KARAPAGAM ACADEMY OF HIGHER EDUCATION, COIMBATORE-21 SEMESTER – I

17PHP101

CONDENSED MATTER PHYSICS

L T P C 4 - - 4

Scope: Study of properties of materials is very important at all times, to choose the correct material for the correct use. Especially with the development of nanotechnology, it is important to give an idea about the preparation methods and characterization of different materials.

Objectives: This paper is intended to give the students an idea about importance of crystals and their properties. An introduction to nanotechnology is also given in this paper.

UNIT – I

Inter planar spacing: Inter planar spacing for SC, FCC, BCC lattices - diamond cubic structure - NaCl structure - The reciprocal lattice and their properties - Bragg condition in terms of reciprocal lattice - Rotatory crystal method of X ray diffraction -Neutron diffraction – experiment.

Lattice: Vibrations of one dimensional diatomic linear lattice-acoustic and optical branches -Semi conductors and their properties - Hall effect - Dielectrics - Lorentz field in dielectrics - The Clausius – Mossoti equation - Ferro electric crystals - Ferro electric domains.

UNIT - II

Crystal defects: Classification of defects - Points defect - The Schottky defect - The Frenkel defect -colour centers - F center - other colour centers - Production of colour centers by X rays or practice irradiation – Defect and energy state.

Dislocations - Slip and plastic deformation - Shear strength of single crystals - Edge dislocation - Screw dislocation - Stress field around an edge dislocation.

Ultrasonics: Non destructive testing and applications.

UNIT - III

Heat capacity of the electron gas: Experimental electrical resistivity of metals – Free electron theory of metals – Debye's equation - superconductivity - Electron phonon interaction - Cooper pairs – BCS theory - Energy gap and its temperature dependence - London equation – Josephson effect and its applications.

Langevin theory of Para magnetism: Quantum theory of Para Magnetism - Curie law- Ferro Magnetism - Weiss molecular field theory - Domain theory - Anti Ferro magnetism - Neel theory - Ferri Magnetism – Ferrites – spin – waves - Experimental techniques to study the magnetic properties.

UNIT - IV NANOSCIENCE

Structure: Size dependence of properties – Crystal Structures – Face centred nano particles – Particle size determination – Surface structure - Metal nano particles - Magic numbers – Theoretical model of nano particles – Geometric structure – Reactivity – Fluctuations –

Magnetic clusters – Bulk to nano transitions Semi conducting nano particles – optical properties – photo fragmentation – Coulombic explosion.

Polymers: Forming and Characterizing polymers – Polymerisation – Sizes of polymers – Nano crystals – Condensed ring types – Poly diacetylene types – Polymers – Conductive polymers – Supra molecular structures – Transition-metal mediated types – Dendritic molecules – Supra molecular dendrimers – Micellers

UNIT - V

Instrumentation: Working principle, and applications of scanning electron microscope - transmission electron microscope - scanning tunneling microscope - atomic force microscope, and surface plasmon resonance – theories and principles of soft lithography, self assembled monolayers and multilayers

TEXT BOOKS:

- 1. Kittel. C. 2015, Introduction to Solid State Physics, 8th Edition, Willey Eastern Ltd., New Delhi.
- 2. Saxena. B.S., R.C.Gupta and P.N.Saxena, 2012, Fundamentals of Solid State Physics, 15th edition, Pragati Prakashan, Meeru.
- Charles P. Poole Jr., Frank J.Owens, 2013, Introduction to Nano-technology, 1st edition, Wiley India, New Delhi

REFERENCES

- 1. Dekkar. A.J., revised edition, 2010, Solid State Physics, Macmillan India Ltd., New Delhi.
- 2. Keer. H.V. 1st edition , 2012, Principles of Solid State, New age international., New Delhi.
- 3. Pillai S.O., 2015, Solid State Physics, 4th Edition, New Age International Publishers Ltd.
- 4. Mark Ratner, Daniel Ratner, 1st edition ; 2009, Nano-Technology, A gentle introduction to the new big idea, Pearson Education (Singapore) (P) Ltd., New Delhi.
- 5. Jean-Marie Lehn, 2016, Supramolecular Chemistry Concepts and Perspectives, Wiley-VCH, Weinheim, Germany Volume 106
- 6. Jonathan Steed and Jerry Atwood, 2st edition; 2010, Supramolecular Chemistry, Wiley Interscience, London.

KARAPAGAM ACADEMY OF HIGHER EDUCATION, COIMBATORE-21

DEPARTMENT OF PHYSICS

LECTURE PLAN (2017-2018 ODD SEMESTER)

I M.SC PHYSICS (2017-2019 BATCH)

CONDENSED MATTER PHYSICS

$\boldsymbol{UNIT-I}$

S.No	Lecture duration	Topic to be covered	Support material
1	1 hr	Inter planar spacing for SC, FCC, BCC lattices, Diamond cubic structure and NaCl structure	T1 (212-213), (215- 216)
2	1 hr	Continuation	
3	1 hr	The reciprocal lattice and their properties, Bragg condition in terms of reciprocal lattice, Rotatory crystal method of X ray diffraction, Neutron diffraction experiment	T2 (598-600), T3 (34-35, 43-47)
4	1 hr	Continuation	
5	1 hr	Vibrations of one dimensional diatomic linear lattice, acoustic and optical branches, Semi conductors and their properties	T1 (232-234), (251- 252)
6	1 hr	Continuation	
7	1 hr	Hall effect, Dielectrics	T3 (211-214), (355- 360)
8	1 hr	Continuation	
9	1 hr	Lorentz field in dielectrics	T3 (360-362)
10	1 hr	Continuation	
11	1 hr	The Clausius – Mossotti equation	T3 (362-363)
12	1 hr	Continuation	
13	1 hr	Ferroelectric crystals, Ferroelectric domains	T3 (389-395)
14	1 hr	REVISION	

Textbooks

- T1-G. Aruldhas and P. Rajagopal, Modern Physics, PHI Pvt Ltd, New Delhi
- T2 R. Murugeshan and Kiruthiga Sivaprasath, Modern Physics, S. Chand & Co. Ltd, New Delhi

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T3 – Saxena, Gupta and Saxena,, Solid State Physics, Pragati Prakashan, Meerut.

S.No	Lecture duration	Topic to be covered	Support material
1	1 hr	Classification of defects, Point T3 (107-111) defect, The Schottky defect, The Frenkel defect	
2	1 hr	Continuation	
3	1 hr	Colour centers, F center, otherT3 (112-117)colour centers, Production of colourrays or practiceirradiationirradiation	
4	1 hr	Continuation	
5	1 hr	Defect and energy state	T3 (117)
6	1 hr	Dislocations, Slip and plastic deformation	T3 (117-118)
7	1 hr	Shear strength of single crystals,T3 (118-121)Edge dislocation, Screw dislocation	
8	1 hr	Continuation	
9	1 hr	Stress field around an edge dislocation	T3 (122-124)
10	1 hr	Ultrasonics, Non destructive testing and applications T4 (1-4, 259-301)	
11	1 hr	Continuation	
12	1 hr	REVISION	

UNIT – II

Textbooks

- T3 Saxena, Gupta and Saxena, Solid State Physics, Pragati Prakashan, Meerut.
- T4 Dale Ensminger and Leonard J. Bond, Ultasonics: Fundamentals, Technologies and Applications, CRC Press, Finland.

Reference Books

- R1 Kittel. C, Introduction to Solid State Physics
- R2 Dekkar. A. J, Solid State Physics

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S.No	Lecture	Topic to be covered	Support material
	duration		
1	1 hr	Heat capacity of the electron gas, Experimental electrical resistivity of metals, Free electron theory of metals, Debye's equation	T3 (165-166) T2 (657-659) T3 (158-161, 171-179)
2	1 hr	Continuation	
3	1 hr	Superconductivity, Electron phonon interaction, Cooper pairs, BCS theory, Energy gap and its temperature dependence	
4	1 hr	Continuation	
5	1 hr	London equation, Josephson effect and its applications, Langevin theory of Para magnetism, Quantum theory of Paramagnetism T3 (419-420, 423-426 T3 (295-300)	
6	1 hr	Continuation	
7	1 hr	Curie law, Ferromagnetism, Weiss T3 (303-306), (311-313) molecular field theory, Domain theory	
8	1 hr	Continuation	
9	1 hr	Anti Ferromagnetism, Neel theory T3 (315-316)	
10	1 hr	Ferrimagnetism, Ferrites, spin, wavesT1 (267-268)	
11	1 hr	Continuation	
12	1 hr	Experimental techniques to study the magnetic properties	http://phys.thu.edu.tw/~hlh siao/mse-web_ch20.pdf
13	1 hr	REVISION	
10	1 hr	Revision	

UNIT – III

Textbooks

- T1 G. Aruldhas and P. Rajagopal, Modern Physics, PHI Pvt Ltd, New Delhi
- T2 R. Murugeshan and Kiruthiga Sivaprasath, Modern Physics, S. Chand & Co. Ltd, New Delhi
- T3 Saxena, Gupta and Saxena,, Solid State Physics, Pragati Prakashan, Meerut.

S.No	Lecture duration	Topic to be covered	Support material
1	1 hr	Size dependence of properties, Crystal Structures, Face centred nano particles, Particle size determination, Surface structure, Metal nano particles, Magic numbersT5 (8-15), (42-48, 74-1000)	
2	1 hr	Continuation	
3	1 hr	Theoretical model of nano particles, Geometric structure, Reactivity, Fluctuations, Magnetic clusters, Bulk to nano transitions	T5 (75-81), (83-89)
4	1 hr	Continuation	
5	1 hr	Semi conducting nano particles, T5 (90-94 optical properties, photo fragmentation, Coulombic explosion	
6	1 hr	Continuation	
7	1 hr	Polymers, Forming and Characterizing polymers, Polymerization, Sizes of polymers, Nano crystals, Condensed ring types, Poly diacetylene types	T5 (283-292)
8	1 hr	Polymers, Conductive polymers, Supra molecular structures, Transition-metal mediated types	T5 (292-293), (295-296)
9	1 hr	Revision	

$\mathbf{UNIT} - \mathbf{IV}$

Textbooks

T5 - Charles P. Poole Jr. and Frank J.Owens, Introduction to Nano-technology, Wiley India, New Delhi

Reference Books

R1 - Mark Ratner and Daniel Ratner, Nano-Technology, A gentle introduction to the new big idea, Pearson Education (Singapore) (P) Ltd., New Delhi.

S.No	Lecture	Topic to be covered	Support material
	duration		
1	1 hr	Working principle and applications of scanning electron microscope, Working principle and applications of transmission electron microscope	http://serc.carleton.edu//SEM.html, http://web.stanford.edu/group/snl/tem.htm
	1 hr	Continuation	
2	1 hr	Working principle and applications of scanning tunneling microscope, Working principle and applications of atomic force microscope	http://www.britannica.com//scanning- tunneling-microscope-STM, http://www.shu.ac.uk//atomic-force- microscope-afm-0
3	1 hr	Working principle and applications of surface plasmon resonance, Theories and principles of soft lithography	http://www.bionavis.com/technology/spr/ http://gmwgroup.harvard.edu//index.php? page=22
	1 hr	Theories and principles of self assembled monolayers, Theories and principles of multilayers	http://en.wikipedia.org/wiki/Self-assembly http://www.ncbi.nlm.nih.gov/pubmed/1726 1075
4	1 hr	REVISION	
	1 hr	OLD QUESTION PAPER DISCUSSION	
5	1 hr	OLD QUESTION PAPER DISCUSSION	
6	1 hr	OLD QUESTION PAPER DISCUSSION	

UNIT – V

Textbooks

Reference Books

R1 - T. Pradeep, Nano: The Essentials, McGraw Hill Professional, USA.

Prepared by Dr.V. Senthil Kumar Head Department of Physics

KAHE, COIMBATORE-21

UNIT – I

Inter planar spacing: Inter planar spacing for SC, FCC, BCC lattices - diamond cubic structure - NaCl structure - The reciprocal lattice and their properties - Bragg condition in terms of reciprocal lattice - Rotatory crystal method of X ray diffraction -Neutron diffraction – experiment.

Lattice: Vibrations of one dimensional diatomic linear lattice-acoustic and optical branches -Semi conductors and their properties - Hall effect - Dielectrics - Lorentz field in dielectrics - The Clausius –Mossoti equation - Ferro electric crystals - Ferro electric domains.

SIMPLE CRYSTAL STRUCTURES

Cesium chloride

Cesium chloride is the inorganic compound with the formula CsCl. This colorless solid is an important source of cesium ions in a variety of applications. Its crystal structure forms a major structural type where each cesium ion is coordinated by 8 chlorine ions. Cesium chloride crystals are thermally stable, but easily dissolve in water and concentrated hydrochloric acid, and therefore gradually disintegrate in the ambient conditions due to moisture. Cesium chloride naturally in mineral waters and impurity in carnallite (up occurs as an to 0.002%), sylvite andkainite. Less than 20 tonnes of CsCl is produced annually worldwide, mostly from a cesium-bearing mineral pollucite.

Cesium chloride is widely used in isopycnic centrifugation for separating various types of DNA. It is a reagent in analytical chemistry, where it is used to identify ions by the color and morphology of the precipitate. When enriched in radioisotopes, such as ¹³⁷CsCl or ¹³¹CsCl, cesium chloride is used in nuclear medicine applications such as treatment of cancer and diagnosis of myocardial infarction. Another form of cancer treatment was studied using conventional non-radioactive CsCl. Whereas conventional cesium chloride has a rather low toxicity to humans and animals, the radioactive form easily contaminates the environment due to the high solubility of CsCl in water. Spread of ¹³⁷CsCl powder from a 93-gram container in 1987

in Goiânia, Brazil, resulted in one of the worst-ever radiation spill accidents killing four and directly affecting more than 100,000 people.

Crystal structure



Ball-and-stick model of the coordination of Cs and Cl in CsCl

The cesium chloride structure adopts a primitive cubic lattice with a two-atom basis, where both atoms have eight fold coordination. The chloride atoms lie upon the lattice points at the edges of the cube, while the cesium atoms lie in the holes in the center of the cubes. This structure is shared with CsBr and CsI and many binary metallic alloys. In contrast, the other alkaline halides have the sodium chloride (rocksalt) structure. When both ions are similar in size (Cs⁺ ionic radius 174 pm for this coordination number, Cl⁻ 181 pm) the CsCl structure is adopted, when they are different (Na⁺ ionic radius 102 pm, Cl⁻ 181 pm) the sodium chloride structure is adopted. Upon heating to above 450 °C, the normal cesium chloride structure (α -CsCl) converts to the β -CsCl form with the rocksalt structure (space group*Fm3m*).

Uses

Precursor to Cs metal

- Cesium chloride is the main precursor to cesium metal by high temperature reduction:
 2 CsCl + Mg → MgCl₂ + Cs
- An analogous reaction heating CsCl with calcium in vacuum in presence of phosphorus was first reported in 1905 by the French chemist M. L. Hackspill and is still used industrially.

Cesium hydroxide is obtained by electrolysis of aqueous cesium chloride solution:
 2 CsCl + 2 H₂O → 2 CsOH + Cl₂ + H₂

Solute for ultracentrifugation

Cesium chloride is widely used in centrifugation in a technique known as isopycnic centrifugation. Centripetal and diffusive forces establish a density gradient that allow separation of mixtures on the basis of their molecular density. This technique allows separation of DNA of different densities (e.g. DNA fragments with differing A-T or G-C content). This application requires a solution with high density and yet relatively low viscosity, and CsCl suits it because of its high solubility in water, high density owing to the large mass of Cs, as well as low viscosity and high stability of CsCl solutions.

Medicine

Medical properties of cesium chloride were studied back in 1888 by Ivan Pavlov and S. S. Botkin. They found that CsCl and RbCl induce long-term narrowing of the blood vessels (vasoconstriction) and the associated increase in the blood pressure (hypertension), stimulating the cardiovascular activity. These properties were then applied in the treatment of cardiovascular deceases.

Later research indicated that CsCl alleviates cardiac dysrhythmia and that the life expectancy is higher in regions characterized by elevated levels of CsCl in water and food. Preliminary results indicate that CsCl can be used in the treatment of depressions. The neurological action of CsCl is related to the protection of neurons from apoptosis and activation of caspase 3 caused by reduced potassium content.

Several reports suggested that non-radioactive cesium chloride can be used in a complex treatment of some forms of cancer. However, it has been linked to the deaths of over 50 patients, when it was used as part of a scientifically unvalidated cancer treatment. The American Cancer Society considers cesium chloride therapy as requiring a further study for benefits and side effects.

Nuclear medicine and radiography

Cesium chloride composed of radioisotopes such as ¹³⁷CsCl and ¹³¹CsCl, is used in nuclear medicine, including treatment of cancer(brachytherapy) and diagnosis of myocardial infarction. In the production of radioactive sources, it is normal to choose a chemical form of the radioisotope which would not be readily dispersed in the environment in the event of an accident. For instance, radiothermal generators (RTGs) often use strontium titanate, which is insoluble in water. For teletherapy sources, however, the radioactive density (Ci in a given volume) needs to be very high, which is not possible with known insoluble cesium compounds. A thimble-shaped container of radioactive cesium chloride provides the active source.

Miscellaneous applications

Cesium chloride is used in the preparation of electrically conducting glasses and screens of cathode ray tubes. It is a non-toxic provider of a halogen gas in exciplex lamps (exilamps) – a gas-discharge source of ultraviolet light which uses, for example, electrically excited XeCl molecules. Other uses include activation of electrodes in welding; manufacture of mineral water, beer and drilling muds; repellents and high-temperature solders. High-quality CsCl single crystals have a wide transparency range from UV to the infrared and therefore had been used for cuvettes, prisms and windows in optical spectrometers; this use was discontinued with the development of less hygroscopic materials.

HEXAGONAL CLOSE-PACKED STRUCTURE



Dr. V. Senthil Kumar Head Department of Physics

In a hexagonal close-packed (hcp) arrangement of atoms, the unit cell consists of three layers of atoms. The top and bottom layers (a) contain six atoms at the corners of a hexagon and one atom at the center of each hexagon. The middle layer (b) contains three atoms nestled between the atoms of the top and bottom layers, hence, the name close-packed. The hexagonal close packed structure can be made by piling layers in the a-b-a-b-a-b... sequence.

CUBIC ZINC SULPHIDE STRUCTURE



Zinc sulfide (or zinc sulphide) is a inorganic compound with the formula ZnS. ZnS is the main form of zinc in nature, where it mainly occurs as the mineral sphalerite. Although the mineral is black owing to impurities, the pure material is white and is in fact used widely as a pigment.

Structure of ZnS

ZnS exists in two main forms, and this dualism is often a textbook example of polymorphism. In both polymorphs, the coordination geometry at Zn and S are tetrahedral. The more stable form cubic form is known also as zinc blende or sphalerite. The hexagonal form is known as the mineral wurtzite, although it also can be produced synthetically. The transition

from the sphalerite form to the wurtzite form occurs at around 1020 °C. A tetragonal form is also known as the very rare mineral called polhemusite, with the formula (Zn,Hg)S.

Applications

Luminescent material

Zinc sulfide, with addition of few ppm of suitable activator, is used as phosphor in many applications, from cathode ray tubes through X-ray screens to glow in the dark products. When silver is used as activator, the resulting color is bright blue, with maximum at 450 nm. Manganese yields an orange-red color at around 590 nm. Copper provides long glow time and the familiar glow-in-the-dark greenish color. Copper-doped zinc sulfide ("ZnS+Cu") is used also in electroluminescent panels. It also exhibits phosphorescence due to impurities on illumination with blue or ultraviolet light.

Optical material

Zinc sulfide is also used as an infrared optical material, transmitting from visible wavelengths to over 12 micrometres. It can be used planar as an optical window or shaped into a lens. It is made as microcrystalline sheets by the synthesis from hydrogen sulfide gas and zinc vapour and sold as FLIR (Forward Looking IR) grade ZnS a pale milky yellow visibly opaque form. This material when hot isostatically pressed (HIPed) can be converted to a water-clear form known as Cleartran (trademark). Early commercial forms were marketed as Irtran-2 but this designation is now obsolete.

Pigment

Zinc sulfide is a common pigment. When compounded with barium sulfate, zinc sulfide form slithopone.

Semiconductor properties

Both sphalerite and wurtzite are intrinsic, wide-bandgap semiconductors. It is a prototypical II-VI semiconductor and adopts structures related to many other semiconductors such as gallium arsenide. The cubic form has a band gap of 3.54 eV at 300 K whereas the hexagonal form has a band gap of 3.91 eV. It can be doped as both n-type semiconductor and p-type semiconductor.

Condensed Matter Physics UNIT I (17PHP101) INTERPLANAR SPACING

DIAMOND STRUCTURE



In mineralogy, diamond is an allotrope of carbon, where the carbon atoms are arranged in a variation of the face-centered cubic crystal structure called a diamond lattice. Diamond is less stable than graphite, but the conversion rate from diamond to graphite is negligible at ambient conditions. Diamond is renowned as a material with superlative physical qualities, most of which originate from the strong covalent bonding between its atoms. In particular, diamond has the highest hardness and thermal conductivity of any bulk material. Those properties determine the major industrial application of diamond in cutting and polishing tools.

Diamond has remarkable optical characteristics. Because of its extremely rigid lattice, it can be contaminated by very few types of impurities, such as boron and nitrogen. Combined with wide transparency, this results in the clear, colorless appearance of most natural diamonds. Small amounts of defects or impurities (about one per million of lattice atoms) color diamond blue (boron), yellow (nitrogen), brown (lattice defects), green (radiation exposure), purple, pink, orange or red. Diamond also has relatively high optical dispersion (ability to disperse light of

different colors), which results in its characteristic luster. Excellent optical and mechanical properties, combined with efficient marketing, make diamond the most popular gemstone.

Most natural diamonds are formed at high-pressure high-temperature conditions existing at depths of 140 to 190 kilometers (87 to 120 mi) in the Earth mantle. Carbon-containing minerals provide the carbon source, and the growth occurs over periods from 1 billion to 3.3 billion years (25% to 75% of the age of the Earth). Diamonds are brought close to the Earth surface through deep volcanic eruptions by a magma, which cools into igneous rocks known as kimberlites and lamproites. Diamonds can also be produced synthetically in a high-pressure high-temperature process which approximately simulates the conditions in the Earth mantle. An alternative and completely different growth technique is chemical vapor deposition (CVD). Several non-diamond materials, which include cubic zirconia and silicon carbide and are often called diamond simulants, resemble diamond in appearance and many properties. Special gemological techniques have been developed to distinguish natural and synthetic diamonds and diamond simulants.

SODIUM CHLORIDE STRUCTURE

Sodium chloride, also known as salt, common salt, table salt or halite, is an ionic compound with the formula NaCl. Sodium chloride is the salt most responsible for the salinity of the ocean and of the extracellular fluid of many multicellular organisms. As the major ingredient in edible salt, it is commonly used as a condiment and food preservative.

Chemistry of solid and dissolved sodium chloride

Solid sodium chloride

In solid sodium chloride, each ion is surrounded by six ions of the opposite charge as expected on electrostatic grounds. The surrounding ions are located at the vertices of a regular octahedron. In the language of close-packing, the larger chloride ions are arranged in a cubic array whereas the smaller sodium ions fill all the cubic gaps (octahedral voids) between them. This same basic structure is found in many other compounds and is commonly known as the halite or rock-salt crystal structure. It can be represented as a face-centered cubic (fcc) lattice with a two-atom basis or as two interpenetrating face centered cubic lattices. The first atom is

located at each lattice point, and the second atom is located half way between lattice points along the fcc unit cell edge.

Thermal conductivity of NaCl as a function of temperature has a maximum of 2.03 W/(cm K) at 8 K and decreases to 0.069 at 314 K (41 $^{\circ}$ C). It also decreases with doping.

Aqueous solutions

The attraction between the Na⁺ and Cl⁻ ions in the solid is so strong that only highly polar solvents like water dissolve NaCl well.

When dissolved in water, the sodium chloride framework disintegrates as the Na⁺ and Cl⁻ ions become surrounded by the polar water molecules. These solutions consist of metal aquo complex with the formula $[Na(H_2O)_x]^+$, where x is 8 with the Na-O distance of 250 pm. The chloride ions are also strongly solvated, each being surrounded by an average of 6 molecules of water. Solutions of sodium chloride have very different properties from pure water. The freezing point is -21.12 °C for 23.31 wt% of salt, and the boiling point of saturated salt solution is near 108.7 °C. From cold solutions, salt crystallizes as the dihydrateNaCl·2H₂O.

Uses

Chemicals production

Salt is the source, directly or indirectly, for the production of many chemicals, which consume most of the world's production.

Chlor-alkali industry

It is the starting point for the Chloralkali process, which provides the world with chlorine and sodium hydroxide according to the chemical equation:

$2 \text{ NaCl} + 2 \text{ H}_2\text{O} \rightarrow \text{Cl}_2 + \text{H}_2 + 2 \text{ NaOH}$

This electrolysis is conducted in either a mercury cell, a diaphragm cell, or a membrane cell. Each of those use a different method to separate the chlorine from the sodium hydroxide. Other technologies are under development due to the high energy consumption of the electrolysis, whereby small improvements in the efficiency can have large economic paybacks. Some application of chlorine includes PVC, disinfectants, and solvents. From sodium hydroxide enables industries that produce paper, soap, and aluminium.

Soda ash industry

Via the Solvay process, sodium chloride is used to produce sodium carbonate and calcium chloride. Sodium carbonate is used to produce glass, sodium bicarbonate, and dyes as well as myriad other chemicals. In the Mannheim process and in the Hargreaves process, it is used for the production of sodium sulfate and hydrochloric acid.

Miscellaneous industrial uses

Sodium chloride is heavily used, so even miscellaneous applications can consume massive quantities. In oil and gas exploration, salt is an important component of drilling fluids in well drilling. It is used to flocculate and increase the density of the drilling fluid to overcome high down well gas pressures. Whenever a drill hits a salt formation, salt is added to the drilling fluid to saturate the solution and to minimize the dissolution within the salt stratum. Salt is also used to increase the curing of concrete in cemented casings.

In textiles and dyeing, salt is used as a brine rinse to separate organic contaminants, to promote "salting out" of dyestuff precipitates, and to blend with concentrated dyes to standardize them. One of its main roles is to provide the positive ion charge to promote the absorption of negatively charged ions of dyes.

It also is used in processing aluminium, beryllium, copper, steel and vanadium. In the pulp and paper industry, salt is used to bleach wood pulp. It also is used to make sodium chlorate, which is added along with sulfuric acid and water to manufacture chlorine dioxide, an excellent oxygen-based bleaching chemical. The chlorine dioxide process, which originated in Germany after World War I, is becoming more popular because of environmental pressures to reduce or eliminate chlorinated bleaching compounds. In tanning and leather treatment, salt is added to animal hides to inhibit microbial activity on the underside of the hides and to attract moisture back into the hides.

In rubber manufacture, salt is used to make buna, neoprene and white rubber types. Salt brine and sulfuric acid are used to coagulate an emulsified latex made from chlorinated butadiene.

Salt also is added to secure the soil and to provide firmness to the foundation on which highways are built. The salt acts to minimize the effects of shifting caused in the subsurface by changes in humidity and traffic load.

Water softening

Hard water contains calcium and magnesium ions that interfere with action of soap and contribute to the buildup of a scale or film of alkaline mineral deposits in household and industrial equipment and pipes. Commercial and residential water-softening units use ion exchange resins to remove the offending ions that cause the hardness. These resins are generated and regenerated using sodium chloride.

Road salt

The second major application of salt is for deicing and anti-icing of roads, both in grit bins and spread by winter service vehicles. In anticipation of snowfall, roads are optimally "antiiced" with brine (concentrated solution of salt in water), which prevents bonding between the snow-ice and the road surface. This procedure precludes the heavy use of salt after the snowfall. For de-icing, mixtures of brine and salt are used, sometimes with additional agents such as calcium and magnesium chloride. The use of salt or brine becomes ineffective below -10 °C.

Salt for de-icing in the United Kingdom predominantly comes from a single mine in Winsford in Cheshire. Prior to distribution it is mixed with <100 ppm of sodium hexacyanoferrate (II) as an anti-caking agent, which enables rock salt to flow freely out of the gritting vehicles despite being stockpiled prior to use. In recent years this additive has also been used in table salt. Other additives had been used in road salt to reduce the total costs. For example, in the US, a byproduct carbohydrate solution from sugar beet processing was mixed with rock salt and adhered to road surfaces about 40% better than loose rock salt alone. Because it stayed on the road longer, the treatment did not have to be repeated several times, saving time and money.

In the technical terms of physical chemistry, the minimum freezing point of a water-salt mixture is -21.12 °C for 23.31 wt% of salt. Freezing near this concentration is however so slow that the eutectic point of -22.4 °C can be reached with about 25 wt% of salt.

Environmental effect

Road salt ends up in fresh water bodies and could harm aquatic plants and animals by disrupting their osmoregulation ability. The omnipresence of salt poses a problem in any coastal coating application, as trapped salts cause great problems in adhesion. Naval authorities and ship builders monitor the salt concentrations on surfaces during construction. Maximum salt concentrations on surfaces are dependent on the authority and application. The IMO regulation is mostly used and sets salt levels to a maximum of 50 mg/m² soluble salts measured as sodium chloride. These measurements are done by means of a Bresle test.

In highway deicing, salt has been associated with corrosion of bridge decks, motor vehicles, reinforcement bar and wire, and unprotected steel structures used in road construction. Surface runoff, vehicle spraying, and windblown actions also affect soil, roadside vegetation, and local surface water and groundwater supplies. Although evidence of environmental loading of salt has been found during peak usage, the spring rains and thaws usually dilute the concentrations of sodium in the area where salt was applied.

Food industry, medicine and agriculture

Many micro organisms cannot live in an overly salty environment: water is drawn out of their cells by osmosis. For this reason salt is used to preserve some foods, such as smoked bacon or fish. It can also be used to detach leeches that have attached themselves to feed. It is also used to disinfect wounds.

Salt is added in most food items, by the food processor or by the consumer, as a flavor enhancer, preservative, binder, fermentation-control additive, texture-control agent and color developer. The salt consumption in the food industry is subdivided, in descending order of consumption, into other food processing, meat packers, canning, baking, dairy and grain mill products. Salt is added to promote color development in bacon, ham and other processed meat products. As a preservative, salt inhibits the growth of bacteria. Salt acts as a binder in sausages to form a binding gel made up of meat, fat, and moisture. Salt also acts as a flavor enhancer and as a tenderizer.

In the dairy industry, salt is added to cheese as a color-, fermentation-, and texturecontrol agent. The dairy subsector includes companies that manufacture creamery butter, condensed and evaporated milk, frozen desserts, ice cream, natural and processed cheese, and specialty dairy products. In canning, salt is primarily added as a flavor enhancer and preservative. It also is used as a carrier for other ingredients, dehydrating agent, enzyme inhibitor and tenderizer. In baking, salt is added to control the rate of fermentation in bread dough. It also is used to strengthen the gluten (the elastic protein-water complex in certain doughs) and as a flavor enhancer, such as a topping on baked goods. The food-processing category also contains grain mill products. These products consist of milling flour and rice and manufacturing cereal breakfast food and blended or prepared flour. Salt is also used a seasoning agent, e.g. in potato chips, pretzels, cat and dog food.

Sodium chloride is used in veterinary medicine as emesis causing agent. It is given as warm saturated solution. Emesis can also be caused by pharyngeal placement of small amount of plain salt or salt crystals.

Firefighting

Sodium chloride is the principal extinguishing agent in fire extinguishers (Met-L-X, Super D) used on combustible metal fires such as magnesium, potassium, sodium, and NaK alloys (Class D). Thermoplastic powder is added to the mixture, along with waterproofing (metal stearates) and anti-caking materials (tricalcium phosphate) to form the extinguishing agent. When it is applied to the fire, the salt acts like a heat sink, dissipating heat from the fire, and also forms an oxygen-excluding crust to smother the fire. The plastic additive melts and helps the crust maintain its integrity until the burning metal cools below its ignition temperature. This type of extinguisher was invented in the late 1940s in the cartridge-operated type shown here, although stored pressure versions are now popular. Common sizes are 30 lb portable and 350 lb wheeled.

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Cleanser

Since at least medieval times, people have used salt as a cleansing agent rubbed on household surfaces. It is also used in many brands of shampoo, toothpaste and popularly to deice driveways and patches of ice.

DIFFRACTION OF WAVES BY CRYSTALS: BRAGG'S LAW

In physics, Bragg's law gives the angles for coherent and incoherent scattering from a crystal lattice. When X-rays are incident on an atom, they make the electronic cloud move as does any electromagnetic wave. The movement of these charges re-radiates waves with the same frequency (blurred slightly due to a variety of effects); this phenomenon is known as Rayleigh scattering (or elastic scattering). The scattered waves can themselves be scattered but this secondary scattering is assumed to be negligible.

A similar process occurs upon scattering neutron waves from the nuclei or by a coherent spin interaction with an unpaired electron. These re-emitted wave fields interfere with each other either constructively or destructively (overlapping waves either add together to produce stronger peaks or subtract from each other to some degree), producing a diffraction pattern on a detector or film. The resulting wave interference pattern is the basis of diffraction analysis. This analysis is called *Bragg diffraction*.

Bragg diffraction (also referred to as the Bragg formulation of X-ray diffraction) was first proposed by William Lawrence Bragg and William Henry Bragg in 1913 in response to their discovery that crystalline solids produced surprising patterns of reflected X-rays (in contrast to that of, say, a liquid). They found that these crystals, at certain specific wavelengths and incident angles, produced intense peaks of reflected radiation (known as *Bragg peaks*). The concept of Bragg diffraction applies equally to neutron diffraction and electron diffraction processes. Both neutron and X-ray wavelengths are comparable with inter-atomic distances (~150 pm) and thus are an excellent probe for this length scale.

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X-rays interact with the atoms in a crystal.

W. L. Bragg explained this result by modeling the crystal as a set of discrete parallel planes separated by a constant parameter *d*. It was proposed that the incident X-ray radiation would produce a Bragg peak if their reflections off the various planes interfered constructively. The interference is constructive when the phase shift is a multiple of 2π ; this condition can be expressed by Bragg's law,

$$n\lambda = 2d\sin\theta$$

Where *n* is an integer, λ is the wavelength of incident wave, *d* is the spacing between the planes in the atomic lattice, and θ is the angle between the incident ray and the scattering planes. Note that moving particles, including electrons, protons and neutrons, have an associated De Broglie wavelength.



According to the 2θ deviation, the phase shift causes constructive (left figure) or destructive (right figure) interferences.

Bragg's Law was derived by physicist Sir William Lawrence Bragg in 1912 and first presented on 11 November 1912 to the Cambridge Philosophical Society. Although simple, Bragg's law confirmed the existence of real particles at the atomic scale, as well as providing a

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powerful new tool for studying crystals in the form of X-ray and neutron diffraction. William Lawrence Bragg and his father, Sir William Henry Bragg, were awarded the Nobel Prize in physics in 1915 for their work in determining crystal structures beginning with NaCl, ZnS, and diamond. They are the only father-son team to jointly win. W. L. Bragg was 25 years old, making him the youngest Nobel laureate.

Bragg condition



Bragg diffraction. Two beams with identical wavelength and phase approach a crystalline solid and are scattered off two different atoms within it. The lower beam traverses an extra length of $2d\sin\theta$. Constructive interference occurs when this length is equal to an integer multiple of the wavelength of the radiation.

Bragg diffraction occurs when electromagnetic radiation or subatomic particle waves with wavelength comparable to atomic spacings are incident upon a crystalline sample, are scattered in a specular fashion by the atoms in the system, and undergo constructive interference in accordance to Bragg's law. For a crystalline solid, the waves are scattered from lattice planes separated by the interplanar distance *d*. Where the scattered waves interfere constructively, they remain in phase since the path length of each wave is equal to an integer multiple of the wavelength. The path difference between two waves undergoing constructive interference is given by $2d\sin\theta$, where θ is the scattering angle. This leads to **Bragg's law**, which describes the condition for constructive interference from successive crystallographic planes (*h*, *k*, and *l*, as given in Miller Notation) of the crystalline lattice:

$2d\sin\theta = n\lambda,$

where *n* is an integer determined by the order given, and λ is the wavelength. A diffraction pattern is obtained by measuring the intensity of scattered waves as a function of scattering angle. Very strong intensities known as Bragg peaks are obtained in the diffraction pattern when scattered waves satisfy the Bragg condition.

RECIPROCAL LATTICE VECTORS

In physics, the reciprocal lattice of a lattice (usually a Bravais lattice) is the lattice in which the Fourier transform of the spatial function of the original lattice (or *direct lattice*) is represented. This space is also known as *momentum space* or less commonly *k-space*, due to the relationship between the Pontryagin duals momentum and position. The reciprocal lattice of a reciprocal lattice is the original or *direct lattice*.

Mathematical description

Consider a set of points R constituting a Bravais lattice, and a plane wave defined by:

$$e^{i\mathbf{K}\cdot\mathbf{r}} = \cos\left(\mathbf{K}\cdot\mathbf{r}\right) + i\sin\left(\mathbf{K}\cdot\mathbf{r}\right)$$

If this plane wave has the same periodicity as the Bravais lattice, then it satisfies the equation:

$$e^{i\mathbf{K}\cdot(\mathbf{r}+\mathbf{R})} = e^{i\mathbf{K}\cdot\mathbf{r}}$$
$$\therefore e^{i\mathbf{K}\cdot\mathbf{r}}e^{i\mathbf{K}\cdot\mathbf{R}} = e^{i\mathbf{K}\cdot\mathbf{r}}$$
$$\Rightarrow e^{i\mathbf{K}\cdot\mathbf{R}} = 1$$

Mathematically, we can describe the reciprocal lattice as the set of all vectors K that satisfy the above identity for all lattice point position vectors R. This reciprocal lattice is itself a Bravais lattice, and the reciprocal of the reciprocal lattice is the original lattice, which reveals the Pontryagin duality of their respective vector spaces.

For an infinite three dimensional lattice, defined by its primitive vectors $(\mathbf{a_1}, \mathbf{a_2}, \mathbf{a_3})$, its reciprocal lattice can be determined by generating its three reciprocal primitive vectors, through the formulae

$$\mathbf{b_1} = 2\pi \frac{\mathbf{a_2} \times \mathbf{a_3}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})}$$

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$$\mathbf{b_2} = 2\pi \frac{\mathbf{a_3} \times \mathbf{a_1}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})}$$
$$\mathbf{b_3} = 2\pi \frac{\mathbf{a_1} \times \mathbf{a_2}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})}$$

Note that the denominator is the scalar triple product. Using column vector representation of (reciprocal) primitive vectors, the formulae above can be rewritten using matrix inversion:

$$\left[\mathbf{b_1 b_2 b_3}\right]^T = 2\pi \left[\mathbf{a_1 a_2 a_3}\right]^{-1}$$

This method appeals to the definition, and allows generalization to arbitrary dimensions. The cross product formula dominates introductory materials on crystallography.

The above definition is called the "physics" definition, as the factor of 2π comes naturally from the study of periodic structures. An equivalent definition, the "crystallographer's" definition, comes from defining the reciprocal lattice to be $e^{2\pi i \mathbf{K} \cdot \mathbf{R}} = 1$ which changes the definitions of the reciprocal lattice vectors to be

$$\mathbf{b_1} = \frac{\mathbf{a_2} \times \mathbf{a_3}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})}$$

and so on for the other vectors. The crystallographer's definition has the advantage that the definition of $\mathbf{b_1}$ is just the reciprocal magnitude of $\mathbf{a_1}$ in the direction of $\mathbf{a_2} \times \mathbf{a_3}$, dropping the factor of 2π . This can simplify certain mathematical manipulations, and expresses reciprocal lattice dimensions in units of spatial frequency. It is a matter of taste which definition of the lattice is used, as long as the two are not mixed.

Each point (hkl) in the reciprocal lattice corresponds to a set of lattice planes (hkl) in the real space lattice. The direction of the reciprocal lattice vector corresponds to the normal to the real space planes. The magnitude of the reciprocal lattice vector is given in reciprocal length and is equal to the reciprocal of the interplanar spacing of the real space planes.

The reciprocal lattice plays a fundamental role in most analytic studies of periodic structures, particularly in the theory of diffraction. For Bragg reflections in neutron and X-ray diffraction, the momentum difference between incoming and diffracted X-rays of a crystal is a reciprocal lattice vector. The diffraction pattern of a crystal can be used to determine the

reciprocal vectors of the lattice. Using this process, one can infer the atomic arrangement of a crystal.

The Brillouin zone is a primitive unit cell of the reciprocal lattice.

Reciprocal lattice to Simple cubic lattice

The simple cubic Bravais lattice, with cubic primitive cell of side a, has for its reciprocal a simple cubic lattice with a cubic primitive cell of side $\frac{2\pi}{a}(\frac{1}{a}$ in the crystallographer's definition). The cubic lattice is therefore said to be self-dual, having the same symmetry in reciprocal space as in real space.

Reciprocal lattice to Face-centered cubic (FCC) lattice

The reciprocal lattice to an FCC lattice is the body-centered cubic (BCC) lattice.

Consider an FCC compound unit cell. Locate a primitive unit cell of the FCC, i.e., a unit cell with one lattice point. Now take one of the vertices of the primitive unit cell as the origin. Give the basis vectors of the real lattice. Then from the known formulae you can calculate the basis vectors of the reciprocal lattice. These reciprocal lattice vectors of the FCC represent the basis vectors of a BCC real lattice. Note that the basis vectors of a real BCC lattice and the reciprocal lattice of an FCC resemble each other in direction but not in magnitude.

Reciprocal lattice to Body-centered cubic (BCC) lattice

The reciprocal lattice to a BCC lattice is the FCC lattice.

It can be easily proven that only the Bravais lattices which have 90 degrees between $(\mathbf{a_1}, \mathbf{a_2}, \mathbf{a_3})_{(\text{cubic, tetragonal, orthorhombic) have}} (\mathbf{b_1}, \mathbf{b_2}, \mathbf{b_3})_{\text{parallel to their real-space vectors.}}$

ROTATING CRYSTAL METHOD BY X-RAYS



In the rotating crystal method, a single crystal is mounted with an axis normal to a monochromatic X-ray beam. A cylindrical film is placed around it and the crystal is rotated about the chosen axis. As the crystal rotates, sets of lattice planes will at some point make the correct Bragg angle for the monochromatic incident beam, and at that point a diffracted beam will be formed. Lattice constant of the crystal can be determined by means of this method; for a given wavelength if the angle at which a reflection occurs is known, can be determined.

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

The reflected beams are located on the surface of imaginary cones. By recording the diffraction patterns (both angles and intensities) for various crystal orientations; one can determine the shape and size of unit cell as well as arrangement of atoms inside the cell.

Reflected beam Incident beam Cylindrical film X-ray source

NEUTRON DIFFRACTION EXPERIMENT

Neutron diffraction or elastic neutron scattering is the application of neutron scattering to the determination of the atomic and/or magnetic structure of a material: A sample to be examined is placed in a beam of thermal or cold neutrons to obtain a diffraction pattern that provides information of the structure of the material. The technique is similar to X-ray diffraction but due to the different scattering properties of neutrons versus x-rays complementary information can be obtained.

Description

Principle

Neutrons are particles found in the atomic nucleus of almost all atoms, but they are bound. The technique requires free neutrons and these normally do not occur in nature, because they have limited life-time. In a nuclear reactor, however, neutrons can be set free through nuclear decay particularly when fission occurs. All quantum particles can exhibit wave phenomena we typically associate with light or sound. Diffraction is one of these phenomena; it occurs when waves encounter obstacles whose size is comparable with the wavelength. If the wavelength of a quantum particle is short enough, atoms or their nuclei can serve as diffraction obstacles. When a beam of neutrons emanating from a reactor is slowed down and selected properly by their speed, their wavelength lies near one angstrom (0.1 nanometer), the typical

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separation between atoms in a solid material. Such a beam can then be used to perform a diffraction experiment. Impinging on a crystalline sample it will scatter under a limited number of well-defined angles according to the same Bragg's law that describes X-ray diffraction.

Instrumental requirements

A neutron diffraction measurement requires a neutron source (e.g. a nuclear reactor or spallation source), a sample (the material to be studied), and a detector. Samples sizes are large compared to those used in X-ray diffraction. The technique is therefore mostly performed as powder diffraction. At a research reactor other components such as crystal monochromators or filters may be needed to select the desired neutron wavelength. Some parts of the setup may also be movable. At a spallation source the time of flight technique is used to sort the energies of the incident neutrons (Higher energy neutrons are faster), so no monochromator is needed, but rather a series of aperture elements synchronized to filter neutron pulses with the desired wavelength.

Nuclear scattering

Neutrons interact with matter differently than X-rays. X-rays interact primarily with the electron cloud surrounding each atom. The contribution to the diffracted x-ray intensity is therefore larger for atoms with a large atomic number (Z) than it is for atoms with a small Z. On the other hand, neutrons interact directly with the *nucleus* of the atom, and the contribution to the diffracted intensity is different for each isotope; for example, regular hydrogen and deuterium contribute differently. It is also often the case that light (low Z) atoms contribute strongly to the diffracted intensity even in the presence of large Z atoms. The scattering length varies from isotope to isotope rather than linearly with the atomic number. An element like vanadium is a strong scatterer of X-rays, but its nuclei hardly scatter neutrons, which is why it often used as a container material. Non-magnetic neutron diffraction is directly sensitive to the positions of the nuclei of the atoms.

A major difference with X-rays is that the scattering is mostly due to the tiny nuclei of the atoms. That means that there is no need for anatomic form factor to describe the shape of the electron cloud of the atom and the scattering power of an atom does not fall off with the

scattering angle as it does for X-rays. Diffractograms therefore can show strong well defined diffraction peaks even at high angles, particularly if the experiment is done at low temperatures. Many neutron sources are equipped with liquid helium cooling systems that allow data collection at temperatures down to 4.2 K. The superb high angle (i.e. high *resolution*) information means that the data can give very precise values for the atomic positions in the structure. On the other hand, Fourier maps (and to a lesser extent difference Fourier maps) derived from neutron data suffer from series termination errors, sometimes so much that the results are meaningless.

Magnetic scattering

Although neutrons are uncharged, they carry a spin, and therefore interact with magnetic moments, including those arising from the electron cloud around an atom. Neutron diffraction can therefore reveal the microscopic magnetic structure of a material.

Magnetic scattering does require an atomic form factor as it is caused by the much larger electron cloud around the tiny nucleus. The intensity of the magnetic contribution to the diffraction peaks will therefore dwindle towards higher angles.

Uses

Neutron diffraction can be used to determine the static structure factor of gases, liquids or amorphous solids. Most experiments, however, aim at the structure of crystalline solids, making neutron diffraction an important tool of crystallography.

Neutron diffraction is closely related to X-ray powder diffraction. In fact the single crystal version of the technique is less commonly used because currently available neutron sources require relatively large samples and large single crystals are hard or impossible to come by for most materials. Future developments, however, may well change this picture. Because the data is typically a 1D powder diffractogram they are usually processed using Rietveld refinement. In fact the latter found its origin in neutron diffraction (at Petten in the Netherlands) and was later extended for use in X-ray diffraction.

One practical application of elastic neutron scattering/diffraction is that the lattice constant of metals and other crystalline materials can be very accurately measured. Together with an accurately aligned micropositioner a map of the lattice constant through the metal can be

derived. This can easily be converted to the stress field experienced by the material. This has been used to analyze stresses in aerospace and automotive components to give just two examples. This technique has led to the development of dedicated stress diffractometers, such as the ENGIN-X instrument at the ISIS neutron source.

Neutron Diffraction can also be employed to give insight into the 3D structure of novel molecules such as Nanoparticles, Nanorods, Nanotubes, Fullerenes.

Hydrogen, null-scattering and contrast variation

Neutron diffraction can be used to establish the structure of low atomic number materials like proteins and surfactants much more easily with lower flux than at a synchrotron radiation source. This is because some low atomic number materials have a higher cross section for neutron interaction than higher atomic weight materials.

One major advantage of neutron diffraction over X-ray diffraction is that the latter is rather insensitive to the presence of hydrogen (H) in a structure, whereas the nuclei ¹H and ²H (i.e. Deuterium, D) are strong scatterers for neutrons. This means that the position of hydrogen in a crystal structure and its thermal motions can be determined far more precisely with neutrons. In addition the neutron scattering lengths $b_{\rm H} = -3.7406(11)$ fm and $b_{\rm D} = 6.671(4)$ fm, for H and D respectively, have opposite sign allowing for contrast variation. In fact there is a particular isotope ratio for which the contribution of the element would cancel; this is called nullscattering. In practice however it is not desirable to work with the relatively high concentration of H in such a sample. The scattering intensity by H-nuclei has a large inelastic component and this creates a large continuous background that is more or less independent of scattering angle. The elastic pattern typically consists of sharp Bragg reflections if the sample is crystalline. They tend to drown in the inelastic background. This is even more serious when the technique is used for the study of liquid structure. Nevertheless, by preparing samples with different isotope ratios it is possible to vary the scattering contrast enough to highlight one element in an otherwise complicated structure. The variation of other elements is possible but usually rather expensive. Hydrogen is inexpensive and particularly interesting because it plays an exceptionally large role in biochemical structures and is difficult to study structurally in other ways.

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LATTICE

ACOUSTIC AND OPTICAL BRANCHES

Many solid materials, including all metals, are composed of atoms arranged in a lattice arrangement called crystals. There are a variety of crystal structures like cubic, hexagonal, cubic with an atom in the center of the cube, called body centered cubic, cubic with an atom in the center of each face of the cube, called face centered cubic, and others. The particular structure depends on the relative sizes of the atoms that are nestled together to form the crystal. The reason that materials take crystal form is that these neat geometrical structures represent the lowest energy configuration of the collection of atoms making up the material. To dislodge an atom from the crystal structure requires the addition of energy.



Theoretically, at a temperature of absolute zero, the atoms of a crystal lie at their lowest energy position without moving at all. As thermal energy is added to the crystal it is manifest by vibration of the atoms about this equilibrium location. Within the limits of fairly small vibrations the electric forces bonding the atoms together stretch or compress a bit to a higher energy configuration. Each atom acts as though it were connected to its neighbors by little springs. The added energy is stored in the crystal as the kinetic energy of the atoms in motion and the potential energy of the compressed or stretched springs.

Let us consider the oscillation of the atoms in one-dimensional crystal simulated by the chain of the balls with the masses m_1 and m_2 . The force applied to every atom depends upon the relative displacement of the nearby atoms and stiffness c of the virtual springs. Therefore, the displacement u of every atom in one-dimensional crystal is described by the equations:

$$\begin{cases} m_1 \ddot{u}_n = -\chi (2u_n - u_{m-1} - u_m) \\ m_2 \ddot{u}_m = -\chi (2u_m - u_n - u_{n+1}) \end{cases}$$

These equations determine the oscillatory motion of the atoms:

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 $\begin{cases} u_n = A_1 \exp \bigl(i (kan - \omega t) \bigr) \\ u_m = A_2 \exp \bigl(i (kam - \omega t) \bigr) \end{cases}$

where a/2 is the distance between the nearest atoms; k=2p/l is the wave factor, l is the wavelength of the wave in crystal. The equations mentioned above have two solutions for w :

$$\omega_1^2 = \frac{\omega_0^2}{2} \left(1 - \sqrt{1 - \gamma^2 \sin^2(ak/2)} \right) - \text{acoustic branch}$$
$$\omega_2^2 = \frac{\omega_0^2}{2} \left(1 + \sqrt{1 - \gamma^2 \sin^2(ak/2)} \right) - \text{optical branch}$$

where $g^2 = 4m_1m_2/(m_1+m_2)^2$; $w_0^2 = 2c (m_1+m_2)/m_1m_2$. These equations determine two branches of the dispersion curve (so called acoustic and optical branches).

Let us consider the types of oscillation in a crystal for these two branches. In the case of the long-wave approximation ($ak \ll 1$) in acoustic branch the k atoms move synchronously and deviation of every atom is about the same at

any moment of the time (see this case at the bottom of the animation); in optical branch the atoms move in antiphase (it is shown on top of animation). For the shortest waves ($k = 2\pi/\lambda = 2\pi/a$) in acoustic branch the lighter atoms are still and more heavy atoms oscillate; in the optical branch the situation is inverse (these cases are shown in the middle of animation). Oscillation of atoms in optical branch polarizes the matter electrically and this type of oscillation can be excited by infra-red optical radiation. This is the reason why this branch was called "optical". We can see that the modes differ in the details of how the atoms move, but they both represent energy stored in the crystal, being passed back and forth between the kinetic energy of the atoms and the potential energy of the "springs". The temperature of the crystal is proportional to the average kinetic energy of the atoms.

There are some limitations to this mechanical description of what is going on in crystal vibrations. Because we are dealing with objects as small as individual atoms, quantum mechanical effects may not be neglected. For example, in a metal sample large enough to work with in a laboratory, there may be millions of individual crystals each with millions of individual atoms. On a laboratory size scale, it appears that we can add energy to the sample in any amount, as if the crystal were really composed of weights and springs. In fact, energy may only be added

in multiples of some minimum amount. We call that minimum amount of vibrational energy a "phonon" analogous to the photon energy packet familiar in electromagnetic radiation. Energy addition appears continuous on the laboratory scale because the phonon is so small. On the scale of the atoms in the crystals however, the phonon magnitude is significant and only vibration modes and amplitudes which differ in energy by whole phonon multiples are allowed.

SEMI CONDUCTORS AND THEIR PROPERTIES

A semiconductor is a substance, usually a solid chemical element or compound, which can conduct electricity under some conditions but not others, making it a good medium for the control of electrical current. Its conductance varies depending on the current or voltage applied to a control electrode, or on the intensity of irradiation by infrared (IR), visible light, ultraviolet (UV), or X rays.

The specific properties of a semiconductor depend on the impurities, or dopants, added to it. An N-type semiconductor carries current mainly in the form of negatively-charged electrons, in a manner similar to the conduction of current in a wire. A P-type semiconductor carries current predominantly as electron deficiencies called holes. A hole has a positive electric charge, equal and opposite to the charge on an electron. In a semiconductor material, the flow of holes occurs in a direction opposite to the flow of electrons.

Elemental semiconductors include antimony, arsenic, boron, carbon, germanium, selenium, silicon, sulfur, and tellurium. silicon is the best-known of these, forming the basis of most integrated circuits (ICs). Common semiconductor compounds include gallium arsenide, indium antimonide, and the oxides of most metals. Of these, gallium arsenide (GaAs) is widely used in low-noise, high-gain, weak-signal amplifying devices.

A semiconductor device can perform the function of a vacuum tube having hundreds of times its volume. A single integrated circuit (IC), such as a microprocessor chip, can do the work of a set of vacuum tubes that would fill a large building and require its own electric generating plant.

Conductivity of semiconductors

A semiconductor is very different from a conductor. In fact, a semiconductor is almost an insulator. The only difference between semiconductor and insulator is energy levels. An insulator requires a great deal of energy (maybe 10 eV) to break an electron free from an atom. A semiconductor requires only about 1 eV to free an electron. A conductor has some electrons free to move without any added energy.

When a semiconductor is extremely cold, almost all electrons are held tightly by individual atoms. It is hard to make them move through the material. When a semiconductor is heated, the heat energy knocks loose some of the electrons. These loose electrons can move through the material easily. The conductivity is higher. As more heat energy is added, more electrons break away from individual atoms, becoming free to move through the semiconductor. Higher temperature means greater conductivity. This is NOT true for conductors. Conductors already have plenty of loose electrons. Higher temperature tends to go into these loose electrons. Adding energy makes the loose electrons move in less organized patterns. It becomes more difficult to control the direction of the electrons. This makes the conductor have less conductivity when temperature is higher.

Intrinsic Semiconductor

A silicon crystal is different from an insulator because at any temperature above absolute zero temperature, there is a finite probability that an electron in the lattice will be knocked loose from its position, leaving behind an electron deficiency called a "hole".

If a voltage is applied, then both the electron and the hole can contribute to a small current flow.
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The conductivity of a semiconductor can be modeled in terms of the band theory of solids. The band model of a semiconductor suggests that at ordinary temperatures there is a finite possibility that electrons can reach the conduction band and contribute to electrical conduction.

The term intrinsic here distinguishes between the properties of pure "intrinsic" silicon and the dramatically different properties of doped n-type or p-type semiconductors.



Extrinsic semiconductor

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An extrinsic semiconductor is a semiconductor that has been *doped*, that is, into which a doping agent has been introduced, giving it different electrical properties than the intrinsic (pure) semiconductor. Doping involves adding dopant atoms to an intrinsic semiconductor, which changes the electron and hole carrier concentrations of the semiconductor at thermal equilibrium. Dominant carrier concentrations in an extrinsic semiconductor classify it as either an n-type or p-type semiconductor. The electrical properties of extrinsic semiconductors make them essential components of many electronic devices.

Semiconductor doping

Semiconductor doping is the process that changes an intrinsic semiconductor to an extrinsic semiconductor. During doping, impurity atoms are introduced to an intrinsic semiconductor. Impurity atoms are atoms of a different element than the atoms of the intrinsic semiconductor. Impurity atoms act as either donors or acceptors to the intrinsic semiconductor, changing the electron and hole concentrations of the semiconductor. Impurity atoms are classified as donor or acceptor atoms based on the effect they have on the intrinsic semiconductor. Donor impurity atoms have more valence electrons than the atoms they replace in the intrinsic semiconductor lattice. Donor impurities "donate" their extra valence electrons to a semiconductor.

Excess electrons increase the electron carrier concentration (n_0) of the semiconductor, making it n-type.

Acceptor impurity atoms have less valence electrons than the atoms they replace in the intrinsic semiconductor. They "accept" electrons from the semiconductor's valence band. This provides excess holes to the intrinsic semiconductor. Excess holes increase the hole carrier concentration (p_0) of the semiconductor, creating a p-type semiconductor.

Semiconductors and dopant atoms are defined by the column of the periodic table of elements they fall in. The column definition of the semiconductor determines how many valence electrons its atoms have and whether dopant atoms act as the semiconductor's donors or acceptors. Group IV semiconductors use group V atoms as donors and group III atoms as acceptors.

Group III-V semiconductors use group VI atoms as donors and group II atoms as acceptors. Group III-V semiconductors can also use group IV atoms as either donors or acceptors. When a group IV atom replaces the group III element in the semiconductor lattice, the group IV atom acts as a donor. Conversely, when a group IV atom replaces the group V element, the group IV atom acts as an acceptor. Group IV atoms can act as both donors and acceptors; therefore, they are known as amphoteric impurities.

	Intrinsic semiconductor	Donor atoms	Acceptor atoms
Group IV semiconductors	Silicon, Germanium	Phosphorus, Arsenic	Boron, Aluminium
Group III-V semiconductors	Aluminum phosphide, Aluminum arsenide, Gallium arsenide	Selenium, Tellurium, Silicon, Germanium	Beryllium, Zinc, Cadmium, Silicon, Germanium

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The two types of extrinsic semiconductor

N-type semiconductors



Band structure of an n-type semiconductor. Dark circles in the conduction band are electrons and light circles in the valence band are holes. The image shows that the electrons are the majority charge carrier.

Extrinsic semiconductors with a larger electron concentration than hole concentration are known as n-type semiconductors. The phrase 'n-type' comes from the negative charge of the electron. In n-type semiconductors, electrons are the majority carriers and holes are the minority carriers. N-type semiconductors are created by doping an intrinsic semiconductor with donor impurities. In an n-type semiconductor, the Fermi energy level is greater than the that of the intrinsic semiconductor and lies closer to the conduction band than the valence band.

P-type semiconductors



Band structure of a p-type semiconductor. Dark circles in the conduction band are electrons and light circles in the valence band are holes. The image shows that the holes are the majority charge carrier

As opposed to n-type semiconductors, p-type semiconductors have a larger hole concentration than electron concentration. The phrase 'p-type' refers to the positive charge of the hole. In p-type

semiconductors, holes are the majority carriers and electrons are the minority carriers. P-type semiconductors are created by doping an intrinsic semiconductor with acceptor impurities. P-type semiconductors have Fermi energy levels below the intrinsic Fermi energy level. The Fermi energy level lies closer to the valence band than the conduction band in a p-type semiconductor.

Utilization of extrinsic semiconductors

Extrinsic semiconductors are components of many common electrical devices. A semiconductor diode (devices that allow current flow in only one direction) consists of p-type and n-type semiconductors placed in junction with one another. Currently, most semiconductor diodes use doped silicon or germanium.

Transistors (devices that enable current switching) also make use of extrinsic semiconductors. Bipolar junction transistors (BJT) are one type of transistor. The most common BJTs are NPN and PNP type. NPN transistors have two layers of n-type semiconductors sandwiching a p-type semiconductor. PNP transistors have two layers of p-type semiconductors sandwiching an n-type semiconductor.

Field-effect transistors (FET) are another type of transistor implementing extrinsic semiconductors. As opposed to BJTs, they are unipolar and considered either N-channel or P-channel. FETs are broken into two families, junction gate FET (JFET) and insulated gate FET (IGFET).

Other devices implementing the extrinsic semiconductor:

- Lasers
- Solar cells
- Photodetectors
- Light-emitting diodes
- Thyristors

HALL EFFECT

Experiment that shows the sign of the charge carriers in a conductor. In 1879 E. H. Hall discovered that when he placed a metal strip carrying a current in a magnetic field, a voltage

difference was produced across the strip. The side of the strip that is at the higher voltage depends on the sign of the charge carrier; Hall's work demonstrated that in metals the charge carriers are negative. Today it is known that this negative charge carrier is the electron. The Hall effect has again become an active area of research with the discovery of the quantized Hall effect, for which Klaus von Klitzing was awarded the 1985 Nobel Prize in physics. Before von Klitzing's work it was thought that the amount of voltage difference across the strip varied in direct proportion to the strength of the magnetic field—the greater the magnetic field, the greater the voltage difference. Von Klitzing showed that under the special conditions of low temperature, high magnetic field, and two-dimensional electronic systems (in which the electrons are confined to move in planes), the voltage difference increases as a series of steps with increasing magnetic field.



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Schematic of the Hall effect in a long, thin bar of semiconductor with four ohmic contacts. The direction of the magnetic field B is along the z-axis and the sample has a finite thickness d.

DIELECTRICS

A dielectric is a nonconducting substance, i.e. an insulator. The term was coined by William Whewell in response to a request from Michael Faraday. Whewell considered "diaelectric", from the Greek "*dia*" meaning "through", since an electric field passes through the material but felt that "dielectric" was easier to pronounce. Although "dielectric" and "insulator" are generally considered synonymous, the term "dielectric" is more often used when considering the effect of alternating electric fields on the substance while "insulator" is more often used when the material is being used to withstand a high electric field. Von Hippel, in his seminal book takes this definition further. He states,

"*Dielectrics*... are not a narrow class of so-called insulators, but the broad expanse of *nonmetals* considered from the standpoint of their interaction with electric, magnetic, of electromagnetic fields. Thus we are concerned with gases as well as with liquids and solids, and with the storage of electric and magnetic energy as well as its dissipation."

Dielectrics is the study of dielectric materials and involves physical models to describe how an electric field behaves inside a material. It is characterized by how an electric field interacts with an atom and is therefore possible to approach from either a classical interpretation or a quantum one.

Many phenomena in electronics, solid state and optical physics can be described using the underlying assumptions of the dielectric model. This can mean that the same mathematical objects can go by many different names.

Applications

Capacitors

Commercially manufactured capacitors typically use a solid dielectric material with high permittivity as the intervening medium between the stored positive and negative charges. This material is often referred to in technical contexts as the "capacitor dielectric". The most obvious advantage to using such a dielectric material is that it prevents the conducting plates on which

the charges are stored from coming into direct electrical contact. More significantly however, a high permittivity allows a greater charge to be stored at a given voltage.

Dielectric materials used for capacitors are also chosen such that they are resistant to ionization. This allows the capacitor to operate at higher voltages before the insulating dielectric ionizes and begins to allow undesirable current flow.

Cable insulation

The term "dielectric" may also refer to the insulation used in power and RF cables.

Some practical dielectrics

Dielectric materials can be solids, liquids, or gases. In addition, a high vacuum can also be a useful, lossless dielectric even though its relative dielectric constant is only unity.

Solid dielectrics are perhaps the most commonly used dielectrics in electrical engineering, and many solids are very good insulators. Some examples include porcelain, glass, and most plastics. Air, nitrogen and sulfur hexafluoride are the three most commonly used gaseous dielectrics.

- Industrial coatings such as parylene provide a dielectric barrier between the substrate and its environment.
- Mineral oil is used extensively inside electrical transformers as a fluid dielectric and to assist in cooling. Dielectric fluids with higher dielectric constants, such as electrical grade castor oil, are often used in high voltage capacitors to help prevent corona discharge and increase capacitance.

• Because dielectrics resist the flow of electricity, the surface of a dielectric may retain *stranded* excess electrical charges. This may occur accidentally when the dielectric is rubbed (the triboelectric effect). This can be useful, as in a Van de Graaff generator or electrophorus, or it can be potentially destructive as in the case of electrostatic discharge.

• Specially processed dielectrics, called electrets (also known as ferroelectrics), may retain excess internal charge or "frozen in" polarization. Electrets have a semipermanent external electric field, and are the electrostatic equivalent to magnets. Electrets have numerous practical applications in the home and industry.

• Some dielectrics can generate a potential difference when subjected to mechanical stress, or change physical shape if an external voltage is applied across the material. This property is called piezoelectricity. Piezoelectric materials are another class of very useful dielectrics.

• Some ionic crystals and polymer dielectrics exhibit a spontaneous dipole moment which can be reversed by an externally applied electric field. This behavior is called the ferroelectric effect. These materials are analogous to the way ferromagnetic materials behave within an externally applied magnetic field. Ferroelectric materials often have very high dielectric constants, making them quite useful for capacitors.

CLAUSIUS-MOSSOTTI RELATION

The Clausius–Mossotti equation is named after the Italian physicist Ottaviano-Fabrizio Mossotti, whose 1850 book analyzed the relationship between the dielectric constants of two different media, and the German physicist Rudolf Clausius, who gave the formula explicitly in his 1879 book in the context not of dielectric constants but of indices of refraction. The same formula also arises in the context of conductivity, in which it is known as Maxwell's formula. It arises yet again in the context of refractivity, in which it is known as the Lorentz–Lorenz equation.

Clausius-Mossotti factor

The Clausius–Mossotti factor can be expressed in terms of complex permittivities:

$$\begin{split} K(\omega) &= \frac{\epsilon_p^* - \epsilon_m^*}{\epsilon_p^* + 2\epsilon_m^*} \\ \epsilon^* &= \epsilon + \frac{\sigma}{i\omega} = \epsilon - \frac{i\sigma}{\omega} \end{split}$$

Where

 ε is the permittivity

(where the subscript p refers to a lossless dielectric sphere suspended in a medium m)

 σ is the conductivity

 ω is the angular frequency of the applied electric field

i is the square root of -1

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In the context of electro kinetic manipulation, the real part of the Clausius-Mossotti factor is a determining factor for the dielectrophoretic force on a particle, where as the imaginary part is a determining factor for the electro rotational torque on the particle. Other factors are, of course, the geometries of the particle to be manipulated and the electric field.

FERROELECTRIC CRYSTALS

Ferroelectricity is a physical property of a material whereby it exhibits a spontaneous electric polarization, the direction of which can be switched between equivalent states by the application of an external electric field. The experimental evidence for this domain switching is a hysteresis loop. The term is used in analogy to ferromagnetism, in which a material exhibits a permanent magnetic moment. Ferromagnetism was already known when ferroelectricity was discovered in 1920 in Rochelle salt by Valasek. Thus, the prefix "ferro", meaning iron, was used to describe the property despite the fact that most ferroelectric materials do not have iron in their lattice.

Ferroelectrics are key materials in microelectronics. Their excellent dielectric properties make them suitable for electronic components such as tunable capacitors and memory cells.

Applications

The nonlinear nature of ferroelectric materials can be used to make capacitors with tunable capacitance. Typically, a ferroelectric capacitor simply consists of a pair of electrodes sandwiching a layer of ferroelectric material. The permittivity of ferroelectrics is not only tunable but commonly also very high in absolute value, especially when close to the phase transition temperature. This fact makes ferroelectric capacitors small in size compared to dielectric (non-tunable) capacitors of similar capacitance.

The spontaneous polarization of ferroelectric materials implies a hysteresis effect which can be used as a memory function. Indeed, ferroelectric capacitors are used to make ferroelectric RAM for computers and RFID cards. These applications are usually based on thin films of ferroelectric materials as this allows the high coercive field required to switch the polarization to be achieved with a moderate voltage, though a side effect of this is that a great deal of attention needs to be paid to the interfaces, electrodes and sample quality for devices to work reliably.

All ferroelectrics are required by symmetry considerations to be also piezoelectric and pyroelectric. The combined properties of memory, piezoelectricity, and pyroelectricity make ferroelectric capacitors very useful, e.g. for sensor applications. Ferroelectric capacitors are used in medical ultrasound machines (the capacitors generate and then listen for the ultrasound ping used to image the internal organs of a body), high quality infrared cameras (the infrared image is projected onto a two dimensional array of ferroelectric capacitors capable of detecting temperature differences as small as millionths of a degree Celsius), fire sensors, sonar, vibration sensors, and even fuel injectors on diesel engines. As well, the electro-optic modulators that form the backbone of the Internet are made with ferroelectric materials.

One new idea of recent interest is the *ferroelectric tunnel junction (FTJ)* in which a contact made up by nanometer-thick ferroelectric film placed between metal electrodes. The thickness of the ferroelectric layer is thin enough to allow tunneling of electrons. The piezoelectric and interface effects as well as the depolarization field may lead to a giant electro resistance (GER) switching effect.

Another hot topic is multi ferroics, where researchers are looking for ways to couple magnetic and ferroelectric ordering within a material or hetero structure; there are several recent reviews on this topic.

FERROELECTRIC DOMAINS

Ferroelectric domains, sometimes known as Weiss domains, are areas of local dipole alignment - with an associated net dipole moment and net polarization.



Domains are separated from one another by 'domain walls'. These domain boundaries are usually described according to the angle between the domains that they separate. The most common found are 90° and 180° boundaries.

The picture above shows an area of a ferroelectric material clearly displaying a domain structure. The dark lines are 90° domain walls.

The domain structure and behaviour of a material will critically affect its operational performance

Most importantly, the domain wall mobility will affect the high frequency performance of the material when used as an actuator.

In the presence of an applied electric field, domains that are aligned with the direction of the field will grow at the expense of the less well aligned domains. This may be visualized in terms of the boundary between the domains moving.

Several synthesis and processing techniques may be adopted to control the mobility of the domain wall and hence reduce losses.

The domain structure can also change over time by a process known as ageing. This causes degradation to the dielectric properties and often causes device failure due to loss of insulation resistance.

If high frequency operation is required with very low losses and no domain ageing then electrostrictive materials may offer a solution. Electrostrictive ceramics possess no spontaneous polarization and no domain structure. Examples of such materials are lead magnesium niobate titanate (PMNT) and various lead lanthanum zirconate titanate (PLZT) compositions

KARAPAGAM ACADEMY OF HIGHER EDUCATION, COIMBATORE-21 POSSIBLE QUESTIONS

UNIT I

- 1. Define Hall Effect. Explain the dielectric materials with significance properties.
- 2. Define the reciprocal lattice. Explain the various properties of reciprocal lattice
- 3. Describe about the Clausius –Mossoti equation.
- 4. Describe in detail about interplanar spacing for SC, FCC, BCC.
- 5. Describe the Bragg condition in terms of reciprocal lattice and explain NaCl structure
- 6. Describe the neutron scattering and explain how it is different from X-ray diffraction.
- 7. Describe the rotatory crystal method of X-ray diffraction.
- 8. What is mean by Hall effect? Explain briefly the physical origin and uses of Hall effect.
- 9. What is Dielectric? Explain Clausius Mossoti equation.
- 10. Explain the vibrations of one dimensional diatomic lattice

KARPAGAM ACADEMY OF HIGHER EDUCATION, COIMBATORE-21

DEPARTMENT OF PHYSICS

I M.SC PHYSICS

BATCH: 2017-2019

CONDENSED MATTER PHYSICS (17PHP101) MULTIPLE CHOICE QUESTIONS

Questions	option 1	option 2	option 3	option 4	Answer
UNIT I					
The correct order of the coordination number is SC, BCC, FCC and HCP unit cells is	12, 8, 12, 6	6, 8, 12, 12	8, 6, 12, 12	6, 12, 12, 8	6, 8, 12, 12
The number of atoms present in the unit cell of HCP structure is	2	4	6	7	6
Which of the following elements is a covalently bonded crystal?	aluminium	sodium chloride	germanium	lead	germanium
The forbidden energy gap of carbon in diamond structure is	7.0 eV	1.0 eV	0.01 eV	none	7.0 eV
For silicon doped with trivalent impurity,	ne >> nh	ne > nh	nh >> ne	nh > ne	nh >> ne
Metallic bond is not characterized by	ductility	high conductivity.	directionality	opacity	directionality
If the Fermi energy of silver at 0 K is 5 electron volt, the mean energy of electron in silver at 0 K is	6 electron volt.	12 electron volt.	1.5 electron volt.	3 electron volt.	3 electron volt.
The Fermi level in an n-type semiconductor at 0 K lies	below the donor level.	Half way between the bottom of conduction band and donor level.	Exactly in the middle of hand gap.	Half way between the top of valence band and the acceptor level.	Half way between the bottom of conduction band and donor level.
Piezoelectric effect is the production of electricity by	chemical effect.	pressure		temperature	pressure
Electromigration in metallization refers to the diffusion (under the influence of current) of	Al	Cu in A1-Cu alloy.	Si	Na	Al
Fine grain sizes are obtained by	slow cooling.	increasing nucleation rate	decreasing growth rate	fast cooling	slow cooling
Zinc has hcp structure. In a unit cell of zinc, the zinc atoms occupy	74% of volume of unit cell.	80% of volume of unit cell.	68% of volume of unit cell.	90% of volume of unit cell.	74% of volume of unit cell.
The density of carriers in a pure semiconductor is proportional to	exp(-Eg/kT)	exp(-2Eg/kT)	exp(-2Eg / kT2)	exp(-Eg/2kT)	exp(-Eg/kT)
The probability of occupation of an energy level E, when $E - EF = kT$, is given by	0.73	0.63	0.5	0.27	0.27
majority charge carriers in p-type semiconductor are	ions	holes	free electrons.	conduction electrons.	holes
Polarization in a dielectric on application of electric field is	Displacement/separat ion of opposite charge centres.	Passing of current through dielectric.	Breaking of insulation.	Excitation of electrons to higher energy level.	Displacement/separat ion of opposite charge centres.
The radius of first Bohr orbit in the hydrogen atom is about	0.053 Å	0.530 Å	5.31 Å	53.10 Å	0.530 Å
The Fermi level is	an average value of all available energy levels.	an energy level at the top of the valence band.	the highest occupied energy level at 0 0C.	the highest occupied energy level at 0 K.	the highest occupied energy level at 0 K.
Among the common dielectric materials, the highest dielectric strength is possessed by	mica.	polyethylene.	PVC	transformer oil.	mica.

In intrinsic semiconductor there are	no mobile holes.	no free electrons.	as many free electrons as there are holes.	neither free electrons nor mobile holes.	as many free electrons as there are holes.
Mobility of electron is	Average flow of electrons per unit field.	Average applied field per unit drift velocity.	Average drift velocity per unit field.	Reciprocal of conductivity per unit charge.	Average drift velocity per unit field.
In a dielectric, the power loss is proportional to	ω	ω ^2	1/ω	1/ω2	ω
Above curie temperature, the spontaneous polarization for ferro electric materials is	zero	1	half	infinity	zero
Fermi level represents the energy level with probability of its occupation of	0 %.	25 %.	50 %.	100 %.	50 %.
The acceptor type impurity is formed by adding impurity of valency	6	5	4	3	3
If the atomic number of an element is Z, and its atomic mass number is A, the number of protons in its nucleus is	А	Z	A-Z	A/Z	Z
Miller indices of the diagonal plane of a cube are	2,0,0	1,1,1	0,1,0	1,1,0	1,1,0
Highest electrical resistivity exists in	platinum wire.	nichrome wire.	silver wire.	kanthal wire.	nichrome wire.
Hall effect can be used to measure	mobility of semiconductors.	conductivity of semiconductors.	resistivity of semiconductors.	all of these.	all of these.
The unit of dielectric constant is	Dimensionless	Fm-1	CV-1	Fc-1	Fm-1
Pure silicon at zero K is an	intrinsic semiconductor.	extrinsic semiconductor.	metal.	insulator.	insulator.
The dielectric strength of a material is the highest	current which can pass through it.	voltage that can be applied to it.	field (voltage per meter thickness) that can be with-stood by it.	current density that can be transmitted by it.	field (voltage per meter thickness) that can be with-stood by it.
A Ge atom contains	four protons	four valence electrons	six valence electrons	only two electron orbits	four valence electrons
The energy required to break a covalent bond in a semiconductor	is equal to 1 eV	is equal to the width of the forbidden gap	is greater in Ge than in Si	is the same in Ge and Si	is equal to the width of the forbidden gap
An electron in the conduction band	is located near the top of the crystal	has no charge	has a higher energy than an electron in the valence band	is bound to its parent atom	has a higher energy than an electron in the valence band
At 0° K, all the valence electrons in an intrinsic semiconductor	are in the valence band	are in the forbidden gap	are in the conduction band	are free electrons	are in the valence band
Insulating material used in spark plug is	rubber	porcelain	mica	Polysterene	porcelain
Which of the following has piezoelectric properties:	corundum	neoprene	quartz	glass	quartz
For metallization, the property not desirable is	reproducibility	quick dissipation of heat	low thermal conductivity	high melting point	reproducibility
The correct order of the co-ordination number in simple cubic, body centered cubic and face centered cubic of unit cell is	6, 8, 12.	8, 12, 12.	12, 8, 12.	6, 8, 8.	6, 8, 12.

At absolute zero temperature, the probability of finding an electron at an energy level E is zero when	E < EF	E > Ef	E = Ef/2	None	E > Ef
In an intrinsic semiconductor, there are	no mobile holes.	no free electrons.	neither free electrons nor mobile holes.	equal number of free electrons and mobile holes.	equal number of free electrons and mobile holes.
The probability of occupancy of electrons above Fermi level at T=0°K is	0 %.	25%.	50%.	100%.	0 %.
In a ferroelectric material, the spontaneous polarization vanishes above	Transition temperature.	Debye temperature.	Fermi temperature.	Curie temperature.	Curie temperature.
P-type and N-type extrinsic semiconductors are formed by adding impurities of valency	5 and 3 respectively.	5 and 4 respectively.	3 and 5 respectively.	3 and 4 respectively.	3 and 5 respectively.
Which one is a secondary form of energy?	Furnace oil	natural gas	electricity	coal	electricity
In an intrinsic semiconductor, the Fermi level	Lies at the center of forbidden energy gap.	Is near the conduction band.	Is near the valence band.	May be anywhere in the forbidden energy gap.	Lies at the center of forbidden energy gap.
Most commonly used semiconductor material is	Silicon	Germanium	Mixture of silicon and germanium	None of the above.	Silicon
At room temperature a semiconductor material is	Perfect insulator	Conductor	Slightly conducting	Any one of the above.	Slightly conducting
The process of adding impurities to a pure semiconductor is called	Mixing	Doping	Diffusing	None of the above	Doping
Impurities like boron, aluminum, gallium or indium are added to intrinsic semiconductor to form	N-type doped semiconductor	P-type doped semiconductor	A junction diode	All of these	P-type doped semiconductor
In a N-type semiconductor, the position of Fermi-level	Is lower than the center of energy gap	Is at the center of energy gap	Is higher than the center of energy gap	Can be any where	Is higher than the center of energy gap
In a metal	The electrical conduction is by electrons and holes	The conductivity decreases with the rise in temperature	The conduction band is empty	None of the above	The conductivity decreases with the rise in temperature
The energy gap in a semiconductor	Increases with temperature	Does not change with temperature	Decreases with temperature	Is zero	Decreases with temperature
In a single-component condensed system, if degree of freedom is zero, maximum number of phases that can co-exist	0	1	2	3	2
Impurity not responsible for temper embrittlement	Sn	Sb	Si	As	Si
Miller indices for Octahedral plane in cubic crystal	1,0,0	1,1,0	1,1,1	none	1,1,1
Repeatable entity of a crystal structure is known as	Crystal	Lattice	Unit cell	Miller indices	Unit cell
Coordination number for closest packed crystal structure	16	12	8	4	12
Coordination number in simple cubic crystal structure	1	2	3	4	2
The atomic diameter of an BCC crystal (if a is lattice parameter) is	a	a/2	a/(4√3)	a/(4√2)	a/(4√3)
Which of the following is not the characteristic of ionic solids?	electrical conductivity in the	Brittle nature.	Very strong forces of interactions.	Anisotropic nature.	electrical conductivity in the

Graphite is a good conductor of electricity due to the presence of	lone pair of electrons	free valence electrons	cations	anions	free valence electrons
Electrical conductivity of insulators is the range	10-10(Ω-mm)-1	10-10(Ω-cm)-1	10-10(Ω-m)-1	10-8(Ω-m)-1	10-10(Ω-mm)-1
Units for electric field strength	A/cm2	mho/meter	cm2/V.s	V/cm	cm2/V.s
Energy band gap size for semiconductors is in the rangeeV.	1 to 2	2 to 3	3 to 4	> 4	2 to 3
Energy band gap size for insulators is in the range eV.	1 to 2	2 to 3	3 to 4	> 4	3 to 4
Flow of electrons is affected by the following	Thermal vibrations	Impurity atoms	Crystal defects	all	all
Not a super conductive metallic element	Fe	Al	Ti	W	Al
Fermi energy level for intrinsic semiconductors lies	At middle of the band gap	Close to conduction band	Close to valence band	None	Close to valence band
Fermi energy level for p-type extrinsic semiconductors lies	At middle of the band gap	Close to conduction band	Close to valence band	None	Close to conduction band
Fermi energy level for n-type extrinsic semiconductors lies	At middle of the band gap	Close to conduction band	Close to valence band	None	Close to conduction band
Not an example for intrinsic semiconductor	Silicon	Al	germanium	Sn	Silicon
	Equal	Greater than	Less than	Can not define	Less than
alectrons	Equal	Greater than	Less than	Can not define	Can not define
ni p-type semiconductors, number of notes number of	Equal	Greater than	Less than	Can not define	Equal
Mobility of holes is mobility of electrons in intrinsic semiconductors.	Equal	Greater than	Less than	Can not define	Can not define
Fermi level for extrinsic semiconductor depends on	Donor element	Impurity concentration	Temperature	All	All
Value of dielectric constant for a material	Equal to 1	Greater than 1	Less than 1	Zero.	Equal to 1
High dielectric constant material is must for	Insulation of wires	Generators	Switch bases	Generators.	Insulation of wires
Example for ferro-electric material	Potassium niobate	Lead titanate	Lead zirconate	quartz	Lead titanate

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UNIT - II

Crystal defects: Classification of defects - Points defect - The Schottky defect - The Frenkel defect -colour centers - F center - other colour centers - Production of colour centers by X rays or practice irradiation – Defect and energy state.

Dislocations - Slip and plastic deformation - Shear strength of single crystals - Edge dislocation - Screw dislocation - Stress field around an edge dislocation.

Ultrasonics: Non destructive testing and applications.

CLASSIFICATION OF DEFECTS

POINT DEFECT

Point defects are defects which are not extended in space in any dimension. There is not strict limit for how small a "point" defect should be, but typically the term is used to mean defects which involve at most a few extra or missing atoms without an ordered structure of the defective positions. Larger defects in an ordered structure are usually considered dislocation loops. For historical reasons, many point defects especially in ionic crystals are called 'centers': for example the vacancy in many ionic solids is called an F-center.

Vacancies are sites which are usually occupied by an atom but which are unoccupied. If a neighboring atom moves to occupy the vacant site, the vacancy moves in the opposite direction to the site which used to be occupied by the moving atom. The stability of the surrounding crystal structure guarantees that the neighboring atoms will not simply collapse around the vacancy. In some materials, neighboring atoms actually move away from a vacancy, because they can better form bonds with atoms in the other directions. A vacancy (or pair of vacancies in an ionic solid) is sometimes called a Schottky defect.

Interstitials are atoms which occupy a site in the crystal structure at which there is usually not an atom. They are generally high energy configurations. Small atoms in some crystals can occupy interstices without high energy, such as hydrogen in palladium



Schematic illustration of some simple point defect types in a monatomic solid

A nearby pair of a vacancy and an interstitial is often called a Frenkel defect or Frenkel pair. Impurities occur because materials are never 100% pure. In the case of an impurity, the atom is often incorporated at a regular atomic site in the crystal structure. This is neither a vacant site nor is the atom on an interstitial site and it is called a substitutional defect. The atom is not supposed to be anywhere in the crystal, and is thus an impurity.

Anti-site defects occur in an ordered alloy. For example, some alloys have a regular structure in which every other atom is a different species, for illustration assume that type A atoms sit on the cube corners of a cubic lattice, and type B atoms sit in center of the cubes. If one cube has an A atom at its center, the atom is on a site usually occupied by an atom, but it is not the correct type. This is neither a vacancy nor an interstitial, nor an impurity.

Topological defects are regions in a crystal where the normal chemical bonding environment is topologically different from the surroundings. For instance, in a perfect sheet of graphite (graphene) all atoms are in rings containing six atoms. If the sheet contains regions where the number of atoms in a ring is different from six, while the total number of atoms remains the same, a topological defect has formed. An example is the Stone Wales defect in nanotubes, which consists of two adjacent 5-membered and two 7-membered atom rings.



Schematic illustration of defects in a compound solid, using GaAs as an example.

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M.Sc Physics

2017-2018

Also amorphous solids may contain defects. These are naturally somewhat hard to define, but sometimes their nature can be quite easily understood. For instance, in ideally bonded amorphous silica all Si atoms have 4 bonds to O atoms and all O atoms have 2 bonds to Si atom. Thus e.g. an O atom with only one Si bond can be considered a defect in silica.

Complexes can form between different kinds of point defects. For example, if a vacancy encounters an impurity, the two may bind together if the impurity is too large for the lattice. Interstitials can form 'split interstitial' or 'dumbbell' structures where two atoms effectively share an atomic site, resulting in neither atom actually occupying the site.

THE SCHOTTKY DEFECT

A Schottky defect is a type of point defect in a crystal lattice named after Walter H. Schottky.

The defect forms when oppositely charged ions leave their lattice sites, creating vacancies. These vacancies are formed in stoichiometric units, to maintain an overall neutral charge in the ionic solid. The vacancies are then free to move about as their own entities. Normally these defects will lead to a decrease in the density of the crystal. The following are the chemical equations in Kröger-Vink Notation for the formation of Schottky defects in TiO2 and BaTiO3.

$$\emptyset \Leftrightarrow V_{Ba}'' + V_{Ti}'''' + 3V_O^{\bullet \bullet}$$

This can be illustrated schematically with a two-dimensional diagram of a sodium chloride crystal lattice:



The defect-free NaCl structure



Schottky defects within the NaCl structure

Definition

If in an ionic crystal of type A+B- an equal number of cations and anions are missing from their lattice sites so that electrical neutrality as well as stoichiometry is maintained this is called a Schottky Defect.

It is a vacancy defect (due to missing ions) and also a stoichiometric defect, as the ratio of the number of cations and anions remains the same.

Examples

This type of defect is shown in compounds with:

- highly ionic compounds
- high co-ordination number
- small difference in sizes of cations and anions

Examples : NaCl, KCl, CsCl, KBr, AgCl. etc.

Experimental observations show that at room temperature in an NaCl crystal there is one Schottky defect per 1016 ions.

FRENKEL DEFECT

The Frenkel Defect is shown by ionic solids. The smaller ion (usually the cation) is displaced from its lattice position to an interstitial site. It creates a vacancy defect at its original site and an interstitial defect at its new location.

Definition

A Frenkel defect, Frenkel point defect in a crystal lattice. The defect forms when an atom or cation leaves its place in the lattice, creating avacancy, and becomes an interstitial by

lodging in a nearby location not usually occupied by an atom. Frenkel defects occur due to thermal vibrations, and it is theorized that there will be no defects in a crystal at 0 K. The phenomenon is named after the Soviet physicist Yakov Frenkel, who discovered it in 1926.

Examples

It is shown in ionic solids with large size difference between the anion and cation (with the cation usually smaller due to an increased effective nuclear charge) Some solids which display this defect - ZnS, AgCl, AgBr, AgI (due to the comparatively smaller size of Zn2+ and Ag+ ions)

To be noted : AgBr shows both Frenkel as well as Schottky defects.

For example, consider a lattice formed by X and M ions. Suppose an M ion leaves the M sublattice, leaving the X sublattice unchanged. The number of interstitials formed will equal the number of vacancies formed.

One form of a Frenkel defect reaction in MgO with the oxygen ion leaving the lattice and going into the interstitial site written in Kröger–Vink notation:

$$Mg^{\times}_{Mg+}O^{\times}_{O\to}O^{''}_{i}+V^{\bullet\bullet}_{O}+Mg^{\times}_{Mg}$$

This can be illustrated with the example of the sodium chloride crystal structure. The diagrams below are schematic two-dimensional representations.



The defect-free NaCl structure



Two Frenkel defects within the NaCl structure

F-CENTER

An F-Center or Farbe (German for color) center is a type of crystallographic defect in which an anionic vacancy in a crystal is filled by one or more electrons, depending on the charge of the missing ion in the crystal. Electrons in such a vacancy tend to absorb light in the visible spectrum such that a material that is usually transparent becomes colored. Thus the origin of the name, F-center, which originates from the German Farbzentrum. The translation of this term also provides the synonym color center, which can also refer to such defects. F-centers are often paramagnetic and can then be studied by electron paramagnetic resonance techniques. The greater the number of F-centers, the more intense is the color of the compound. A way of producing F centers is to heat a crystal in the presence of an atmosphere of the metal that constitutes the material, e.g.: NaCl heated in a metallic Na atmosphere.

$Na0 \rightarrow$		Na++	e-	
Na+ is	incorporated	at	NaCl	crystal.
Cl-vacancies	are generated, because of the	e excess of Na+.		

These vacancies capture available e-, neutralizing and forming F-centers; that is, the electrons released in this process diffuse to occupy the vacant places. Also, ionizing radiation can produce F-centers.

An H-center (a halogen interstitial) is in a sense the opposite, and hence a F-center and a H-center can combine and clear the lattice of a defect. This process can be photo induced, e.g. by a laser.

OTHER COLOUR CENTERS

Atomic and electronic defects of various types which produce optical absorption bands in otherwise transparent crystals such as the alkali halides, alkaline earth fluorides, or metal oxides. They are general phenomena found in a wide range of materials. Color centers are produced by gamma radiation or x-radiation, by addition of impurities or excess constituents, and sometimes through electrolysis. A well-known example is that of the F-center in alkali halides such as sodium chloride, NaCl. The designation F-center comes from the German word Farbe, which means color. F-centers in NaCl produce a band of optical absorption toward the blue end of the visible spectrum; thus the colored crystal appears yellow under transmitted light. On the other hand, KCl with F-centers appears magenta, and KBr appears blue.

Color centers have been under investigation for many years. Theoretical studies guided by detailed experimental work have yielded a deep understanding of specific centers. The crystals in which color centers appear tend to be transparent to light and to microwaves. Consequently, experiments which can be carried out include optical spectroscopy, luminescence and Raman scattering, magnetic circular dichroism, magnetic resonance, and electromodulation. Color centers find practical application in radiation dosimeters; schemes have been proposed to use color centers in high-density memory devices; and tunable lasers have been made from crystals containing color centers.

The illustration shows the absorption bands due to color centers produced in potassium bromide by exposure of the crystal at the temperature of liquid nitrogen (81 K) to intense penetrating x-rays. Several prominent bands appear as a result of the irradiation. The F-band appears at 600 nanometers and the so-called V-bands appear in the ultraviolet.

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Absorption bands produced in a KBr crystal by exposure to x-rays at 81 K

Color bands such as the F-band and the V-band arise because of light absorption at defects dispersed throughout the lattice. This absorption is caused by electronic transitions at the centers. On the other hand, colloidal particles, each consisting of many atoms, dispersed through an optical medium also produce color bands. In this case, if the particles are large enough, the extinction of light is due to both light scattering and light absorption. Colloidal gold is responsible for the color of some types of ruby glass. Colloids may also form in alkali halide crystals—for example, during heat treatment of an additively colored crystal with an excess of alkali metal.

Atomically dispersed centers such as F-centers are part of the general phenomena of trapped electrons and holes in solids. The accepted model of the F-center is an electron trapped at a negative ion vacancy. Many other combinations of electrons, holes, and clusters of lattice vacancies have been used to explain the various absorption bands in ionic crystals.

Impurities can play an important role in color-center phenomena. Certain impurities in ionic crystals produce color bands characteristic of the foreign ion. For example, hydrogen can be incorporated into the alkali halides with resultant appearance of an absorption band (the U-band) in the ultraviolet. In this case, the U-centers interact with other defects. The rate at which F-centers are produced by x-irradiation is greatly increased by the incorporation of hydrogen, the U-centers being converted into F-centers with high efficiency.

DISLOCATIONS - SLIP AND PLASTIC DEFORMATION

Until the 1930s, one of the enduring challenges of materials science was to explain plasticity in microscopic terms. A naive attempt to calculate the shear stress at which neighbouring atomic planes slip over each other in a perfect crystal suggests that, for a material with shear modulus G, shear strength τm is given approximately by:

$$\tau_m = \frac{G}{2\pi}.$$

As shear modulus in metals is typically within the range 20 000 to 150 000 MPa, this is difficult to reconcile with shear stresses in the range 0.5 to 10 MPa observed to produce plastic deformation in experiments.

In 1934, Egon Orowan, Michael Polanyi and G. I. Taylor, roughly simultaneously, realized that plastic deformation could be explained in terms of the theory of dislocations. Dislocations can move if the atoms from one of the surrounding planes break their bonds and rebond with the atoms at the terminating edge. In effect, a half plane of atoms is moved in response to shear stress by breaking and reforming a line of bonds, one (or a few) at a time. The energy required to break a single bond is far less than that required to break all the bonds on an entire plane of atoms at once. Even this simple model of the force required to move a dislocation shows that plasticity is possible at much lower stresses than in a perfect crystal. In many materials, particularly ductile materials, dislocations are the "carrier" of plastic deformation, and the energy required to move them is less than the energy required to fracture the material. Dislocations give rise to the characteristic malleability of metals.

When metals are subjected to "cold working" (deformation at temperatures which are relatively low as compared to the material's absolute melting temperature, Tm, i.e., typically less than 0.3 Tm) the dislocation density increases due to the formation of new dislocations and dislocation multiplication. The consequent increasing overlap between the strain fields of adjacent dislocations gradually increases the resistance to further dislocation motion. This causes a hardening of the metal as deformation progresses. This effect is known as strain hardening (also "work hardening"). Tangles of dislocations are found at the early stage of deformation and appear as non well-defined boundaries; the process of dynamic recovery leads

eventually to the formation of a cellular structure containing boundaries with misorientation lower than 15° (low angle grain boundaries). In addition, adding pinning points that inhibit the motion of dislocations, such as alloying elements, can introduce stress fields that ultimately strengthen the material by requiring a higher applied stress to overcome the pinning stress and continue dislocation motion.

The effects of strain hardening by accumulation of dislocations and the grain structure formed at high strain can be removed by appropriate heat treatment (annealing) which promotes the recovery and subsequent recrystallisation of the material.

The combined processing techniques of work hardening and annealing allow for control over dislocation density, the degree of dislocation entanglement, and ultimately the yield strength of the material.

EDGE DISLOCATIONS



Figure B Schematic diagram (lattice planes) showing an edge dislocation. Burgers vector in black, dislocation line in blue.

An edge dislocation is a defect where an extra half-plane of atoms is introduced mid way through the crystal, distorting nearby planes of atoms. When enough force is applied from one side of the crystal structure, this extra plane passes through planes of atoms breaking and joining bonds with them until it reaches the grain boundary. A simple schematic diagram of such atomic planes can be used to illustrate lattice defects such as dislocations. (Figure B represents the "extra half-plane" concept of an edge type dislocation). The dislocation has two properties, a line direction, which is the direction running along the bottom of the extra half plane, and the Burgers vector which describes the magnitude and direction of distortion to the lattice. In an edge dislocation, the Burgers vector is perpendicular to the line direction. (see also Jog (dislocations))

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The stresses caused by an edge dislocation are complex due to its inherent asymmetry. These stresses are described by three equations:

$$\sigma_{xx} = \frac{-\mu b}{2\pi(1-\nu)} \frac{y(3x^2+y^2)}{(x^2+y^2)^2}$$
$$\sigma_{yy} = \frac{\mu b}{2\pi(1-\nu)} \frac{y(x^2-y^2)}{(x^2+y^2)^2}$$
$$\tau_{xy} = \frac{\mu b}{2\pi(1-\nu)} \frac{x(x^2-y^2)}{(x^2+y^2)^2}$$

where μ is the shear modulus of the material, b is the Burgers vector, v is Poisson's ratio and x and y are coordinates.

These equations suggest a vertically oriented dumbbell of stresses surrounding the dislocation, with compression experienced by the atoms near the "extra" plane, and tension experienced by those atoms near the "missing" plane.

SCREW DISLOCATIONS



Top right: edge dislocation.

Bottom right: screw dislocation.



Figure C Schematic diagram (lattice planes) showing a screw dislocation.

A screw dislocation is much harder to visualize. Imagine cutting a crystal along a plane and slipping one half across the other by a lattice vector, the halves fitting back together without leaving a defect. If the cut only goes part way through the crystal, and then slipped, the boundary of the cut is a screw dislocation. It comprises a structure in which a helical path is traced around the linear defect (dislocation line) by the atomic planes in the crystal lattice (Figure C). Perhaps the closest analogy is a spiral-sliced ham. In pure screw dislocations, the Burgers vector is parallel to the line direction.

Despite the difficulty in visualization, the stresses caused by a screw dislocation are less complex than those of an edge dislocation. These stresses need only one equation, as symmetry allows only one radial coordinate to be used:

$$\tau_r = \frac{-\mu b}{2\pi r}$$

where μ is the shear modulus of the material, b is the Burgers vector, and r is a radial coordinate. This equation suggests a long cylinder of stress radiating outward from the cylinder and decreasing with distance. Please note, this simple model results in an infinite value for the core of the dislocation at r=0 and so it is only valid for stresses outside of the core of the dislocation. If the Burgers vector is very large, the core may actually be empty resulting in a micropipe, as commonly observed in silicon carbide.

STRESS FIELD AROUND AN EDGE DISLOCATION

Here is a well known representation of the stress field surrounding an edge dislocation.

On the left half of the picture, the stresses on the elementary cube are shown around the dislocation. Since there is no stress perpendicular to the image plane, a two-dimensional representation is sufficient. On the right half, contours of equal stress are shown for the normal component and the shear components of the stress tensor.

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ULTRASONICS

NON DESTRUCTIVE TESTING AND APPLICATIONS

Nondestructive testing or Non-destructive testing (NDT) is a wide group of analysis techniques used in science and industry to evaluate the properties of a material, component or system without causing damage. The terms Nondestructive examination (NDE), Nondestructive inspection (NDI), and Nondestructive evaluation (NDE) are also commonly used to describe this technology. Because NDT does not permanently alter the article being inspected, it is a highlyvaluable technique that can save both money and time in product evaluation, troubleshooting, NDT research. Common methods include ultrasonic, magnetic-particle, liquid and penetrant, radiographic, remote visual inspection (RVI), eddy-current testing, and low coherence interferometry. NDT is a commonly-used tool in forensic engineering, mechanical engineering, electrical engineering, civil engineering, systems engineering, aeronautical engineering, medicine, and art.

METHODS

NDT methods may rely upon use of electromagnetic radiation, sound, and inherent properties of materials to examine samples. This includes some kinds of microscopy to examine external surfaces in detail, although sample preparation techniques for metallography, optical microscopy and electron microscopy are generally destructive as the surfaces must be made smooth through polishing or the sample must be electron transparent in thickness. The inside of a sample can be examined with penetrating electromagnetic radiation, such as X-rays or3D X-rays for volumetric inspection. Sound waves are utilized in the case of ultrasonic testing.

Contrast between a defect and the bulk of the sample may be enhanced for visual examination by the unaided eye by using liquids to penetrate fatigue cracks. One method (liquid penetrant testing) involves using dyes, fluorescent or non-fluorescing, in fluids for non-magnetic materials, usually metals. Another commonly used method for magnetic materials involves using a liquid suspension of fine iron particles applied to a part while it is in an externally applied magnetic field (magnetic-particle testing). Thermoelectric effect (or use of the Seebeck effect) uses thermal properties of an alloy to quickly and easily characterize many alloys. The chemical test, or chemical spot test method, utilizes application of sensitive chemicals that can indicate the presence of individual alloying elements.

APPLICATIONS WELD VERIFICATION



- 1. Section of material with a surface-breaking crack that is not visible to the naked eye.
- 2. Penetrant is applied to the surface.
- 3. Excess penetrant is removed.
- 4. Developer is applied, rendering the crack visible.

In manufacturing, welds are commonly used to join two or more metal surfaces. Because these connections may encounter loads and fatigue during product lifetime, there is a chance that they may fail if not created to proper specification. For example, the base metal must reach a

certain temperature during the welding process, must cool at a specific rate, and must be welded with compatible materials or the joint may not be strong enough to hold the surfaces together, or cracks may form in the weld causing it to fail. The typical welding defects, lack of fusion of the weld to the base metal, cracks or porosity inside the weld, and variations in weld density, could cause a structure to break or a pipeline to rupture.

Welds may be tested using NDT techniques such as industrial radiography or industrial CT scanning using X-rays or gamma rays, ultrasonic testing, liquid penetrant testing or via eddy current. In a proper weld, these tests would indicate a lack of cracks in the radiograph, show clear passage of sound through the weld and back, or indicate a clear surface without penetrant captured in cracks.

Welding techniques may also be actively monitored with acoustic emission techniques before production to design the best set of parameters to use to properly join two materials.

STRUCTURAL MECHANICS

Structures can be complex systems that undergo different loads during their lifetime. Some complex structures, such as the turbo machinery in a liquid-fuel rocket, can also cost millions of dollars. Engineers will commonly model these structures as coupled second-order systems, approximating dynamic structure components with springs, masses, and dampers. These sets of differential equations can be used to derive a transfer function that models the behaviour of the system.

In NDT, the structure undergoes a dynamic input, such as the tap of a hammer or a controlled impulse. Key properties, such as displacement or acceleration at different points of the structure, are measured as the corresponding output. This output is recorded and compared to the corresponding output given by the transfer function and the known input. Differences may indicate an inappropriate model (which may alert engineers to unpredicted instabilities or performance outside of tolerances), failed components, or an inadequate control system. Radiography in medicine

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Chest radiography indicating a peripheral bronchial carcinoma.

As a system, the human body is difficult to model as a complete transfer function. Elements of the body, however, such as bones or molecules, have a known response to certain radiographic inputs, such as X-rays or magnetic resonance. Coupled with the controlled introduction of a known element, such as digested barium, radiography can be used to image parts or functions of the body by measuring and interpreting the response to the radiographic input. In this manner, many bone fractures and diseases may be detected and localized in preparation for treatment. X-rays may also be used to examine the interior of mechanical systems in manufacturing using NDT techniques, as well.

Condensed Matter Physics UNIT II (17PHP101) CRYSTAL DEFECTS

KARAPAGAM ACADEMY OF HIGHER EDUCATION, COIMBATORE-21

POSSIBLE QUESTIONS

UNIT II

- 1. Describe various classifications of defects with a clear picture.
- 2. Explain about Non destructive testing and applications.
- 3. Explain the experimental facts on F-centers.
- 4. Explain the following: (i) Points defect, (ii) The Schottky defect & (iii) F center
- Explain the following: i) Colour centers, ii) Production of colour by X-rays & iii) Points defect
- 6. Explain the following: i) Shear strength of materials and (ii) Edge dislocation.
- 7. Explain the various classifications of crystal defects.
- 8. What is Ultrasonics? Explain a Non- destructive testing along with its applications.
- 9. What do you mean by dislocations? Explain Shear strength and Stress field around an edge dislocations

CARPAGAM ACADEMY OF HIGHER EDUCATION, COIMBATORE-21 DEPARTMENT OF PHYSICS I M.SC PHYSICS BA CONDENSED MATTER PHYSICS (17PHP101)

BATCH: 2017-2019

MULTIPLE CHOICE QUESTIONS

Questions	option 1	option 2	option 3	option 4	Answer
UNIT II					
Atomic packing factor is	Distance between two adjacent atoms	Projected area fraction of atoms on a plane	Volume fraction of atoms in cell	None	Volume fraction of atoms in cell
Schottky-defect in ceramic material is	Interstitial impurity	Vacancy- interstitial pair of cations	Pair of nearby cation and anion vacancies	Substitutional impurity	Pair of nearby cation and anion vacancies
Theoretical strength is about times to average real strength of a material.	1	10	100	1000	100
Hooke's law	Elastic range, strain is proportional to stress		Plastic range, strain is proportional to stress	None	Elastic range, strain is proportional to stress
Following is not the 2-dimensional imperfection	Twin boundary	Dislocation	Surface	Grain boundary	Dislocation
Figure out the odd one in the following	Frenkel defect	Tilt boundary	Twist boundary	Stacking fault	Frenkel defect
Thermodynamically stable defects	Point defects	Line defects	Surface defects	Volume defects	Point defects
Taylor dislocation can not move by the following way	Slip	Climb	Cross-slip	All	Climb
Conservative movement of dislocations	Slip	Climb	Both slip and climb	none	Slip
Burger's vector changes with	Kind of dislocation	Length of dislocation	Both kind and length of dislocation	None	None
Which of the following is false?	Line defects are thermodynamically stable	Dislocation can end inside a crystal without forming loop	ABC ABC ABCis stacking sequence for HCP crystal	All	All
Average frequency of atomic vibrations in a solid (in Hz)	10^-12	10^-13	10^12	10^13	10^13
Requirement for cross-slip movement of dislocation	Preferred slip plane	Preferred slip direction	No preferred slip plane	No preferred slip direction	No preferred slip plane
Beneficial property of foreign particles	Reduces density	Act as stress raisers	Obstructs dislocation motion	None	Obstructs dislocation motion
Stacking fault energies are in the range of	0.01-0.1 J/m2	0.01-0.1 J/cm2	0.1-10 J/m2	0.1-10 J/m2	0.01-0.1 J/m2
Frankel and Schottky imperfections are	dislocations in ionic crystals.	Grain boundaries in covalent crystals.	Vacancies in ionic crystals.	Vacancies in covalent crystals.	Vacancies in ionic crystals.
In normalizing, one of the following is not correct:	it relieves internal stresses	it produces a uniform structure.	the rate of cooling is rapid	the rate of cooling is slow.	the rate of cooling is slow.
Imperfection arising due to the displacement of an ion from a regular site to an interstitial site maintaining overall electrical neutrality of the ionic crystal is called.	Frenkel imperfection	Schottky imperfection	Point imperfection	Volume imperfection	Frenkel imperfection
Annealing is generally done to impart	hardness to the material	softness to the material	brittleness to the material	high conductivity to the material	softness to the material
Which of the following processes is used to harden a steel?	Normalizing	Annealing	Carburizing	Quenching	Quenching

The steady state conditions in diffusion are governed by	Fick's second law.	Fick's first law.	both (A) and (B).	Maxwell-Boltzmann's law.	Fick's first law.
A pair of one cation and one anion missing in a crystal of the type AB is called	Schottky defect.	Frenkel defect.	Pair of vacancies.	None of these.	Schottky defect.
The property of a material by which it can be drawn into wires is known as	ductility	elasticity	softness	tempering	ductility
Malleability of a metal is the	ability to withstand compressive stresses	ability to withstand deformation under shear	property by which a material can be cold- worked	ability to undergo permanent deformation	ability to undergo permanent deformation
The hardness of quenched Martensite	increases with increasing carbon percentage.		first increases and then remains almost constant as the carbon percentage increases.	first increases and then decreases as carbon percentage increases.	first increases and then remains almost constant as the carbon percentage increases.
Missing of one cation and one anion in an ionic crystal (having charge neutrality) is called	Frenkel imperfections.	Compositional imperfections.	Electronic imperfections.	Schottky imperfections.	Schottky imperfections.
Ultrasonic waves have frequency	as that of audible range	above audible range	below audible range	below as well as above audible range	above audible range
Ultrasonic waves are produced by utilizing	piezoelectric effect	Peltier effect	Doppler effects	magneto-optic effect	piezoelectric effect
The velocity of ultrasonic waves is generally greater in solids than in gases because	the density of solids is high but the elasticity is low	both the density and the elasticity of solids are low	the density of solids is low but the elasticity is high	both the density and elasticity of solids are high	both the density and elasticity of solids are high
Ultrasonic waves travel with a velocity	equal to the velocity of light	more than velocity of sound waves	equal to the velocity of sound waves	less than the velocity of sound waves	equal to the velocity of sound waves
Ultrasonic waves produced in a medium can be detected by	a telephone	Kundt's tube	discharge tube	spectrometer	Kundt's tube
Ultrasonic waves are used for stirring liquid solutions because	they do not cause chemical reactions	they cause chemical reactions	they produce perfectly homogenous solutions	they produce heating	they produce perfectly homogenous solutions
The waves used in sonography are	microwaves	light waves	sound waves	ultrasonic waves	ultrasonic waves
The wavelength of a wave produced in air is 0.60 cm. and it travels with a velocity 300 m/s. Then it is,	ultrasonic waves	sound waves	light waves	micro waves	ultrasonic waves
The wavelength of ultrasonic waves in air is in the order of	1 cm	5 × 10- 6 m	$5 \times 10.4 \text{ m}$	$1 \times 10.6 \text{ m}$	1 cm
The instrument used to measure the depth of the sea using ultrasonic waves is	lactometer	speedometer	galvanometer	fathometer	fathometer
Bats detect the obstacles in their path by receiving the reflected	infrasonic waves	radio waves	electromagnetic waves	ultrasonic waves	ultrasonic waves
The frequency which is not audible to the human ear is	50 Hz	500 Hz	5000 Hz	50,000 Hz	50,000 Hz
The technique used by bats to find their way or to locate food	SONAR	RADAR	Echo location	Flapping	Echo location
The audible range of sound for human ear	below 20 Hz	above 20 kHz	20 Hz to 20 kHz	none of the above	20 Hz to 20 kHz
The frequency of infrasonic sound is	above 20 Hz	above 20 kHz	20 Hz to 20 kHz	below 20 Hz	below 20 Hz
You would generally select a high frequency ultrasound transducer to get	better tissue penetration	better image detail	faster imaging	decreased attenuation	better image detail
The wavelength of ultrasonic waves in air is 1.65 cm. Its frequency is :	20 Hz	200 Hz	2000 Hz	20000 Hz	20000 Hz
In ultrasound imaging, increasing the number of scan times in the image will generally	increase imaging depth	Increase visibility of anatomical detail	increase pulse velocity	none of the above	Increase visibility of anatomical detail

transducer frequency	th of vessel	direction of vessel	size of the vessel.	direction of vessel
ultrasonic are sound waves of very long wavelength	ultrasonic are sound waves of very high frequency	ultrasonic waves moves faster than sound wave	ultrasonic waves moves with the same velocity as sound waves	ultrasonic waves moves with the same velocity as sound waves
165 Hz	68 × 103 Hz	1.5 × 10- 9 Hz	170 Hz	68 × 103 Hz
with the speed less than the speed of sound	with the speed of sound	with the speed of greater than the sound	with the speed of light.	with the speed of sound
infrasonic	ultrasonic waves	bats can see at night	none of the above.	ultrasonic waves
infrasonic waves	ultrasonic waves	radio waves	micro waves.	infrasonic waves
vu = vi = va	vu > va > vi	vu > va > vi	$va \le vu$ and $vu \approx vi$	vu = vi = va
e.m.w	Elastic waves	Mechanical waves	Mechanical waves	Mechanical waves
Long wavelength	High frequency	Low frequency	Velocity equal to c	High frequency
Flaws of the solid	Thickness of the metal plate	Distance of the objects	All the above	All the above
Having high frequency	Travel long distances	Reflects back when medium changes	All the above	All the above
J.J. Thomson	Curie brothers	Earnest Rutherford	Sommerfeld Arnold	Curie brothers
electromagnetic waves	ultrasonic waves	infra-red radiation	ultrasonic let radiation	ultrasonic waves
2 - 3 kW/m2	3 - 4 kW/m2	4 - 5 kW/m2	1 - 2 kW/m2	1 - 2 kW/m2
asymmetric	symmetric	isotropic	anisotropic	asymmetric
Y - cut crystal	Z - cut crystal	X - cut crystal	Y -Z cut crystal	Z - cut crystal
	transducer frequency ultrasonic are sound waves of very long wavelength 165 Hz with the speed less than the speed of sound infrasonic infrasonic waves vu = vi = va e.m.w Long wavelength Flaws of the solid Having high frequency J.J. Thomson electromagnetic waves 2 - 3 kW/m2 asymmetric Y - cut crystal	transducer frequencyth of vesselultrasonic are sound waves of very long wavelengthultrasonic are sound waves of very high frequency165 Hz 68×103 Hzwith the speed less than the speed of soundwith the speed of soundinfrasonicultrasonic wavesvu = vi = vavu > va > vie.m.wElastic wavesLong wavelengthHigh frequencyFlaws of the solidThickness of the metal plateHaving high frequencyTravel long distancesJ.J. ThomsonCurie brothers electromagnetic waves2 - 3 kW/m2 $3 - 4$ kW/m2 asymmetricY - cut crystalZ - cut crystal	transducer frequencyth of vesseldirection of vesselultrasonic are sound waves of very long wavelengthultrasonic are sound waves of very high frequencyultrasonic waves moves faster than sound wave165 Hz 68×103 Hz $1.5 \times 10-9$ Hzwith the speed less than the speed of soundwith the speed of soundwith the speed of greater than the soundinfrasonicultrasonic wavesbats can see at nightinfrasonicultrasonic wavesradio wavesvu = vi = vavu > va > vivu > va > vie.m.wElastic wavesMechanical wavesLong wavelengthHigh frequencyLow frequencyFlaws of the solidThickness of the metal plateDistance of the objectsHaving high frequencyTravel long distancesReflects back when medium changesJ.J. ThomsonCurie brothersEarnest Rutherfordelectromagnetic wavesultrasonic wavesinfra-red radiation2 - 3 kW/m23 - 4 kW/m24 - 5 kW/m2asymmetricsymmetricisotropicY - cut crystalZ - cut crystalX - cut crystal	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $

PREPARED BY : Dr. V. Senthil Kumar, Head, Department Of Physics, KAHE-CBE-21
UNIT - III

Heat capacity of the electron gas: Experimental electrical resistivity of metals – Free electron theory of metals – Debye's equation - superconductivity - Electron phonon interaction - Cooper pairs – BCS theory - Energy gap and its temperature dependence - London equation – Josephson effect and its applications.

Langevin theory of Para magnetism: Quantum theory of Para Magnetism - Curie law- Ferro Magnetism - Weiss molecular field theory - Domain theory - Anti Ferro magnetism - Neel theory - Ferri Magnetism – Ferrites – spin – waves - Experimental techniques to study the magnetic properties.

FREE-ELECTRON THEORY OF METALS

The treatment of a metal as containing a gas of electrons completely free to move within it. The theory was originally proposed in 1900 to describe and correlate the electrical and thermal properties of metals. Later, quantum mechanics became the basis for the theory of most of the general properties of simple metals such as sodium, with one free electron per atom, magnesium with two, and aluminum with three. Transition metals, such as iron, have partially filled electronic d states and are not treated by the free-electron model.

Three years after J. J. Thomson's 1897 discovery of the electron, P. Drude suggested that the transport properties of metals might be understood by assuming that their electrons are free and in thermal equilibrium with their atoms. This theory was made more quantitative by H. A. Lorentz. Assuming that the mean free path of electrons was limited by collisions, he was able to derive Ohm's law for the electrical conductivity and obtain the ratio of thermal to electrical conductivity in excellent agreement with experiment. This ratio, divided by the absolute temperature, is called the Wiedemann-Franz ratio and had been observed to be universal 50 years earlier.

The theory, however, had two major shortcomings. First, it predicted a large component of the specific heat of a metal, not present in insulators, which was not observed. Second, comparison of the theory with experiment indicated that the mean free path of the electrons became extremely large at low temperatures; the model offered no justification.

In 1928 A. Sommerfeld revised Lorentz's treatment by using quantum statistics, which removed the difficulty of the specific heat without losing the successful description of transport properties. The resulting theory remains the basis for the understanding of most transport properties of metals and semiconductors. At about the same time, W. V. Houston and F. Bloch solved the quantum-mechanical wave equation for electrons in a regular periodic structure, finding that they could indeed have arbitrarily large mean free paths if there were no defects in the periodicity, thereby putting the free-electron theory on a firm basis.

Even in the context of a free-electron gas, there are strong Coulomb interactions between electrons which are frequently neglected in the free-electron theory of metals. This neglect was justified in the late 1950s by L. D. Landau, who asserted that, even with strong electron–electron interactions, there is a one-to-one correspondence between the excited states, called quasiparticle states, of the real system and the one-electron excitations from the ground state of the noninteracting electron gas. Thus, the formulations for free-electron theory still follow, but perhaps with modifications of parameters such as mass. Subsequent theory indicates that indeed these modification due to the electron-electron interaction are extremely small for the low-energy excitations present in thermal equilibrium, and so again the simplest theory succeeds for many properties, although substantial modifications are required for the higher-energy excitations caused by light. There are additional corrections, which are much larger than those from the electron-electron interaction, arising from the interaction between electrons and phonons, the quantum-mechanical term for lattice vibrations. In many metals these vibrations reduce the electron velocities by factors of as much as 2, increasing the electronic specific heat although they turn out not to modify the conductivity itself.

Another feature of the electron-phonon interaction is a resulting interaction among electrons, which is attractive and tends to cancel or exceed the repulsive electron-electron interaction. At low temperatures the net attraction binds electrons in pairs in a superconducting state. The theory of J. Bardeen, J. R. Schrieffer, and L. N. Cooper (the BCS theory of superconductivity), which first explained this phenomenon, is also a free-electron theory, but assumes that the free electrons have such a net attractive interaction. In contrast, it is generally believed that the high-temperature superconductors discovered in 1986 are very far from free-

electron in character, and most workers do not believe that phonons are primarily responsible for the attractive interaction.

SUPERCONDUCTIVITY

Mercury Zero resistancel G H = 4.2 K 4.1 4.3 42 Temperature (K)

If mercury is cooled below 4.1 K, it loses all electric resistance. This discovery of superconductivity by H. Kammerlingh Onnes in 1911 was followed by the observation of other metals, which exhibit zero resistivity below a certain critical temperature. The fact that the resistance is zero has been demonstrated by sustaining currents in superconducting lead rings for many years with no measurable reduction. An induced current in an ordinary metal ring would decay rapidly from the dissipation of ordinary resistance, but superconducting rings had exhibited a decay constant of over a billion years!

One of the properties of a superconductor is that it will exclude magnetic fields, a phenomenon called the Meissner effect.

The disappearance of electrical resistivity was modeled in terms of electron pairing in the crystal lattice by John Bardeen, Leon Cooper, and Robert Schrieffer in what is commonly called the BCS theory.

A new era in the study of superconductivity began in 1986 with the discovery of high critical temperature superconductors.

CRITICAL TEMPERATURE FOR SUPERCONDUCTORS

The critical temperature for superconductors is the temperature at which the electrical resistivity of a metal drops to zero. The transition is so sudden and complete that it appears to be a transition to a different phase of matter; this superconducting phase is described by the BCS theory. Several materials exhibit superconducting phase transitions at low temperatures. The

highest critical temperature was about 23 K until the discovery in 1986 of some high temperature superconductors.

Materials with critical temperatures in the range 120 K have received a great deal of attention because they can be maintained in the superconducting state with liquid nitrogen (77 K).

Material	T-Critical
Gallium	1.1 K
Aluminum	1.2 K
Indium	3.4 K
Tin	3.7 K
Mercury	4.2 K
Lead	7.2 K
Niobium	9.3 K
Niobium-Tin	17.9 K
La-Ba-Cu-oxide	30 K
Y-Ba-Cu-oxide	92 K
Tl-Ba-Cu-oxide	125 K

Types I and II Superconductors

There are thirty pure metals, which exhibit zero resistivity at low temperatures and have the property of excluding magnetic fields from the interior of the superconductor (Meissner effect). They are called Type I superconductors. The superconductivity exists only below their critical temperatures and below a critical magnetic field strength. Type I superconductors are well described by the BCS theory.

Starting in 1930 with lead-bismuth alloys, a number of alloys were found which exhibited superconductivity; they are called Type II superconductors. They were found to have much

higher critical fields and therefore could carry much higher current densities while remaining in the superconducting state.

The variations on barium-copper-oxide ceramics which achieved the superconducting state at much higher temperatures are often just referred to as high temperature superconductors and form a class of their own.

Type I Superconductors

The thirty pure metals listed at right below are called Type I superconductors. The identifying characteristics are zero electrical resistivity below a critical temperature, zero internal magnetic field (Meissner effect), and a critical magnetic field above which superconductivity ceases.

The superconductivity in Type I superconductors is modeled well by the BCS theory which relies upon electron pairs coupled by lattice vibration interactions. Remarkably, the best conductors at room temperature (gold, silver, and copper) do not become superconducting at all. They have the smallest lattice vibrations, so their behavior correlates well with the BCS Theory.

While instructive for understanding superconductivity, the Type I superconductors have been of limited practical usefulness because the critical magnetic fields are so small and the superconducting state disappears suddenly at that temperature. Type I superconductors are sometimes called "soft" superconductors while the Type II are "hard", maintaining the superconducting state to higher temperatures and magnetic fields.

Mat.	Тс	Mat.	Тс	
Be	0	Al	1.2	
Rh	0	Pa	1.4	
W	0.015	Th	1.4	
Ir	0.1	Re	1.4	
Lu	0.1	T1	2.39	
Hf	0.1	In	3.408	
Ru	0.5	Sn	3.722	

Os	0.7	Hg	4.153
Мо	0.92	Та	4.47
Zr	0.546	V	5.38
Cd	0.56	La	6.00
U	0.2	Pb	7.193
Ti	0.39	Тс	7.77
Zn	0.85	Nb	9.46
Ga	1.083		•

Type II Superconductors

Superconductors made from alloys are called Type II superconductors. Besides being mechanically harder than Type I superconductors, they exhibit much higher critical magnetic fields. Type II superconductors such as niobium-titanium (NbTi) are used in the construction of high field superconducting magnets.

Type-II superconductors usually exist in a mixed state of normal and superconducting regions. This is sometimes called a vortex state, because vortices of superconducting currents surround filaments or cores of normal material.

Material	Transition Temp (K)	Critical Field (T)
NbTi	10	15
PbMoS	14.4	6.0
V₃Ga	14.8	2.1
NDN	15.7	1.5
V ₃ Si	16.9	2.35
Nb ₃ Sn	18.0	24.5
Nb ₃ A1	18.7	32.4
Nb ₃ (A1G)	e) 20.7	44
Nb ₃ Ge	23.2	38

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ELECTRON-PHONON INTERACTION

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The strength of the electron-phonon interaction has been addressed in several ways, both via ab initio calculations and via analysis of experiment. A very early theoretical estimate was obtained within the rigid muffin-tin, using an empirical phonon model. Later a full potential LMTO calculation was performed to obtain ab initio phonon frequencies, eigenvectors and electron-phonon couplings in a frozen phonon approach.

The electron-phonon coupling has also been deduced from photoemission measurements for free, negatively charged, C60 molecule. In this approach the coupling strengths are deduced from the weights of the phonon satellites in the photoemission spectrum

The electron-phonon coupling can also be deduced from Raman scattering data. These estimates differ substantially from the once deduced from photoemission. We have therefore analyzed the methods for extracting the electron-phonon coupling from Raman scattering data and shown that the two types of experiment can be partly reconciled.

To obtain the electron-phonon coupling, it is important to also know the density of states, since this quantity enters as a multiplying factor. Different estimates of density of states have therefore been analyzed.

The theoretical estimates generally give a rather weak coupling to the low-lying Hg phonons in contradiction to the experimental estimates. The reason for this discrepance is not known.

COOPER PAIR

In condensed matter physics, a Cooper pair is the name given to electrons that are bound together at low temperatures in a certain manner first described in 1956 by Leon Cooper. Cooper showed that an arbitrarily small attraction between electrons in a metal can cause a paired state of electrons to have a lower energy than the Fermi energy, which implies that the pair is bound. In normal superconductors, this attraction is due to the electron - phonon interaction. The Cooper pair state is responsible for superconductivity, as described in the BCS theory developed by John Bardeen, John Schrieffer and Leon Cooper for which they shared the 1972 Nobel Prize.

The reason for the pairing can be seen from a simplified explanation. An electron in a metal normally behaves as a free particle. The electron is repelled from other electrons due to their similar charge, but it also attracts the positive ions that make up the rigid lattice of the

metal. This attraction can distort the positively charged ion lattice in such a way as to attract other electrons (the electron-phonon interaction). At long distances this attraction between electrons due to the displaced ions can overcome the electrons' repulsion due to their negative charge, and cause them to pair-up.

The energy of the pairing interaction is quite weak, of the order of 10-3eV, and thermal energy can easily break the pairs up. So only at low temperatures are a significant number of the electrons in a metal in Cooper pairs. The electrons in a pair are not necessarily close together; because the interaction is long range, paired electrons may still be many hundreds of nanometers apart. This distance is usually greater than the average inter electron distance, so many Cooper pairs can occupy the same space. Since electrons are spin-1/2 fermions, a Cooper pair is a boson, to which the Pauli exclusion principle doesn't apply, so they are allowed to be in the same state. The tendency for all the Cooper pairs in a body to 'condense' into the same ground quantum state is responsible for the peculiar properties of superconductivity.

RELATIONSHIP TO SUPERCONDUCTIVITY

Cooper originally just considered the case of an isolated pair forming in a metal. When one considers the more realistic state consisting of many electrons forming pairs as is done in the full BCS Theory one finds that the pairing opens a gap in the continuous spectrum of allowed energy states of the electrons, meaning that all excitations of the system must possess some minimum amount of energy. This gap to excitations leads to superconductivity, since small excitations such as scattering of electrons are forbidden.

Herbert Fröhlich was first to suggest that the electrons might act as pairs coupled by lattice vibrations in the material. This was indicated by the isotope effect observed in superconductors. The isotope effect showed that materials with heavier ions (different nuclear isotopes) had lower superconducting transition temperatures. This can be explained nicely by the theory of Cooper pairing; since heavier ions are harder to move they would be less able to attract the electrons resulting in a smaller binding energy for Cooper pairs.

The pair are still Cooperic if $k_1 = k_2$ and $k_1 - q = -(k_1 - q) = -(-k_2 - q) = -(k_2 + q)$

The theory of Cooper pairs is quite general and does not depend on the specific electronphonon interaction. Condensed matter theorists have proposed pairing mechanisms based on

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other attractive interactions such as electron-exciton interactions or electron-plasmon interactions. Currently, none of these alternate pairing interactions has been observed in any material.

BCS theory

BCS theory is a microscopic theory of superconductivity, proposed by Bardeen, Cooper, and Schrieffer. It describes superconductivity as a microscopic effect caused by Bose condensation of pairs of electrons.

Overview

In the BCS framework, superconductivity is a macroscopic effect which results from Bose condensation of electron (Cooper) pairs. These behave as bosons which, at sufficiently low temperature, form a large Bose-Einstein condensate. At sufficiently low temperatures, electrons near the Fermi surface become unstable against the formation of cooper pairs. Cooper showed such binding will occur in the presence of an attractive potential, no matter how weak. In conventional superconductors, such binding is generally attributed to an electron-lattice interaction. The BCS theory, however, requires only that the potential be attractive, regardless of its origin. Superconductivity was simultaneously explained by Nikolay Bogoliubov, by means of the so-called Bogoliubov transformations.

In many superconductors, the attractive interaction between electrons (necessary for pairing) is brought about indirectly by the interaction between the electrons and the vibrating crystal lattice (the phonons). Roughly speaking the picture is the following:

An electron moving through a conductor will attract nearby positive charges in the lattice. This deformation of the lattice causes another electron, with opposite "spin", to move into the region of higher positive charge density. The two electrons are then held together with a certain binding energy. If this binding energy is higher than the energy provided by kicks from oscillating atoms in the conductor (which is true at low temperatures), then the electron pair will stick together and resist all kicks, thus not experiencing resistance.

More details

- BCS theory starts from the assumption that there is some attraction between electrons, which can overcome the Coulomb repulsion. In most materials (in low temperature superconductors), this attraction is brought about indirectly by the coupling of electrons to the crystal lattice (as explained above). However, the results of BCS theory do not depend on the origin of the attractive interaction. The original results of BCS (discussed below) described an "s-wave" superconducting state, which is the rule among low-temperature superconductors but is not realized in many "unconventional superconductors", such as the "d-wave" high-temperature superconductors. Extensions of BCS theory exist to describe these other cases, although they are insufficient to completely describe the observed features of high-temperature superconductivity.
- BCS is able to give an approximation for the quantum-mechanical state of the system of (attractively interacting) electrons inside the metal. This state is now known as the "BCS state". In the normal state of a metal, electrons move independently, whereas in the BCS state, they are bound into "Cooper pairs" by the attractive interaction.
- BCS derived several important theoretical predictions that are independent of the details of the interaction, since the quantitative predictions mentioned below hold for any sufficiently weak attraction between the electrons and this last condition is fulfilled for many low temperature superconductors the so-called "weak-coupling case". These have been confirmed in numerous experiments:
- Since the electrons are bound into Cooper pairs, a finite amount of energy is needed to break these apart into two independent electrons. This means there is an "energy gap" for "single-particle excitation", unlike in the normal metal (where the state of an electron can be changed by adding an arbitrarily small amount of energy). This energy gap is highest at low temperatures but vanishes at the transition temperature when superconductivity ceases to exist. BCS theory correctly predicts the variation of this gap with temperature. It also gives an expression that shows how the gap grows with the strength of the attractive interaction and the (normal phase) single particle density of states at the Fermi energy. Furthermore, it describes how the density of states is changed on entering the superconducting state, where there are no electronic states any more at the Fermi energy.

The energy gap is most directly observed in tunneling experiments and in reflection of microwaves from the superconductor.

- The ratio between the value of the energy gap at zero temperature and the value of the superconducting transition temperature (expressed in energy units) takes the universal value of 3.5, independent of material.
- Due to the energy gap, the specific heat of the superconductor is suppressed strongly (exponentially) at low temperatures, there being no thermal excitations left. However, before reaching the transition temperature, the specific heat of the superconductor becomes even higher than that of the normal conductor (measured immediately above the transition) and the ratio of these two values is found to be universally given by 2.5.
- BCS theory correctly predicts the Meissner effect, i.e. the expulsion of a magnetic field from the superconductor and the variation of the penetration depth (the extent of the screening currents flowing below the metal's surface) with temperature.
- It also describes the variation of the critical magnetic field (above which the superconductor can no longer expel the field but becomes normal conducting) with temperature. BCS theory relates the value of the critical field at zero temperature to the value of the transition temperature and the density of states at the Fermi energy.
- In its simplest form, BCS gives the superconducting transition temperature in terms of the electron-phonon coupling potential and the Debye cutoff energy:
- $k_B T_c = 1.14 E_D e^{-1/N(0)V}$.

ENERGY GAP IN SUPERCONDUCTORS AS A FUNCTION OF TEMPERATURE

The effective energy gap in superconductors can be measured in microwave absorption



The reduction of the energy gap as you approach the critical temperature can be taken as an indication that the charge carriers have some sort of collective nature. That is, the charge carriers must consist of at least two things which are bound together, and the binding energy is weakening as you approach the critical temperature. Above the critical temperature, such collections do not exist, and normal resistivity prevails. This kind of evidence, along with the isotope effect which showed that the crystal lattice was involved, helped to suggest the picture of paired electrons bound together by phonon interactions with the lattice.

LONDON EQUATIONS

The London equations, developed by brothers Fritz and Heinz London in 1935, relate current to electromagnetic fields in and around a superconductor. Arguably the simplest meaningful description of superconducting phenomena, they form the genesis of almost any modern introductory text on the subject. A major triumph of the equations is their ability to explain the Meissner effect, wherein a material exponentially expels all internal magnetic fields as it crosses the superconducting threshold.



As a material drops below its superconducting critical temperature, magnetic fields within the material are expelled via the Meissner effect. The London equations give a quantitative explanation of this effect.

Formulations

There are two London equations when expressed in terms of measurable fields:

$$rac{\partial \mathbf{j}_s}{\partial t} = rac{n_s e^2}{m} \mathbf{E}, \qquad
abla imes \mathbf{j}_s = -rac{n_s e^2}{mc} \mathbf{B}.$$

Here \mathbf{j}_s is the superconducting current, E and B are respectively the electric and magnetic fields within the superconductor, *e* is the charge of an electron, *m* is electron mass, and

 n_s is a phenenological constant loosely associated with a number density of superconducting carriers. Throughout this article Gaussian (cgs) units are employed.

On the other hand, if one is willing to abstract away slightly, both the expressions above can more neatly be written in terms of a single "London Equation" in terms of the vector potential A:

$$\mathbf{j}_s = -\frac{n_s e_s^2}{mc} \mathbf{A}.$$

The last equation suffers from only the disadvantage that it is not gauge invariant, but is true only in the London gauge, where the divergence of A is zero.

JOSEPHSON EFFECT

The Josephson effect is the phenomenon of current flow across two weakly coupled superconductors, separated by a very thin insulating barrier. This arrangement—two superconductors linked by a non-conducting barrier—is known as a Josephson junction; the current that crosses the barrier is the Josephson current. The terms are named after British physicist Brian David Josephson, who predicted the existence of the effect in 1962. It has important applications in quantum-mechanical circuits, such as SQUIDs.

The effect

The basic equations governing the dynamics of the Josephson effect are

$$U(t) = \frac{\hbar}{2e} \frac{\partial \phi}{\partial t}$$
 (superconducting phase evolution equation)

 $I(t) = I_c \sin(\phi(t))_{\text{(Josephson or weak-link current-phase relation)}}$

where $U(t)_{and} I(t)_{are}$ the voltage and current across the Josephson junction, $\phi(t)_{is}$ the "phase difference" across the junction (i.e., the difference in phase factor, or equivalently, argument, between the Ginzburg-Landau complex order parameter of the two superconductors comprising the junction), and I_{cis} a constant, the *critical current* of the junction. The critical current is an important phenomenological parameter of the device that can be affected by

temperature as well as by an applied magnetic field. The physical constant, $\overline{2e}$ is the magnetic flux quantum, the inverse of which is the Josephson constant.

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The three main effects predicted by Josephson follow from these relations:

1. The DC Josephson effect. This refers to the phenomenon of a direct current crossing the insulator in the absence of any external electromagnetic field, owing to tunneling. This DC Josephson current is proportional to the sine of the phase difference across the insulator, and may take values between $-I_{cand} I_{c}$.

2. The AC Josephson effect. With a fixed voltage U_{DC} across the junctions, the phase will vary linearly with time and the current will be an AC current with amplitude I_{cand} frequency

 $\frac{2e}{h} \cdot U_{DC}$. The complete expression for the current drive I_{ext} becomes $I_{ext} = C_J \frac{dv}{dt} + I_J sin\phi + \frac{V}{R}$. This means a Josephson junction can act as a perfect

voltage-to-frequency converter.

3. The inverse AC Josephson effect. If the phase takes the form $\phi(t) = \phi_0 + n\omega t + a\sin(\omega t)$, the voltage and current will be

$$U(t) = \frac{\hbar}{2e}\omega(n + a\cos(\omega t)), \quad I(t) = I_c \sum_{m = -\infty}^{\infty} J_n(a)\sin(\phi_0 + (n + m)\omega t)$$

The DC components will then be

$$U_{DC} = n \frac{\hbar}{2e} \omega, \quad I(t) = I_c J_{-n}(a) \sin \phi_0$$

Hence, for distinct DC voltages, the junction may carry a DC current and the junction acts like a perfect frequency-to-voltage converter.

Applications

The Josephson effect has found wide usage, for example in the following areas:

- SQUIDs, or superconducting quantum interference devices, are very sensitive magnetometers that operate via the Josephson effect. They are widely used in science and engineering. (See main article: SQUID.)
- In precision metrology, the Josephson effect provides an exactly reproducible conversion between frequency and voltage. Since the frequency is already defined precisely and

practically by the cesium standard, the Josephson effect is used, for most practical purposes, to give the definition of a volt (although, as of July 2007, this is not the official BIPM definition).

- Single-electron transistors are often constructed of superconducting materials, allowing use to be made of the Josephson effect to achieve novel effects. The resulting device is called a "superconducting single-electron transistor".
- Josephson junctions are integral in Superconducting quantum computing as qubits where the phase and charge act as the Conjugate variables.

CURIE'S LAW

In a paramagnetic material the magnetization of the material is directly proportional to an applied magnetic field. However, if the material is heated, this proportionality is reduced: for a fixed value of the field, the magnetization is inversely proportional to temperature. This fact is encapsulated by Curie's law:

$$\mathbf{M} = C \cdot \frac{\mathbf{B}}{T},$$

where

M is the resulting magnetisationB is the magnetic field, measured in teslasT is absolute temperature, measured in kelvins

C is a material-specific Curie constant

This relation was discovered experimentally (by fitting the results to a correctly guessed model) by Pierre Curie. It only holds for high temperatures, or weak magnetic fields. As the derivations below show, the magnetization saturates in the opposite limit of low temperatures, or strong fields.

Simple Derivation (Statistical Mechanics)



Magnetization of a paramagnet as a function of inverse temperature.

A simple model of a paramagnet concentrates on the particles which compose it, call them *paramagnetons*, which do not interact with each other. Each paramagneton has a magnetic moment given by $\vec{\mu}$. The energy of a magnetic moment in a magnetic field is given by

$$E = -\vec{\mu} \cdot \vec{B}$$

To simplify the calculation, we are going to work with a 2-state paramagneton: the particle may either align its magnetic moment with the magnetic field, or against it. So the only possible values of magnetic moment are then μ and $-\mu$. If so, then such a particle has only two possible energies

$$E_0 = -\mu B$$

and

$$E_1 = \mu B$$

When one seeks the magnetization of a paramagnet, one is interested in the likelihood of a paramagneton to align itself with the field. In other words, one seeks the expectation value of the magnetization μ :

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M.Sc PhysicsCondensed Matter Physics2017-2018UNIT III(17PHP101)HEAT CAPACITY OF THE ELECTRON GAS $\langle \mu \rangle = \mu P(\mu) + (-\mu) P(-\mu) = \frac{1}{Z} \left(\mu e^{\mu B \beta} - \mu e^{-\mu B \beta} \right) = \frac{2\mu}{Z} \sinh(\mu B \beta),$

where the probability of a configuration is given by its Boltzmann factor, and the partition function Z provides the necessary normalization for probabilities (so that the sum of all of them is unity.) The partition function of one paramagneton is:

$$Z = \sum_{n=0,1} e^{-E_n \beta} = e^{\mu B \beta} + e^{-\mu B \beta} = 2 \cosh(\mu B \beta)$$

Therefore, in this simple case we have:

 $\langle \mu \rangle = \mu \tanh{(\mu B \beta)}$

This is magnetization of one paramagneton, the total magnetization of the solid is given by

$$M = N \langle \mu \rangle = N \mu \tanh\left(\frac{\mu B}{kT}\right)$$

The formula above is known as the Langevin Paramagnetic equation. Pierre Curie found an approximation to this law which applies to the relatively high temperatures and low, magnetic fields used in his experiments. Let's see what happens to the magnetization as we specialize it to large T and small B. As temperature increases and magnetic field decreases, the argument of hyperbolic tangent decreases. Another way to say this is

$$\left(\frac{\mu B}{kT}\right) \ll 1$$

this is sometimes called the Curie regime. We also know that if $|x| \ll 1$, then

$$anh \, x pprox x$$

So

$$\mathbf{M}(T\to\infty)=\frac{N\mu^2}{k}\frac{\mathbf{B}}{T}$$

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Q.E.D., with a Curie constant given by $C = N\mu^2 / k$. Also, in the opposite regime of low temperatures or high fields, *M* tends to a maximum value of $N\mu$, corresponding to all the paramagnetons being completely aligned with the field.

FERROMAGNETISM

Iron, nickel, cobalt and some of the rare earths (gadolinium, dysprosium) exhibit a unique magnetic behavior which is called ferromagnetism because iron (ferrum in Latin) is the most common and most dramatic example. Samarium and neodymium in alloys with cobalt have been used to fabricate very strong rare-earth magnets.

Ferromagnetic materials exhibit a long-range ordering phenomenon at the atomic level which causes the unpaired electron spins to line up parallel with each other in a region called a domain. Within the domain, the magnetic field is intense, but in a bulk sample the material will usually be unmagnetized because the many domains will themselves be randomly oriented with respect to one another. Ferromagnetism manifests itself in the fact that a small externally imposed magnetic field, say from a solenoid, can cause the magnetic domains to line up with each other and the material is said to be magnetized. The driving magnetic field will then be increased by a large factor which is usually expressed as a relative permeability for the material. There are many practical applications of ferromagnetic materials, such as the electromagnet.

Ferromagnets will tend to stay magnetized to some extent after being subjected to an external magnetic field. This tendency to "remember their magnetic history" is called hysteresis. The fraction of the saturation magnetization which is retained when the driving field is removed is called the remanence of the material, and is an important factor in permanent magnets.

All ferromagnets have a maximum temperature where the ferromagnetic property disappears as a result of thermal agitation. This temperature is called the Curie temperature. Ferromagnetic materials will respond mechanically to an impressed magnetic field, changing length slightly in the direction of the applied field. This property, called magnetostriction, leads to the familiar hum of transformers as they respond mechanically to 60 Hz AC voltages.

WEISS MOLECULAR FIELD

Some materials present very strong magnetization, typically in the order of the saturation magnetization, also in absence of external field, i.e. they present spontaneous magnetization.

These kinds of materials are referred to as *ferromagnetic materials* (Fe, Co, Ni, Gd, alloys, etc.). Typical properties of some ferromagnetic materials can be found in Appendix A. The behavior of very small regions of ferromagnetic materials can be treated by following the same line of reasoning used for paramagnetism. With respect to the continuum model introduced in section 1.1.1, we are now dealing with phenomena occurring inside our elementary volume $dV_{\mathbf{r}}$, which involve the interactions between single spins. Here we report the theory developed by Weiss which is very similar to the one used for paramagnetism. In fact, the main difference stays in the postulation of an additional magnetic field H w whose non magnetic (Maxwellian) origin $H_{\mathbf{w}} = N$ is not investigated. This field was called *molecular field* by Weiss; by adding the field $W_{\mathbf{w}}$

w M (^N w is characteristic of the material) to the external field in Eq. (1.24), one ends up with the following equation:

$$M = M_s \mathcal{L} \left(\frac{\mu_0 m_0 (H_a + N_w M)}{kT} \right) \quad .$$
(1.28)

The latter equation can be linearized for high temperatures, which corresponds to small β as seen before. Then, one can find the well-known *Curie-Weiss law* that once again expresses

the dependence of the susceptibility on the temperature

$$\chi \propto \frac{1}{T - T_c}$$
 , $T_c = \frac{\mu_0 M_s m_0 N_w}{3k}$,
(1.29)

where T_c is the Curie temperature, characteristic of the material. Thus, for temperatures $T > T_c$ the ferromagnetic materials behave like paramagnetic. For temperature $T < T_c$, one can use Eq. (1.28) to derive the relationship between the saturation magnetization M_s and the

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temperature T. The resulting relationship
$$M_s = M_s(T)$$
 be

behaves like in Fig. 1.2. This behavior

qualitatively matches with experimental observations [5].



Figure 1.2: Typical behaviour of spontaneous magnetization as function of temperature

In addition, the phenomenological approach of molecular field was theoretically justified when Heisenberg introduced the exchange interaction on the basis of quantum theory (1931). Nevertheless, the Weiss theory gives information about the magnitude of magnetization, but nothing can be said about the direction. In this respect micromagnetics has the purpose to find the direction of magnetization at every location within the magnetic body. In this respect, for

constant temperature, the magnetization vector field $\mathbf{M}(\mathbf{r},t)$ can be written as

$$\mathbf{M}(\mathbf{r},t) = M_s \,\mathbf{m}(\mathbf{r},t) \quad , \tag{1.30}$$

where $\mathbf{m}(\mathbf{r},t)$ is the magnetization unit-vector field.

DOMAIN THEORY

A more modern theory of magnetism is based on the electron spin principle. From the study of atomic structure it is known that all matter is composed of vast quantities of atoms, each atom containing one or more orbital electrons. The electrons are considered to orbit in various shells and subshells depending upon their distance from the nucleus. The structure of the atom has

previously been compared to the solar system, wherein the electrons orbiting the nucleus correspond to the planets orbiting the sun. Along with its orbital motion about the sun, each planet also revolves on its axis. It is believed that the electron also revolves on its axis as it orbits the nucleus of an atom.

It has been experimentally proven that an electron has a magnetic field about it along with an electric field. The effectiveness of the magnetic field of an atom is determined by the number of electrons spinning in each direction. If an atom has equal numbers of electrons spinning in opposite directions, the magnetic fields surrounding the electrons cancel one another, and the atom is unmagnetized. However, if more electrons spin in one direction than another, the atom is magnetized. An atom with an atomic number of 26, such as iron, has 26 protons in the nucleus and 26 revolving electrons orbiting its nucleus. If 13 electrons are spinning in a clockwise direction and 13 electrons are spinning in a counterclockwise direction, the opposing magnetic fields will be neutralized. When more than 13 electrons spin in either direction, the atom is magnetized. An example of a magnetized atom of iron is shown in figure below:



ANTIFERROMAGNETISM



Antiferromagnetic ordering

In materials that exhibit antiferromagnetism, the magnetic moments of atoms or molecules, usually related to the spins of electrons, align in a regular pattern with neighboring spins (on different sublattices) pointing in opposite directions. This is, like ferromagnetism and ferrimagnetism, a manifestation of ordered magnetism. Generally, antiferromagnetic order may exist at sufficiently low temperatures, vanishing at and above a certain temperature, the Néel temperature (named after Louis Néel, who had first identified this type of magnetic ordering). Above the Néel temperature, the material is typically paramagnetic.

Geometric frustration

Unlike ferromagnetism, anti-ferromagnetic interactions can lead to multiple optimal states (ground states—states of minimal energy). In one dimension, the anti-ferromagnetic ground state is an alternating series of spins: up, down, up, down, etc. Yet in two dimensions, multiple ground states can occur.

Consider an equilateral triangle with three spins, one on each vertex. If each spin can take on only two values (up or down), there are $2^3 = 8$ possible states of the system, six of which are ground states! The two situations which are not ground states are when all three spins are up or are all down. In any of the other six states, there will be two favorable interactions and one unfavorable one. This illustrates frustration: the inability of the system to find a single ground state. This type of magnetic behavior has been found in minerals that have a crystal stacking structure such as a Kagome lattice or hexagonal lattice.

Antiferromagnetic materials

Antiferromagnetic materials occur commonly among transition metal compounds, especially oxides. An example is the heavy-fermion superconductor URu₂Si₂. Better known examples include hematite, metals such as chromium, alloys such as iron manganese (FeMn), and oxides such as nickel oxide (NiO). There are also numerous examples among high nuclearity metal clusters. Organic molecules can also exhibit antiferromagnetic coupling under rare circumstances, as seen in radicals such as 5-dehydro-m-xylylene.

Antiferromagnets can couple to ferromagnets, for instance, through a mechanism known as exchange bias, in which the ferromagnetic film is either grown upon the antiferromagnet or annealed in an aligning magnetic field, causing the surface atoms of the ferromagnet to align with the surface atoms of the antiferromagnet. This provides the ability to "pin" the orientation of a ferromagnetic film, which provides one of the main uses in so-called spin valves, which are the basis of magnetic sensors including modern hard drive read heads. The temperature at or above which an antiferromagnetic layer loses its ability to "pin" the magnetization direction of an adjacent ferromagnetic layer is called the blocking temperature of that layer and is usually lower than the Néel temperature.

Other properties

Antiferromagnetism plays a crucial role in giant magnetoresistance, as had been discovered in 1988 by the Nobel prize winners Albert Fertand Peter Grünberg (awarded in 2007).

There are also examples of disordered materials (such as iron phosphate glasses) that become antiferromagnetic below their Néel temperature. These disordered networks 'frustrate' the antiparallelism of adjacent spins; i.e. it is not possible to construct a network where each spin is surrounded by opposite neighbour spins. It can only be determined that the average correlation of neighbour spins is antiferromagnetic. This type of magnetism is sometimes called speromagnetism.

ESSENTIAL NÉEL THEORY

The theoretical basis for how ancient magnetic fields might be preserved was established over fifty years ago with the work of Nobel prize winner Louis Néel (1949, 1955). In the introduction to this chapter, we suggested that the mechanism which controls the approach to magnetic equilibrium is relaxation time. In the sheep analogy this would be the frequency of fence jumping. We defined relaxation time by Equation 4.11 in Chapter 4, sometimes called the Néel equation, which relates τ to volume v, the anisotropy constant (K) and absolute temperature (T).

Relaxation time is controlled by the competition between anisotropy energy Kv and thermal energy, so will be constant at a given temperature with constant Kv. Iso- τ s of equal

relaxation time are curves in v - K space. Figure 7.2b shows the family of curves with τ s ranging from ~100 seconds to the age of the Earth. The inset to Figure 7.2b illustrates the effect of temperature on the iso- τ s, which move up and to the right with increasing temperature. This behavior gives us a clue as to how a rise in temperature could change a "blocked" remanence at 0°C (273K) (one that is stable for long periods of time) to an unblocked one. In fact, Figure 7.2b (and the inset) suggests two other ways of manipulating the approach to equilibrium besides temperature: by changing the time span of observation and by changing grain volume. Each of these mechanisms represents a different mode of remanence acquisition (thermal, viscous, and chemical remanences respectively). Naturally acquired remanences are generally referred to as natural remanent magnetizations or NRMs. In this chapter we will introduce these and other forms of NRM and how they are acquired. We will also introduce useful unnatural remanences where appropriate.

In the "sheep in the rain" scenario, jumping over the fence into the sun would occur more frequently than jumping into the rain. It is also true that the energy barrier for magnetic particles to flip into the direction of the applied field H requires less energy than to flip the other way, so relaxation time must also be a function of the applied field. This tendency is reflected in the more general form of the Néel equation:

$$\tau = \frac{1}{C} \exp \frac{[Kv]}{[kT]} [1 - \frac{H}{H_c}]^2.$$
(7.1)

In this chapter we are concerned mainly with magnetic remanences acquired in the presence of the Earth's magnetic field, which is tiny compared to the coercivity of the minerals in question and so we can neglect the effect of H on τ in the next few sections.

In Equation 7.1, the product Kv is an energy barrier to the rotation of m and we will call it the blocking energy. High blocking energies will promote more stable magnetizations. We learned in Chapter 4 that K for uniaxial shape anisotropy, K_u , is related to the coercivity H_c (the field required to flip the magnetization) by:

$$H_c = \frac{2K_u}{\mu_o M_s},$$

where M_s is the saturation magnetization. Substituting for K_u in Equation 4.11 from Chapter 4 we get:

$$\tau = \frac{1}{C} \exp \frac{\left[\mu_o H_c M_s v\right]}{\left[2kT\right]}, (7.2)$$

where M_s is itself a strong function of temperature. We can see from Equation 7.2 that relaxation time is a function of magnetization, as well as volume, coercivity and temperature, properties that we will return to later in the chapter and in future chapters through out the course.



Figure 7.3:Lines of equal blocking energy in plot of grain volume, v, against the anisotropy energy density, K. Lines of equal blocking energy (product Kv) are also lines of equal relaxation time, τ , at a given temperature (here assumed to be room temperature). Contours are for a hypothetical population of magnetic grains. Grains with short τ plot toward the lower left. Grains with long τ plot toward the upper right; superparamagnetic grains with $\tau < 100$ s plot to the left or below the "superparamagnetic line" when $\tau \approx 100$ s. Stable single domain grains with $\tau > 100$ s plot above or to right of superparamagnetic line.

It is instructive to plot distributions of grains on the v - K diagrams as shown in Figure 7.3b. By definition, superparamagnetic grains are those grains whose remanence relaxes quickly. A convenient critical relaxation time, for purposes of laboratory experiments may be taken as ~ 100 s. Effective paleomagnetic recorders must have relaxation times on the order of geological time. So it might be more appropriate to choose τ s of the age of the Earth (4.5 Gyr) as the relevant relaxation for geological time scales.

FERRIMAGNETISM



Ferrimagnetic ordering

In physics, a ferrimagnetic material is one in which the magnetic moments of the atoms on different sub lattices are opposed, as in antiferromagnetism; however, in ferrimagnetic materials, the opposing moments are unequal and a spontaneous magnetization remains. This happens when the sub lattices consist of different materials or ions (such as Fe^{2+} and Fe^{3+}).

Ferrimagnetic materials are like ferromagnets in that they hold a spontaneous magnetization below the Curie temperature, and show no magnetic order (are paramagnetic) above this temperature. However, there is sometimes a temperature *below* the Curie temperature at which the two sub lattices have equal moments, resulting in a net magnetic moment of zero; this is called the *magnetization compensation point*. This compensation point is observed easily in garnets and rare earth - transition metal alloys (RE-TM). Furthermore, ferrimagnets may also exhibit an *angular momentum compensation point* at which the angular momentum of the magnetic sub lattices is compensated. This compensation point is a crucial point for achieving high speed magnetization reversal in magnetic memory devices .

Ferrimagnetism is exhibited by ferrites and magnetic garnets. The oldest-known magnetic substance, magnetite (iron (II, III) oxide; Fe_3O_4), is a ferrimagnet; it was originally classified as a ferromagnet before Néel's discovery of ferrimagnetism and antiferromagnetism in 1948.

Some ferrimagnetic materials are YIG (yttrium iron garnet) and ferrites composed of iron oxides and other elements such as aluminum, cobalt, nickel, manganese and zinc.

Properties

Ferrimagnetic materials have high resistivity and have anisotropic properties. The anisotropy is actually induced by an external applied field. When this applied field aligns with the magnetic dipoles it causes a net magnetic dipole moment and causes the magnetic

dipoles to precess at a frequency controlled by the applied field, called *Larmor* or *precession frequency*. As a particular example, a microwave signal circularly polarized in the same direction as this precession strongly interacts with the magnetic dipole moments; when it is polarized in the opposite direction the interaction is very low. When the interaction is strong, the microwave signal can pass through the material. This directional property is used in the construction of microwave devices like isolators, circulators and gyrators. Ferrimagnetic materials are also used to produce optical insulators and circulators.

FERRITE

Ferrites are a class of chemical compounds with the formula AB_2O_4 , where A and B represent various metal cations, usually including iron. These magnetic ceramic materials are used to make permanent magnets, ferrite cores for transformers, and in various other high tech applications.

Ferrites are a class of spinels, materials that adopt a crystal motif consisting of cubic close-packed (FCC) oxides (O^{2-}) with A cations occupying one eighth of the tetrahedral holes and B cations occupying half of the octahedral holes. The magnetic material known as "ZnFe" has the deceptively simple formula ZnFe₂O₄, with Fe³⁺ occupying the octahedral sites and half of the tetrahedral sites. The remaining tetrahedral sites in this spinel are occupied by Zn²⁺.

Properties

Ferrites are usually non-conductive ferrimagnetic ceramic compounds derived from iron oxides such as hematite (Fe_2O_3) or magnetite (Fe_3O_4) as well as oxides of other metals. Ferrites are, like most other ceramics, hard and brittle. In terms of the magnetic properties, ferrites are often classified as "soft" and "hard" which refers to their low or high coercivity of their magnetism, respectively.

Soft ferrites

Ferrites that are used in transformer or electromagnetic cores contain nickel, zinc, and/or manganese compounds. They have a low coercivity and are called soft ferrites. The low coercivity means the material's magnetization can easily reverse direction without dissipating

much energy (hysteresis losses), while the material's high resistivity prevents eddy currents in the core, another source of energy loss. Because of their comparatively low losses at high frequencies, they are extensively used in the cores of switched-mode power supply (SMPS) and RF transformers and inductors. A common ferrite, chemical symbol MnZn, is composed of the oxides of manganese and zinc.

The most common ferrites are manganese-zinc (MnZn, with the formula $Mn_aZn_{(1-a)}Fe_2O_4$) and nickel-zinc (NiZn, with the formula $Ni_aZn_{(1-a)}Fe_2O_4$). NiZn ferrites exhibit higher resistivity than MnZn, and are therefore more suitable for frequencies above 1 MHz. MnZn have in comparison higher permeability and saturation induction.

Hard ferrites

In contrast, permanent ferrite magnets are made of hard ferrites, which have a high coercivity and high remanence after magnetization. These are composed of iron and barium or strontium oxides. In a magnetically saturated state they conduct magnetic flux well and have a high magnetic permeability. This enables these so-called *ceramic magnets* to store stronger magnetic fields than iron itself. They are cheap, and are widely used in household products such as refrigerator magnets. The maximum magnetic field *B* is about 0.35 tesla and the magnetic field strength *H* is about 30 to 160 kiloampere turns per meter (400 to 2000 oersteds). (Hill 2006)

Production

Ferrites are produced by heating an intimate mixture of powdered precursors pressed into a mold. During the heating process, calcination of carbonates occurs:

$MCO_3 \rightarrow MO + CO_2$

The oxides of barium and strontium are typically supplied as their carbonates, BaCO₃ or SrCO₃. The resulting mixture of oxides undergoes sintering. Sintering is a high temperature process similar to the firing of ceramic ware.

Afterwards the cooled product is milled to particles smaller than 2 μ m, small enough that each particle consists of a single Weiss domain. Next the powder is pressed into a shape, dried, and re-sintered. The shaping may be performed in an external magnetic field, in order to achieve a preferred orientation of the particles (anisotropy).

Small and geometrically easy shapes may be produced with dry pressing. However, in such a process small particles may agglomerate and lead to poorer magnetic properties compared to the wet pressing process. Direct calcination and sintering without re-milling is possible as well but leads to poor magnetic properties.

Electromagnets are pre-sintered as well (pre-reaction), milled and pressed. However, the sintering takes place in a specific atmosphere, for instance one with an oxygen shortage. The chemical composition and especially the structure vary strongly between the precursor and the sintered product.

To allow efficient stacking of product in the furnace during sintering and prevent parts sticking together, many manufacturers separate ware using Ceramic Powder Separator Sheets. These sheets are available in various materials such as alumina, zirconia and magnesia. They are also available in fine medium and coarse particle sizes. By matching the material and particle size to the ware being sintered, surface damage and contamination can be reduced while maximizing furnace loading.

Uses

- Ferrite cores are used in electronic inductors, transformers, and electromagnets where the high electrical resistance of the ferrite leads to very low eddy current losses. They are commonly seen as a lump in a computer cable, called a ferrite bead, which helps to prevent high frequency electrical noise (radio frequency interference) from exiting or entering the equipment.
- Early computer memories stored data in the residual magnetic fields of hard ferrite cores, which were assembled into arrays of *core memory*. Ferrite powders are used in the coatings of magnetic recording tapes. One such type of material is iron (III) oxide.
- Ferrite particles are also used as a component of radar-absorbing materials or coatings used in stealth aircraft and in the expensive absorption tiles lining the rooms used for electromagnetic compatibility measurements.
- Most common radio magnets, including those used in loudspeakers, are ferrite magnets. Ferrite magnets have largely displaced Alnico magnets in these applications.

• It is a common magnetic material for electromagnetic instrument pickups, because of price and relatively high output. However, such pickups lack certain sonic qualities found in other pickups, such as those that use Alnico alloys or more sophisticated magnets.

SPIN WAVES

Spin waves are propagating disturbances in the ordering of magnetic materials. These low-lying collective excitations occur in magnetic lattices with continuous symmetry. From the equivalent quasiparticle point of view, spin waves are known as magnons, which are boson modes of the spin lattice that correspond roughly to the phonon excitations of the nuclear lattice. As temperature is increased, the thermal excitation of spin waves reduces a ferromagnet's spontaneous magnetization. The energies of spin waves are typically only µeV in keeping with typical Curie points at room temperature and below.



An illustration of the precession of a spin wave about an applied magnetic field with a wavevector that is eleven times the lattice constant.

KARAPAGAM ACADEMY OF HIGHER EDUCATION, COIMBATORE-21 POSSIBLE QUESTIONS

UNIT III

- 1. Describe quantum theory of paramagnetism.
- 2. Explain the free electron theory of metals and Debye's equation.

- 3. Explain the Langevin theory of paramagnetism
- 4. Explain Weiss molecular field theory.
- 5. Give an account of Neel's theory of antiferromagnetism and show how ferromagnetic behaviour of ferrites can be explained from Neel's theory.
- 6. How to measure the resistivity of metals? Give the explanation of free electron theory of metals
- 7. What do you mean by specific heat capacity? Explain the superconductivity with any two significant properties.
- 8. What is energy gap of metals? Explain BCS theory and Josephson effect of superconductors.
- 9. Write the experimental techniques to study the magnetic properties.

KARPAGAM ACADEMY OF HIGHER EDUCATION, COIMBATORE-21

DEPARTMENT OF PHYSICS I M.SC PHYSICS

BATCH: 2017-2019

CONDENSED MATTER PHYSICS (17PHP101)

MULTIPLE CHOICE QUESTIONS

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Questions	option 1	option 2	option 3	option 4	Answer
UNIT III					
The SI unit of heat capacity is	joule	joule/kilogram	joule/(kilogram × kelvin)	joule/kelvin	joule/kelvin
Aluminum has the specific heat capacity of	450 J kg ⁻¹ °C ⁻¹	900 J kg ⁻¹ °C ⁻¹	1350 J kg ⁻¹ °C ⁻¹	1800 J kg ⁻¹ °C ⁻¹	900 J kg ⁻¹ °C ⁻¹
In a laboratory, bunsen burner is used to increase the temperature of lime from 10 °C to 50 °C with the thermal energy of 80000 J. If the mass of the lime is 20 kg the specific heat capacity of the lime would be	25 J kg ⁻¹ °C ⁻¹	50 J kg ⁻¹ °C ⁻¹	75 J kg ⁻¹ °C ⁻¹	100 J kg ⁻¹ °C ⁻¹	100 J kg ⁻¹ °C ⁻¹
The heat capacity of sodium metal is 1500 J K ⁻¹ , if the mass of the sodium metal is 75 kg, the specific heat capacity would be	10 J kg ⁻¹ °C ⁻¹	20 J kg ⁻¹ °C ⁻¹	40 J kg ⁻¹ °C ⁻¹	80 J kg ⁻¹ °C ⁻¹	$20 \text{ J kg}^{-1} \text{ °C}^{-1}$
The internal energy comprises of two types of energies, those are	mechanical and electrical energy	magnetic and electrical energy	kinetic and potential energy	kinetic and magnetic energy	kinetic and potential energy
What substance is attracted to a magnet?	silver	lead	water	iron	iron
What characteristics do magnetic substances have?	They can give a "shock" when you touch them.	They can push or pull objects they are not touching.	They are always black and cold to touch.	They fall faster than other objects when you drop them.	They can push or pull objects they are not touching.
Ancient people discovered magnetic rocks called lodestone. What did they use them for?	to start fires	compasses	sculptures	telephone receivers	compasses
What must happen for an electromagnet to have a magnetic field?	It must be heated.	It has to be touching another magnet.	It must be lined up with Earth's magnetic field.	It must be connected to an electrical source.	It must be connected to an electrical source.
What happens when two north poles of magnets are placed together?	They repel.	They attract.	They cancel each other out.	The strength of the magnet is doubled.	They repel.
How is Earth's magnetic field similar to that of a magnet?	It has North and South poles.	It is hundreds of miles long.	It is made in Earth's core.	It is shaped like a horseshoe.	It has North and South poles.
What is our best evidence that Earth has a magnetic field?	All things fall toward Earth's center.	A compass needle lines up with it.	Winds blow from east to west.	Earth's oceans all have currents.	A compass needle lines up with it.
The study of phenomena at very low temperatures is called	heat transfer	morphology	crystallography	cryogenics	cryogenics
Thermal insulation is used to:	stop the flow of heat.	reduce the flow of heat.	absorb heat.	reverse the heat flow direction.	reverse the heat flow direction.
On which of the following factors does the resistivity of a material depend ?	Resistance of the conductor	Area of the conductor section	Length of the conductor	All of the above	All of the above
is a negatively charged particle present in an atom.	Proton	Neutron	Electron	None of the above	Electron
A perfect conductor has	zero conductivity	unity conductivity	infinite conductivity	none of the above	infinite conductivity
The metal having the lowest temperature coefficient of resistance is	gold	copper	aluminium	kanthal	gold
Commonly used conducting materials are	copper	aluminium	both (a) and (b)	copper and silver	both (a) and (b)
Which of the following materials is preferred for transmitting electrical energy over long distance ?	Copper	Aluminium	Steel reinforced copper	Steel reinforced aluminium	Steel reinforced aluminium

The kingtic energy of a bounded electron is	less than that of	greater than that of	equal to that of	infinite	less than that of
The kinetic chergy of a bounded electron is	unbounded electron	unbounded electron	unbounded electron	mmme	unbounded electron
The conductivity of a conductor can be increased by	decreasing its	increasing its	deereesing its vibration	increasing its vibration	decreasing its
The conductivity of a conductor can be increased by	temperature	temperature	decreasing its vioration		temperature
Superconductivity is observed for	infrared frequencies	d.c. and low frequency	a.c. and high frequency	frequencies having no effect	d.c. and low frequency
	the crystal structure	all electrons interact in	the electrons jump into		the crystal structure
The superconductivity is due to	having no atomic	the super-conducting	nucleus at 0°K	none of the above	having no atomic
	vibration at 0°K	state	nucleus at 0 K		vibration at 0°K
The value of critical field below the transition temperature will	increase	decrease	remain unchanged	any of the above	increase
In a superconductor the value of critical density depends upon	magnetic field strength	temperature	either (a) or (b)	both (a) and (b)	both (a) and (b)
Superconductors are becoming popular for use in	generating very strong	manufacture of bubble	generating electrostatic	generating regions free	generating very strong
Superconductors are occoming popular for use in	magnetic field	memories	field	from magnetic field	magnetic field
High resistivity materials are used in	precision instruments	heating elements	motor starters	all of the above	all of the above
Mercury as an electric contact material is	a liquid	a metal	a metal liquid	a gas	a metal liquid
An H.P.C. fuse is	a ceramic body having	a wire of platinum	a heavy cross-section of	a ceramic tube having	a ceramic body having
All II.K.C. luse is	metal and caps	a wife of platinum	copper or aluminium	carbon rod inside it	metal and caps
Which of the following resistive materials has the lowest temperature co- efficient of resistance ?	Nichrome	Constantan	Kanthal	Molybdenum	Nichrome
The conductors have transport phenomena of electrons due to	electric field	magnetic field	electromagnetic field	none of the above	electric field
The transition temperature of mercury is	18.0°K	9.22°K	4.12°K	1.14'K	4.12°K
By increasing impurity content in the metal alloy the residual resistivity always	decreases	increases	remains constant	becomes temperature independent	increases
The structure sensitive property of a super conductor is	critical magnetic field	transition temperature	critical current density	none of the above	critical current density
At transition temperature the value of critical field is	zero	negative real value	positive real value	complex value	zero
Which of the following is the poorest conductor of electricity ?	Carbon	Steel	Silver	Aluminium	Carbon
has zero temperature co-efficient of resistance.	Aluminium	Carbon	Porcelain	Manganin	Manganin
In thermocouples which of the following pairs is commonly used ?	Copper-constantan	Aluminium-tin	Silver-German silver	Iron-steel	Copper-constantan
is most commonly used for making magnetic recording tape	Silver nitrate	Ferric oxide	Small particles of iron	Silicon-iron	Ferric oxide
A good electric contact material should have all of the following properties	high resistivity	high resistance to	good thermal	high malting point	high resistivity
except	nigh tesistivity	corrosion	conductivity	nigh mennig point	ingli resistivity
Most of the common metals have structure.	linear	hexagonal	orthorhombic	cubic	cubic
Which of the following affect greatly the resistivity of electrical conductors ?	Composition	Pressure	Size	Temperature	Composition
Addition of 0.3 to 4.5% silicon to iron the electrical resistivity of iron.	increases	decreases	does not change	zero	increases
Super conductivity can be destroyed by	adding impurities	reducing temperatures	application of magnetic field	any of the above	application of magnetic field
In graphita handing is	aavalant	matallia	Vandar Waala	Vander Waals and	Vander Waals and
	covalent	metanic	vanuel waals	covalent	covalent
The resistivity of a metal is a function of temperature because	the amplitude of vibration of the atoms varies with temperature	the electron density varies with temperature	the electron gas density varies with temperature	None	the amplitude of vibration of the atoms varies with temperature

he impurity atoms is semiconductors	inject more charge carriers	reduce the energy gap	increase the kinetic energy of valence electrons	all of the above	reduce the energy gap
Which of the following are non-conductors of electricity?	Non-metal solids except carbon	Air and most other gases	Pure water and liquids in general except mercury	All of the above	All of the above
Which of the following high resistance materials has the highest operating temperature ?	Kanthal	Manganin	Nichrome	Eureka	Kanthal
Low resistivity materials are used in	transformer, motor and generator windings	transmission and distribution lines	house wiring	all above applications	all above applications
Which of the following is an advantage of stranded conductor over equivalent single conductor ?	Less liability to kink	Greater flexibility	Less liability to break	All of the above	All of the above
Due to which of the following reasons copper and aluminium are not used for heating elements ?	Both have great tendency for oxidation	Both have low melting point	Very large length of wires will be required	All of the above	All of the above
Which of the following materials is used for making coils of standard resistances ?	Copper	Nichrome	Platinum	Manganin	Manganin
Substances whose specific resistance abruptly decreases at very low temperature are called	insulators	conductors	semiconductors	superconductors	superconductors
Which of the following materials is the best conductor of electricity?	Tungsten	Aluminium	Copper	Carbon	Copper
The conduction of electricity, in semiconductors, takes place due to movement of	positive ions only	negative ions only	positive and negative ions	electrons and holes	electrons and holes
Which of the following is a semiconductor material?	Phosphorous	Rubber	Silicon	Aluminium	Silicon
If the resistance of a conductor does not vary in accordance with Ohm's law it is known as	non-linear conductor	reverse conductor	bad-conductor	non-conductor	non-linear conductor
The forbidden gap in an insulator is	large	small	nil	any of the above	large
Which of the following factors affect resistivity of metals ?	Age hardening	Alloying	Temperature	All of the above	All of the above

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UNIT - IV

NANOSCIENCE

Structure: Size dependence of properties – Crystal Structures – Face centred nano particles – Particle size determination – Surface structure - Metal nano particles - Magic numbers – Theoretical model of nano particles – Geometric structure – Reactivity – Fluctuations – Magnetic clusters – Bulk to nano transitions Semi conducting nano particles – optical properties – photo fragmentation – Coulombic explosion.

Polymers: Forming and Characterizing polymers – Polymerisation – Sizes of polymers – Nano crystals – Condensed ring types – Poly diacetylene types – Polymers – Conductive polymers – Supra molecular structures – Transition-metal mediated types – Dendritic molecules – Supra molecular dendrimers – Micellers

STRUCTURE: SIZE DEPENDENCE OF PROPERTIES

Many properties of solids depend on the size range over which they are measured. Microscopic details become averaged when investigating bulk materials. At the macro- or large-scale range ordinarily studied in traditional fields of physics such as mechanics, electricity and magnetism, and optics, the sizes of the objects under study range from millimeters to kilometers. The properties that we associate with mechanics, the resistivity and magnetization in electricity and magnetism, and the dielectric constant in optics. When measurements are made in the micrometer or nanometer range, many properties of materials change, such as mechanical, ferroelectric, and ferromagnetic properties. The aim of the present book is to examine characteristics of solids at the next lower level of size, namely, the nanoscale level, perhaps from 1 to 100nm. Below this there is the atomic scale near 0.1 nm, followed by the nuclear scale near a femtometer m). In order to understand properties at the macroscopic and mesoscopic levels, and the present chapter aims to provide some of this background.

Many important nanostmetures are composed of the group IV elements Si or Ge, type **111-V** semiconducting compounds such as GaAs, or type **11-VI** semiconducting materials such as CdS, so these semiconductor materials will be used to illustrate some of the bulk properties
that become modified with incorporation into nanostructures. The Roman numerals **IV**, **111**, V, and so on, refer to columns of the periodic table. Appendix B provides tabulations of various properties of these semiconductors.

CRYSTAL STRUCTURES

Most solids are crystalline with their atoms arranged in a regular manner. They have what is called *long-range order* because the regularity can extend throughout the crystal. In contrast to this, amorphous materials such as glass and wax lack long range order, but they have what is called *short-range order* so the local environment of each atom is similar to that of other equivalent atoms, but this regularity does not persist over appreciable distances. Liquids also have short-range order, but lack long-range order. Gases lack both long-range and short-range order. Figure 1 shows the five regular arrangements of lattice points that can occur in two dimensions: the square (a), primitive rectangular (b), centered rectangular (c), hexagonal (d), and oblique (e) types. These arrangements are called *Bravais lattices.* The general or oblique Bravais lattice has two unequal lattice constants a # b and an arbitrary angle 8 between them. For the perpendicular case when $19 = 90^{\circ}$, the lattice becomes the rectangular type. For the special case a = b and $8 = 60^{\circ}$, the lattice is the hexagonal type formed from equilateral triangles. Each lattice has a unit cell, indicated in the figures, which can replicate throughout the plane and generate the lattice.



Figure 1. The five Bravais lattices that occur in two dimensions, with the unit cells indicated: (a) square; (b) primitive rectangular; (c) centered rectangular; (d) hexagonal; (e) oblique.

A crystal structure is formed by associating with a lattice a regular arrangement of atoms or molecules. Figure 2 presents a two-dimensional crystal structure based on a primitive rectangular lattice containing two diatomic molecules A-B in each unit cell. A single unit cell can generate the overall lattice. In three dimensions there are three lattice constants, a, b, and c, and three angles: c(between b and c; b between a and c, and y between lattice constants a and b.

There are 14 Bravais lattices, ranging from the lowest-symmetry triclinic type in which all three lattice constants and all three angles differ from each other (a # b # c and c(# b # y)), to the highest-symmetry cubic case in which all the lattice constants are equal and all the angles are 90" (a = b = c and c(= b = y = 90"). There are three Bravais lattices in the cubic system, namely, a primitive or simple cubic (SC) lattice in which the atoms occupy the eight apices of the cubic unit cell, as shown in Fig. 2a, a body-centered cubic (BCC) lattice with lattice points occupied at the apices and in the center of the unit cell, as indicated in Fig. 2b, and a face-centered cubic (FCC) Bravais lattice with atoms at the apices and in the centers of the faces, as shown in Fig. 2.3~. In two dimensions the most efficient way to pack identical circles (or spheres) is the equilateral triangle arrangement shown in Fig. 2a, corresponding to the hexagonal Bravais lattice of Fig. 2d. A second hexagonal layer of spheres can be placed on top of the first to form the most efficient packing of two layers, as shown in Fig. 2b. For efficient packing, the third layer can be placed either above the first layer with an atom at the location indicated by Tor in the third possible arrangement with an atom above the position marked by X on the figure. In the first case a hexagonal lattice with a hexagonal close-packed (HCP) structure is generated, and in the second case a face-centered cubic lattice results. The former is easy to visualize, but the latter is not so easy to picture.



(a) (b) (c) Figure 2 Unit cells of the three cubic Bravais lattices: (a) simple cubic (SC); (b) body-centered cubic (BCC); (c) face-centered cubic (FCC).



Figure 3. Close packing of spheres on a flat surface: (a) for a monolayer; (b) with a second layer added. The circles of the second layer are drawn smaller for clarity. The location of an octahedral site is indicated by x, and the position of a tetrahedral site is designated by T on panel (b).

In the three-dimensional case of close-packed spheres there are spaces or sites between the spheres where smaller atoms can reside. The point marked by X on Fig. 3b, called an octahedral site, is equidistant from the three spheres 0 below it, and from the three spheres 0 above it. An atom A at this site has the local coordination AO₂. The radius *aoct*, of this octahedral site is where a is the lattice constant and a. is the radius of the spheres. The number of octahedral sites is equal to the number of spheres. There are also smaller sites, called tetrahedral sites, labeled T in the figure that are equidistant from four nearest neighbor spheres, one below and three above, corresponding to AO, for the local coordination. This is a smaller site since its radius aT is There are twice as many tetrahedral sites as there are spheres in the structure. Many diatomic oxides and sulfides such as MgO, MgS, MnO, and MnS have their larger oxygen or sulfur anions in a perfect FCC arrangement with the smaller metal cations located at octahedral sites. This is called the NaCZ Zattice type, where we use the term anion for a negative ion (e.g., Cl-) and cation for a positive ion (e.g., Na+). The mineral spinel MgAI,O, has a face-centered arrangement of divalent oxygens 0,- (radius 0.132 nm) with the A13+ ions (radius 0.05 1 nm) occupying one-half of the octahedral sites and Mg2+ (radius 0.066 nm) located in one-eighth of the tetrahedral sites in a regular manner.

FACE CENTRED NANO PARTICLES

Most metals in the solid state form close-packed lattices; thus Ag, Al, Au, Co, Cu, Pb, Pt, and Rh, as well as the rare gases Ne, Ar, Kr, and Xe, are face-centered cubic (FCC), and Mg, Nd, Os, Re, Ru, Y, and Zn, are hexagonal close-packed (HCP). A number of other metallic atoms crystallize in the not so closely packed body centered cubic (BCC) lattice, and a few such as Cr, Li, and Sr crystallize in all three structure types, depending on the temperature. An atom in each of the two close packed lattices has 12 nearest neighbors. Figure 4 shows the 12 neighbors that surround an atom (darkened circle) located in the center of a cube for a FCC lattice. These 13 atoms constitute the smallest theoretical nanoparticle for an FCC lattice. Figure 2.6 shows the 14-sided polyhedron, called a *dekatessarahedron*, that is generated by connecting the atoms with planar faces. Sugano and Koizumi (1998) call this polyhedron a *cuboctahedron*. The three open circles at the upper right of Fig. 5 are the three atoms in the top layer of Fig. 10.18, the six darkened circles plus an atom in the center of the cube of Fig. 5 constitute the middle layer of that figure, and the open circle at the lower left of Fig. 4 is one of the three obscured atoms in the plane below the cluster pictured in Fig. 10.18. This 14-sided polyhedron has six square faces and eight equilateral triangle faces. If another layer of 42 atoms is layed down around the 13-atom nanoparticle, one obtains a 55-atom nanoparticle with the same dekatessarahedron shape. Larger



Figure 4 Face-centered cubic unit cell showing the 12 nearest-neighbor atoms that surround

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the atom (darkened circle) in the center.



Figure 5Thirteen-atom nanoparticle set in its FCC unit cell, showing the shape of the 14sided polyhedron associated with the nanocluster. The three open circles at the upper right correspond to the atoms of the top layer of the nanoparticle sketched in Fig. 10.8 (of Chapter lo), the six solid circles plus the atom (not pictured) in the center of the cube constitute the middle hexagonal layer of that figure, and the open circle at the lower left corner of the cube is one of the three atoms at the bottom of the cluster

layers, and the sequence of numbers in the resulting particles, N = 1,13,55,147,309,561,..., are called *structural magic numbers*. For *n* layers the number of atoms *N* in this FCC nanoparticle is given by the formula

N = i[10n3 - 15n2 + 11n - 31 (2.3)]

and the number of atoms on the surface Nsud is

Nsud = 10n2 - 20n + 12 (2.4)

For each value of n, Table 2.1 lists the number of atoms on the surface, as well as the percentage of atoms on the surface. The table also lists the diameter of each nanoparticle, which is given by the expression (2n - 1)d, where d is the distance between the centers of nearest-neighbor atoms, and d = a/& where a is the lattice constant. If the same procedure is used to construct nanoparticles with the hexagonal close-packed structure that was discussed in the

previous section, a slightly different set of structural magic numbers is obtained, namely, 1,13,57,153,321,581, . . . Purely metallic FCC nanoparticles such as Au,, tend to be very reactive and have short lifetimes. They can be ligand-stabilized by adding atomic groups between their atoms and on their surfaces. The Au,, nanoparticle has been studied in the ligand14 stabilized form Au55(PPh3)12C16w hich has the diameter of -1.4nm, where PPh, is an organic group. Further examples are the magic number nanoparticles Pt3,9(1, 10-phenantroline),,O,, and Pd561(1,10-phenantroline),,,0~,,. The magic numbers that we have been discussing are called structural magic numbers because they arise from minimum-volume, maximum-density nanoparticles that approximate a spherical shape, and have close-packed structures characteristic of a bulk solid. These magic numbers take no account of the electronic structure of the consitituent atoms in the nanoparticle. Sometimes the dominant factor in determining the minimum-energy structure of small nanoparticles is the interactions of the valence electrons of the constituent atoms with an averaged molecular potential, so that the electrons occupy orbital levels associated with this potential. Atomic cluster configurations in which these electrons fill closed shells are especially stable, and constitute electronic magic numbers. Their atomic structures differ from the FCC arrangement. When mass spectra were recorded for sodium nanoparticles Na., it was found that mass peaks corresponding to the first 15 electronic magic numbers $N = 3,9,20,36,61,\ldots$ were observed for cluster sizes up to N = 1220 atoms (n = 15), and FCC structural magic numbers starting with N = 1415 for n = 8 were observed for larger sizes [Martin et al. (1 990); see also Sugano and Koizumi (1 998), p. 901. The mass spectral data are plotted versus the cube root of the number of atoms N'I3, and it is clear that the lines from both sets of magic numbers are approximately equally spaced, with the spacing between the structural magic numbers about 2.6 times that between the electronic ones. This result provides evidence that small clusters tend to satisfy electronic criteria and large structures tend to be structurally determined.

PARTICLE SIZE DETERMINATION

Earlier we discussed determining the sizes of grains in polycrystalline materials via X-ray diffraction. These grains can range from nanoparticles with size distributions much larger micrometer-sized particles, held together tightly to form the polycrystalline material. This is the

bulk or clustered grain limit. The opposite limit is that of grains or nanoparticles dispersed in a matrix so that the distances between them are greater than their average diameters or dimensions. It is of interest to know how to measure the sizes, or ranges of sizes, of these dispersed particles. The most straightforward way to determine the size of a micrometer-sized grain is to look at it in a microscope, and for nanosized particles a transmission electron microscope (TEM). Another method for determining the sizes of particles is by measuring how they scatter light. The extent of the scattering depends on the relationship between the particle size d and the wavelength 1 of the light, and it also depends on the polarization of the incident light beam. For example, the scattering of white light, which contains wavelengths in the range from 400 nrn for blue to 750 nrn for red, off the nitrogen and oxygen molecules in the atmosphere with respective sizes d = 0.11 and 0.12 nm, explains why the light reflected from the sky during the day appears blue, and that transmitted by the atmosphere at sunrise and sunset appears red. Particle size determinations are made using a monochromatic (single-wavelength) laser beam scattered at a particular angle (usually 90°) for parallel and perpendicular polarizations. The detected intensities can provide the particle size, the particle concentration, and the index of refraction. The Rayleigh-Gans theory is used to interpret the data for particles with sizes d less than O.IA, which corresponds to the case for nanoparticles measured by optical wavelengths. The example of a laser beam nanoparticle determination shown in Fig. 3.7 shows an organic solvent dispersion with sizes ranging from 9 to 30 nrn, peaking at 12 nm. This method is applicable for use with nanoparticles that have diameters above 2 nm, and for smaller nanoparticles other methods must be used.



Figure 6. Sketch of a mass spectrometer utilizing a 90" magnetic field mass analyzer, showing details of the ion source: A-amlerator or extractor plate, Eelectron trap, Milament, lionization chamber, L-focusing lenses, Fkepeller, *Clits.* The magnetic lidd 01 the mass analyzer is perpendicular to the plane of the page.

The mass spectrometer that has been described made use of the typical magnetic field mass analyzer. Modern mass spectrometers generally employ other types of mass analyzers, such as the quadrupole model, or the time-of-flight type in which each ion acquires the same kinetic energy *;mu2* during its acceleration out of the ionization chamber, so the lighter mass ions move faster and arrive at the detector before the heavier ions, thereby providing a separation by mass.

SURFACE STRUCTURE

To obtain crystallographic information about the surface layers of a material a technique called low-energy electron diffraction (LEED) can be employed because at low energies (10-100 eV) the electrons penetrate only very short distances into the surface, so their diffraction pattern reflects the atomic spacings in the surface layer. If the diffraction pattern arises from more than one surface layer, the contribution of lower-lying crystallographic planes will be weaker in intensity. The electron beam behaves like a wave and reflects from crystallographic planes in analogy with an X-ray beam, and its wavelength I, called the *de Broglie Wavelength*, depends on the energy E expressed in the units of electron volts through the expression

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	1.226			

$$\lambda = \frac{1.226}{\sqrt{E}} \text{ nm}$$

Thus an electron energy of 25.2 eV gives a de Broglie wavelength I equal to the Ga-As bond distance in gallium arsenide (3'I2a/4 = 0.2442 nm), where the lattice constant a = 0.565 nm, so we see that low energies are adequate for crystallographic electron diffraction measurements. Another technique for determining surface layer lattice constants is reflection high energy electron diffraction (WEED) carried out at grazing incidence angles where the surface penetration is minimal. When 8 is small in the Bragg expression, then I must be small, so the energy E must be large, hence the need for higher energies for applying MEED diffraction at grazing incidence.

METAL NANO PARTICLES

MAGIC NUMBERS

Figure 7 is an illustration of a device used to form clusters of metal atoms. A high intensity laser beam is incident on a metal rod, causing evaporation of atoms from the surface of the metal. The atoms are then swept away by a burst of helium and passed through an orifice into a vacuum where the expansion of the gas causes cooling and formation of clusters of the metal atoms. These clusters are then ionized by *UV* radiation and passed into a mass spectrometer that measures their mass : charge ratio. Figure 8 shows the mass spectrum data of lead clusters formed in such an experiment where the number of ions (counts) is plotted as a function of the number of atoms in the cluster. (Usually mass spectra data are plotted as counts versus mass over charge.) The data show that clusters of 7 and 10 atoms are more likely than other clusters, which means that these clusters are more stable than clusters of other sizes. The ionization potential is the energy necessary to remove the outer electron from the



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Figure 7. Apparatus to make metal nanoparticles by laser induced evaporation of atoms from the surface of a metal. Various gases such as oxygen can be introduced to study the chemical interaction of the nanoparticles and the gases. (With permission from F. J. Owens and C. P. Poole, Jr., *New Superconductors*, Plenum Press, 1999.)



Figure 8. Mass spectrum of Pb clusters. [Adapted from M. A. Duncan and D. H. Rouvray, Sci.

Am. 110 (Dec. 1989).]

atom. The maximum ionization potentials occur for the rare-gas atoms *He, '%e, and **18Ar** because their outermost **s** andp orbitals are filled. More energy is required to remove electrons from filled orbitals than from unfilled orbitals. Peaks are observed at clusters having two and eight atoms. These numbers are referred to as *electronic magic numbers*. Their existence suggests that clusters can be viewed as superatoms, and this result motivated the development of the jellium model of clusters. In the case of larger clusters stability, is determined by structure and the magic numbers are referred to as *structural magic numbers*.

THEORETICAL MODEL OF NANO PARTICLES

The jellium model envisions a cluster of atoms as a large atom. The positive nuclear charge of each atom of the cluster is assumed to be uniformly distributed over a sphere the size of the cluster. A spherically symmetric potential well is used to represent the potential describing the interaction of the electron with the positive spherical charge distribution. Thus the energy levels can be obtained by solving the Schrodinger equation for this system in a fashion analogous to that for the hydrogen atom. The superscripts refer to the number of electrons that fill a

particular energy level. The electronic magic number corresponds to the total number of electrons on the superatom when the top level is filled. Notice that the order of the levels in the jellium model is different from that of the hydrogen atom. In this model the magic numbers correspond to those clusters having a size in which all the energy levels are filled. An alternative model that has been used to calculate the properties of clusters is to treat them as molecules and use existing molecular orbital theories such as density functional theory to calculate their properties. This approach can be used to calculate the actual geometric and electronic structure of small metal clusters. In the quantum theory of the hydrogen atom, the electron circulating about the nucleus is described by a wave. The mathematical function for this wave, called the *wavefunction* \$, is obtained by solving the Schrodinger equation, which includes the electrostatic potential between the electron and the positively charged nucleus. The square of the amplitude of the nucleus. The wavefunction of the lowest level of the hydrogen atom designated the 1s level has the form

$$\psi(1s) = A \exp\left(-\frac{r}{\rho}\right) \tag{4.1}$$

where r is the distance of the electron from the nucleus and p is the radius of the first Bohr orbit. This comes from solving the Schrodinger equation for an electron having an electrostatic interaction with a positive nucleus given by e/r. The equation of the hydrogen atom is one of the few exactly solvable problems in physics, and is one of the best understood systems in the Universe. In the case of a molecule such as the H,+ ion, molecular orbital theory assumes that the wavefinction of the electron around the two H nuclei can be described as a linear combination of the wavefunction of the isolated H atoms.

The Schrodinger equation for the molecular ion is

$$\left[\left(\frac{-\hbar^2}{2m}\right)\nabla^2 - \frac{e^2}{r_a} - \frac{e^2}{r_b}\right]\psi = E\psi$$

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The symbol V * denotes a double differentiation operation. The last two terms in the brackets are the electrostatic attraction of the electron to the two positive nuclei, which are at distances r, and rb from the electron. For the hydrogen molecule, which has two electrons, a term for the electrostatic repulsion of the two electrons would be added. The Schrodinger equation is solved with this linear combination of wavefunctions. When there are many atoms in the molecule and many electrons, the problem becomes complex, and many approximations are used to obtain the solution. Density functional theory represents one approximation. With the development of large fast computer capability and new theoretical approaches, it is possible using molecular orbital theory to determine the geometric and electronic structures of large molecules with a high degree of accuracy. The calculations can find the structure with the lowest energy, which will be the equilibrium geometry. These molecular orbital methods with some modification have been applied to metal nanoparticles.

GEOMETRIC STRUCTURE

Generally the crystal structure of large nanoparticles is the same as the bulk structure with somewhat different lattice parameters. X-ray diffraction studies of **80-nm** aluminum particles have shown that it has the face-centered cubic (FCC) unit cell shown in Fig. 9a, which is the structure of the unit cell of bulk aluminum. However, in some instances it has been shown that small particles having diameters of <5 nm may have different structures. For example, it has been shown that 3-5-nm gold particles have an icosahedral structure rather than the bulk FCC structure. It is of interest to consider an aluminum cluster of 13 atoms because this is a magic number. Figure 9b shows three possible arrangements of atoms for the cluster. On the basis of criteria of maximizing the number of bonds and minimizing the number of atoms on the surface, as well as the fact that the structure of bulk aluminum is FCC, one might expect the structure of the particle to be FCC.



Figure 9. (a) The unit cell of bulk aluminum; (b) three possible structures of Alj3: a

However, molecular face-centered cubic structure (FCC), an hexagonal close-packed structure (HCP), and an icosahedral (ICOS) structure. Orbital calculations based on the density functional method predict that the icosahedral form has a lower energy than the other forms, suggesting the possibility of a structural change. There are no experimental measurements of the All3 structure to verify this prediction. The experimental determination of the structure of small metal nanoparticles is difficult, and there are not many structural data available. In the late 1970s and early 1980s, G. D. Stien was able to determine the structure of BiN, PbN, InN, and AgN nanoparticles. The particles were made using an oven to vaporize the metal and a supersonic expansion of an inert gas to promote cluster formation. Deviations from the face-centered cubic structure were observed for clusters smaller than 8 nm in diameter. Indium clusters undergo a change of structure when the size is smaller than 5.5 nm. Above 6.5 nm, a diameter corresponding to about 6000 atoms, the clusters have a face-centered tetragonal structure with a c/a ratio of 1.075. In a tetragonal unit cell the edges of the cell are perpendicular, the long axis is denoted by c, and the two short axes by a. Below -6.5 nm the c/a ratio begins to decrease, and at 5 nm c/a = 1, meaning that the structure is face-centered cubic. Figure 4.7 is a plot of c/a versus the diameter of indium nanoparticles. It needs to be pointed out that the structure of isolated nanoparticles may differ from that of ligand-stabilized structures. Ligand stabilization refers to associating nonmetal ion groups with metal atoms or ions.

REACTIVITY

Since the electronic structure of nanoparticles depends on the size of the particle, the ability of the cluster to react with other species should depend on cluster size. This has important implications for the design of catalytic agents. There is experimental evidence for the effect of

size on the reactivity of nanoparticles. A laser beam aimed at a metal disk dislodges metallic particles that are carried along to a mass spectrometer by a flow of helium gas. Down stream before the particles in the cluster beam enter the mass spectrometer, various gases are introduced, as shown in the figure. The results show that two peaks have these data provide clear evidence for the dependence of the reactivity of aluminum clusters on the number of atoms in the cluster. Similar size dependences have been observed for the reactivity of other metals. The data show that particles of certain sizes such as the one with 10 atoms and sizes greater than 18 atoms are more reactive with hydrogen than others. A group at Osaka National research Institute in Japan discovered that high catalytic activity is observed to switch on for gold nanoparticles smaller than 3-5nm, where the structure is icosahedral instead of the bulk FCC arrangement. This work has led to the development of odor eaters for bathrooms based on gold nanoparticles on a Fe_2O_3 substrate.

FLUCTUATIONS

Very small nanoparticles, have all or almost all of their atoms on the surface. Surface atoms are less restricted in their ability to vibrate than those in the interior, and they are able to make larger excursions from their equilibrium positions. This can lead to changes in the structure of the particle. Observations of the changes in the geometry with time of gold clusters have been made using an electron microscope. The gold clusters of 1CrIOO-8, radii are prepared in vacuum and deposited on a silicon substrate, which is then covered with an SiOz film. At higher temperatures these fluctuations can cause a breakdown in the symmetry of the nanoparticle, resulting in the formation of a liquid-like droplet of atoms.

BULK TO NANO TRANSITIONS

The most studied non-oxide semiconductors are cadmium chalcogenides (CdE, with E = sulfide, selenide and telluride). CdE nanocrystals were probably the first material used to demonstrate quantum size effects corresponding to a change in the electronic structure with size, i.e., the increase of the band gap energy with the decrease in size of particles (**Figure 10**). These semiconductors nanocrystals are commonly synthesized by thermal decomposition of an organometallic precursor dissolved in an anhydrous solvent containing the source of

chalcogenide and a stabilizing material (polymer or capping ligand). Stabilizing molecules bound to the surface of particles control their growth and prevent particle aggregation.



Figure 10: Picture of cadmium selenide (CdSe) quantum dots, dissolved in toluene, fluorescing brightly, as they are exposed to an ultraviolet lamp, in three noticeable different colors (blue ~481 nm, green ~520 nm, and orange ~612 nm) due to the quantum dots' bandgap (and thus the wavelength of emitted light) depends strongly on the particle size; the smaller the dot, the shorter the emitted wavelength of light. The "blue" quantum dots have the smallest particle size, the "green" dots are slightly larger, and the "orange" dots are the largest.

Although cadmium chalcogenides are the most studies semiconducting nanoparticles, the methodology for the formation of semiconducting nanoparticles was first demonstrated

independently for InP and GaAs, e.g., **Equation 1**. This method has been adapted for a range of semiconductor nanoparticles.

 $InCl_3 + P(SiMe_3)_3 \rightarrow InP + 3 Me_3SiCl$

(1)

In the case of CdE, dimethylcadmium $Cd(CH_3)_2$ is used as a cadmium source and bis(trimethylsilyl)sulfide, $(Me_3Si)_2S$, trioctylphosphine selenide or telluride (TOPSe, TOPTe) serve as sources of selenide in trioctylphosphine oxide (TOPO) used as solvent and capping molecule. The mixture is heated at 230-260 °C over a few hours while modulating the temperature in response to changes in the size distribution as estimated from the absorption spectra of aliquots removed at regular intervals. These particles, capped with TOP/TOPO molecules, are non-aggregated (**Figure 11**) and easily dispersible in organic solvents forming optically clear dispersions. When similar syntheses are performed in the presence of surfactant, strongly anisotropic nanoparticles are obtained, e.g., rod-shaped CdSe nanoparticles can be obtained.



Figure 11: TEM image of CdSe nanoparticles.

Dr. V. Senthil Kumar Head Department of Physics Because Cd(CH₃)₂ is extremely toxic, pyrophoric and explosive at elevated temperature, other Cd sources have been used. CdO appears to be an interesting precursor. CdO powder dissolves in TOPO and HPA or TDPA (tetradecylphosphonic acid) at about 300 °C giving a colorless homogeneous solution. By introducing selenium or tellurium dissolved in TOP, nanocrystals grow to the desired size.

Nanorods of CdSe or CdTe can also be produced by using a greater initial concentration of cadmium as compared to reactions for nanoparticles. This approach has been successfully applied for synthesis of numerous other metal chalcogenides including ZnS, ZnSe, and Zn₁. $_xCd_xS$. Similar procedures enable the formation of MnS, PdS, NiS, Cu₂S nanoparticles, nano rods, and nano disks.

COULOMBIC EXPLOSION

A Coulomb explosion is a mechanism for coupling electronic excitation energy from intense electromagnetic fields into atomic motion. The Coulombic repulsion of particles having the same electric charge can break the bonds that hold solids together. When done with a narrow laser beam, a small amount of solid explodes into a plasma of ionized atomic particles.

With their low mass, outer valence electrons responsible for chemical bonding are easily stripped from atoms, leaving them positively charged. Given a mutually repulsive state between atoms whose chemical bonds are broken, the material explodes into a small plasma cloud of energetic ions with higher velocities than seen in thermal emission.

A Coulomb explosion is one particular mechanism that permits laser-based machining.

Coulomb explosions for industrial machining are made with brief (picosecond or high femtoseconds) laser pulses. The enormous beam intensities required (10–400 terawatt per square centimeter thresholds, depending on material) are only practical to generate, shape and deliver for very brief instants of time.

A Coulomb explosion is a "cold" alternative to the dominant laser etching technique of thermal ablation, which depends on local heating, melting, and vaporization of molecules and atoms using less-intense beams. Pulse brevity down only to the nanosecond regime is sufficient to localize thermal ablation – before the heat is conducted far, the energy input (pulse) has ended. Nevertheless, thermally ablated materials may seal pores important in catalysis or battery

operation, and recrystallize or even burn the substrate, thus changing the physical and chemical properties at the etch site. In contrast, even light foams remain unsealed after ablation by Coulomb explosion.

Coulomb explosion etching can be used in any material to bore holes, remove surface layers, and texture and microstructure surfaces; e.g., to control ink loading in printing presses.

POLYMERS

FORMING AND CHARACTERIZING POLYMERS

A polymer is a large molecule (macromolecule) composed of repeating structural units. These sub-units are typically connected by covalent chemical bonds. Although the term *polymer* is sometimes taken to refer to plastics, it actually encompasses a large class of compounds comprising both natural and synthetic materials with a wide variety of properties. Because of the extraordinary range of properties of polymeric materials, they play an essential and ubiquitous role in everyday life. This role ranges from familiar synthetic plastics

and elastomers to natural biopolymers such as nucleic acids and proteins that are essential for life.

Natural polymeric materials such as shellac, amber, and natural rubber have been used for centuries. A variety of other natural polymers exist, such as cellulose, which is the main constituent of wood and paper. The list of synthetic polymers includes synthetic rubber, Bakelite, neoprene, nylon, PVC,polystyrene, polyethylene, polypropylene, polyacrylonitr ile, PVB, silicone, and many more.

Most commonly, the continuously linked backbone of a polymer used for the preparation of plastics consists mainly of carbon atoms. A simple example is polyethylene ('polythene' in British English), whose repeating unit is based on ethylene monomer. However, other structures do exist; for example, elements such as silicon form familiar materials such as silicones, examples being Silly Putty and waterproof plumbing sealant. Oxygen is also commonly present in polymer backbones, such as those of polyethylene glycol, polysaccharides (in glycosidic bonds), and DNA (in phosphodiester bonds).

Polymers are studied in the fields of polymer chemistry, polymer physics, and polymer science.

POLYMERIZATION

In polymer chemistry, polymerization is a process of reacting monomer molecules together in achemical reaction to form three-dimensional networks or polymer chains. There are many forms of polymerization and different systems exist to categorize them.

In chemical compounds, polymerization occurs via a variety of reaction mechanisms that vary in complexity due to functional groups present in reacting compounds and their inherent steric effects explained by VSEPR Theory. In more straightforward polymerization, alkenes, which are relatively stable due to σ bonding between carbon atoms, form polymers through relatively simple radical reactions; in contrast, more complex reactions such as those that involve substitution at the carbonyl group require more complex synthesis due to the way in which reacting molecules polymerize.

As alkenes can be formed in somewhat straightforward reaction mechanisms, they form useful compounds such as polyethylene andpolyvinyl chloride (PVC) when undergoing radical reactions, which are produced in high tonnages each year due to their usefulness in manufacturing processes of commercial products, such as piping, insulation and packaging. In general, polymers such as PVC are referred to as "homopolymers," as they consist of repeated long chains or structures of the same monomer unit, whereas polymers that consist of more than one molecule are referred to as copolymers (or co-polymers).

Other monomer units, such as formaldehyde hydrates or simple aldehydes, are able to polymerize themselves at quite low temperatures (>-80 °C) to form trimers; molecules consisting of 3 monomer units, which can cyclize to form ring cyclic structures, or undergo further reactions to form tetramers, or 4 monomer-unit compounds. Further compounds either being referred to as oligomers in smaller molecules. Generally, because formaldehyde is an exceptionally reactive electrophile it allows nucleophillic addition of hemiacetal intermediates, which are in general short-lived and relatively unstable "mid-stage" compounds that react with other molecules present to form more stable polymeric compounds.

Polymerization that is not sufficiently moderated and proceeds at a fast rate can be very hazardous. This phenomenon is known asHazardous polymerization and can cause fires and explosions.

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Step-growth

Step-growth polymers are defined as polymers formed by the stepwise reaction between functional groups of monomers. Most step-growth polymers are also classified as condensation polymers, but not all step-growth polymers (like polyurethanes formed from isocyanate and alcohol bifunctional monomers) release condensates; in this case, we talk about addition polymers. Step-growth polymers increase in molecular weight at a very slow rate at lower conversions and reach moderately high molecular weights only at very high conversion (i.e., >95%).

To alleviate inconsistencies in these naming methods, adjusted definitions for condensation and addition polymers have been developed. A condensation polymer is defined as a polymer that involves loss of small molecules during its synthesis, or contains functional groups as part of its backbone chain, or its repeat unit does not contain all the atoms present in the hypothetical monomer to which it can be degraded.

Chain-growth

Chain-growth polymerization (or addition polymerization) involves the linking together of molecules incorporating double or triple chemical bonds. These unsaturated *monomers* (the identical molecules that make up the polymers) have extra internal bonds that are able to break and link up with other monomers to form the repeating chain. Chain-growth polymerization is involved in the manufacture of polymers such aspolyethylene, polypropylene, and polyvinyl chloride (PVC). A special case of chain-growth polymerization leads to living polymerization.

In the radical polymerization of ethylene, its pi bond is broken, and the two electrons rearrange to create a new propagating center like the one that attacked it. The form this propagating center takes depends on the specific type of addition mechanism. There are several mechanisms through which this can be initiated. The free radical mechanism is one of the first methods to be used. Free radicals are very reactive atoms or molecules that have unpaired electrons. Taking the polymerization of ethylene as an example, the free radical mechanism can be divided in to three stages: chain initiation, chain propagation, and chain termination.

Free radical addition polymerization of ethylene must take place at high temperatures and pressures, approximately 300 °C and 2000 atm. While most other free radical polymerizations do

not require such extreme temperatures and pressures, they do tend to lack control. One effect of this lack of control is a high degree of branching. Also, as termination occurs randomly, when two chains collide, it is impossible to control the length of individual chains. A newer method of polymerization similar to free radical, but allowing more control involves the Ziegler-Natta catalyst, especially with respect to polymer branching.

Other forms of chain growth polymerization include cationic addition polymerization and anionic addition polymerization. While not used to a large extent in industry yet due to stringent reaction conditions such as lack of water and oxygen, these methods provide ways to polymerize some monomers that cannot be polymerized by free radical methods such as polypropylene. Cationic and anionic mechanisms are also more ideally suited for living polymerizations, although free radical living polymerizations have also been developed.

NANOCRYSTAL

More properly, any material with a dimension of less than 1 micrometre, i.e., 1000 nanometers, should be referred to as a nanoparticle, not a nanocrystal. For example, any particle which exhibits regions of crystallinity should be termed nanoparticle or nanocluster based on dimensions. These materials are of huge technological interest since many of their electrical and thermodynamic properties show strong size dependence and can therefore be controlled through careful manufacturing processes.

Crystalline nanoparticles are also of interest because they often provide single-domain crystalline systems that can be studied to provide information that can help explain the behaviour of macroscopic samples of similar materials, without the complicating presence of grain boundaries and other defects. Semiconductor nanocrystals in the sub-10nm size range are often referred to as quantum dots.

Crystalline nanoparticles made with zeolite are used as a filter to turn crude oil onto diesel fuel at an ExxonMobil oil refinery in Louisiana, a method cheaper than the conventional way.

A layer of crystalline nanoparticles is used in a new type of solar panel named SolarPly made by Nanosolar. It is cheaper than other solar panels, more flexible, and claims 12% efficiency. (Conventionally inexpensive organic solar panels convert 9% of the sun's energy into

electricity.) Crystal tetrapods 40 nanometers wide convert photons into electricity, but only have 3% efficiency.

CONDUCTIVE POLYMER

Conductive polymers or, more precisely, intrinsically conducting polymers (ICPs) are organic polymers that conduct electricity. Such compounds may have metallic conductivity or can be semiconductors. The biggest advantage of conductive polymers is their processability, mainly by dispersion. Conductive polymers are generally not plastics, i.e., they are not thermoformable. But, like insulating polymers, they are organic materials. They can offer high electrical conductivity but do not show mechanical properties as other commercially used polymers do. The electrical properties can be fine-tuned using the methods of organic synthesis and by advanced dispersion techniques.

Properties and applications

Conductive polymers enjoy few large-scale applications due to their poor processability. They have been known to have promise in antistatic materials and they have been incorporated into commercial displays and batteries, but there have had limitations due to the manufacturing costs, material inconsistencies, toxicity, poor solubility in solvents, and inability to directly melt process. Literature suggests they are also promising in organic solar cells, printing electronic circuits, organic light-emitting diodes, actuators, electrochromism, supercapacitors, biosensors, flexible transparent displays, electromagnetic shielding and possibly replacement for the popular transparent conductor indium tin oxide. Conducting polymers are rapidly gaining attraction in new applications with increasingly processable materials with better electrical and physical properties and lower costs. The new nanostructured forms of conducting polymers particularly, provide fresh air to this field with their higher surface area and better dispersability.

With the availability of stable and reproducible dispersions, PEDOT and polyaniline have gained some large scale applications. While PEDOT (poly(3,4-ethylenedioxythiophene)) is mainly used in antistatic applications and as a transparent conductive layer in form of PEDOT:PSS dispersions (PSS=polystyrene sulfonic acid), polyaniline is widely used for printed circuit board manufacturing – in the final finish, for protecting copper from corrosion and preventing its solderability.

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Electroluminescence

Electroluminescence is light emission stimulated by electrical current. In organic compounds, electroluminescence has been known since the early 1950s, when Bernanose and coworkers first produced electroluminescence in crystalline thin films of acridine orange and quinacrine. In 1960, researchers at Dow Chemical developed AC-driven electroluminescent cells using doping. In some cases, similar light emission is observed when a voltage is applied to a thin layer of a conductive organic polymer film. While electroluminescence was originally mostly of academic interest, the increased conductivity of modern conductive polymers means enough power can be put through the device at low voltages to generate practical amounts of light. This property has led to the development of flat panel displays using organic LEDs,solar panels, and optical amplifiers.

Barriers to applications

Since most conductive polymers require oxidative doping, the properties of the resulting state are crucial. Such materials are salt-like (polymer salt), which diminishes their solubility in organic solvents and water and hence their processability. Furthermore, the charged organic backbone is often unstable towards atmospheric moisture. Compared to metals, organic conductors can be expensive requiring multi-step synthesis. The poor processability for many polymers requires the introduction of solubilizing or substituents, which can further complicate the synthesis.

Experimental and theoretical thermodynamical evidence suggests that conductive polymers may even be completely and principally insoluble so that they can only be processed by dispersion.

Trends

Most recent emphasis is on organic light emitting diodes and organic polymer solar cells. The Organic Electronics Association is an international platform to promote applications of organic semiconductors. Conductive polymer products with embedded and improved electromagnetic interference (EMI) and electrostatic discharge (ESD) protection have led to both prototypes and products. For example, Polymer Electronics Research Center at University of Auckland is developing a range of novel DNA sensor technologies based on conducting

polymers, photoluminescent polymers and inorganic nanocrystals (quantum dots) for simple, rapid and sensitive gene detection. Typical conductive polymers must be "doped" to produce high conductivity. To date, there remains to be discovered an organic polymer that is*intrinsically* electrically conducting.

SUPRA MOLECULAR STRUCTURES

Supramolecular structures are large molecules formed by grouping or bonding smaller molecules

together. It belongs to the realm of nanoscience since it is often possible to develop molecules of a desired shape or functionality. Supramolecular structures can be used to develop numerous different shapes of molecules, including 2D triangles, squares, pentagons, hexagons and 3D octahedrons and cubes.

DENDRITIC MOLECULES



Dendrimer and dendron

Dendrimers are repetitively branched molecules. The name comes from the Greek word "δένδρον" (pronounced dendron), which translates to "tree". Synonymous terms for dendrimer include **arborols** and **cascade molecules**. However, dendrimer is currently the internationally accepted term. A dendrimer is typically symmetric around the core, and often adopts a spherical three-dimensional morphology. The word **dendron** is also encountered frequently. A dendron usually contains a single chemically addressable group called the focal point. The difference between dendrons and dendrimers is illustrated in figure one, but the terms are typically encountered interchangeably.



Crystal structure of a first-generation polyphenylene dendrimer reported by Müllen et al.

Properties

Dendritic molecules are characterized by structural perfection. Dendrimers and dendrons are monodisperse and usually highly symmetric, spherical compounds. The field of dendritic molecules can be roughly divided into low-molecular weight and high-molecular weight species. The first category includes dendrimers and dendrons, and the latter includes dendronized polymers, hyperbranched polymers, and thepolymer brush.

The properties of dendrimers are dominated by the functional groups on the molecular surface, however, there are examples of dendrimers with internal functionality. Dendritic encapsulation of functional molecules allows for the isolation of the active site, a structure that mimics that of active sites in biomaterials. Also, it is possible to make dendrimers water soluble, unlike most polymers, by functionalizing their outer shell with charged species or other hydrophilic groups. Other controllable properties of dendrimers include toxicity, crystallinity, tecto-dendrimer formation, and chirality.

Dendrimers are also classified by generation, which refers to the number of repeated branching cycles that are performed during its synthesis. For example if a dendrimer is made by convergent synthesis (see below), and the branching reactions are performed onto the core molecule three times, the resulting dendrimer is considered a third generation dendrimer. Each successive generation results in a dendrimer roughly twice the molecular weight of the previous

generation. Higher generation dendrimers also have more exposed functional groups on the surface, which can later be used to customize the dendrimer for a given application.

Applications

Applications of dendrimers typically involve conjugating other chemical species to the dendrimer surface that can function as detecting agents (such as a dye molecule), affinity ligands, targeting components, radioligands, imaging agents, or pharmaceutically active compounds. Dendrimers have very strong potential for these applications because their structure can lead to multivalentsystems. In other words, one dendrimer molecule has hundreds of possible sites to couple to an active species. Researchers aimed to utilize the hydrophobic environments of the dendritic media to conduct photochemical reactions that generate the products that are synthetically challenged. Carboxylic acid and phenol terminated water soluble dendrimers were synthesized to establish their utility in drug delivery as well as conducting chemical reactions in their interiors. This might allow researchers to attach both targeting molecules and drug molecules to the same dendrimer, which could reduce negative side effects of medications on healthy cells.

Dendrimers can also be used as a solubilizing agent. Since their introduction in the mid-1980s, this novel class of dendrimer architecture has been a prime candidate for hosts guest chemistry. Dendrimers with hydrophobic core and hydrophilic periphery have shown to exhibit micelle-like behavior and have container properties in solution. The use of dendrimers as unimolecular micelles was proposed by Newkome in 1985. This analogy highlighted the utility of dendrimers as solubilizing agents. The majority of drugs available in pharmaceutical industry are hydrophobic in nature and this property in particular creates major formulation problems. This drawback of drugs can be ameliorated by dendrimeric scaffolding, which can be used to encapsulate as well as to solubilize the drugs because of the capability of such scaffolds to participate in extensive hydrogen bonding with water. Dendrimer labs throughout the planet are persistently trying to manipulate dendrimer's solubilizing trait, in their way to explore dendrimer as drug delivery and target specific carrier.

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Drug Delivery



Schematic of a G-5 PAMAM dendrimer conjugated to both a dye molecule and a strand of DNA.

Approaches for delivering unaltered natural products using polymeric carriers is of widespread dendrimers interest. have been explored for the encapsulation of hydrophobic compounds and for the delivery of anticancer drugs. The physical characteristics of dendrimers, including their monodispersity, water solubility, encapsulation ability, and large number of functionalizable peripheral groups, make these macromolecules appropriate candidates for evaluation as drug delivery vehicles. There are three methods for using dendrimers in drug delivery: first, the drug is covalently attached to the periphery of the dendrimer to form dendrimer prodrugs, second the drug is coordinated to the outer functional groups via ionic interactions, or third the dendrimer acts as a unimolecular micelle by encapsulating a pharmaceutical through the formation of a dendrimer-drug supramolecular

assembly. The use of dendrimers as drug carriers by encapsulating hydrophobic drugs is a potential method for delivering highly active pharmaceutical compounds that may not be in clinical use due to their limited water solubility and resulting suboptimal pharmacokinetics. Dendrimers have been widely explored for controlled delivery of antiretroviral bioactives. The inherent antiretroviral activity of dendrimers enhances their efficacy as carriers for antiretroviral drugs. The dendrimer enhances both the uptake and retention of compounds within cancer cells, a finding that was not anticipated at the onset of studies. The encapsulation increases with dendrimer generation and this method may be useful to entrap drugs with a relatively high therapeutic dose. Studies based on this dendritic polymer also open up new avenues of research into the further development of drug-dendrimer complexes specific for a cancer and/or targeted organ system. These encouraging results provide further impetus to design, synthesize, and evaluate dendritic polymers for use in basic drug delivery studies and eventually in the clinic.

Gene Delivery

The ability to deliver pieces of DNA to the required parts of a cell includes many challenges. Current research is being performed to find ways to use dendrimers to traffic genes into cells without damaging or deactivating the DNA. To maintain the activity of DNA during dehydration, the dendrimer/DNA complexes were encapsulated in a water soluble polymer, and then deposited on or sandwiched in functional polymer films with a fast degradation rate to mediate gene transfection. Based on this method, PAMAM dendrimer/DNA complexes were used to encapsulate functional biodegradable polymer films for substratemediated gene delivery. Research has shown that the fast degrading functional polymer has great potential for localized transfection.

Sensors

Scientists have also studied dendrimers for use in sensor technologies. Studied systems include proton or pH sensors using poly(propylene imine), cadmium-sulfide/polypropylenimine tetrahexacontaamine dendrimer composites to detect fluorescence signal quenching, and poly(propylenamine) first and second generation dendrimers for metal cation photodetection amongst others. Research in this field is vast and ongoing due to the potential for multiple detection and binding sites in dendritic structures.

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Blood substitution

Dendrimers are also being investigated for use as blood substitutes. Their steric bulk surrounding a heme-mimetic centre significantly slows degradation compared to free heme, and prevents the cytotoxicity exhibited by free heme.

MICELLES

A micelle is an aggregate of surfactant molecules dispersed in a liquid colloid. A typical micelle in aqueous solution forms an aggregate with the hydrophilic "head" regions in contact with surrounding solvent, sequestering the hydrophobic single tail regions in the micelle centre. This phase is caused by the insufficient packing issues of single tailed lipids in a bilayer. The difficulty filling all the volume of the interior of a bilayer, while accommodating the area per head group forced on the molecule by the hydration of the lipid head group leads to the formation of the micelle. This type of micelle is known as a normal phase micelle (oil-in-water micelle). Inverse micelles have the headgroups at the centre with the tails extending out (water-in-oil micelle). Micelles are approximately spherical in shape. Other phases, including shapes such as ellipsoids, cylinders, and bilayers are also possible. The shape and size of a micelle is a function of the molecular geometry of its surfactant molecules and solution conditions such as surfactant concentration, temperature, pH, and ionic strength. The process of forming micellae is known as micellization and forms part of the phase behavior of many lipids according to their polymorphism. This is usually takes place in soaps when hydrophylic occupies the water and hydrophobic catch hold of the dirt in clothes that are washed.



Scheme of a micelle formed by phospholipids in an aqueous solution.

Uses

- When surfactants are present above the CMC (Critical micelle concentration), they can act as emulsifiers that will allow a compound that is normally insoluble (in the solvent being used) to dissolve. This occurs because the insoluble species can be incorporated into the micelle core, which is itself solubilized in the bulk solvent by virtue of the head groups' favorable interactions with solvent species. The most common example of this phenomenon is detergents, which clean poorly soluble lipophilic material (such as oils and waxes) that cannot be removed by water alone. Detergents also clean by lowering the surface tension of water, making it easier to remove material from a surface. The emulsifying property of surfactants is also the basis for emulsion polymerization.
- Micelle formation is essential for the absorption of fat-soluble vitamins and complicated lipids within the human body. Bile salts formed in the liver and secreted by the gall bladder allow micelles of fatty acids to form. This allows the absorption of complicated lipids (e.g., lecithin) and lipid soluble vitamins (A, D, E and K) within the micelle by the small intestine.

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POSSIBLE QUESTIONS

UNIT IV

- 1. Define polymers. Explain the following: i) Conductive polymers and (ii) Supra molecular structures.
- Define polymers. Explain the following: i) Nanocrystals, ii) Dendritic molecules & iii) Micelles
- 3. Define polymers. Explain the various significant properties of polymers.
- 4. Discuss about the photo fragmentation.
- 5. Explain in detail about Metal Nano particles.
- 6. Explain the face centred nano particles. Describe the size dependent properties of semiconducting nanoparticle.
- 7. Explain the formation and characterization of polymers.
- 8. Explain the size dependent properties of different nanomaterials. Describe the size dependent properties of semiconducting nanoparticles.
- 9. What do you mean by nanoscience? Explain metal nanoparticles along with surface structure.
- 10. What do you mean by single crystal? Describe optical properties of metal nanoparticles.
- 11. What are some of the polymers that you encounter every day? Describe their physical properties.

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DEPARTMENT OF PHYSICS I M SC DIIVSICS

Which one of the following is used in making nanowires?

Which of the following can be used as nanocarriers?

Nanoparticles that are used as pharmaceutical delivery systems are called as

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ZnO.

dots.

nanocapsules.

Liposomes, quantum

I M.SC PHYSICS	BATCH: 2017-2019				
CONDENSED MATTER PHYSICS (17PHP101)					
MULTIPLE CHOICE QUESTIONS					
Questions	option 1	option 2	option 3	option 4	Answer
UNIT IV					
In Nanobiotechnology, size of nanomaterials is of a meter.	hundred billionth.	ten billionth.	one billionth.	twenty billionth.	one billionth.
Bucky balls are made up of	nickel.	DNA.	RNA.	carbon	carbon
technology is used in making memory chips.	Nano design.	Nano fabrication.	Microassay.	Tissue engineering.	
Which of the following is NOT a potential application of nano fabrication technology?	DNA chip assays.	Integrated photonic devices and diode displays.	Amulti lambda high density optical data storage material.	Textile industry.	Amulti lambda high density optical data storage material.
The art and science of etching, writing or printing at the microscopic level in the order of nanometer is	NEMS.	nano lithography.	nano fabrication.	nano paltcinins	nano lithography.
What are the approaches used in making nano systems?	Top down.	Bottom up.	Both a and b.	Neither a nor b.	Both a and b.
Ceramic powders find application in	pigments.	abrasives.	catalysts.	all the above.	all the above.
Nano powders are defined as powders having an average particle size of less that nm.	100	1000	10	1	100
Which of the following are 1-D nano systems?	Rods, Cylinders.	Rods, Cylinders, Prisms.	Rods, Cylinders, Prisms, wires.	Cylinders, wires.	Rods, Cylinders, Prisms, wires.
Which techniques is mostly used for the synthesis of 2-D nano structures?	Anisotropic crystal growth.	Top up.	Bottom down.	Microscopic.	Anisotropic crystal growth.
Nanomembranes have a pore size ofnm.	1-10.	10-100.	0.1-1.	100-1000.	1-10.
Silicon or polymer devices that perform non-electronic functions such as sensing and activation are called as	microsystems.	nanosystems.	sensors.	smart systems.	microsystems.
Mention the nanomaterial used in the remediation of waste?	Titanium oxide	Nanoprobes.	Nanomembranes.	Sodium ions.	Titanium oxide
The study that involves the behavior, manipulation and control of fluids that are confined to nanometers is called as	nanoarray.	nanocapillary.	nanofluids.	nanofringes	nanofluids.
The concentration at which surfactants begin to form micelle is known as	critical micelle concentration.	crucial micelle concentration.	circular micelle concentration.	critical molecule concentration.	critical micelle concentration.
Compounds that lower the surface tension of a liquid are called as	detergents.	surfactants.	wetting agents.	soaps.	surfactants.
Nanoemulsion are oil-in-water emulsion with mean droplet diameters of what size.	50-100 nm	100-500 nm.	50-100 nm.	500-1000 nm.	50-100 nm
Machanics and Electronics that are on the nanoscale are called as	MEMS.	NEMS.	MEM.	NEM.	NEMS.
Asemiconductor whose excitons are confined in all three spatial dimensions is called as	qubit.	bucky ball.	quantum dot.	dot.	quantum dot.
Which of the following are applications of quantum dots?	Immunolabelling and fluorescence imaging.	Drug delivery.	As tags for other drug carries.	All the above.	All the above.
Structures that have a thickness or diameter constrained to tens of nms or less and an unconstrained length are called as	nano tubes.	nano wires.	nano crystals.	bucky balls.	nano wires.

TiO

nanocarriers.

Micelles, dendrimers.

Heavy metals.

Microcapsules.

nanotubes.

Hydrogen.

nanocubes

All the above.

ZnO.

nanocarriers.

All the above.

Self-assembled nanosystems used for targeting subcellular organelles such as mitochondria are called	nanoparticles.	nanoassemblers.	nanocarriers.	nanofilms.	nanoassemblers.
Nanopores are made up of	carbon.	titanium.	titanium.	silicon.	silicon.
Nanopore sequencing is a method for determining the order in which nucleotides occur on a strand of	RNA.	DNA.	cDNA.	Template.	DNA.
Fullerences are	bionanomaterials	carbon based carriers.	polymers.	dendrimers.	carbon based carriers.
Nano particles in biomedical application are	nano capsules.	nano spheres.	both a and b.	neither a nor b.	both a and b.
Nanodevices use to move linearly by rotation.	ATP	electricity.	motor proteins.	nano machine.	motor proteins.
Two dimensional protein crystals that might provide useful scaffolds for Nanobiotechnology are called	proteins.	protein arrays.	ordered protein arrays.	planar protein arrays.	ordered protein arrays.
Which metal is used with nanoparticles for antibiotic delivery?	Gold.	Titanium	Zinc.	Silver.	Silver.
Which of the following is NOT an application of fullerenes?	Organic photovoltaics.	Antioxidants.	Additives.	Imaging	Imaging
Expand CNT.	Copper Nano Tube.	Carbon Nano Tube.	Cell Nano Tube.	Crystal Nano tube.	Carbon Nano Tube.
Which of the following is NOT a type of fullerene?	Nano onions.	Nano tubes.	Bucky balls.	Quantum dots.	Quantum dots.
is essentially miniaturized in laboratories that can perform 100s or 1000s of simultaneous biochemical reactions.	Chip	Biochip	Nanochip	Biosensors	Biochip
Which one of the following is NOT an important microfabrication technology?	Film deposition.	Bonding	Etching.	Electron beam lithography.	Electron beam lithography.
Which one of the following is NOT a nano fabrication technology?	Electrically induced nano patterning.	Electron beam lithography.	Photolithography.	Focussed lithography.	Photolithography.
Which one of the following is NOT a nano fabrication technology?	Ion projection lithography.	Ion projection lithography.	X-ray lithography.	Soft lithography.	Soft lithography.
Which one of the following is NOT a nanofabrication technology?	Colloid monolayer lithography.	Rapid phototyping.	Electrically induced nanopatterning.	Film deposition.	Film deposition.
Which one of the following is NOT used as a material for fabricating microneedles?	Silicon	Metal	Iron	Glass	Iron
have been used as quantum dots and as chemical catalysts.	Micro particles.	Metals.	Nano particles.	Biological particles.	Nano particles.
What is the application of Nanobiotechnology?	Nano scale studies.	sub microscopic fabrication	Understanding the biological activity at molecular scale.	All the above.	All the above.
Strongest element in the earth is	Silicon	Metal	Iron	Diamond	Diamond
Fullerence are	molecules made up of carbon.	buckyballs.	hollow carbon tubes.	All the above.	All the above.
Nanoshells are	Gold-coated glass nano particles used to assay whole blood.	Zinc coated glass nanoparticles.	Copper coated nanoparticles.	Iron coated nanoparticles.	Gold-coated glass nano particles used to assay whole blood.
Bottom up approach is building starts	from smaller from large.	from larger to smaller.	equally.	horizontally.	from smaller from large.
Nano lithography means	nano writing.	nano drawing.	writing.	drawing.	nano writing.
The temperature used in chemical deposition method of carbon nano tube fabrication is Degree Celsius.	110	100	1100	90	110
Nanonose is	nano biosensor .	nanocell.	nanodevice.	biosensor.	nano biosensor .
Self-assemble layers are structures.	1D	3D	0D	2D	Self-assemble layers are structures.
Polymers have thermal conductivities in the range of	< 1	1 to 10	10 to 100	>100	< 1
Polymers have thermal expansion coefficients in the range ofx10-6.	0.5-15	5 to 25	25 to 50	50 to 400	50 to 400
Thermal conductivity in polymers increases with	Increase in crystallinity	Decrease in crystallinity	Either	None	None

The following material can be used for filling in sandwich structures	Polymers	Cement	Wood	All	All
The word 'polymer' meant for material made from	Single entity	Two entities	Multiple entities	Any entity	Multiple entities
One of characteristic properties of polymer material	High temperature stability	High mechanical strength	High elongation	Low hardness	High elongation
Polymers are in nature.	Organic	Inorganic	Both (a) and (b)	None	Both (a) and (b)
These polymers can not be recycled:	Thermoplasts	Thermosets	Elastomers	All polymers	Thermosets
In general, strongest polymer group is	Thermoplasts	Thermosets	Elastomers	All polymers	Thermosets
Strong covalent bonds exists between polymer chains in	Thermoplasts	Thermosets	Elastomers	All polymers	Thermosets
Following is the unique to polymeric materials:	Elasticity	Viscoelasticity	Plasticity	None	Viscoelasticity
Elastic deformation in polymers is due to	Slight adjust of molecular chains	Slippage of molecular chains	Straightening of molecular chains	Severe of Covalent bonds	Slight adjust of molecular chains
Kevlar is commercial name for	Glass fibers	Carbon fibers	Aramid fibers	Cermets	Aramid fibers
Repeatable unit of polymers	isomer	copolymer	homopolymer	mer	mer
Composite materials are	made mainly to improve temperature resistance	used for improved optical properties	made with strong fibres embedded in weaker and softer matrix to obtain strength better than strength of matrix.	made with strong fibres embedded in weaker and softer matrix to obtain strength of both matrix and filler. strength better than	made with strong fibres embedded in weaker and softer matrix to obtain strength better than strength of matrix.
Which one are inorganic materials	biological materials	minerals and ceramics	plastics	wood	minerals and ceramics
Graphite is a good conductor of electricity due to the presence of	lone pair of electrons	free valence electrons	cations	anions	free valence electrons
Graphite cannot be classified as	conducting solid	network solid	covalent solid	ionic solid	ionic solid

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Condensed Matter Physics UNIT V (17PHP101) INSTRUMENTATION

UNIT - V

Instrumentation: Working principle, and applications of scanning electron microscope - transmission electron microscope - scanning tunneling microscope - atomic force microscope, and surface plasmon resonance – theories and principles of soft lithography, self assembled monolayers and multilayers

UNIT V

SCANNING ELECTRON MICROSCOPY (SEM)

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions (using EDS), crystalline structure, and crystal orientations (using EBSD). The design and function of the SEM is very similar to the EPMA and considerable overlap in capabilities exists between the two instruments.

Fundamental Principles of Scanning Electron Microscopy (SEM)

Accelerated electrons in an SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light (cathodoluminescence--CL), and heat. Secondary electrons and backscattered electrons are

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commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination). X-ray generation is produced by inelastic collisions of the incident electrons with electrons in discrete orbitals (shells) of atoms in the sample. As the excited electrons return to lower energy states, they yield X-rays that are of a fixed wavelength (that is related to the difference in energy levels of electrons in different shells for a given element). Thus, characteristic X-rays are produced for each element in a mineral that is "excited" by the electron beam. SEM analysis is considered to be "non-destructive"; that is, x-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly.

Scanning Electron Microscopy (SEM) Instrumentation - How Does It Work?



Essential components of all SEMs include the following:

- Electron Source ("Gun")
- Electron Lenses
- Sample Stage

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- Detectors for all signals of interest
- Display / Data output devices
- Infrastructure Requirements:
 - Power Supply
 - Vacuum System
 - Cooling system
 - Vibration-free floor
 - Room free of ambient magnetic and electric fields

SEMs always have at least one detector (usually a secondary electron detector), and most have additional detectors. The specific capabilities of a particular instrument are critically dependent on which detectors it accommodates.

Applications

The SEM is routinely used to generate high-resolution images of shapes of objects (SEI) and to show spatial variations in chemical compositions: 1) acquiring elemental maps or spot chemical analyses using EDS, 2)discrimination of phases based on mean atomic number (commonly related to relative density) using BSE, and 3) compositional maps based on differences in trace element "activitors" (typically transition metal and Rare Earth elements) using CL. The SEM is also widely used to identify phases based on qualitative chemical analysis and/or crystalline structure. Precise measurement of very small features and objects down to 50 nm in size is also accomplished using the SEM. Back scattered electron images (BSE) can be used for rapid discrimination of phases in multiphase samples. SEMs equipped with diffracted backscattered electron detectors (EBSD) can be used to examine microfabric and crystallographic orientation in many materials.

Strengths and Limitations of Scanning Electron Microscopy

Strengths

There is arguably no other instrument with the breadth of applications in the study of solid materials that compares with the SEM. The SEM is critical in all fields that require characterization of solid materials. While this contribution is most concerned with geological applications, it is important to note that these applications are a very small subset of the scientific

and industrial applications that exist for this instrumentation. Most SEM's are comparatively easy to operate, with user-friendly "intuitive" interfaces. Many applications require minimal sample preparation. For many applications, data acquisition is rapid (less than 5 minutes/image for SEI, BSE, spot EDS analyses.) Modern SEMs generate data in digital formats, which are highly portable.

Limitations

Samples must be solid and they must fit into the microscope chamber. Maximum size in horizontal dimensions is usually on the order of 10 cm, vertical dimensions are generally much more limited and rarely exceed 40 mm. For most instruments samples must be stable in a vacuum on the order of 10⁻⁵ - 10⁻⁶ torr. Samples likely to outgas at low pressures (rocks saturated with hydrocarbons, "wet" samples such as coal, organic materials or swelling clays, and samples likely to decrepitate at low pressure) are unsuitable for examination in conventional SEM's. However, "low vacuum" and "environmental" SEMs also exist, and many of these types of samples can be successfully examined in these specialized instruments. EDS detectors on SEM's cannot detect very light elements (H, He, and Li), and many instruments cannot detect elements with atomic numbers less than 11 (Na). Most SEMs use a solid state x-ray detector (EDS), and while these detectors are very fast and easy to utilize, they have relatively poor energy resolution and sensitivity to elements present in low abundances when compared to wavelength dispersive x-ray detectors (WDS) on most electron probe microanalyzers (EPMA). An electrically conductive coating must be applied to electrically insulating samples for study in conventional SEM's, unless the instrument is capable of operation in a low vacuum mode.

User's Guide - Sample Collection and Preparation

Sample preparation can be minimal or elaborate for SEM analysis, depending on the nature of the samples and the data required. Minimal preparation includes acquisition of a sample that will fit into the SEM chamber and some accommodation to prevent charge build-up on electrically insulating samples. Most electrically insulating samples are coated with a thin layer of conducting material, commonly carbon, gold, or some other metal or alloy. The choice of material for conductive coatings depends on the data to be acquired: carbon is most desirable if elemental analysis is a priority, while metal coatings are most effective for high resolution

electron imaging applications. Alternatively, an electrically insulating sample can be examined without a conductive coating in an instrument capable of "low vacuum" operation.

TRANSMISSION ELECTRON MICROSCOPE

Transmission electron microscopy (TEM) is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera.

TEMs are capable of imaging at a significantly higher resolution than light microscopes, owing to the small de Broglie wavelength of electrons. This enables the instrument's user to examine fine detail—even as small as a single column of atoms, which is tens of thousands times smaller than the smallest resolvable object in a light microscope. TEM forms a major analysis method in a range of scientific fields, in both physical and biological sciences. TEMs find application in cancer research, virology, materials science as well as pollution and semiconductor research.

At smaller magnifications TEM image contrast is due to absorption of electrons in the material, due to the thickness and composition of the material. At higher magnifications complex wave interactions modulate the intensity of the image, requiring expert analysis of observed images. Alternate modes of use allow for the TEM to observe modulations in chemical identity, crystal orientation, electronic structure and sample induced electron phase shift as well as the regular absorption based imaging.

The first TEM was built by Max Knoll and Ernst Ruska in 1931, with this group developing the first TEM with resolving power greater than that of light in 1933 and the first commercial TEM in 1939.

Instrumentation

A TEM works much like a slide projector. A projector shines a beam of light through (transmits) the slide, as the light passes through it is affected by the structures and objects on the slide. These effects result in only certain parts of the light beam being transmitted through certain parts of the slide. This transmitted beam is then projected onto the viewing screen, forming an enlarged image of the slide.

TEMs work the same way except that they shine a beam of electrons (like the light) through the specimen (like the slide). Whatever part is transmitted is projected onto a phosphor screen for the user to see. A more technical explanation of typical TEMs working is as follows (refer to the diagram below):



1. The "Virtual Source" at the top represents the electron gun, producing a stream of monochromatic electrons.

2. This stream is focused to a small, thin, coherent beam by the use of condenser lenses 1 and 2. The first lens(usually controlled by the "spot size knob") largely determines the "spot size"; the general size range of the final spot that strikes the sample. The second lens(usually controlled by the "intensity or brightness knob" actually changes the size of the spot on the sample; changing it from a wide dispersed spot to a pinpoint beam.

3. The beam is restricted by the condenser aperture (usually user selectable), knocking out high angle electrons (those far from the optic axis, the dotted line down the center)

4. The beam strikes the specimen and parts of it are transmitted

5. This transmitted portion is focused by the objective lens into an image

6. Optional Objective and Selected Area metal apertures can restrict the beam; the Objective aperture enhancing contrast by blocking out high-angle diffracted electrons, the Selected Area aperture enabling the user to examine the periodic diffraction of electrons by ordered arrangements of atoms in the sample

7. The image is passed down the column through the intermediate and projector lenses, being enlarged all the way

8. The image strikes the phosphor image screen and light is generated, allowing the user to see the image. The darker areas of the image represent those areas of the sample that fewer electrons were transmitted through (they are thicker or denser). The lighter areas of the image represent those areas of the sample that more electrons were transmitted through (they are thinner or less dense)

Principles of operation:

The transmission electron microscope uses a high energy electron beam transmitted through a very thin sample to image and analyze the microstructure of materials with atomic scale resolution. The electrons are focused with electromagnetic lenses and the image is observed on a fluorescent screen, or recorded on film or digital camera. The electrons are accelerated at several hundred kV, giving wavelengths much smaller than that of light: 200kV electrons have a wavelength of 0.025Å. However, whereas the resolution of the optical microscope is limited by the wavelength of light, that of the electron microscope is limited by aberrations inherent in electromagnetic lenses, to about 1-2 Å.

Because even for very thin samples one is looking through many atoms, one does not usually see individual atoms. Rather the high resolution imaging mode of the microscope images the crystal lattice of a material as an interference pattern between the transmitted and diffracted beams. This allows one to observe planar and line defects, grain boundaries, interfaces, etc. with atomic scale resolution. The bright field/dark field imaging modes of the microscope, which operate at intermediate magnification, combined with electron diffraction, are also invaluable for giving information about the morphology, crystal phases, and defects in a material. Finally the microscope is equipped with a special imaging lens allowing for the observation of micro magnetic domain structures in a field-free environment.

The TEM is also capable of forming a focused electron probe, as small as 20 Å, which can be positioned on very fine features in the sample for micro diffraction information or analysis of x-rays for compositional information. The latter is the same signal as that used for EMPA and SEM composition analysis (see EMPA facility), where the resolution is on the order of one micron due to beam spreading in the bulk sample. The spatial resolution for this compositional analysis in TEM is much higher, on the order of the probe size, because the sample is so thin. Conversely the signal is much smaller and therefore less quantitative. The high brightness field-emission gun improves the sensitivity and resolution of x-ray compositional analysis over that available with more traditional thermionic sources.

Restrictions on Samples:

Sample preparation for TEM generally requires more time and experience than for most other characterization techniques. A TEM specimen must be approximately 1000 Å or less in thickness in the area of interest. The entire specimen must fit into a 3mm diameter cup and be less than about 100 microns in thickness. A thin, disc shaped sample with a hole in the middle, the edges of the hole being thin enough for TEM viewing, is typical. The initial disk is usually formed by cutting and grinding from bulk or thin film/substrate material, and the final thinning done by ion milling. Other specimen preparation possibilities include direct deposition onto a TEM-thin substrate (Si3N4, carbon); direct dispersion of powders on such a substrate; grinding and polishing using special devices (t-tool, tripod); chemical etching and electropolishing; lithographic patterning of walls and pillars for cross-section viewing; and focused ion beam (FIB) sectioning for site specific samples.

Artifacts are common in TEM samples, due both to the thinning process and to changing the form of the original material. For example surface oxide films may be introduced during ion milling and the strain state of a thin film may change if the substrate is removed. Most artifacts can either be minimized by appropriate preparation techniques or be systematically identified and separated from real information.

SCANNING TUNNELING MICROSCOPE

A scanning tunneling microscope (STM) is an instrument for imaging surfaces at the atomic level. Its development in 1981 earned its inventors, Gerd Binnig and Heinrich

Rohrer (at IBMZürich), the Nobel Prize in Physics in 1986. For an STM, good resolution is considered to be 0.1 nm lateral resolution and 0.01 nm depth resolution. With this resolution, individual atoms within materials are routinely imaged and manipulated. The STM can be used not only in ultra high vacuum but also in air, water, and various other liquid or gas ambients, and at temperatures ranging from near zero Kelvin to a few hundred degrees Celsius.

The STM is based on the concept of quantum tunneling. When a conducting tip is brought very near to the surface to be examined, a bias (voltage difference) applied between the two can allow electrons to tunnel through the vacuum between them. The resulting *tunneling current* is a function of tip position, applied voltage, and the local density of states (LDOS) of the sample. Information is acquired by monitoring the current as the tip's position scans across the surface, and is usually displayed in image form. STM can be a challenging technique, as it requires extremely clean and stable surfaces, sharp tips, excellent vibration control, and sophisticated electronics.

Procedure

First, a voltage bias is applied and the tip is brought close to the sample by some coarse sample-to-tip control, which is turned off when the tip and sample are sufficiently close. At close range, fine control of the tip in all three dimensions when near the sample is typically piezoelectric, maintaining tip-sample separation W typically in the 4-7 Å range, which is the equilibrium position between attractive (3<W<10Å) and repulsive (W<3Å) interactions. In this situation, the voltage bias will cause electrons to tunnel between the tip and sample, creating a current that can be measured. Once tunneling is established, the tip's bias and position with respect to the sample can be varied (with the details of this variation depending on the experiment) and data is obtained from the resulting changes in current.

If the tip is moved across the sample in the x-y plane, the changes in surface height and density of states cause changes in current. These changes are mapped in images. This change in current with respect to position can be measured itself, or the height, z, of the tip corresponding to a constant current can be measured. These two modes are called constant height mode and constant current mode, respectively. In constant current mode, feedback electronics adjust the height by a voltage to the piezoelectric height control mechanism. This leads to a height variation

and thus the image comes from the tip topography across the sample and gives a constant charge density surface; this means contrast on the image is due to variations in charge density. In constant height mode, the voltage and height are both held constant while the current changes to keep the voltage from changing; this leads to an image made of current changes over the surface, which can be related to charge density. The benefit to using a constant height mode is that it is faster, as the piezoelectric movements require more time to register the change in constant current mode than the voltage response in constant height mode. All images produced by STM are grayscale, with color optionally added in post-processing in order to visually emphasize important features.

In addition to scanning across the sample, information on the electronic structure at a given location in the sample can be obtained by sweeping voltage and measuring current at a specific location. This type of measurement is called scanning tunneling spectroscopy (STS) and typically results in a plot of the local density of states as a function of energy within the sample. The advantage of STM over other measurements of the density of states lies in its ability to make extremely local measurements: for example, the density of states at an impurity site can be compared to the density of states far from impurities.

Frame rates of at least 1 Hz enable so called Video-STM (up to 50 Hz is possible). This can be used to scan surface diffusion.

Instrumentation



Schematic view of an STM

Dr. V. Senthil Kumar Head Department of Physics The components of an STM include scanning tip, piezoelectric controlled height and x,y scanner, coarse sample-to-tip control, vibration isolation system, and computer.

The resolution of an image is limited by the radius of curvature of the scanning tip of the STM. Additionally, image artifacts can occur if the tip has two tips at the end rather than a single atom; this leads to "double-tip imaging," a situation in which both tips contribute to the tunneling. Therefore it has been essential to develop processes for consistently obtaining sharp, usable tips. Recently, carbon nanotubes have been used in this instance.

The tip is often made of tungsten or platinum-iridium, though gold is also used. Tungsten tips are usually made by electrochemical etching, and platinum-iridium tips by mechanical shearing.

Due to the extreme sensitivity of tunnel current to height, proper vibration isolation or an extremely rigid STM body is imperative for obtaining usable results. In the first STM by Binnig and Rohrer, magnetic levitation was used to keep the STM free from vibrations; now mechanical spring or gas spring systems are often used. Additionally, mechanisms for reducing eddy currents are sometimes implemented.

Maintaining the tip position with respect to the sample, scanning the sample and acquiring the data is computer controlled. The computer may also be used for enhancing the image with the help of image processing as well as performing quantitative measurements.



ATOMIC FORCE MICROSCOPE



Dr. V. Senthil Kumar Head Department of Physics

Atomic force microscopy (AFM) or scanning force microscopy (SFM) is a very highresolution type of scanning probe microscopy, with demonstrated resolution on the order of fractions of a nanometer, more than 1000 times better than the optical diffraction limit. The precursor to the AFM, the scanning tunneling microscope, was developed by Gerd Binnig and Heinrich Rohrer in the early 1980s at IBM Research - Zurich, a development that earned them the Nobel Prize for Physics in 1986. Binnig, Quate and Gerber invented the first atomic force microscope (also abbreviated as AFM) in 1986. The first commercially available atomic force microscope was introduced in 1989. The AFM is one of the foremost tools for imaging, measuring, and manipulating matter at the nanoscale. The information is gathered by "feeling" the surface with a mechanical probe. Piezoelectric elements that facilitate tiny but accurate and precise movements on (electronic) command enable the very precise scanning. In some variations, electric potentials can also be scanned using conducting cantilevers. In newer more advanced versions, currents can even be passed through the tip to probe the electrical conductivity or transport of the underlying surface, but this is much more challenging with very few research groups reporting reliable data.

Basic principles

The AFM consists of a cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. The cantilever is typically silicon or silicon nitride with a tip radius of curvature on the order of nanometers. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke's law. Depending on the situation, forces that are measured in AFM include mechanical contact force, van der Waals forces, capillary forces, chemical bonding, electrostatic forces, magnetic forces (see magnetic force microscope, MFM), Casimir forces, solvation forces, etc. Along with force, additional quantities may simultaneously be measured through the use of specialized types of probe (see scanning thermal microscopy, scanning joule expansion microscopy, photothermal microspectroscopy, etc.). Typically, the deflection is measured using a laser spot reflected from the top surface of the cantilever into an array ofphotodiodes. Other methods that are used include optical interferometry, capacitive sensing or piezoresistive AFM cantilevers. These cantilevers are fabricated with piezoresistive elements that act as a strain

gauge. Using a Wheatstone bridge, strain in the AFM cantilever due to deflection can be measured, but this method is not as sensitive as laser deflection or interferometry.

If the tip was scanned at a constant height, a risk would exist that the tip collides with the surface, causing damage. Hence, in most cases a feedback mechanism is employed to adjust the tip-to-sample distance to maintain a constant force between the tip and the sample. Traditionally, the sample is mounted on a piezoelectric tube, that can move the sample in the *z* direction for maintaining a constant force, and the *x* and *y* directions for scanning the sample. Alternatively a 'tripod' configuration of three piezo crystals may be employed, with each responsible for scanning in the x,y and z directions. This eliminates some of the distortion effects seen with a tube scanner. In newer designs, the tip is mounted on a vertical piezo scanner while the sample is being scanned in X and Y using another piezo block. The resulting map of the area s = f(x,y) represents the topography of the sample.

The AFM can be operated in a number of modes, depending on the application. In general, possible imaging modes are divided into static (also called *contact*) modes and a variety of dynamic (or non-contact) modes where the cantilever is vibrated.

Imaging modes

The primary modes of operation for an AFM are static mode and dynamic mode. In static mode, the cantilever is "dragged" across the surface of the sample and the contours of the surface are measured directly using the deflection of the cantilever. In the dynamic mode, the cantilever is externally oscillated at or close to its fundamental resonance frequency or a harmonic. The oscillation amplitude, phase and resonance frequency modified bv are tipsample interaction forces. These changes in oscillation with respect to the external reference oscillation provide information about the sample's characteristics.

Contact mode

In the static mode operation, the static tip deflection is used as a feedback signal. Because the measurement of a static signal is prone to noise and drift, low stiffness cantilevers are used to boost the deflection signal. However, close to the surface of the sample, attractive forces can be quite strong, causing the tip to "snap-in" to the surface. Thus static mode AFM is almost always done in contact where the overall force is repulsive. Consequently, this technique is typically

called "contact mode". In contact mode, the force between the tip and the surface is kept constant during scanning by maintaining a constant deflection.

Non-contact mode

In this mode, the tip of the cantilever does not contact the sample surface. The cantilever is instead oscillated at a frequency slightly above its resonance frequency where the amplitude of oscillation is typically a few nanometers (<10 nm). The van der Waals forces, which are strongest from 1 nm to 10 nm above the surface, or any other long range force which extends above the surface acts to decrease the resonance frequency of the cantilever. This decrease in resonance frequency combined with the feedback loop system maintains a constant oscillation amplitude or frequency by adjusting the average tip-to-sample distance. Measuring the tip-to-sample distance at each (x,y) data point allows the scanning software to construct a topographic image of the sample surface.

Non-contact mode AFM does not suffer from tip or sample degradation effects that are sometimes observed after taking numerous scans with contact AFM. This makes non-contact AFM preferable to contact AFM for measuring soft samples. In the case of rigid samples, contact and non-contact images may look the same. However, if a few monolayers of adsorbed fluid are lying on the surface of a rigid sample, the images may look quite different. An AFM operating in contact mode will penetrate the liquid layer to image the underlying surface, whereas in noncontact mode an AFM will oscillate above the adsorbed fluid layer to image both the liquid and surface.

Schemes for dynamic mode operation include frequency modulation and the more common amplitude modulation. In frequency modulation, changes in the oscillation frequency provide information about tip-sample interactions. Frequency can be measured with very high sensitivity and thus the frequency modulation mode allows for the use of very stiff cantilevers. Stiff cantilevers provide stability very close to the surface and, as a result, this technique was the first AFM technique to provide true atomic resolution in ultra-high vacuum conditions.

In amplitude modulation, changes in the oscillation amplitude or phase provide the feedback signal for imaging. In amplitude modulation, changes in the phase of oscillation can be used to discriminate between different types of materials on the surface. Amplitude modulation

can be operated either in the non-contact or in the intermittent contact regime. In dynamic contact mode, the cantilever is oscillated such that the separation distance between the cantilever tip and the sample surface is modulated.

Amplitude modulation has also been used in the non-contact regime to image with atomic resolution by using very stiff cantilevers and small amplitudes in an ultra-high vacuum environment.

Tapping mode

In ambient conditions, most samples develop a liquid meniscus layer. Because of this, keeping the probe tip close enough to the sample for short-range forces to become detectable while preventing the tip from sticking to the surface presents a major problem for non-contact dynamic mode in ambient conditions. Dynamic contact mode (also called intermittent contact or tapping mode) was developed to bypass this problem.

In *tapping mode*, the cantilever is driven to oscillate up and down at near its resonance frequency by a small piezoelectric element mounted in the AFM tip holder similar to non-contact mode. However, the amplitude of this oscillation is greater than 10 nm, typically 100 to 200 nm. Due to the interaction of forces acting on the cantilever when the tip comes close to the surface, Van der Waals force, dipole-dipole interaction, electrostatic forces, etc. cause the amplitude of this oscillation to decrease as the tip gets closer to the sample. An electronic servo uses the piezoelectric actuator to control the height of the cantilever above the sample. The servo adjusts the height to maintain a set cantilever oscillation amplitude as the cantilever is scanned over the sample. A *tapping AFM* image is therefore produced by imaging the force of the intermittent contacts of the tip with the sample surface.

This method of "tapping" lessens the damage done to the surface and the tip compared to the amount done in contact mode. Tapping mode is gentle enough even for the visualization of supported lipid bilayers or adsorbed single polymer molecules (for instance, 0.4 nm thick chains of synthetic polyelectrolytes) under liquid medium. With proper scanning parameters, the conformation of single molecules can remain unchanged for hours.

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AFM cantilever deflection measurement



AFM beam deflection detection

Laser light from a solid state diode is reflected off the back of the cantilever and collected by a position sensitive detector (PSD) consisting of two closely spaced photodiodes whose output signal is collected by a differential amplifier. Angular displacement of cantilever results in one photodiode collecting more light than the other photodiode, producing an output signal (the difference between the photodiode signals normalized by their sum) which is proportional to the deflection of the cantilever. It detects cantilever deflections <10 nm (thermal noise limited). A long beam path (several centimeters) amplifies changes in beam angle.

Force spectroscopy

Another major application of AFM (besides imaging) is force spectroscopy, the direct measurement of tip-sample interaction forces as a function of the gap between the tip and sample (the result of this measurement is called a force-distance curve). For this method, the AFM tip is extended towards and retracted from the surface as the deflection of the cantilever is monitored as a function of piezoelectric displacement. These measurements have been used to measure nanoscale contacts, atomic bonding, Van der Waals forces, and Casimir forces, dissolution forces in liquids and single molecule stretching and rupture forces. Furthermore, AFM was used to measure in aqueous environment dispersion force due to polymer adsorbed on the substrate. Forces of the order of a few piconewtons can now be routinely measured with a

vertical distance resolution of better than 0.1 nanometers. Force spectroscopy can be performed with either static or dynamic modes. In dynamic modes, information about the cantilever vibration is monitored in addition to the static deflection.

Problems with the technique include no direct measurement of the tip-sample separation and the common need for low stiffness cantilevers which tend to 'snap' to the surface. The snap-in can be reduced by measuring in liquids or by using stiffer cantilevers, but in the latter case a more sensitive deflection sensor is needed. By applying a small dither to the tip, the stiffness (force gradient) of the bond can be measured as well.

Identification of individual surface atoms

The AFM can be used to image and manipulate atoms and structures on a variety of surfaces. The atom at the apex of the tip "senses" individual atoms on the underlying surface when it forms incipient chemical bonds with each atom. Because these chemical interactions subtly alter the tip's vibration frequency, they can be detected and mapped. This principle was used to distinguish between atoms of silicon, tin and lead on an alloy surface, by comparing these 'atomic fingerprints' to values obtained from large-scale density functional theory (DFT) simulations.

The trick is to first measure these forces precisely for each type of atom expected in the sample, and then to compare with forces given by DFT simulations. The team found that the tip interacted most strongly with silicon atoms, and interacted 23% and 41% less strongly with tin and lead atoms, respectively. Thus, each different type of atom can be identified in the matrix as the tip is moved across the surface.

Such a technique has been used now in biology and extended recently to cell biology. Forces corresponding to (i) the unbinding of receptor ligand couples (ii) unfolding of proteins (iii) cell adhesion at single cell scale have been gathered.

Advantages and disadvantages

Just like any other tool, an AFM's usefulness has limitations. When determining whether or not analyzing a sample with an AFM is appropriate, there are various advantages and disadvantages that must be considered.

Advantages

AFM has several advantages over the scanning electron microscope (SEM). Unlike the electron microscope which provides a two-dimensional projection or a two-dimensional image of a sample, the AFM provides a three-dimensional surface profile. Additionally, samples viewed by AFM do not require any special treatments (such as metal/carbon coatings) that would irreversibly change or damage the sample. While an electron microscope needs an expensive vacuum environment for proper operation, most AFM modes can work perfectly well in ambient air or even a liquid environment. This makes it possible to study biological macromolecules and even living organisms. In principle, AFM can provide higher resolution than SEM. It has been shown to give true atomic resolution in ultra-high vacuum (UHV) and, more recently, in liquid environments. High resolution AFM is comparable in resolution to scanning tunneling microscopy and transmission electron microscopy.

Disadvantages

A disadvantage of AFM compared with the scanning electron microscope (SEM) is the single scan image size. In one pass, the SEM can image an area on the order of square millimeters with a depth of field on the order of millimeters. Whereas the AFM can only image a maximum height on the order of 10-20 micrometers and a maximum scanning area of about 150×150 micrometers. One method of improving the scanned area size for AFM is by using parallel probes in a fashion similar to that of millipede data storage.

The scanning speed of an AFM is also a limitation. Traditionally, an AFM cannot scan images as fast as a SEM, requiring several minutes for a typical scan, while a SEM is capable of scanning at near real-time, although at relatively low quality. The relatively slow rate of scanning during AFM imaging often leads to thermal drift in the image making the AFM microscope less suited for measuring accurate distances between topographical features on the image. However, several fast-acting designs were suggested to increase microscope scanning productivity including what is being termed video AFM (reasonable quality images are being obtained with video AFM at video rate: faster than the average SEM). To eliminate image distortions induced by thermal drift, several methods have been introduced.

AFM images can also be affected by hysteresis of the piezoelectric material and crosstalk between the x, y, z axes that may require software enhancement and filtering. Such filtering could "flatten" out real topographical features. However, newer AFMs utilize closed-loop scanners which practically eliminate these problems. Some AFMs also use separated orthogonal scanners (as opposed to a single tube) which also serve to eliminate part of the cross-talk problems.

As with any other imaging technique, there is the possibility of image artifacts, which could be induced by an unsuitable tip, a poor operating environment, or even by the sample itself. These image artifacts are unavoidable however, their occurrence and effect on results can be reduced through various methods.

Due to the nature of AFM probes, they cannot normally measure steep walls or overhangs. Specially made cantilevers and AFMs can be used to modulate the probe sideways as well as up and down (as with dynamic contact and non-contact modes) to measure sidewalls, at the cost of more expensive cantilevers, lower lateral resolution and additional artifacts.

Piezoelectric scanners

AFM scanners are made from piezoelectric material, which expands and contracts proportionally to an applied voltage. Whether they elongate or contract depends upon the polarity of the voltage applied. The scanner is constructed by combining independently operated piezo electrodes for X, Y, and Z into a single tube, forming a scanner which can manipulate samples and probes with extreme precision in 3 dimensions.

Scanners are characterized by their sensitivity which is the ratio of piezo movement to piezo voltage, i.e., by how much the piezo material extends or contracts per applied volt. Because of differences in material or size, the sensitivity varies from scanner to scanner. Sensitivity varies non-linearly with respect to scan size. Piezo scanners exhibit more sensitivity at the end than at the beginning of a scan. This causes the forward and reverse scans to behave differently and display hysteresis between the two scan directions. This can be corrected by applying a non-linear voltage to the piezo electrodes to cause linear scanner movement and calibrating the scanner accordingly.

The sensitivity of piezoelectric materials decreases exponentially with time. This causes most of the change in sensitivity to occur in the initial stages of the scanner's life. Piezoelectric scanners are run for approximately 48 hours before they are shipped from the factory so that they are past the point where they may have large changes in sensitivity. As the scanner ages, the sensitivity will change less with time and the scanner would seldom require recalibration.

SURFACE PLASMON RESONANCE

The excitation of surface plasmons by light is denoted as a surface plasmon resonance (SPR) for planar surfaces or localized surface plasmon resonance (LSPR) for nanometer-sized metallic structures.

This phenomenon is the basis of many standard tools for measuring adsorption of material onto planar metal (typically gold and silver) surfaces or onto the surface of metal nanoparticles. It is the fundamentals behind many color based biosensor applications and different lab-on-a-chip sensors.

Explanation

Surface plasmons, also known as surface plasmon polaritons, are surface electromagnetic waves that propagate in a direction parallel to the metal/dielectric (or metal/vacuum) interface. Since the wave is on the boundary of the metal and the external medium (air or water for example), these oscillations are very sensitive to any change of this boundary, such as the adsorption of molecules to the metal surface.

To describe the existence and properties of surface plasmons, one can choose from various models (quantum theory, Drude model, etc.). The simplest way to approach the problem is to treat each material as a homogeneous continuum, described by a frequency-dependent relative permittivity between the external medium and the surface. This quantity, hereafter referred to as the materials' "dielectric constant," is complex-valued. In order for the terms which describe the electronic surface plasmons to exist, the real part of the dielectric constant of the metal must be negative and its magnitude must be greater than that of the dielectric. This condition is met in the IR-visible wavelength region for air/metal and water/metal interfaces (where the real dielectric constant of a metal is negative and that of air or water is positive).

Localized surface plasmon polaritions (LSPRs) are collective electron charge oscillations in metallic nanoparticles that are excited by light. They exhibit enhanced near-field amplitude at the resonance wavelength. This field is highly localized at the nanoparticle and decays rapidly away from the nanoparticle/dieletric interface into the dielectric background, though far-field scattering by the particle is also enhanced by the resonance. Light intensity enhancement is a very important aspect of LSPRs and localization means the LSPR has very high spatial resolution (subwavelength), limited only by the size of nanoparticles. Because of the enhanced field amplitude, effects that depend on the amplitude such as magneto-optical effect are also enhanced by LSPRs.

Realisation



Kretschmann configuration

In order to excite surface plasmons in a resonant manner, one can use an electron or light beam(visible and infrared are typical). The incoming beam has to match its impulse to that of the plasmon. In the case of p-polarized light (polarization occurs parallel to the plane of incidence), this is possible by passing the light through a block of glass to increase the wavenumber (and theimpulse), and achieve the resonance at a given wavelength and angle. Spolarized (polarization occurs perpendicular to the plane of incidence) light cannot excite

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electronic surface plasmons. Electronic and magnetic surface plasmons obey the following dispersion relation:

$$K(\omega) = \frac{\omega}{c} \sqrt{\frac{\varepsilon_1 \varepsilon_2 \mu_1 \mu_2}{\varepsilon_1 \mu_1 + \varepsilon_2 \mu_2}}$$

where ε stands for the dielectric constant, and μ for the magnetic permeability of the materials (1: the glass block, 2: the metal film).

Typical metals that support surface plasmons are silver and gold, but metals such as copper, titanium or chromium are also known to be applicable.

Using light to excite SP waves, there are two constructions which are well known. In the Otto setup, the light is shone on the wall of a glass block, typically a prism, and totally reflected. A thin metal (for example gold) film is positioned close enough, that the evanescent waves can interact with the plasma waves on the surface and excite the plasmons.

In the Kretschmann configuration, the metal film is evaporated onto the glass block. The light is again illuminating from the glass, and an evanescent wave penetrates through the metal film. The plasmons are excited at the outer side of the film. This configuration is used in most practical applications.

SPR emission

When the surface plasmon wave hits a local particle or irregularity—like on a rough surface—, part of the energy can be re-emitted as light. This emitted light can be detected *behind* the metal film in various directions.

Applications

Surface plasmons have been used to enhance the surface sensitivity of several spectroscopic measurements including fluorescence, Raman scattering, and second harmonic generation. However, in their simplest form, SPR reflectivity measurements can be used to detect molecular adsorption, such as polymers, DNA or proteins, etc. Technically, it is common, that the angle of the reflection minimum (absorption maximum) is measured. This angle changes in the order of 0.1° during thin (about nm thickness) film adsorption. (See also the Examples.) In other cases the changes in the absorption wavelength is followed. The mechanism of detection is based on that the

adsorbing molecules cause changes in the local index of refraction, changing the resonance conditions of the surface plasmon waves.

- If the surface is patterned with different biopolymers, using adequate optics and imaging sensors (i.e. a camera), the technique can be extended to surface plasmon resonance imaging (SPRI). This method provides a high contrast of the images based on the adsorbed amount of molecules, somewhat similar to Brewster angle microscopy (this latter is most commonly used together with a Langmuir-Blodgett trough).
- For nano particles, localized surface plasmon oscillations can give rise to the intense colors of suspensions or sols containing the nano particles. Nano particles or nanowires of noble metals exhibit strong absorption bands in the ultraviolet-visible light regime that are not present in the bulk metal. This extraordinary absorption increase has been exploited to increase light absorption in photovoltaic cells by depositing metal nano particles on the cell surface. The energy (color) of this absorption differs when the light is polarized along or perpendicular to the nanowire. Shifts in this resonance due to changes in the local index of refraction upon adsorption to the nano particles can also be used to detect biopolymers such as DNA or proteins. Related complementary techniques include plasmon waveguide resonance, QCM, extraordinary optical transmission, and Dual Polarisation Interferometry

SOFT LITHOGRAPHY

Soft Lithography is an umbrella term for a set of techniques that rely on printing and molding to make microstructures and nanostructures. It was originally developed in order to circumvent the limitations of photolithography, which has been the basic technology used for making all microelectronic systems. The invention of photolithography is arguably as important as that of the wheel, bronze, or movable type in terms of its impact on society. It is, however, a technology that is specialized for use in microelectronics.

For making other kinds of micro-systems, photolithography is not necessarily the right technology to use. It is not only limited in the materials it can use and in the geometries it can produce, but it is expensive and can only pattern a small area at any given time. In addition, the size of the features one can make with photolithography is limited by diffraction of light. As a

result, to a first approximation, photolithography is confined to extremely flat silicon substrates; curved surfaces, for example, cannot evenly accommodate light beams moving in a straight line. One could not, for example, fabricate electronic circuits on a plastic sheet or a flexible display on a curved car dashboard. While Soft Lithography has different limitations, the physics-based constraints in these techniques are relatively minimal, especially relative to the broad range of capabilities this technique enables.

It is important to emphasize that while Soft Lithography clearly is of value for electronics, it is by no means limited to this field. In fact, Soft Lithography is finding application in a range of different fields from consumer products to industrial processes to life sciences, because the fundamental capability it enables is critical to so many development challenges: the exquisite control over an infinite range of structures and chemistries from the nano- to the meso-scale, and the integration of these into useful systems and devices.

The basic principle of the first phase for any Soft Lithographic technique is illustrated below. We start with the fabrication of a 'Master' using proven techniques, such as photolithography, e-beam, or micro-machining. A Master could also be an existing structure that doesn't require processing like a human hair or some woven fabric. An elastomer, such as polyurethane or a silicone, is poured onto the Master, hardened using heat or ultraviolet light, and peeled off to yield a 'mold'. The resulting mold is the exact structural inverse of the original Master - down to nanometer accuracy depending on the combination of materials used and the precision of the replication process.



Dr. V. Senthil Kumar Head Department of Physics

Thanks to their distinct physical characteristics, such as softness, flexibility, elasticity and minimal stickiness, these polymer molds can be used as stamps for transferring the Master pattern to virtually any surface. While our techniques often begin with polymer stamps and molds, we could just as easily impart structures and chemistries onto a variety of non-plastic surfaces (such as metals, ceramics or oxides) of practically any shape or size. Furthermore, we can pattern these diverse materials with a broad range of materials, including silicon on glass or organic molecules on metal.

Note that a single Master can be used tens to hundreds of times, depending on application, to produce tens to hundreds of molds, and each mold can be used to transfer the pattern tens to a hundred times depending on application. And each mold can also act as a Master from which we can again accurately replicate tens to hundreds of molds. The result is a highly scalable and economical process. It is also important to note that molds can, in principle, be fabricated with meter-sized dimensions and surface feature sizes ranging in size from nanometers to millimeters.

The transfer of a pattern from a patterned stamp, created using Soft Lithography, to a surface requires an 'ink'. We use conventional inks to create color effects on surfaces much like we would use a stamp to imprint a return address on an envelope. Industries are interested in the wide range of specialized 'inks' that we pattern on surfaces that modify the characteristics of the material, including its: water-repellency, interfacial energy, electrical conductance, heat conductance, optical properties, stiffness, strength and other physical properties. The chemical and physical properties of the 'ink' may be just as important for the performance of the integrated system or device as the design on the stamp.

Examples of Patterned Chemistry

- Organic molecules (e.g. self-assembled monolayers)
- Metals
- Charge (electrets)
- Crystals
- Liquid crystals
- Proteins and other biological molecules (e.g. DNA, antigens/antibodies)

- Cells (mammalian; bacterial)
- Solids and liquids

The micro-patterned metal spheres below illustrate the ability to transfer a pattern onto a nonflat surface using Soft Lithography. The rainbow colors visible on the spheres results from our fabrication of nano-scale structures on the sphere's surface.



Micropatterned Metal Spheres

We fabricated the structures enlarged on the right on a Master, which we then replicated into a deformable plastic mold. We used this mold as a conformal phase-mask to transfer the pattern lithographically to the curved surface of a sphere—a surface that is practically impossible to pattern through conventional lithography. Each structure is approximately 500 nanometers in diameter, with line widths in the 50 to 100 nanometer range. Similar in principle to rainbows or butterfly wings, these structures diffract white light with wavelengths of 400 to 800 nanometers hitting the sphere's surfaces into the spectrum of colors visible in the image above. This type of structural color could find practical use in industry as a replacement for die/pigment-based color or as an anti-counterfeiting measure imprinted on packaging or the product itself.

Soft Lithography can be used to pattern or replicate structures ranging from passive components such as electronic interconnects, optical lenses, filtration membranes, or ultraefficient micro-structured heat sinks, to active components such as transistors or display pixels. Additional examples of structures that can be fabricated include:

Examples of Fabricated Structures

• Anti-reflective structures

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Condensed Matter Physics UNIT V (17PHP101) INSTRUMENTATION

- Circuitry for electronics on flexible substrates
- Diffraction gratings
- Heat exchanges
- Micro-lens arrays
- Optical elements
- Filtration membranes

SELF-ASSEMBLED MONOLAYER

A self assembled monolayer (SAM) is an organized layer of amphiphilic molecules in which one end of the molecule, the "head group" shows a special affinity for a substrate. SAMs also consist of a tail with a functional group at the terminal end as seen in Figure 1.



Figure 1. Representation of a SAM structure

SAMs are created by the chemisorption of hydrophilic "head groups" onto a substrate from either the vapor or liquid phase followed by a slow two-dimensional organization of hydrophobic "tail groups". Initially, adsorbate molecules form either a disordered mass of molecules or form a "lying down phase", and over a period of hours, begin to form crystalline or semicrystalline structures on the substrate surface. The hydrophilic "head groups" assemble together on the substrate, while the hydrophobic tail groups assemble far from the substrate. Areas of close-packed molecules nucleate and grow until the surface of the substrate is covered in a single monolayer.

Adsorbate molecules adsorb readily because they lower the surface energy of the substrate and are stable due to the strong chemisorption of the "head groups." These bonds create monolayers that are more stable than the physisorbed bonds of Langmuir–Blodgett films. Thiol-

metal bonds, for example, are on the order of 100 kJ/mol, making the bond stable in a wide variety of temperature, solvents, and potentials. The monolayer packs tightly due to van der Waals interactions, thereby reducing its own free energy. The adsorption can be described by the Langmuir adsorption isotherm if lateral interactions are neglected. If they cannot be neglected, the adsorption is better described by the Frumkin isotherm.

Types of SAMs

Selecting the type of head group depends on the application of the SAM. Typically, head groups are connected to an alkyl chain in which the terminal end can be functionalized (i.e. adding –OH, –NH3, or –COOH groups) to vary the wetting and interfacial properties. An appropriate substrate is chosen to react with the head group. Substrates can be planar surfaces, such as silicon and metals, or curved surfaces, such as nanoparticles. Alkanethiols are the most commonly used molecules for SAMs. Alkanethiols are molecules with an alkyl chain, (C-C)ⁿ chain, as the back bone, a tail group, and a S-H head group. They are used on noble metal substrates because of the strong affinity of sulfur for these metals. The sulfur gold interaction is semi-covalent @45kcal/mol. In addition, gold is an inert and biocompatible material that is easy to acquire. It is also easy to pattern via lithography, a useful feature for applications in nanoelectromechanical systems (NEMS). Additionally, it can withstand harsh chemical cleaning treatments. Silanes are generally used on nonmetallic oxide surfaces.

Preparation of SAMs

Metal substrates for use in SAMs can be produced through physical vapor deposition techniques, electrodeposition or electroless deposition. Alkanethiol SAMs produced by adsorption from solution are made by immersing a substrate into a dilute solution of alkane thiol in ethanol for 12 to 72 hours at room temperature and dried with nitrogen. SAMs can also be adsorbed from the vapor phase. For example, chlorosilane SAMs (which can also be adsorbed from the liquid phase), are often created in a reaction chamber by silanization in which silane vapor flows over the substrate to form the monolayer.

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Applications of SAMs

Thin Film SAMs

SAMs are an inexpensive and versatile surface coating for applications including control of wetting and adhesion, chemical resistance, bio compatibility, sensitization, and molecular recognition for sensors and nano fabrication. Areas of application for SAMs include biology, electrochemistry and electronics, nanoelectromechanical systems (NEMS) and microelectromechanical systems (MEMS), and everyday household goods. SAMs can serve as models for studying membrane properties of cells and organelles and cell attachment on surfaces. SAMs can also be used to modify the surface properties of electrodes for electrochemistry, general electronics, and various NEMS and MEMS. For example, the properties of SAMs can be used to control electron transfer in electrochemistry. They can serve to protect metals from harsh chemicals and etchants. SAMs can also reduce sticking of NEMS and MEMS components in humid environments. In the same way, SAMs can alter the properties of glass. A common household product, Rain-X, utilizes SAMs to create a hydrophobic monolayer on car windshields to keep them clear of rain.

Thin film SAMs can also be placed on nanostructures. In this way they functionalize the nanostructure. This is advantageous because thenanostructure can now selectively attach itself to other molecules or SAMs. This technique is useful in biosensors or other MEMS devices that need to separate one type of molecule from its environment. One example is the use of magnetic nanoparticles to remove a fungus from a blood stream. The nanoparticle is coated with a SAM that binds to the fungus. As the contaminated blood is filtered through a MEMS device the magnetic nanoparticles are inserted into the blood where they bind to the fungus and are then magnetically driven out of the blood stream into a nearby laminar waste stream.

Patterned SAMs

SAMs are also useful in depositing nanostructures, because each adsorbate molecule can be tailored to attract two different materials. Current techniques utilize the head to attract to a surface, like a plate of gold. The terminal group is then modified to attract a specific material like a particular nanoparticle, wire, ribbon, or other nanostructure. In this way, wherever the a SAM is patterned to a surface there will be nanostructures attached to the tail groups. One example is

the use of two types of SAMs to align single wall carbon nanotubes, SWNTs. Dip pen nanolithography was used to pattern a 16-mercaptohexadecanoic acid (MHA)SAM and the rest of the surface was passivated with 1-octadecanethiol (ODT) SAM. As the solvent that was carrying the SWNTs evaporated, the SWNTs became attracted to the MHA SAM because of its hydrophilic nature. Once the SWNTs became close enough to the MHA SAM they attached to it due to Van der Waals forces. Using this technique Chad Mirkin, Schatz and their co-workers were able to make complex two dimensional shapes, a representation of a shape created is shown to the right.

Another application of patterned SAMs is the functionalization of biosensors. The tail groups can be modified so they have an affinity for cells, proteins, or molecules. The SAM can then be placed onto a biosensor so that binding of these molecules can be detected. The ability to pattern these SAMs allows them to be placed in configurations that increase sensitivity and do not damage or interfere with other components of the biosensor.

Condensed Matter Physics UNIT V (17PHP101) INSTRUMENTATION

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POSSIBLE QUESTIONS

UNIT V

- 1. Describe the instrumentation of Scanning electron microscope (SEM)
- 2. Describe the instrumentation of Scanning tunneling microscope (STM).
- 3. Describe the various theories involved in soft lithography along with principles.
- 4. Explain about the theories and principles of soft lithography.
- 5. Explain Surface Plasmon resonance (SPR).
- 6. What is lithography? Explain the theories and principles of soft lithography.
- 7. Explain the working principle of Atomic Force Microscope (AFM).
- 8. Explain the working principle of Scanning Electron Microscope.
- 9. Explain with neat diagram about scanning electron microscope.
- 10. How do you characterize a material with transmission electron microscope (TEM) with a neat sketch?

KARPAGAM ACADEMY OF HIGHER EDUCATION, COIMBATORE-21

DEPARTMENT OF PHYSICS CONDENSED MATTER PHYSICS (17PHP101)

MULTIPLE CHOICE QUESTIONS	
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Questions	option 1	option 2	option 3	option 4	Answer
UNIT V					
	Transmission Electron	Transmit Electron	Transform Electron	Transmit	Transmission Electron
TEM is	Microscope.	Microscope.	Microscope.	ElectricalMicroscope.	Microscope.
		Scanning Light	Scanning Light		
SLMS are	Spatial Light Modulators.	Microscope.	Modulator.	Spatial Light Microscope.	Spatial Light Modulators.
	Magnetic Resonance	Molecule Resonance	Magnetic Resonance		Magnetic Resonance
Expand MRFM.	Force Microscopy.	Microscopy.	Imaging.	None of the above.	Force Microscopy.
microscope has been used to build nano sized structural atom by atom					
on the surface of materials.	TEM.	AFM.	STM.	SEM.	STM.
lithographic pattern a resist by physically deforming the resist sharp with					
a mold having a nano structure pattern on it, rather than by modifying the resist					
surface by radiation, as in conventional lithography.	Micro imprimt.	Nano imprimt.	Micro and nano imprint.	Macro imprint.	Nano imprimt.
is the art and science of etching, writing or printing at the microscopic	*	, î		^	•
level, where that dimensions of characters are on the order of nm.	Nanolithography	Optical lithography.	X-ray lithography.	UV lithography.	Nanolithography
includes various methods of modifying semiconductor chips at the atomic					
level for the purpose of fabricating integrated circuits.	Optical lithography.	Nanolithography.	X-ray lithography.	Micro lithography.	Nanolithography.
is used during the fabrication of leading etch semiconductor integrated					
circuits or nano electromechanical system.	X-ray lithography.	Nanolithography.	Optical lithography.	UV-lithography.	Optical lithography.
lithography and its variants such as step and flash imprint lithography are					
promising nano pattern replication technologies.	Micro imprint.	Nano imprint.	Neutral particle.	Extreme UV.	Nano imprint.
Atomic force microscopic nanolithography is a chemo-mechanical surface					
patterning technology that uses microscope.	electron.	atomic.	atomic force.	atomic particle.	atomic force.
lithography is used to transfer a used generated shape on to a material					
through the selective exposure of a light sensitive polymer.	Photo.	soft	Film	Bonding	Photo.
encompasses three different techniques which are all based on the generation					
and utilization of the mold of a micro structure out of poly dimethyl siloxane					
(PDMS).	Film deposition.	Bonding.	Photolithography.	Softlithography.	Softlithography.
consists of the formation of micron thick films on the surface of a					
substrate.	Film deposition.	Bonding.	Etching.	Softlithography.	Film deposition.
	Quasino contact force	Quantum force	Quasi contact		Quasino contact force
QFM is	microscopy	microscopy.	microscopy.	None of the above.	microscopy
is considered as the most expensive micromechanical process:	Etching	Lift-off technique	Lithography	Masking	Lithography
Types of lithography:	Photolithography	X-ray lithography	E-beam lithography	All of the above	All of the above
In X-ray lithography, the X-ray absorber is usually:	Silver	Gold	Aluminum	None of the above	None of the above
			Doesn't require high		
The electron gun is used in lithography because it is	Inexpensive	Accurate	voltage	Not e of the above	Accurate
Types of etching are	Wet isotropic	Wet anisotropic	Dry	All of the above	All of the above
Etching is always anisotropic if the material is	Crystalline	Polycrystalline	Amorphous	None of the above	None of the above
is the etching through chemical or physical interaction between					
ions:	Wet isotropic etching	Wet anisotropic etching	Dry etching	None of the above	Dry etching

		Combined			
is used for metals that are hard to etch:	Lift-off technique	physical/chemical etching	Physical sputter etching	Chemical plasma etching	Lift-off technique
	Forming resist layers on				Forming resist layers on
Lithography is used for:	the substrate	Cutting tool	Forming electric bonds	None of the above	the substrate
Types of photoresist:	Positive	Negative	a & b	None of the above	a & b
is projecting electron beam directing on photoresist of the wafer :	E-beam lithography	Light emitting	Electron beam gun	Radar beam	E-beam lithography
Used for removing desired areas of the photo resist from the substrate:	LIGA	Lithography	Etching	Not e of the above	Etching
			Combined		
Methods of dry etching are:	Physical sputter etching	Chemical plasma etching	chemical/physical etching	All of the above	All of the above
One of the most used kinds of lasers in microfabrication is:	Excimer	Diamond milling	Bulk micromachining	None of the above	Excimer
process is also called spark erosion	U ultrasonic machining	Powder blasting	Soft lithography	Micro electro discharge machining	Micro electro discharge machining
is the most used in silicon micromachining:	Laser micromachining.	Micro Electro-Discharge machining.	Bulk machining.	Powder Blasting.	Bulk machining.
			Micro-electro discharge		Micro-electro discharge
method removes material through erosive action:	Diamond milling	Soft lithography	machining	Powder blasting	machining
the full wafer thickness range is:	80—200 ms	80—400 ns	80—200 ns	80—200 s	80—200 ms
	he type of heavy metal or dye that is used to stain	the ratio of an object's	the shortest wavelength of light used to illuminate	the type of lens used to magnify the object under	the shortest wavelength of light used to illuminate
What limits the resolving power of a light microscope?	the specimen	image to its real size	the specimen	study	the specimen
When biologists wish to study the internal ultrastructure of cells, they most likely would use	a scanning electron microscope.	a light microscope.	a transmission electronic microscope.	both A and C.	a transmission electronic microscope.

PREPARED BY : Dr. V. Senthil Kumar, Head, Department Of Physics, KAHE-CBE-21

Register No. -----[17PHP101]

KARPAGAM ACADEMY OF HIGHER EDUCATION, COIMBATORE - 641 021 **DEPARTMENT OF PHYSICS** I M. Sc. PHYSICS

INTERNAL TEST I

CONDENSED MATTER PHYSICS

Date: 28.08.2017 Marks: 50

Duration: 2 Hrs.

$PART - A (20 \times 1 = 20 Marks)$

Objective Type Questions:

- 1. The correct order of the coordination number is SC, BCC, FCC and HCP unit cells is d. 6, 12, 12, 8 a. 12, 8, 12, 6 c. 8, 6, 12, 12
- 2. The number of atoms present in the unit cell of HCP structure is a. 2 b. 4 xe. 6 d. 7
- 3. Which of the following elements is a covalently bonded crystal? a. aluminium b . sodium chloride v . germanium d. lead
- 4. The forbidden energy gap of carbon in diamond structure is a. 7.0 eV b. 1.0 eV c. 0.01 eV d. none
- 5. For silicon doped with trivalent impurity, a. ne >> nh b. ne > nh 10. nh >> ne d. nh > ne

6. Metallic bond is not characterized by b. high conductivity a. ductility . directionality d. opacity

- 7. The Fermi level in an n-type semiconductor at 0 K lies a. below the donor level.
- Half way between the bottom of conduction band and donor. level.
 - c. Exactly in the middle of bandgap.
 - d. Half way between the top of valence band and the acceptor level.
- 8. Piezoelectric effect is the production of electricity by a. chemical effect b. pressure c. varying magnetic field d. temperature
- 9. Electromigration in metallization refers to the diffusion (under the influence of current) of A. Al
 - b. Cu in A1-Cu alloy c. Si d. Na

10. Fine grain sizes are obtained by

A. slow cooling b. increasing nucleation rate c. decreasing growth rate d. fast cooling

11. Atomic packing factor is

- a. Distance between two adjacent atoms
- b. Projected area fraction of atoms on a plane
- Volume fraction of atoms in cell d. None
- 12. Schottky-defect in ceramic material is a. Interstitial impurity b. Vacancy- interstitial pair of cations Pair of nearby cation and anion vacancies d. Substitutional impurity
- 13. Theoretical strength is about ______ times to average real strength of a material.

a. 1	b. 10	<u>c</u> 100	d. 1000
14. Followi	ng is not the 2-o	imensional impe	erfection

a. Twin boundary D. Dislocation c. Surface d. Grain boundary

- 15. Figure out the odd one in the following A. Frenkel defect b. Tilt boundary
- c. Twist boundary d. Stacking fault
- 16. Thermodynamically stable defects A. Point defects b. Line defects c. Surface defects d. Volume defects
- 17. The SI unit of heat capacity is a. Joule b. joule/kilogram c. Joule/(kilogram × Kelvin) Joule/Kelvin
- 18. Aluminum has the specific heat capacity of a. 450 J kg-1 °C-1 ₩. 900 J kg-1 °C-1 c. 1350 J kg-1 °C-1 d. 1800 J kg-1 °C-1
- 19. The internal energy comprises of two types of energies, those are a. mechanical & electrical energy b. magnetic & electrical energy kinetic & potential energy
- d. kinetic & magnetic energy
- 20. What substance is attracted to a magnet? a. silver b. lead c. water d. iron

 $PART - B (3 \times 2 = 6 Marks)$

Short Answer Type Questions:

21. Write down the Clausius-Mossoti equation.

- 22. Define dislocation.
- 23. Define resistivity.

$$PART - C (3 \times 8 = 24 Marks)$$

Answer ALL questions:

- 24. a. Write a detailed note on (i) Diamond cubic structure and (ii) NaCl structure.
 - (OR) b. Discuss the properties of semiconductors.
- 25. a. Explain the various classifications of crystal defects. (OR)
 - b. Write a detailed note on ultrasonics. Explain the application of non destructive testing.

(OR)

26. a) Discuss the experimental electrical resistivity of metals?

b) Discuss superconductivity.

****ALL THE BEST****

Register No. -----

[17PHP101]

KARPAGAM ACADEMY OF HIGHER EDUCATION, COIMBATORE – 641 021 DEPARTMENT OF PHYSICS I M. Sc. PHYSICS

INTERNAL TEST I

CONDENSED MATTER PHYSICS

Date: 28.08.2017

Marks: 50 Duration: 2 Hrs.

$PART - A (20 \times 1 = 20 Marks)$

Objective Type Questions:

- The correct order of the coordination number is SC, BCC, FCC and HCP unit cells is

 a. 12, 8, 12, 6
 b. 6, 8, 12, 12
 c. 8, 6, 12, 12
 d. 6, 12, 12, 8
- 2. The number of atoms present in the unit cell of HCP structure is a. 2 b. 4 c. 6 d. 7
- 3. Which of the following elements is a covalently bonded crystal? a. aluminium b . sodium chloride **c. germanium** d. lead
- 4. The forbidden energy gap of carbon in diamond structure is
 a. 7.0 eV
 b. 1.0 eV
 c. 0.01 eV
 d. none
- 5. For silicon doped with trivalent impurity,
 a. ne >> nh b. ne > nh c. nh >> ne d. nh > ne
 6. Metallic bond is not characterized by
- a. ductility b. high conductivity c. directionality d. opacity
- 7. The Fermi level in an n-type semiconductor at 0 K lies a. below the donor level.
 - b. Half way between the bottom of conduction band and donor level.
 - c. Exactly in the middle of bandgap.
 - d. Half way between the top of valence band and the acceptor level.
- 8. Piezoelectric effect is the production of electricity by

a. chemical effectb. pressured. temperature

- 9. Electromigration in metallization refers to the diffusion (under the influence of current) of
 a. Al
 b. Cu in A1-Cu alloy c. Si d. Na
- 10. Fine grain sizes are obtained bya. slow coolingb. increasing nucleation ratec. decreasing growth rated. fast cooling
- 11. Atomic packing factor is
 - a. Distance between two adjacent atoms
 - b. Projected area fraction of atoms on a plane
 - c. Volume fraction of atoms in cell d. None
- 12. Schottky-defect in ceramic material is
 - a. Interstitial impurity b. Vacancy- interstitial pair of cations
 - c. Pair of nearby cation and anion vacancies
 - d. Substitutional impurity

13. Theoretical strength is about ______ times to average real strength of a material.
a. 1 b. 10 c. 100 d. 1000

- 14. Following is not the 2-dimensional imperfectiona. Twin boundaryb. Dislocation
 - c. Surface d. Grain boundary
- 15. Figure out the odd one in the following
 - a. Frenkel defect b. Tilt boundary
 - c. Twist boundary d. Stacking fault
- 16. Thermodynamically stable defects
 - **a. Point defects** b. Line defects
 - c. Surface defects d. Volume defects

17. The SI unit of heat capacity is

a. Joule	b. joule/kilogram
c. Joule/(kilogram × Kelvin)	d. Joule/Kelvin

18. Aluminum has the specific heat capacity of

a. 450 J kg-1 °C-1	b. 900 J kg-1 °C-1
c. 1350 J kg-1 °C-1	d. 1800 J kg-1 °C-1

19. The internal energy comprises of two types of energies, those are

- a. mechanical & electrical energy
- b. magnetic & electrical energy
- c. kinetic & potential energy
- d. kinetic & magnetic energy
- 20. What substance is attracted to a magnet?
 - a. silver b. lead c. water **d. iron**

$PART - B (3 \times 2 = 6 Marks)$

Short Answer Type Questions:

21. Write down the Clausius-Mossoti equation.

The Clausius–Mossotti factor can be expressed in terms of complex permittivities:

$$\begin{split} K(\omega) &= \frac{\epsilon_p^* - \epsilon_m^*}{\epsilon_p^* + 2\epsilon_m^*} \\ \epsilon^* &= \epsilon + \frac{\sigma}{i\omega} = \epsilon - \frac{i\sigma}{\omega} \end{split}$$

Where

 ε is the permittivity

(where the subscript p refers to a lossless dielectric sphere suspended in a medium m)

 σ is the conductivity

 $\boldsymbol{\omega}$ is the angular frequency of the applied electric field

i is the square root of -1

22. Define dislocation.

In materials science, a dislocation or Taylor's dislocation is a crystallographic defect or irregularity within a crystal structure. The presence of dislocations strongly influences many of the properties of materials.

23. Define resistivity.

It is the property of material which opposes the flow of charge carrier. Its value depends on material and also temperature, as for conductor if temperature increases resistivity increases. For semiconductor temperature increases resistivity decreases and for alloy it is almost constant with temperature.

$$PART - C (3 \times 8 = 24 Marks)$$

Answer ALL questions:

24. a. Write a detailed note on (i) Diamond cubic structure and (ii) NaCl structure.
Diamond Cubic Structure

- Typical and well known purely covalent bonded materials are carbon (Diamond), Si, Ge and SiC.
- For example, in diamond, the base lattice is FCC and is built by the C atoms with half of the tetrahedral sites filled by C atoms. Thus, the unit cell of diamond contains a total of 8 atoms.
- The structure is typically called as diamond cubic structure.
- Orbital hybridization of C atoms (sp³) requires that the atoms are tetrahedrally coordinated and thus the structure has high degree of directionality.
- One unit-cell consists of two FCC motifs, one at $(0\ 0\ 0)$ and another at $(\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4})$.
 - What it means is that there are two FCC unit-cells of C intermingled into each other, with origin of one at (0,0,0) and another at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$.
- In case of compounds, FCC lattice can be formed by one type of atom and remaining atoms, usually from the same group, occupy half of the tetrahedral sites.
- Figure 1 shows the crystal structure of diamond where one can clearly observe the tetrahedrally co-ordinated C atoms.



Figure 1 Diamond cubic structure (a) the unit cell showing all the atoms and (b) (001)-plan view of the structure where positions marked show the position in the z-direction only while x- and ypositions are self-explanatory.

NaCl Structure

The three-dimensional structure of solids can be described with the help of certain basic units which are called as unit cell. Unit cell can be defined as the simplest basic units which repeat itself in a certain pattern to form the complete crystal lattice.



The unit cell of NaCl represents that each sodium ion is surrounded by 6 chloride ions and each chloride ion is surrounded by 6 sodium ions. Here small balls represent sodium ions and bigger ones are for chloride ions. So we can say that in sodium chloride crystal lattice, sodium ions and chloride ions alternate with each other in each of the three dimensions. The bond is only between those ions which are joined by lines. At center of unit cell, there is a sodium ion which is being touched by 6 chloride ions. If chloride ion is located at the center, it would be touched by 6 sodium ions. So the coordination ratio in sodium chloride would be 6:6.

(OR)

b. Discuss the properties of semiconductors.

The name "semiconductor" is widely known, but what are semiconductors? Semiconductors possess specific electrical properties. A substance that conducts electricity is called a conductor, and a substance that does not conduct electricity is called an insulator. Semiconductors are substances with properties somewhere between them. Electrical properties can be indicated by resistivity. Conductors such as gold, silver and copper have low resistance and conduct electricity easily. Insulators such as rubber, glass and ceramics have high resistance and are difficult for electricity to pass through. Semiconductors have properties somewhere between these two. Their resistivity might change according to the temperature for example. At a low temperature, almost no electricity passes through them. But temperature electricity when the rises. passes through them easily. Semiconductors containing almost no impurities conduct almost no electricity. But when some elements are added to the semiconductors, electricity passes through them easily. Semiconductors comprising a single element are called elemental semiconductors, including the famous semiconductor material Silicon. On the other hand, semiconductors made up of two or compound semiconductors, more compounds called and are used are in semiconductor lasers, light-emitting diodes, etc.



Energy Band

An atom is consisting of a nucleus and electrons orbiting the nucleus. The electrons cannot orbit the nucleus at any distance in the atomic space surrounding the nucleus, but only certain, very specific orbits are allowed, and only exist in specific discrete levels. These energies are called energy levels. A large number of atoms gather to form a crystal, and interacts in a solid material, then the energy levels became so closely spaced that they form bands. This is the energy band.

Metals, semiconductors and insulators are distinguished from each others by their band structures. Their band structures are shown in the figure below.



In metals, the conduction band and the valence band come very closer to each other and may even overlap, with the Fermi energy (E_f) somewhere inside. This means that the metal always has electrons that can move freely and so can always carry current. Such electrons are known as free electrons. These free electrons are responsible for current that flows through a metal.

In semiconductors and insulators, the valance band and conduction band are separated by a forbidden energy gap (Eg) of sufficient width, and the Fermi energy (E_f) is between the valence and conduction band. To get to the conduction band, the electron has to gain enough energy to jump the band gap. Once this is done, it can conduct.

In semiconductors at room temperature, the band gap is smaller, there is enough thermal energy to allow electrons to jump the gap fairly easily and make the transitions in conduction band, given the semiconductor limited conductivity. At low temperature, no electron possesses sufficient energy to occupy the conduction band and thus no movement of charge is possible. At absolute zero, semiconductors are perfect insulators, The density of electrons in conduction band at room temperature is not as high as in metals, thus cannot conduct current as good as metal. The electrical conductivity of semiconductor is not as high as metal but also not as poor as electrical insulator. That is why, this type of material is called semiconductor - means half conductor.

The bandgap for insulators is large so very few electrons can jump the gap. Therefore, current does not flow easily in insulators. The difference between insulators and semiconductors is the size of the band gap energy. In insulator where forbidden gap is very large and as a result the energy required by the electron to cross over to the conduction band is practically large enough. Insulators do not conduct electricity easily. That means the electrical conductivity of insulator is very poor.

Semiconductor crystal used for IC etc. is high purity single crystal silicon of 99.999999999%, but when actually making a circuit, impurities are added to control the electrical properties. Depending on the added impurities, they become n-type and p-type semiconductors.



Pentavalent phosphorus (P) or arsenic (As) is added to high purity silicon for n-type semiconductors. These impurities are called donors. The energy level of the donor is located close to the conduction band, that is, the energy gap is small. Then, electrons at this energy level are easily excited to the conduction band and contribute to the conductivity.

On the other hand, trivalent boron (B) etc. is added to p type semiconductor. This is called an acceptor. The energy level of the acceptor is close to the valence band. Since there are no electrons here, electrons in the valence band are excited here. As a result, holes are formed in the valence band, which contributes to the conductivity.

25. a. Explain the various classifications of crystal defects.

Types of Defects in Crystal

1. Point Defects

Point defects are localized disruptions in otherwise perfect atomic or ionic arrangements in crystal structure. These imperfections may be introduced by movement of atoms or ions.

i) Vacancy

This is the simplest point defect. In this system, an atom is missing from its regular atomic site. It formed during solidification as a result of atomic vibrations and during recovery as a result of local rearrangement of atoms. Vacancies are also introduced during plastic deformation.

ii) Interstitialcy or Self-interstitial

Self-interstitial defect in a solid is obtained when an atom in a crystal occupies an interstitial site between surrounding atoms in normal atom sites.

Impurities in Solid

A pure metal consisting of just only one type of atom is not possible; impurity or foreign atoms will always be present, and some will exist as crystalline point defects.

Solid Solution

The simplest type of alloy is that of the solid solution. A solid solution is a solid that consists of two or more elements atomically dispersed in a single-phase structure. Impurity point defects are found in two types of solid solutions, namely, i) interstitial and ii) substitutional.

In interstitial solid solution, impurity atoms fill the voids or interstices among the host atoms. For metallic materials that have relatively high atomic packing factors, these interstitial positions are relatively small. Consequently, the atomic diameter of an interstitial impurity must be substantially smaller than that of the host atoms.

In substitutional solid solution, solute or impurity atoms replace the host atoms. The crystal structure of the parent element or solvent is unchanged.

Schottky Imperfections – When two oppositely charged ions are missing from an ionic crystal, a cation-anion vacancy is created which is known as a Schottky imperfection.

Frenkel Imperfection – If a positive cation moves into an interstitial site in an ionic crystal, a cation vacancy is created in the normal ion site. This vacancy-interstitialcy pair is called Frenkel Imperfection.



(a) Schottky defect

(b) Frenkel defect

2. Line Defects

Line imperfections or defects in crystalline solids are defects that cause lattice distortion centered around a line. The main two types of dislocations are edge dislocations and screw dislocation, a combination of these two gives the mixed dislocations.

i) Edge Dislocation

An Edge Dislocation is created in a crystal by the intersection of an extra half plane of atoms. The inverted 'tee' indicates a positive edge dislocation, whereas upright 'tee' indicates a negative edge dislocation. The edge dislocation has a region of compressive strain where the extra half of plan is present and region tensile strain below the extra half plane of atoms

ii) Screw Dislocation

The Screw Dislocation can be formed in a perfect crystal by applying upward and downward shear stresses to regions of a perfect crystal, which have been separated by a cutting plane.

iii) Mixed Dislocation

Most dislocations in crystal are of mixed type having the edge and the screw components with a transition region between them.

Burgers Vector

Burgers vector characterizes a dislocation line. It indicates whether the dislocation line is an edge, screw or mixed dislocation. The Burgers vector is determined by carrying out a conventional procedure by tracing out a Burgers circuit. Burger vector is perpendicular to the edge dislocation.

3. Surface Defects

i) External Surface – One of the most obvious boundaries is the external surface, along which the structure terminates. Surface atoms are not bonded to the maximum number of nearest neighbors and therefore in a higher energy state than the atoms at interior position. To reduce this energy, materials tend to minimize.

ii) Grain Boundary and Interface – In this defect boundary separates two small grains or crystals having different crystallographic orientation in polycrystalline materials. In metals, grain boundaries are created during solidification, it is a narrow region of about two to five atomic diameters in width. Atomic packing in grain boundaries is lower than within the grains because of the atomic mismatch.

iii) Twin Boundary – Twin boundary is a mirror reflection of the atomic arrangement on the other side. Twin boundaries occur in pairs, such that the orientation change introduced by one boundary is restored by the other. The region between twin boundaries is called the twined region. Twins which form during the process of re-crystallization are called annealing twins, Whereas, twins form during plastic deformation are called deformation twins, commonly observed in HCP and BCC crystals.

iv) Stacking Fault – Stacking Faults are also planar surface imperfections created by a fault in stacking sequence of atoms planed in crystals.

ABCABCABC

If A is missing the stacking sequence become ABCABCABC. It is called HCP stacking.

v) Bulk or Volume Defects – These include pores, cracks, foreign inclusion and other phases.

(OR)

b. Write a detailed note on ultrasonics. Explain the application of non destructive testing.

Ultrasonics, vibrations of frequencies greater than the upper limit of the audible range for humans that is, greater than about 20 kilohertz. The term sonic is applied to ultrasound waves of very high amplitudes. Hypersound, sometimes called praetersound or microsound, is sound waves of frequencies greater than 1013 hertz. At such high frequencies it is very difficult for a sound wave to propagate efficiently; indeed, above a frequency of about 1.25×1013 hertz it is impossible for longitudinal waves to propagate at all, even in a liquid or a solid, because the molecules of the material in which the waves are traveling cannot pass the vibration along rapidly enough.

Many animals have the ability to hear sounds in the human ultrasonic frequency range. A presumed sensitivity of roaches and rodents to frequencies in the 40 kilohertz region has led to the manufacture of "pest controllers" that emit loud sounds in that frequency range to drive the pests away, but they do not appear to work as advertised.

Non-destructive testing

Ultrasonic testing is a type of nondestructive testing commonly used to find flaws in materials and to measure the thickness of objects. Frequencies of 2 to 10 MHz are common but for special purposes other frequencies are used. Inspection may be manual or automated and is an essential part of modern manufacturing processes. Most metals can be inspected as well as plastics and aerospace composites. Lower frequency ultrasound (50–500 kHz) can also be used to inspect less dense materials such as wood, concrete and cement.

Ultrasound inspection of welded joints has been an alternative to radiography for nondestructive testing since the 1960s. Ultrasonic inspection eliminates the use of ionizing radiation, with safety and cost benefits. Ultrasound can also provide additional information such as the depth of flaws in a welded joint. Ultrasonic inspection has progressed from manual methods to computerized systems that automate much of the process. An ultrasonic test of a joint can identify the existence of flaws, measure their size, and identify their location. Not all welded materials are equally amenable to ultrasonic inspection; some materials have a large grain size that produces a high level of background noise in measurements.

26. a) Discuss the experimental electrical resistivity of metals?

Electrical conductivity in metals is a result of the movement of electrically charged particles.

The atoms of metal elements are characterized by the presence of valence electrons - electrons in the outer shell of an atom that are free to move about. It is these 'free electrons' that allow metals to conduct an electric current.

Because valence electrons are free to move they can travel through the lattice that forms the physical structure of a metal.

Under an electric field, free electrons move through the metal much like billiard balls knocking against each other, passing an electric charge as they move.

The transfer of energy is strongest when there is little resistance. On a billiard table, this occurs when a ball strikes against another single ball, passing most of its energy onto the next ball. If a single ball strikes multiple other balls, each of those will carry only a fraction of the energy.

By the same token, the most effective conductors of electricity are metals that have a single valence electron that is free to move and causes a strong repelling reaction in other electrons. This is the case in the most conductive metals, such as silver, gold, and copper, who each have a single valence electron that moves with little resistance and causes a strong repelling reaction.

Semi-conductor metals (or metalloids) have a higher number of valence electrons (usually four or more) so, although they can conduct electricity, they are inefficient at the task.

However, when heated or doped with other elements semiconductors like silicon and germanium can become extremely efficient conductors of electricity.

Conduction in metals must follow Ohm's Law, which states that the current is directly proportional to the electric field applied to the metal. The key variable in applying Ohm's Law is a metal's resistivity.

Resistivity is the opposite of electrical conductivity, evaluating how strongly a metal opposes the flow of electric current. This is commonly measured across the opposite faces of a one-meter cube of material and described as an ohm meter ($\Omega \cdot m$). Resistivity is often represented by the Greek letter rho (ρ).

Electrical conductivity, on the other hand, is commonly measured by Siemens per meter $(S \cdot m^{-1})$ and represented by the Greek letter sigma (σ). One Siemens is equal to the reciprocal of one ohm.

(OR)

b) Discuss superconductivity.



If mercury is cooled below 4.1 K, it loses all electric resistance. This discovery of superconductivity by H. Kammerlingh Onnes in 1911 was followed by the observation of other metals, which exhibit zero resistivity below a certain critical temperature. The fact that the resistance is zero has been demonstrated by sustaining currents in superconducting lead rings for many years with no measurable reduction. An induced current in an ordinary metal ring would decay rapidly from the dissipation of ordinary resistance, but superconducting rings had exhibited a decay constant of over a billion years!

One of the properties of a superconductor is that it will exclude magnetic fields, a phenomenon called the Meissner effect.

The disappearance of electrical resistivity was modeled in terms of electron pairing in the crystal lattice by John Bardeen, Leon Cooper, and Robert Schrieffer in what is commonly called the BCS theory.

A new era in the study of superconductivity began in 1986 with the discovery of high critical temperature superconductors.

Critical Temperature for Superconductors

The critical temperature for superconductors is the temperature at which the electrical resistivity of a metal drops to zero. The transition is so sudden and complete that it appears to be a transition to a different phase of matter; this superconducting phase is described by the BCS theory. Several materials exhibit superconducting phase transitions at low temperatures. The highest critical temperature was about 23 K until the discovery in 1986 of some high temperature superconductors.

Materials with critical temperatures in the range 120 K have received a great deal of attention because they can be maintained in the superconducting state with liquid nitrogen (77 K).

Material	T-Critical
Gallium	1.1 K
Aluminum	1.2 K
Indium	3.4 K
Tin	3.7 K
Mercury	4.2 K
Lead	7.2 K
Niobium	9.3 K

Niobium-Tin	17.9 K
La-Ba-Cu-oxide	30 K
Y-Ba-Cu-oxide	92 K
Tl-Ba-Cu-oxide	125 K

Types I and II Superconductors

There are thirty pure metals, which exhibit zero resistivity at low temperatures and have the property of excluding magnetic fields from the interior of the superconductor (Meissner effect). They are called Type I superconductors. The superconductivity exists only below their critical temperatures and below a critical magnetic field strength. Type I superconductors are well described by the BCS theory.

Starting in 1930 with lead-bismuth alloys, a number of alloys were found which exhibited superconductivity; they are called Type II superconductors. They were found to have much higher critical fields and therefore could carry much higher current densities while remaining in the superconducting state.

The variations on barium-copper-oxide ceramics which achieved the superconducting state at much higher temperatures are often just referred to as high temperature superconductors and form a class of their own.

Type I Superconductors

The thirty pure metals listed at right below are called Type I superconductors. The identifying characteristics are zero electrical resistivity below a critical temperature, zero internal magnetic field (Meissner effect), and a critical magnetic field above which superconductivity ceases.

The superconductivity in Type I superconductors is modeled well by the BCS theory which relies upon electron pairs coupled by lattice vibration interactions. Remarkably, the best conductors at room temperature (gold, silver, and copper) do not become superconducting at all. They have the smallest lattice vibrations, so their behavior correlates well with the BCS Theory.

While instructive for understanding superconductivity, the Type I superconductors have been of limited practical usefulness because the critical magnetic fields are so small and the superconducting state disappears suddenly at that temperature. Type I superconductors are sometimes called "soft" superconductors while the Type II are "hard", maintaining the superconducting state to higher temperatures and magnetic fields.

Mat.	Tc	
Be	0	Mat. Tc
Rh	0	Al 1.2

W	0.015	Pa	1.4
Ir	0.1	Th	1.4
Lu	0.1	Re	1.4
Hf	0.1	Tl	2.39
Ru	0.5	In	3.408
Os	0.7	Sn	3.722
Mo	0.92	Hg	4.153
Zr	0.546	Та	4.47
Cd	0.56	V	5.38
U	0.2	La	6.00
Ti	0.39	Pb	7.193
Zn	0.85	Tc	7.77
Ga	1.083	Nb	9.46

Type II Superconductors

Superconductors made from alloys are called Type II superconductors. Besides being mechanically harder than Type I superconductors, they exhibit much higher critical magnetic fields. Type II superconductors such as niobium-titanium (NbTi) are used in the construction of high field superconducting magnets.

Type-II superconductors usually exist in a mixed state of normal and superconducting regions. This is sometimes called a vortex state, because vortices of superconducting currents surround filaments or cores of normal material.

Material	Transition Temp (K)	Critical Field (T)
NbTi	10	15
PbMoS	14.4	6.0
V₃Ga	14.8	2.1
NbN	15.7	1.5
V ₃ Si	16.9	2.35
Nb ₃ Sn	18.0	24.5
Nb ₃ A1	18.7	32.4
Nb ₃ (A1G	e) 20.7	44
Nb ₃ Ge	23.2	38

From Blatt, Modern Physics

****ALL THE BEST****

Register No. -----

[17PHP101]

KARPAGAM ACADEMY OF HIGHER EDUCATION, COIMBATORE - 641 021

DEPARTMENT OF PHYSICS

I M. Sc. PHYSICS

INTERNAL TEST II

CONDENSED MATTER PHYSICS

Date: Marks: 50

Duration: 2 Hrs.

$PART - A (20 \times 1 = 20 Marks)$

Objective Type Questions:

1. Which of the following materials is used for making coils of standard resistances? d Manganin

a. Copper b. Nichrome c. Platinum

2. Substances whose specific resistance abruptly decreases at very low temperature are called

b. conductors a. insulators

d superconductors c. semiconductors

3. Which of the following materials is the best conductor of electricity?

Copper d. Carbon a. Tungsten b. Aluminium

4. The conduction of electricity, in semiconductors, takes place due to movement of

b. negative ions only a. positive ions only

c. positive and negative ions delectrons and holes 5. Which of the following is a semiconductor material? a. Phosphorous b. Rubber d. Aluminium **√**Silicon 6. In Nanobiotechnology, size of nanomaterials is _____ of a meter. a. hundred billionth b. ten billionth d. twenty billionth c. one billionth 7. Bucky balls are made up of a. nickel b. DNA c. RNA d. carbon 8. technology is used in making memory chips. a. Nano design b. Nano fabrication c. Micro assay d. Tissue engineering 9. Which of the following is NOT a potential application of nano fabrication technology? a. DNA chip assays b. Integrated photonic devices and diode displays A multi lambda high density optical data storage material d. Textile industry 10. The art and science of etching, writing or printing at the microscopic level in the order of nanometer is _____ a. NEMS b. nano lithography c. nano fabrication c. nano paltcinins

11. What are the approaches used in making nano systems?

a. Top down b. Bottom up de Both a and b d. Neither a nor b

12. Ceramic powders find application in

ิล	nigments	h abrasives	c catalysts	A all the above
α.	pignients	U. abrasives	c. catalysis	u. all the above

13. Nano powders are defined as powders having an average particle size of less that nm. d. 1

b. 1000 a. 100 c. 10

14. TEM is

a. Transmission Electron Microscope

b. Transmit Electron Microscope

c. Transform Electron Microscope

d. Transmit Electrical Microscope

15. SLMS are

A. Spatial Light Modulators

b. Scanning Light Microscope

c. Scanning Light Modulator

d. Spatial Light Microscope

16. Expand MRFM.

- Magnetic Resonance Force Microscopy
- b. Molecule Resonance Microscopy
- c. Magnetic Resonance Imaging

d. None of the above

microscope has been used to build nano sized structural 17. atom by atom on the surface of materials. b. AFM STM d. SEM a. TEM

lithographic pattern a resist by physically deforming the 18. resist sharp with a mold having a nano structure pattern on it, rather than by modifying the resist surface by radiation, as in conventional lithography.

b. Nano imprint a. Micro imprint c. Micro and nano imprint d. Macro imprint

_ is the art and science of etching, writing or printing at the 19. microscopic level, where that dimensions of characters are on the order of nm.

%. Nanolithography c. X-ray lithography b. Optical lithography d. UV lithography

includes various methods of modifying semiconductor 20. chips at the atomic level for the purpose of fabricating integrated circuits. **b**. Nanolithography

a. Optical lithography c. X-ray lithography

d. Micro lithography

 $PART - B (3 \times 2 = 6 Marks)$

Short Answer Type Questions:

21. Define Curie law.

22. Define magic numbers.

23. Write a short note on soft lithography.

$PART - C (3 \times 8 = 24 Marks)$

Answer ALL questions:

24. a. Explain the free electron theory of metals. (OR)

b. Write the experimental techniques to study the magnetic properties.

25. a. Write a detailed note on semiconducting nano particles.

b. Explain the formation and characterization of polymers.

(OR)

(OR)

26. a) Explain the working principle and applications of SEM.

b) Explain the working principle and applications of TEM.

****ALL THE BEST****

Register No. -----

[17PHP101]

KARPAGAM ACADEMY OF HIGHER EDUCATION, COIMBATORE – 641 021 DEPARTMENT OF PHYSICS I M. Sc. PHYSICS INTERNAL TEST II

CONDENSED MATTER PHYSICS

Date: 23.10.2017/FN

Marks: 50 Duration: 2 Hrs.

$PART - A (20 \times 1 = 20 Marks)$

Objective Type Questions:

- 1. Which of the following materials is used for making coils of standard resistances?
- a. Copper b. Nichrome c. Platinum d. Manganin
- 2. Substances whose specific resistance abruptly decreases at very low temperature are called
- a. insulators b. conductors
- c. semiconductors d. superconductors
- 3. Which of the following materials is the best conductor of electricity?
- a. Tungsten b. Aluminium **c. Copper** d. Carbon
- 4. The conduction of electricity, in semiconductors, takes place due to movement of
- a. positive ions only b. negative ions only
- c. positive and negative ions d. electrons and holes
- 5. Which of the following is a semiconductor material?
- a. Phosphorous b. Rubber c. Silicon d. Aluminium
- 6. In Nanobiotechnology, size of nanomaterials is ______ of a meter.
- a. hundred billionth b. ten billionth
- c. one billionth d. twenty billionth

7. Bucky balls are made up of _____.a. nickelb. DNAc. RNAd. carbon

8. _____technology is used in making memory chips.

- a. Nano design **b. Nano fabrication**
- c. Micro assay d. Tissue engineering

9. Which of the following is NOT a potential application of nano fabrication technology?

- a. DNA chip assays
- b. Integrated photonic devices and diode displays

c. A multi lambda high density optical data storage material

d. Textile industry

10. The art and science of etching, writing or printing at the microscopic level in the order of nanometer is

a. NEMSb. nano lithographyc. nano fabricationc. nano paltcinins

11. What are the approaches used in making nano systems?a. Top down b. Bottom up c. Both a and b d. Neither a nor b

12. Ceramic powders find application in ______.a. pigments b. abrasives c. catalysts d. all the above

13. Nano powders are defined as powders having an average particle size of less that _____ nm.a. 100b. 1000c. 10d. 1

14. TEM is _____.

a. Transmission Electron Microscope

b. Transmit Electron Microscope

c. Transform Electron Microscope

d. Transmit Electrical Microscope

15. SLMS are ____

a. Spatial Light Modulators

- b. Scanning Light Microscope
- c. Scanning Light Modulator
- d. Spatial Light Microscope

16. Expand MRFM.

a. Magnetic Resonance Force Microscopy

- b. Molecule Resonance Microscopy
- c. Magnetic Resonance Imaging
- d. None of the above

17. _____ microscope has been used to build nano sized structural atom by atom on the surface of materials.

a. TEM b. AFM c. STM d. SEM

18. _____ lithographic pattern a resist by physically deforming the resist sharp with a mold having a nano structure pattern on it, rather than by modifying the resist surface by radiation, as in conventional lithography.

a.	Micro imprint	b. Nano imprint
c.	Micro and nano imprint	d. Macro imprint

19. _____ is the art and science of etching, writing or printing at the microscopic level, where that dimensions of characters are on the order of nm.

a. Nanolithography	b. Optical lithography
c. X-ray lithography	d. UV lithography

20. _____ includes various methods of modifying semiconductor chips at the atomic level for the purpose of fabricating integrated circuits.

a. Optical lithography	b. Nanolithography
c. X-ray lithography	d. Micro lithography

c. X-ray lithography	d. Micro lithography
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 $PART - B (3 \times 2 = 6 Marks)$

Short Answer Type Questions:

21. Define Curie law.

A law of magnetism now replaced by the Curie-Weiss law: the susceptibility of a paramagnetic substance is inversely proportional to the absolute temperature.

22. Define magic numbers.

In nuclear physics, a magic number is a number of nucleons (either protons or neutrons, separately) such that they are arranged into complete shells within the atomic nucleus. The seven most widely recognized magic numbers as of 2007 are 2, 8, 20, 28, 50, 82, and 126 (sequence A018226 in the OEIS). For protons, this corresponds to the elements helium, oxygen, calcium, nickel, tin, lead and the hypothetical unbihexium. Atomic nuclei consisting of such a magic number of nucleons have a higher average binding energy per nucleon than one would expect based upon predictions such as the semi-empirical mass formula and are hence more stable against nuclear decay.

23. Write a short note on soft lithography.

In technology, soft lithography is a family of techniques for fabricating or replicating structures using "elastomeric stamps, molds, and conformable photomasks". It is called "soft" because it uses elastomeric materials, most notably PDMS.

Soft lithography is generally used to construct features measured on the micrometer to nanometer scale. According to Rogers and Nuzzo (2005), development of soft lithography expanded rapidly from 1995 to 2005. Soft lithography tools are now commercially available

$PART - C (3 \times 8 = 24 Marks)$

Answer ALL questions:

24. a. Explain the free electron theory of metals.

The treatment of a metal as containing a gas of electrons completely free to move within it. The theory was originally proposed in 1900 to describe and correlate the electrical and thermal properties of metals. Later, quantum mechanics became the basis for the theory of most of the general properties of simple metals such as sodium, with one free electron per atom, magnesium with two, and aluminum with three. Transition metals, such as iron, have partially filled electronic d states and are not treated by the free-electron model.

Three years after J. J. Thomson's 1897 discovery of the electron, P. Drude suggested that the transport properties of metals might be understood by assuming that their electrons are free and in thermal equilibrium with their atoms. This theory was made more quantitative by H. A. Lorentz. Assuming that the mean free path of electrons was limited by collisions, he was able to derive Ohm's law for the electrical conductivity and obtain the ratio of thermal to electrical conductivity in excellent agreement with experiment. This ratio, divided by the absolute temperature, is called the Wiedemann-Franz ratio and had been observed to be universal 50 years earlier.

The theory, however, had two major shortcomings. First, it predicted a large component of the specific heat of a metal, not present in insulators, which was not observed. Second, comparison

of the theory with experiment indicated that the mean free path of the electrons became extremely large at low temperatures; the model offered no justification.

In 1928 A. Sommerfeld revised Lorentz's treatment by using quantum statistics, which removed the difficulty of the specific heat without losing the successful description of transport properties. The resulting theory remains the basis for the understanding of most transport properties of metals and semiconductors. At about the same time, W. V. Houston and F. Bloch solved the quantum-mechanical wave equation for electrons in a regular periodic structure, finding that they could indeed have arbitrarily large mean free paths if there were no defects in the periodicity, thereby putting the free-electron theory on a firm basis.

Even in the context of a free-electron gas, there are strong Coulomb interactions between electrons which are frequently neglected in the free-electron theory of metals. This neglect was justified in the late 1950s by L. D. Landau, who asserted that, even with strong electron–electron interactions, there is a one-to-one correspondence between the excited states, called quasiparticle states, of the real system and the one-electron excitations from the ground state of the noninteracting electron gas. Thus, the formulations for free-electron theory still follow, but perhaps with modifications of parameters such as mass. Subsequent theory indicates that indeed these modification due to the electron-electron interaction are extremely small for the low-energy excitations present in thermal equilibrium, and so again the simplest theory succeeds for many properties, although substantial modifications are required for the higher-energy excitations caused by light. There are additional corrections, which are much larger than those from the electron-electron interaction, arising from the interaction between electrons and phonons, the quantum-mechanical term for lattice vibrations. In many metals these vibrations reduce the electron velocities by factors of as much as 2, increasing the electronic specific heat although they turn out not to modify the conductivity itself.

Another feature of the electron-phonon interaction is a resulting interaction among electrons, which is attractive and tends to cancel or exceed the repulsive electron-electron interaction. At low temperatures the net attraction binds electrons in pairs in a superconducting state. The theory of J. Bardeen, J. R. Schrieffer, and L. N. Cooper (the BCS theory of superconductivity), which first explained this phenomenon, is also a free-electron theory, but assumes that the free electrons have such a net attractive interaction. In contrast, it is generally believed that the high-temperature superconductors discovered in 1986 are very far from free-electron in character, and most workers do not believe that phonons are primarily responsible for the attractive interaction.

(OR)

b. Write the experimental techniques to study the magnetic properties.

Magnetisation measurements (VSM) a vibrating sample magnetometer (VSM) is a device in which the sample is vibrated in a uniform magnetising field and the magnetisation of the sample is detected. The precise measurements of magnetisation as a function of temperature, magnetic field strength and crystallographic orientations can be done by this instrument. When the specimen is placed in a uniform magnetic field, a magnetisation is induced in the sample equal to the product of the susceptibility and the applied magnetic field. Due to the vibration of the sample, a sinusoidal motion begins and electrical signal due to the flux change can be induced in a stationary pick-up coil, placed in a suitable position. The electrical signal is proportional to the magnetic moment, amplitude of vibration and vibrational frequency.

25. a. Write a detailed note on semiconducting nano particles.

Semiconductor nanocrystals (NCs) are made from a variety of different compounds. They are referred to as II-VI, III-V or IV-VI semiconductor nanocrystals, based on the periodic table groups into which these elements are formed. For example, silicon and germanium are group IV, GaN, GaP, GaAs, InP and InAs are III-V, while those of ZnO, ZnS, CdS, CdSe and CdTe are II-VI semiconductors.

Semiconductor nanoparticles exhibit size dependent properties, when their size is comparable to the size of Bohr diameter for exciton. This can be exploited to increase fluorescence efficiency or increase the internal magnetic field strength in doped semiconductors. Nanoparticles are usually unstable and can aggregate. It is therefore necessary to protect them. Surface passivation using capping molecules or by making core–shell particles are some useful ways. Here synthesis and results on doped and undoped nanoparticles of ZnS, CdS and ZnO will be discussed. We shall present results on core–shell particles using some of these nanoparticles and also discuss briefly the effect of Mn doping on hyperfine interactions in case of CdS nanoparticles.

Semiconductor nanocrystals are tiny light-emitting particles on the nanometer scale. Researchers have studied these particles intensely and have developed them for broad applications in solar energy conversion, optoelectronic devices, molecular and cellular imaging, and ultrasensitive detection. A major feature of semiconductor nanocrystals is the quantum confinement effect, which leads to spatial enclosure of the electronic charge carriers within the nanocrystal. Because of this effect, researchers can use the size and shape of these "artificial atoms" to widely and precisely tune the energy of discrete electronic energy states and optical transitions. As a result, researchers can tune the light emission from these particles also span the transition between small molecules and bulk crystals, instilling novel optical properties such as carrier multiplication, single-particle blinking, and spectral diffusion. In addition, semiconductor nanocrystals provide a versatile building block for developing complex nanostructures such as superlattices and multimodal agents for molecular imaging and targeted therapy.

In this Account, we discuss recent advances in the understanding of the atomic structure and optical properties of semiconductor nanocrystals. We also discuss new strategies for band gap and electronic wave function engineering to control the location of charge carriers. New methodologies such as alloying, doping, strain-tuning, and band-edge warping will likely play key roles in the further development of these particles for optoelectronic and biomedical applications.

(OR)

b. Explain the formation and characterization of polymers.

A polymer is a large molecule (macromolecule) composed of repeating structural units. These sub-units are typically connected by covalent chemical bonds. Although the term *polymer* is sometimes taken to refer to plastics, it actually encompasses a large class of compounds comprising both natural and synthetic materials with a wide variety of properties.

Because of the extraordinary range of properties of polymeric materials, they play an essential and ubiquitous role in everyday life. This role ranges from familiar synthetic plastics and elastomers to natural biopolymers such as nucleic acids and proteins that are essential for life.

Natural polymeric materials such as shellac, amber, and natural rubber have been used for centuries. A variety of other natural polymers exist, such as cellulose, which is the main constituent of wood and paper. The list of synthetic polymers includes synthetic rubber, Bakelite, neoprene, nylon, PVC,polystyrene, polyethylene, polypropylene, polyacrylonitr ile, PVB, silicone, and many more.

Most commonly, the continuously linked backbone of a polymer used for the preparation of plastics consists mainly of carbon atoms. A simple example is polyethylene ('polythene' in British English), whose repeating unit is based on ethylene monomer. However, other structures do exist; for example, elements such as silicon form familiar materials such as silicones, examples being Silly Putty and waterproof plumbing sealant. Oxygen is also commonly present in polymer backbones, such as those of polyethylene glycol, polysaccharides (in glycosidic bonds), and DNA (in phosphodiester bonds).

Polymers are studied in the fields of polymer chemistry, polymer physics, and polymer science.

26. a) Explain the working principle and applications of SEM.

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions (using EDS), crystalline structure, and crystal orientations (using EBSD). The design and function of the SEM is very similar to the EPMA and considerable overlap in capabilities exists between the two instruments.

Fundamental Principles of Scanning Electron Microscopy (SEM)

Accelerated electrons in an SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light (cathodoluminescence--CL), and heat. Secondary electrons are most valuable for showing

morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination). X-ray generation is produced by inelastic collisions of the incident electrons with electrons in discrete orbitals (shells) of atoms in the sample. As the excited electrons return to lower energy states, they yield X-rays that are of a fixed wavelength (that is related to the difference in energy levels of electrons in different shells for a given element). Thus, characteristic X-rays are produced for each element in a mineral that is "excited" by the electron beam. SEM analysis is considered to be "non-destructive"; that is, x-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly.

Scanning Electron Microscopy (SEM) Instrumentation - How Does It Work?



Essential components of all SEMs include the following:

- Electron Source ("Gun")
- Electron Lenses
- Sample Stage
- Detectors for all signals of interest
- Display / Data output devices
- Infrastructure Requirements:
 - Power Supply
 - Vacuum System
 - Cooling system
 - Vibration-free floor
 - Room free of ambient magnetic and electric fields

SEMs always have at least one detector (usually a secondary electron detector), and most have additional detectors. The specific capabilities of a particular instrument are critically dependent on which detectors it accommodates.

Applications

The SEM is routinely used to generate high-resolution images of shapes of objects (SEI) and to show spatial variations in chemical compositions: 1) acquiring elemental maps or spot chemical analyses using EDS, 2)discrimination of phases based on mean atomic number (commonly related to relative density) using BSE, and 3) compositional maps based on differences in trace element "activitors" (typically transition metal and Rare Earth elements) using CL. The SEM is also widely used to identify phases based on qualitative chemical analysis and/or crystalline structure. Precise measurement of very small features and objects down to 50 nm in size is also accomplished using the SEM. Back scattered electron images (BSE) can be used for rapid discrimination of phases in multiphase samples. SEMs equipped with diffracted backscattered electron detectors (EBSD) can be used to examine microfabric and crystallographic orientation in many materials.

Strengths and Limitations of Scanning Electron Microscopy

Strengths

There is arguably no other instrument with the breadth of applications in the study of solid materials that compares with the SEM. The SEM is critical in all fields that require characterization of solid materials. While this contribution is most concerned with geological applications, it is important to note that these applications are a very small subset of the scientific and industrial applications that exist for this instrumentation. Most SEM's are comparatively easy to operate, with user-friendly "intuitive" interfaces. Many applications require minimal sample preparation. For many applications, data acquisition is rapid (less than 5 minutes/image for SEI, BSE, spot EDS analyses.) Modern SEMs generate data in digital formats, which are highly portable.

Limitations

Samples must be solid and they must fit into the microscope chamber. Maximum size in horizontal dimensions is usually on the order of 10 cm, vertical dimensions are generally much more limited and rarely exceed 40 mm. For most instruments samples must be stable in a vacuum on the order of 10⁻⁵ - 10⁻⁶ torr. Samples likely to outgas at low pressures (rocks saturated with hydrocarbons, "wet" samples such as coal, organic materials or swelling clays, and samples likely to decrepitate at low pressure) are unsuitable for examination in conventional SEM's. However, "low vacuum" and "environmental" SEMs also exist, and many of these types of samples can be successfully examined in these specialized instruments. EDS detectors on SEM's cannot detect very light elements (H, He, and Li), and many instruments cannot detect elements with atomic numbers less than 11 (Na). Most SEMs use a solid state x-ray detector (EDS), and while these detectors are very fast and easy to utilize, they have relatively poor energy resolution and sensitivity to elements present in low abundances when compared to wavelength dispersive x-ray detectors (WDS) on most electron probe microanalyzers (EPMA). An electrically

conductive coating must be applied to electrically insulating samples for study in conventional SEM's, unless the instrument is capable of operation in a low vacuum mode.

User's Guide - Sample Collection and Preparation

Sample preparation can be minimal or elaborate for SEM analysis, depending on the nature of the samples and the data required. Minimal preparation includes acquisition of a sample that will fit into the SEM chamber and some accommodation to prevent charge build-up on electrically insulating samples. Most electrically insulating samples are coated with a thin layer of conducting material, commonly carbon, gold, or some other metal or alloy. The choice of material for conductive coatings depends on the data to be acquired: carbon is most desirable if elemental analysis is a priority, while metal coatings are most effective for high resolution electron imaging applications. Alternatively, an electrically insulating sample can be examined without a conductive coating in an instrument capable of "low vacuum" operation.

(OR)

b) Explain the working principle and applications of TEM.

Transmission electron microscopy (TEM) is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera.

TEMs are capable of imaging at a significantly higher resolution than light microscopes, owing to the small de Broglie wavelength of electrons. This enables the instrument's user to examine fine detail—even as small as a single column of atoms, which is tens of thousands times smaller than the smallest resolvable object in a light microscope. TEM forms a major analysis method in a range of scientific fields, in both physical and biological sciences. TEMs find application in cancer research, virology, materials science as well as pollution and semiconductor research.

At smaller magnifications TEM image contrast is due to absorption of electrons in the material, due to the thickness and composition of the material. At higher magnifications complex wave interactions modulate the intensity of the image, requiring expert analysis of observed images. Alternate modes of use allow for the TEM to observe modulations in chemical identity, crystal orientation, electronic structure and sample induced electron phase shift as well as the regular absorption based imaging.

The first TEM was built by Max Knoll and Ernst Ruska in 1931, with this group developing the first TEM with resolving power greater than that of light in 1933 and the first commercial TEM in 1939.

Instrumentation

A TEM works much like a slide projector. A projector shines a beam of light through (transmits) the slide, as the light passes through it is affected by the structures and objects on the slide. These effects result in only certain parts of the light beam being transmitted through certain parts of the slide. This transmitted beam is then projected onto the viewing screen, forming an enlarged image of the slide.

TEMs work the same way except that they shine a beam of electrons (like the light) through the specimen (like the slide). Whatever part is transmitted is projected onto a phosphor screen for the user to see. A more technical explanation of typical TEMs working is as follows (refer to the diagram below):



1. The "Virtual Source" at the top represents the electron gun, producing a stream of monochromatic electrons.

2. This stream is focused to a small, thin, coherent beam by the use of condenser lenses 1 and 2. The first lens(usually controlled by the "spot size knob") largely determines the "spot size"; the general size range of the final spot that strikes the sample. The second lens(usually controlled by the "intensity or brightness knob" actually changes the size of the spot on the sample; changing it from a wide dispersed spot to a pinpoint beam.

3. The beam is restricted by the condenser aperture (usually user selectable), knocking out high angle electrons (those far from the optic axis, the dotted line down the center)

4. The beam strikes the specimen and parts of it are transmitted

5. This transmitted portion is focused by the objective lens into an image

6. Optional Objective and Selected Area metal apertures can restrict the beam; the Objective aperture enhancing contrast by blocking out high-angle diffracted electrons, the Selected Area aperture enabling the user to examine the periodic diffraction of electrons by ordered arrangements of atoms in the sample

7. The image is passed down the column through the intermediate and projector lenses, being enlarged all the way

8. The image strikes the phosphor image screen and light is generated, allowing the user to see the image. The darker areas of the image represent those areas of the sample that fewer electrons were transmitted through (they are thicker or denser). The lighter areas of the image represent those areas of the sample that more electrons were transmitted through (they are thinner or less dense)

Principles of operation:

The transmission electron microscope uses a high energy electron beam transmitted through a very thin sample to image and analyze the microstructure of materials with atomic scale resolution. The electrons are focused with electromagnetic lenses and the image is observed on a fluorescent screen, or recorded on film or digital camera. The electrons are accelerated at several hundred kV, giving wavelengths much smaller than that of light: 200kV electrons have a wavelength of 0.025Å. However, whereas the resolution of the optical microscope is limited by the wavelength of light, that of the electron microscope is limited by aberrations inherent in electromagnetic lenses, to about 1-2 Å.

Because even for very thin samples one is looking through many atoms, one does not usually see individual atoms. Rather the high resolution imaging mode of the microscope images the crystal lattice of a material as an interference pattern between the transmitted and diffracted beams. This allows one to observe planar and line defects, grain boundaries, interfaces, etc. with atomic scale resolution. The bright field/dark field imaging modes of the microscope, which operate at intermediate magnification, combined with electron diffraction, are also invaluable for giving information about the morphology, crystal phases, and defects in a material. Finally the microscope is equipped with a special imaging lens allowing for the observation of micro magnetic domain structures in a field-free environment.

The TEM is also capable of forming a focused electron probe, as small as 20 Å, which can be positioned on very fine features in the sample for micro diffraction information or analysis of x-rays for compositional information. The latter is the same signal as that used for EMPA and SEM composition analysis (see EMPA facility), where the resolution is on the order of one micron due to beam spreading in the bulk sample. The spatial resolution for this compositional analysis in TEM is much higher, on the order of the probe size, because the sample is so thin. Conversely the signal is much smaller and therefore less quantitative. The high brightness field-emission gun improves the sensitivity and resolution of x-ray compositional analysis over that available with more traditional thermionic sources.

Restrictions on Samples:

Sample preparation for TEM generally requires more time and experience than for most other characterization techniques. A TEM specimen must be approximately 1000 Å or less in thickness in the area of interest. The entire specimen must fit into a 3mm diameter cup and be less than about 100 microns in thickness. A thin, disc shaped sample with a hole in the middle, the edges of the hole being thin enough for TEM viewing, is typical. The initial disk is usually formed by cutting and grinding from bulk or thin film/substrate material, and the final thinning done by ion milling. Other specimen preparation possibilities include direct deposition onto a TEM-thin substrate (Si3N4, carbon); direct dispersion of powders on such a substrate; grinding and polishing using special devices (t-tool, tripod); chemical etching and electropolishing;

lithographic patterning of walls and pillars for cross-section viewing; and focused ion beam (FIB) sectioning for site specific samples.

Artifacts are common in TEM samples, due both to the thinning process and to changing the form of the original material. For example surface oxide films may be introduced during ion milling and the strain state of a thin film may change if the substrate is removed. Most artifacts can either be minimized by appropriate preparation techniques or be systematically identified and separated from real information.

****ALL THE BEST****

Reg. No.....

[16PHP101]

KARPAGAM UNIVERSITY Karpagam Academy of Higher Education (Established Under Section 3 of UGC Act 1956) COIMBATORE – 641 021 (For the candidates admitted from 2016 onwards)

M.Sc., DEGREE EXAMINATION, NOVEMBER 2016

First Semester PHYSICS

CONDENSED MATTER PHYSICS

Time: 3 hours

Maximum : 60 marks

PART – A (20 x 1 = 20 Marks) (30 Minutes) (Ouestion Nos. 1 to 20 Online Examinations)

(Part - B & C 2 1/2 Hours)

PART B (5 x 6 = 30 Marks) Answer ALL the Questions

- 21. a. What is space lattice?. Find the packing factor value of a crystal belonging to BCC structure.
 - Or b. To derive the Lorentz field equation in dielectrics and to prove that the Lorentz field is greater than that of applied electric field.
- 22. a. Derive an expression for Schottky defect concentration in an ionic crystalline material.

Or b. Give an idea for Slip and Plastic deformations in crystal.

23. a. Explain the classical free electron theory of metals.

Or b. Briefly explain the properties of para magnetic materials using the quantum theory.

1

24. a. How the size dependent properties are varied. Explain in detailed. Or

- b. Explain the working principle of Polymerization. Also give its merits and demerits.
- 25. a. How the transmission electron microscope is worked. Briefly explain its working principle and advantages.
 - Or b. Explain the working principle and instrumentation of atomic force microscope with neat diagram.

PART C (1 x 10 = 10 Marks) (Compulsory)

26. Using atomic polarizabilies, how the dielectric constant of new substances is calculated from Clausis-Mossoti equation, explain with detailed equations.

2

Reg. No.....

[17PHP101]

KARPAGAM UNIVERSITY Karpagam Academy of Higher Education (Established Under Section 3 of UGC Act 1956) COIMBATORE - 641 021

(For the candidates admitted from 2017 onwards)

M.Sc., DEGREE EXAMINATION, NOVEMBER 2017 First Semester

PHYSICS

CONDENSED MATTER PHYSICS

Time: 3 hours

Maximum : 60 marks

PART – A (20 x 1 = 20 Marks) (30 Minutes) (Question Nos. 1 to 20 Online Examinations)

(PART - B & C 2 1/2 Hours)

PART B (5 x 6 = 30 Marks) Answer ALL the Questions

- 21. a. What is interplanar Spacing ? Calculate the interplanar spacing for a (321) Plane in a simple cubic lattice whose lattice constant is 4.2 x 10⁻⁸ cm. Or
 - b. What are ferroelectric materials ? Give the theory of ferroelectricity and mention its applications.

Or

Or

- 22. a. Explain the schottky and Frenkel defects.
 - b. Explain edge and screw dislocations.
- 23. a. Explain quantum theory of paramagnetism.
 - b. Write a short note on ferromagnetism.
- 24. a. Write a short note on Fare- centred cubic nano particles.
 - Or b. What is polymer ? Explain how the sizes of the polymers are estimated.

1

- 25. a. With a neat diagram explain the working principle of a scanning electrons microscope Or
 - b. With a neat diagram explain the working principle of a atomic force microscope.

PART C (1 x 10 = 10 Marks) (Compulsory)

26. What is ultrasonics ? Why use is ultrasonics for non destructive material testing? Explain how the discontinuitics are detected using ultrasonics.

2