Module 7

Module:7	Other Electronic Materials	4 hours
Dielectrics, Insulators, Ferroelectric Materials, Supercapacitors, Graphene, Carbon Nanotubes, Superconductors		

Dielectric Materials and Insulation

- The familiar parallel plate capacitor equation with free space as an insulator is given by

$$C = \frac{\varepsilon_o A}{d}$$

where εo is the absolute permittivity, A is the plate area, and d is the separation between the plates. If there is a material medium between the plates, then the capacitance, the charge storage ability per unit voltage, increases by a factor of εr, where εr is called the **dielectric constant** of the medium or its **relative permittivity**

The increase in the capacitance is due to the **polarization** of the medium in which positive and negative charges are displaced with respect to their equilibrium positions.

- The opposite surfaces of the dielectric medium acquire opposite surface charge densities that are related to the amount of polarization in the material. An important concept in dielectric theory is that of an **electric dipole moment** p, which is a measure of the electrostatic effects of a pair of opposite charges $+Q$ and $-Q$ separated by a finite distance a, and so is defined by

$$p = Qa$$

- Although the net charge is zero, this entity still gives rise to an electric field in space and also interacts with an electric field from other sources. The relative permittivity is a material property that is frequency dependent. Some capacitors are designed to work at low frequencies, whereas others have a wide frequency range.

- Furthermore, even though they are regarded as energy storage devices, all practical capacitors exhibit some losses when used in an electric circuit
- These losses are no different than I^2R losses in a resistor carrying a current. The power dissipation in a practical capacitor depends on the frequency, and for some applications it can be an important factor
- A defining property of a dielectric medium is not only its ability to increase capacitance but also, and equally important, its insulating behavior or low conductivity so that the charges are not conducted from one plate of the capacitor to the other through the dielectric.

- Dielectric materials often serve to insulate current-carrying conductors or conductors at different voltages. Why can we not simply use air as insulation between high-voltage conductors?
- When the electric field inside an insulator exceeds a critical field called the **dielectric strength,** the medium suffers dielectric breakdown and a large discharge current flows through the dielectric
- Some 40 percent of utility generator failures are linked to insulation failures in the generator. Dielectric breakdown is probably one of the oldest electrical engineering problems and that which has been most widely studied and never fully explained.

MATTER POLARIZATION AND RELATIVE PERMITTIVITY

We first consider a parallel plate capacitor with vacuum as the dielectric medium between the plates, as shown in Figure 7.1a. The plates are connected to a constant voltage supply V. Let Q_o be the charge on the plates. This charge can be easily measured. The capacitance C_o of the parallel plate capacitor in free space, as in Figure 7.1a, is defined by

$$C_o = \frac{Q_o}{V} \qquad [7.1]$$

The electric field, directed from high to low potential, is defined by the gradient of the potential $E = -dV/dx$. Thus, the electric field E between the plates is just V/d where d is the separation of the plates.

Figure 7.1 (a) Parallel plate capacitor with free space between the plates. (b) As a slab of insulating material is inserted between the plates, there is an external current flow indicating that more charge is stored on the plates. (c) The capacitance has been increased due to the insertion of a medium between the plates.

Consider now what happens when a dielectric slab (a slab of any nonconducting material) is inserted into this parallel plate capacitor, as shown in Figure 7.1b and c with V kept the same. During the insertion of the dielectric slab, there is an external current flow that indicates that there is additional charge being stored on the plates. The charge on the electrodes increases from Q_o to Q. We can easily measure the extra charge $Q - Q_o$ flowing from the battery to the plates by integrating the observed current in the circuit during the process of insertion, as shown in Figure 7.1b. Because there is now a greater amount of charge stored on the plates, the capacitance of the system in Figure 7.1c is larger than that in Figure 7.1a by the ratio Q to Q_o. The **relative permittivity,** or the **dielectric constant,** ε_r is defined to reflect this increase in the capacitance or the charge storage ability by virtue of having a dielectric medium. If C is the capacitance with the dielectric medium as in Figure 7.1c, then by definition

$$\varepsilon_r = \frac{Q}{Q_o} = \frac{C}{C_o} \qquad [7.2]$$

The increase in the stored charge is due to the polarization of the dielectric by the applied field, as explained below. It is important to remember that when the dielectric medium is inserted, the electric field remains unchanged, provided that the insulator fills the whole space between the plates as shown in Figure 7.1c. The voltage V remains the same and therefore so does the gradient V/d, which means that E remains constant.

DIPOLE MOMENT AND ELECTRONIC POLARIZATION

An electrical dipole moment is simply a separation between a negative and positive charge of equal magnitude Q as shown in Figure 7.2. If **a** is the vector from the negative to the positive charge, the **electric dipole moment** is defined as a vector by

$$\mathbf{p} = Q\mathbf{a} \qquad [7.3]$$

The region that contains the $+Q$ and $-Q$ charges has zero net charge. Unless the two charge centers coincide, this region will nonetheless, by virtue of the definition in Equation 7.3, contain a dipole moment.

The net charge within a neutral atom is zero. Furthermore, on average, the center of negative charge of the electrons coincides with the positive nuclear charge, which means that the atom has no net dipole moment, as indicated in Figure 7.3a. However, when this atom is placed in an external electric field, it will develop an induced dipole moment. The electrons, being much lighter than the positive nucleus, become easily displaced by the field, which results in the separation of the negative charge center from the positive charge center, as shown in Figure 7.3b. This separation of negative and positive charges and the resulting induced dipole moment are termed

Figure 7.2 The definition of electric dipole moment.

Figure 7.3 The origin of electronic polarization.

polarization. An atom is said to be **polarized** if it possesses an effective dipole moment, that is, if there is a separation between the centers of negative and positive charge distributions.

The induced dipole moment depends on the electric field causing it. We define a quantity called the **polarizability** α to relate the induced dipole moment p_{induced} to the field E causing it,

$$p_{\text{induced}} = \alpha E \qquad [7.4]$$

where α is a coefficient called the polarizability of the atom. It depends on the polarization mechanism. Since the polarization of a neutral atom involves the displacement of electrons, α is called **electronic polarization** and denoted as α_e. Inasmuch as the electrons in an atom are not rigidly fixed, all atoms possess a certain amount of electronic polarizability.

In the absence of an electric field, the center of mass C of the orbital motions of the electrons coincides with the positively charged nucleus O and the electronic dipole moment is zero as in Figure 7.3a. Suppose that the atom has Z number of electrons orbiting the nucleus and all the electrons are contained within a certain sphere region of radius r_o. When an electric field E is applied, the light electrons become displaced in the opposite direction to E so that their center of mass C is shifted by some distance x with respect to the nucleus at O, which we take to be the origin as shown in Figure 7.3b. As the electrons are "pushed" away by the applied field, the Coulombic attraction between the electrons and nuclear charge "pulls in" the electrons; tries to restore the electron cloud back to its original position. The force on the electrons, due to E, trying to separate them away from the nuclear charge is ZeE as shown in Figure 7.3b. The restoring force F_r, which is the Coulombic attractive force between the electrons and the nucleus, can be taken to be proportional to the displacement x.[1] The restoring force is obviously zero when C coincides with $O(x = 0)$. We can write $F_r = -\beta x$ where β is a constant and the negative sign indicates that F_r is always directed toward the nucleus O. In equilibrium, the net force on the negative charge center is zero as shown in Figure 7.3b,

$$ZeE = \beta x$$

from which x is known. Therefore, the *magnitude* of the induced electronic dipole moment p_e is given by

$$p_e = (Ze)x = \left(\frac{Z^2e^2}{\beta}\right)E \qquad [7.5]$$

As expected p_e is proportional to the applied field. The electronic dipole moment in Equation 7.5 is valid under static conditions, that is, when the electric field is a dc field. The term in the parentheses in Equation 7.5 is the electronic polarizability. We can use elementary electrostatics to find β by assuming that the negative charge Ze is uniformly distributed within the atomic radius r_o. We can then calculate the electric field E_r at x from center of negative charge C. The force ZeE_r on the nucleus would be pulling the nucleus toward C, which is the same force that pulls the negative charge center C toward O as indicated in Figure 7.3b. We can therefore find β as shown in Example 7.1, and then substitute for β in Equation 7.5 with the final result that α_e is given by

$$\alpha_e \approx 4\pi\varepsilon_o r_o^3 \qquad [7.6]$$

Notice that polarizability depends on the atomic size only in this simple classical view. Suppose that we suddenly remove the applied electric field polarizing the atom. There is then only the restoring force $-\beta x$, which always acts to pull the electrons toward the nucleus O. The equation of motion of the negative charge center is then

$$-\beta x = Zm_e\frac{d^2x}{dt^2}$$

Thus, the displacement at any time is sinusoidal and given by

$$x(t) = x_o \cos(\omega_o t)$$

where

$$\omega_o = \left(\frac{\beta}{Zm_e}\right)^{1/2}$$

is the oscillation frequency of the center of mass of the electron cloud about the nucleus and x_o is the displacement before the removal of the field. After the removal of the field, the electronic charge cloud executes simple harmonic motion about the nucleus with a frequency determined by ω_o; called **electronic polarization resonance frequency**.[2] It is analogous to a mass on a spring being pulled and let go. The system then executes simple harmonic motion. The oscillations of course die out with time. In the atomic case, a sinusoidal displacement $x(t)$ above implies that the electronic charge cloud has an acceleration that is also sinusoidal with $\cos(\omega_o t)$. It is well known from classical electromagnetism that an accelerating charge radiates

electromagnetic energy just like a radio antenna. Consequently, the oscillating charge cloud loses energy, and thus its amplitude of oscillations decreases. (Recall that the average energy is proportional to the square of the amplitude of the displacement.)

We can substitute for β in Equation 7.5 in terms of ω_o and use Equation 7.4 to obtain

$$\alpha_e = \frac{Ze^2}{m_e\omega_o^2} \qquad [7.7]$$

SUPER CAPACITOR

SUPERCAPACITOR

- A **supercapacitor** is an electrochemical capacitor that has a very high power density as compared to common capacitors, about 100 times greater.
- Supercapacitor is also known as Electric Double Layer Capacitor (EDLC) or Ultracapacitor.
- The capacitance range is From 100 Farad to 5KFarad.

CONSTRUCTION

- Supercapacitors are constructed with two metal foils, each coated with an electrode material such as activated carbon.

- The electrodes are kept apart by an ion-permeable membrane (separator) used as an insulator to protect the electrodes against short circuits.

- The construction is subsequently rolled or folded into a cylindrical or rectangular shape and is packed in an aluminum can.

1.Positive electrode

2. Negative electrode

3. Separator

4.Aluminum can

5.Positive pole

6.Separator

7.Carbon electrode

8. Collector

9.Carbon electrode

10. Negative pole

WORKING OF SUPERCAPACITOR

- In a supercapacitor, there is no conventional dielectric.
- Both plates are soaked in an electrolyte and separated by a very thin insulator.
- When the plates are charged, an opposite charge forms on either side of the separator, creating what's called an electric **double-layer.**
- This is why supercapacitors are often referred to as double-layer capacitors.

Double Layer Capacitor

ELECTRIC DOUBLE LAYER

- Electrochemical capacitor has two electrodes, separated by a separator, which are electrically connected to each other via the electrolyte.
- When voltage is applied, and plates get charged, an opposite charge forms on the either side of the separator creating a electric double layer.

STRUCTURE OF EDLC

FEATURES

- Stores high amount of energy.
- Have high capacitance.
- High rates of charge and discharge.
- Low toxicity.
- High cycle efficiency (95%)

APPLICATIONS

- In start up mechanism for Automobiles.
- Used in Diesel engine start up in submarines & tanks.
- Backup power system in missiles.
- Power source for laptops, flash in cameras.
- Voltage stabilizer.

Super Capacitor Buses

It is a new form of electric bus powered via energy store in large onboard super-capacitors. A connector in the roof connects to the stationary electrical installation when the bus stops to let the passenger on to the bus.

- Electric Bus Technology
  - Super / Outer Capacitors (Energy Storage device)
  - Collector (fitted on the top)
- Super capacitors can be charged much faster than batteries, but hold less energy (at the current time).

BOOSTCAP
ULTRACAPACITOR
650 Farads | 2.7 VDC
DO NOT REVERSE POLARITY

ADVANTAGES

- High energy storage.
- Wide working temperature(-40°c to 60°c).
- Eco-friendly.
- Quick charging time.
- Maximum life cycle.
- High cycle efficiency (95%).
- High specific power up to 17 kW/kg.
- Extremely low internal resistance.
- Safe.

DISADVANTAGES

- Low energy density.
- The voltage varies with the energy stored.
- Have high self-discharge rate.
- Requires expert electronic control.
- Cannot be used in AC and high frequency circuits.
- High cost.

CONCLUSION

- Supercapacitors may be used where high power or energy storage is required.
- Supercapacitors can be used widely because of their long life & short charging time.
- On the other hand it has limitations due to its high cost, self discharge, packaging problems etc.

Carbon Nanotubes

- Introduction
- Applications
- Growth Techniques
- Growth Mechanism

What is a Carbon Nanotube?

CNT is a tubular form of carbon with diameter as small as 1nm.

Length: few nm to microns.

CNT is configurationally equivalent to a two dimensional graphene sheet rolled into a tube.

A CNT is characterized by its Chiral Vector: $\mathbf{C}_h = n\,\hat{a}_1 + m\,\hat{a}_2$,

θ → Chiral Angle with respect to the zigzag axis.

Chiral Angle with respect to the zigzag axis.

Armchair (n,m) = (5,5)
$\theta = 30°$

Zig Zag (n,m) = (9,0)
$\theta = 0°$

Chiral (n,m) = (10,5)
$0° < \theta < 30°$

Why do Carbon Nanotubes form?

Carbon →

Graphite (Ambient conditions)

sp^2 hybridization: planar

graphite

Diamond (High temperature and pressure)

sp^3 hybridization: cubic

diamond

Nanotube/Fullerene (certain growth conditions)

sp^2 + sp^3 character: cylindrical

(10, 10) nanotube

C_{60} fullerene

Finite size of graphene layer has dangling bonds. These dangling bonds correspond to high energy states.

Nanotube formation → Eliminates dangling bonds + Increases Strain Energy → Total Energy decreases

Types of CNTs

- Single Wall CNT (SWCNT)
- Multiple Wall CNT (MWCNT)
- Can be metallic or semiconducting depending on their geometry.

The Graphene sheet

Graphene sheet

Mads Brandbyge, MIC 2003

”Metallic directions”

Nanotube: Metallic

Nanotube: Semi-conductor

Mads Brandbyge, MIC 2003

Metallic: *n - m= 3j*

$$C = n\,a_1 + m\,a_2$$

$$C \bullet k = 2\pi\, j$$

Non-chiral (”Straight”) nanotubes

Philip G. Collins and Phaedon Avouris

SCIENTIFIC AMERICAN December 2000

Chiral (”Spiral”) Nanotubes

Philip G. Collins and Phaedon Avouris

SCIENTIFIC AMERICAN December 2000

CNT Properties

- The strongest and most flexible molecular material because of C-C covalent bonding and seamless hexagonal network architecture

- Young's modulus of over 1 TPa vs 70 GPa for Aluminum, 700 GPA for C-fiber
  - strength to weight ratio 500 time > for Al; similar improvements over steel and titanium; one order of magnitude improvement over graphite/epoxy

- Maximum strain ~10% much higher than any material

- Thermal conductivity ~ 3000 W/mK in the axial direction with small values in the radial direction

CNT Properties (cont.)

- Electrical conductivity six orders of magnitude higher than copper
- Can be metallic or semiconducting depending on chirality
  - 'tunable' bandgap
  - electronic properties can be tailored through application of external magnetic field, application of mechanical deformation…
- Very high current carrying capacity
- Excellent field emitter; high aspect ratio and small tip radius of curvature are ideal for field emission

CNT: Implications for electronics

- Carrier transport is 1-D.
- All chemical bonds are satisfied $\Rightarrow$ CNT Electronics not bound to use SiO_2 as an insulator.
- High mechanical and thermal stability and resistance to electromigration $\Rightarrow$ Current densities upto 10^9 A/cm^2 can be sustained.
- Diameter controlled by chemistry, not fabrication.
- Both active devices and interconnects can be made from semiconducting and metallic nanotubes.

Nanotube Growth Methods

a) Arc Discharge b) Laser Abalation

- Involve condensation of C-atoms generated from evaporation of solid carbon sources. Temperature ~ 3000-4000K, close to melting point of graphite.
- Both produce high-quality SWNTs and MWNTs.
- MWNT: 10's of μm long, very straight & have 5-30nm diameter.
- SWNT: needs metal catalyst (Ni,Co etc.).

  Produced in form of ropes consisting of 10's of individual nanotubes close packed in hexagonal crystals.

Nanotubes Growth Methods

c) Chemical Vapor Deposition:

Hydrocarbon + Fe/Co/Ni catalyst $\xrightarrow{550\text{-}750^{\circ}C}$ CNT

Steps:

- Dissociation of hy
- Dissolution and s
  of C atoms in met
- Precipitation of C

Choice of catalyst material?

Base Growth Mode or Tip Growth Mode?

- Metal support interactions

Controlled Growth by CVD

Methane + Porous Si + Fe pattern $\xrightarrow{\text{CVD}}$ Aligned MWNTs

a) SEM image of aligned nanotubes.

a) SEM image of side view of towers. Self-alignment due to Van der Walls interaction.

a) High magnification SEM image showing aligned nanotubes.

d) Growth Process: Base growth mode.

Growth Mechanisms

- Electronic and Mechanical Properties are closely related to the atomic structure of the tube.
- Essential to understand what controls the size, number of shells, helicity & structure during synthesis.
- Mechanism should account for the experimental facts: metal catalyst necessary for SWNT growth, size dependent on the composition of catalyst, growth temperature etc.

- MWNT Growth Mechanism:
  - Open or close ended?
  - Lip Lip Interaction Models

- SWNT Growth Mechanism:
  - Catalytic Growth Mechanism

Open-Ended Growth of Multi Walled Nanotube

- Role of Hexagons, Pentagons & Heptagons

Fig. 2. Growth mechanism of a carbon nanotube (white ball-and-stick atomic structure) at an open end by the absorption of C_2 dimers and C_3 trimers (in *black*), respectively [14]

MWNT: The possibilities

SWNT Growth Mechanism

Is uncatalyzed growth possible?

- Simulations & Observations ⇒ No!
- Spontaneous closure at experimental tempera
- Closure reduces reactivity.

Catalytic SWNT Growth Mechanism

- Transition metal surface c
  fullerene nucleates SWNT
  around periphery.

- Catalyst atom chemis
  the open edge. Cataly
  tube open by scootin
  open edge, ensuring a
  and heptagons do no

Conclusion

- Their phenomenal mechanical properties, and unique electronic properties make them both interesting

  as well as potentially useful in future technologies.
- Significant improvement over current state of electronics can be achieved if controllable growth is achieved.
- Growth conditions play a significant role in deciding the electronic and mechanical properties of CNTs.
- Growth Mechanisms yet to be fully established.

Ferroelectrics

An overview

- Non-conducting materials may have a net electrostatic polarisation induced by an external electric field.
- Where the affects upon observable properties such as elastic, optical and thermal behaviour is large, these materials are termed *ferroelectrics*.
- To gain some understanding, we'll start with a simple model…

A naïve picture

Energetics

A naïve picture

A naïve picture

A naïve picture

A naïve picture

- The local alignment of dipoles can exist over any length scale.
- Different regions may exist with different polarisation orientations:
  - Call these “domains” in line with magnetic materials.
  - In contrast with magnetism, domain walls are abrupt.

Applied field

- Suppose we now apply an electric field, horizontal in the figure.
- If it is of sufficient strength, the small ions will be able to overcome the barrier and dipoles will switch direction
  - The dipoles are polarised by the applied field.
  - Domain walls move.

Polarisation vs. E-field

- Suppose we start with a material where there are **many domains** which are **aligned randomly**.
  - What is the initial polarisation?

Polarisation vs. E-field

- If we apply a small electric field, such that it is not able to switch domain alignments, then the material will behave as a normal dielectric:
  - $P \propto E$
- As E is increased, we start to flip domains and rapidly increase P.
- When all domains are switched, we reach saturation.
- What happens if the E-field is now removed?

Polarisation vs. E-field

- The value at zero field is termed the ***remnant polarisation***.
- The value of P extrapolated back from the saturation limit is the ***spontaneous polarisation***.
- Reversal of the field will eventually remove all polarisation
  - The field required is the ***coercive field***.
- Further increasing the reverse field will completely reverse the polarisation, and so a hysteresis loop is formed…

Polarisation hysteresis

Polarisation hysteresis

Polarisation hysteresis

- The essential feature of a ferroelectric is ***not*** that there is a spontaneous polarisation, but that ***the spontaneous polarisation can be reversed by the application of an electric field.***

ΔE

- Now, ΔE is small enough for the applied field to reverse the direction of the dipoles, i.e. move the atoms within the crystal, what else might affect this change?
- What are the relative sized of ΔE and $k_B T$?
- What will happen if $\Delta E \leq k_B T$?

Curie temperature

- Above a *critical temperature* the spontaneous polarisation will be lost due to one of two effects:
  - A change of structure such that there is a single minimum in the energy mid-way between sites
  - The rate that the small ions hop is so high that on average there is no net polarisation

Curie temperature

- This temperature is termed the Curie temperature, T_c, in light of the analogy with the transition temperature between ferromagnetism and paramagnetism.
- Above the Curie temperature, ferroelectrics behave as non-polar dielectrics, *sometimes* termed a ***paraelectric*** phase.
- Some ferroelectrics do not have a Curie temperature – why might this be?

Other temperature effects

- In addition to the change in spontaneous polarisation, temperature affects the ***dielectric constant*** of the material, normally defined as the rate of change of dielectric displacement with electric field.
- For ferroelectrics where there is a non-linear relationship between D and P, we use
  - $\varepsilon=(\partial D/\partial E)_{E=0}$

Other temperature effects

- In some ferroelectrics, the temperature dependence of ε can be reasonably accurately represented by the ***Curie-Weiss*** law:
  - $\varepsilon = \varepsilon_0 + C/(T-T_0)$
  - C is the Curie constant
  - T_0 is the Curie-Weiss temperature, which in general differs from the Curie temperature (T_c)
- Close to T_0 ε becomes very large.
- In some ferroelectrics, $T_c \approx T_0$, and the phase transition is of second order.
- In others T_c is far from T_0 and the phase transition is first order.

Beyond the naïve model

- In the model, we have picked out pairs of atoms, and attributed point dipoles associated with the combination of their charges and separations.
- More realistically, each unit cell carries a dipole moment:
  - $\mathbf{d} = \iiint \rho(\boldsymbol{r}).\boldsymbol{r}.\mathrm{d}v \neq 0$
  - $\rho(\boldsymbol{r})$ is the charge density (inc. ions), the integral is with respect to an arbitrary origin, and **d** is independent of its choice.
  - The definition allows the polarisation to be as influenced by distortions in the electron density as it is by displacements in the point-like ion sites.

Crystallography and ferroelectrics

- The crystal classification of a material has immediate implications for ferroelectric effects
  - There are 32 crystal classes

- $T\ T_h\ O\ T_d\ O_h$
- $C_4\ S_4\ C_{4h}\ D_4\ C_{4v}\ D_{2d}\ D_{4h}$
- $D_2\ C_{2v}\ D_{2h}$
- $C_2\ C_s\ C_{2h}$
- $C_1\ C_i$
- $C_3\ S_6\ D_3\ C_{3v}\ D_{3d}$
- $C_6\ C_{3h}\ C_{6h}\ D_6\ C_{6v}\ D_{3h}\ D_{6h}$

Crystallography and ferroelectrics

- The crystal classification of a material has immediate implications for ferroelectric effects
  - There are 32 crystal classes
  - 11 of them have a centre of symmetry (centrosymmetric) and cannot support ferroelectricity

- T T_h O T_d O_h
- C_4 S_4 C_{4h} D_4 C_{4v} D_{2d} D_{4h}
- D_2 C_{2v} D_{2h}
- C_2 C_s C_{2h}
- C_1 C_i
- C_3 S_6 D_3 C_{3v} D_{3d}
- C_6 C_{3h} C_{6h} D_6 C_{6v} D_{3h} D_{6h}

Crystallography and ferroelectrics

- The crystal classification of a material has immediate implications for ferroelectric effects
  - There are 32 crystal classes
  - 11 of them have a centre of symmetry (centrosymmetric) and cannot support ferroelectricity
  - Of the remaining 21, the O-point group (432) also excludes ferroelectricity.
  - The remaining 20 classes all exhibit the ***piezoelectric effect***…

- T T_h O T_d O_h
- C_4 S_4 C_{4h} D_4 C_{4v} D_{2d} D_{4h}
- D_2 C_{2v} D_{2h}
- C_2 C_s C_{2h}
- C_1 C_i
- C_3 S_6 D_3 C_{3v} D_{3d}
- C_6 C_{3h} C_{6h} D_6 C_{6v} D_{3h} D_{6h}

Piezoelectric effect

- The application of an electric field induces a geometrical change.
- Alternatively, a distortion of the material induces a potential difference.
- Used in many electrical devices, e.g. sound-to-electricity

Crystallography and ferroelectrics

- The crystal classification of a material has immediate implications for ferroelectric effects
  - There are 32 crystal classes
  - 11 of them have a centre of symmetry (centrosymmetric) and cannot support ferroelectricity
  - Of the remaining 21, the O-point group (432) also excludes ferroelectricity.
  - The remaining 20 classes all exhibit the ***piezoelectric effect***
  - Of these, 10 have a unique polar direction.

- T T_h O T_d O_h
- C_4 S_4 C_{4h} D_4 C_{4v} D_{2d} D_{4h}
- D_2 C_{2v} D_{2h}
- C_2 C_s C_{2h}
- C_1 C_i
- C_3 S_6 D_3 C_{3v} D_{3d}
- C_6 C_{3h} C_{6h} D_6 C_{6v} D_{3h} D_{6h}

Crystallography and ferroelectrics

- Crystal classes with a unique polar axis are called ***polar***.
- The spontaneous polarisation can be seen in terms of its change with temperature:
  - the ***pyroelectric effect***.
- The 10 polar classes are therefore sometimes referred to as the ***pyroelectric classes.***
- http://www.staff.ncl.ac.uk/j.p.goss/symmetry/PP_classes.html
- Ferroelectric crystals must belong to the pyroelectric classes.
- But Ferroelectrics must exhibit the hysteresis, so we **define** ferroelectric crystals as ***pyroelectric crystals that exhibit reversible polarisation.***

Classification of ferroelectrics

i. "Crystal-chemical": hydrogen-bonded (e.g. KH_2PO_4) or otherwise (e.g. double oxides).

ii. No. of polarisation directions: single direction (e.g. $PbTa_2O_6$), several equivalent directions (e.g. $BaTiO_3$).

iii. Centrosymmetric non-polar phase: E.g. Rochelle salts exhibit piezoelectric phase above T_c, whereas $BaTiO_3$ is centrosymmetric.

iv. First vs. second order phase change at T_c. It turns out this corresponds to the value of the Curie constant (C), one group being of the order of 10^3K, and the other 10^5K.

These four classifications do not necessarily coincide.

Antiferroelectrics

Polar

Antipolar

Antiferroelectrics

- If the free energy of an antipolar phase is comparable to the polar state then the material is termed ***antiferroelectric***.
- If a material exhibits ferroelectric effects in one polar direction, and antiferroelectric effects perpendicular, it may be termed ***ferrielectric***.

Antipolar

Polar

Perovskites

- Perovskite is a naturally occurring mineral with chemical formula $CaTiO_3$.
- This is a prototype for many ABO_3 materials which are very important in ferroelectrics.
- These materials may be envisaged by consideration of a non-polar, cubic basic building block…

Perovskites

Perovskites

- Below the Curie temperature, these crystals undergo symmetry lowering distortions. We'll initially focus up the distortions of $BaTiO_3$.
- There are three phase transitions in order of decreasing temperature: 120°C, 5°C, and -90°C.

$BaTiO_3$

- Above 120°C $BaTiO_3$ is cubic (non-polar)

$BaTiO_3$

- From 120°C down to ~5°C, there is a distortion to a tetragonal phase.
- All of the cube directions can undergo this type of distortion: this leads to complexity in domain formation.

$BaTiO_3$

- From 5°C down to around -90°C the structure is orthorhombic by dilation along [110] directions and contraction along [1-10].
- There are 12 possible orientations.

$BaTiO_3$

- Finally the lowest temperatures yield rhombohedra (distortions along the body diagonal).
- There are therefore 8 equivalent distortion directions

$PbTiO_3$ internal structure

- The foregoing analysis of $BaTiO_3$ focuses on the shape of the unit cell. However, for the ferroelectric effect, we also require internal structural changes.
- In light of current interest in Cu-related defects in lead titanium tri-oxide, we'll review this tetragonal system at room temperature…

$PbTiO_3$ internal structure

- X-ray and neutron scattering yield the internal structure:
- a=3.904Å, c=4.150Å, so that c/a=1.063.
- Taking the Pb site as the origin, the displacements are
  - δz_{Ti}=+0.040
  - δz_{OI}=+0.112
  - δz_{OII}=+0.112
- Here OI are the polar O-sites, and OII are the equatorial.
- Thus, since the oxygen atoms are all displaced by the same amount, the oxygen cage remains intact, and shifts relative to the Ti and Pb sites.

$PbTiO_3$

$PbTiO_3$

- It should be clear that this system has a net dipole in each unit cell, and furthermore that the distortion can be along any of the x, y and z directions.
- In real $PbTiO_3$, there is a non-trivial role for point defects, especially O-vacancies.

Superconductors

Introduction

– **What are superconductors?**

- *Superconductors are the material having almost zero resistivity and behave as diamagnetic below the superconducting transiting temperature*
- *Superconductivity* is the flow of electric current without resistance in certain metals, alloys, and ceramics at temperatures near absolute zero, and in some cases at temperatures hundreds of degrees above absolute zero = -273ºK.

Discoverer of Superconductivity

- Superconductivity was first discovered in 1911 by the Dutch physicist,Heike Kammerlingh Onnes.

The Discovery

- Onnes, felt that a cold wire's resistance would dissipate. This suggested that there would be a steady decrease in electrical resistance, allowing for better conduction of electricity.
- At some very low temperature point, scientists felt that there would be a leveling off as the resistance reached some ill-defined minimum value allowing the current to flow with little or no resistance.
- Onnes passed a current through a very pure mercury wire and measured its resistance as he steadily lowered the temperature. Much to his surprise there was no resistance at 4.2K.

At 4.2K, the Electrical Resistance (opposition of a material to the flow of electrical current through it)Vanished, Meaning Extremely Good Conduction of Electricity-Superconductivity

General Properties of Superconductors

- **Electrical resistance**: Virtually zero electrical resistance.

- **Effect of impurities**: When impurities are added to superconducting elements, the superconductivity is not loss but the T_c is lowered.

- **Effects of pressures and stress**: certain materials exhibits superconductivity on increasing the pressure in superconductors, the increase in stress results in increase of the T_c value.

- **Isotope effect**: The critical or transition temperature Tc value of a superconductors is found to vary with its isotopic mass. i.e. "*the transition temperature is inversely proportional to the square root of isotopic mass of single superconductors.*"

$$T_C \ \alpha \ 1/\sqrt[2]{M}$$

- **Magnetic field effect**: If Strong magnetic field applied to a superconductors below its T_c, the superconductors undergoes a transition from superconducting state to normal state.

Meissner effect

The complete expulsion of all magnetic field by a superconducting material is called "Meissner effect"

- Normal state: $T > T_c$
- Superconducting state : $T < T_c$
- The Meissner effect is a distinct characteristics of a superconducting from a normal perfect conductor. In addition, this effect is exhibited by the superconducting materials only when the applied field is less then the critical field Hc.

Important Factors to define a Superconducting State

- The superconducting state is defined by three very important factors:
  1. critical temperature (Tc)
  2. critical field (Hc)
  3. critical current density (Jc).

Each of these parameters is very dependant on the other two properties present

CRITICAL TEMPERATURE

- The temperature at which a material electrical resistivity drops to absolute zero is called the Critical Temperature or Transition Temperature.
- Below critical temperature, material is said to be in superconducting and above this it is said to in normal state. Below this temperature the superconductors also exhibits a variety of several astonishing magnetic and electrical properties.

Metal	Critical T(K)
Aluminum	1.2K
Tin	3.7K
Mercury	4.2K
Niobium	9.3K
Niobium-Tin	17.9K
Tl-Ba-Cu-oxide	125K

Electrical Resistivity Vs Temperature Plot for Superconductors and Normal Metals

From the figure it can be seen that the electrical resistivity of normal metal decreases steadily as the temperature is decreased and reaches a low value at 0K called Residual Resistivity.

- **Critical magnetic field (Hc)** Above this value of an externally applied magnetic field a superconductor becomes non-superconducting .*This minimum magnetic fields required to destroy the superconducting state is called the* ***critical magnetic field*** H_c

$$H_c = H_o[1-(T/Tc)^2]$$

TYPES OF SUPERCONDUCTORS

TYPE I	TYPE II
Soft superconductors are those which can tolerate impurities without affecting the superconducting properties.	Hard superconductors are those which cannot tolerate impurities, i.e., the impurity affects the superconducting property
Also called SOFT SUPERCONDUCTORS.	Also called HARD SUPERCONDUCTORS.
Only one critical field exists for these superconductors.	Two critical fields H_{c1}(lower) & H_{c2}(upper) for these.
Critical field value is very low.	Critical field value is very high.
Exhibits perfect and complete Meissner effect.	Don't exhibit perfect and complete Meissner effect.
The current flows through the surface only.	It is found that current flows throughout the material.
These materials have limited technical applications because of very low field strength value	These materials have wider technology of very high field strength value.
.e.g :-Pb,Hg,Zn,etc.	e.g. Nb_3Ge, Nb_3Si

TYPES OF SUPERCONDUCTORS

TYPE 1

Fig. 10

TYPE 2

Fig. 11

HIGH T_c SUPERCONDUCTORS

Low T_c Superconductors

- Superconductors that require liquid helium coolant are called low temperature superconductors.
- Liquid helium temperature is 4.2K above absolute zero

High T_c superconductors

- Superconductors having their T_c values above the temperature of liquid nitrogen (77K) are called the high temperature superconductors.

MAGNETIC LEVITATION

- **Magnetic levitation**, **maglev**, or **magnetic suspension** is a method by which an object is suspended with no support other than magnetic fields. Magnetic force is used to counteract the effects of the gravitational and any other accelerations.
- The two primary issues involved in magnetic levitation are *lifting force*: providing an upward force sufficient to counteract gravity, and *stability*: insuring that the system does not spontaneously slide or flip into a configuration where the lift is neutralized.

Picture below is the levitation of a magnet above a cooled superconductor, the **Meissner Effect**

APPLICATIONS

Magnetically levitated vehicles are called Maglev vehicles

- Maglev trains:
- Based on two techniques:
  1)Electromagnetic suspension
  2)Electrodynamic suspension
- In EMS,the electromagnets installed on the train bogies attract the iron rails. The magnets wrap around the iron & the attractive upward force is lift the train.
- In EDS levitation is achieved by creating a repulsive force between the train and guide ways.
- The basic idea of this is to levitate it with magnetic fields so that there is no physical contact between the trains and guideways. Consequently the maglev train can travel at hihg speed of 500 km/h.

Maglev Train

JOSEPHSON EFFECT

- Two superconductors separated by a very thin strip of an installer forms a Josephson junction.
- The wave nature of moving particles make electrons to tunnel through the barrier. As a consequence of tunneling of electrons across the insulator there is net current across the junction. This is called d.c.josephson effect. The current flows even in absence of potential difference.
- The magnitude of current depends on the thickness of the insulators, the nature of the materials and the temperature.
- On the other hand when potential difference V is applied between the two sides of the junction there will be an oscillation of tunneling current with angular frequency $v=2eV/h$. This is called a.c.josephson effect.

JOSEPHSON DEVICES

Current increases due to tunneling effect
Super conductor 2
Insulator
Super conductor 1

APPLICATION OF SUPERCONDUCTORS

- The production of sensitive magnetometers based on SQUIDs

A SQUID (Superconducting QUantum Interference Device) is the most sensitive type of detector known to science. Consisting of a superconducting loop with two Josephson junctions, SQUIDs are used to measure magnetic fields.

- Powerful superconducting electromagnets used in maglev trains, Magnetic Resonance Imaging (MRI) and Nuclear magnetic resonance (NMR) machines, magnetic confinement fusion reactors (e.g. tokomaks), and the beam-steering and focusing magnets used in particle accelerators.
- Superconducting generators has the benefit of small size and low energy consumption than the conventional generators.
- Very fast and accurate computers can be constructed using superconductors and the power consumption is also very low. Superconductors can be used to transmit electrical power over very long distances without any power or any voltage drop

Graphene

- The wonder material

European Union granted in **1 billion** euro to Chalmers University (Sweden) in 2013.

Fact that it is currently one of the most researched material in the world

Companies around the world urges to invest in this material.

Just for discovering of it from **Scotch Tape** –Andre Gein & Konstantin Novoselov won Nobel Prize.

Researchers around the world, race in for R&D for this material

Patents around the world

Samsung	-149
Chinese entities	-2,204
US entities	-1,754
South Korean entities	-1,160
United Kingdom entities	-54

Insight

Graphene is a substance composed of pure carbon, with atoms arranged in a regular hexagonal pattern similar to graphite, but in a one atom thick sheet.

Or

Flat monolayer of carbon atoms tightly packed into a two dimensional honeycomb lattice

or

Isolated Single Layer of Graphite

Family of Carbon

2-D

3-D

1-D

0-D

Thermal & Optical Properties

- Thermal Conductivity - 5000 W/m.K
  - (Diamond 1200W/m.k)
- Transparent in nature
- 98% visual transmission rate, absorbs 2.3% white light
- Thinnest 0.335 nm

Electrical Properties

- High electrical conductivity 5000 W/mK.
- Zero Gap conductivity
- Resistivity 10^{-6} Ωcm
- Charge carriers behave massless
- Little Scattering
- High mobility

Applications

Integrated Circuits

- High mobility of charge can be integral in IC
- Fast processing
- Replaces Silicon

Distillation

- It allows only water to pass through it.
- Making ideal for purification process. Eradication of Water scarcity
- Desalination

Gas Sensors

- Can detect effect of a single molecule associating with graphene
- Effects the electric properties with addition of any foreign atom

Transistors

- More Efficient than silicon transistors
- Can be easily controlled by electric field
- Can run at higher frequency
- Increase speed of Circuits

Ultra-Capacitor

- High surface to mass ratio
- Two sheet of graphene with electrolyte in between
- May replace batteries
- High recharge rate and slow discharge
- Long life

Bionic Devices

- Non corrosive
- Biodegradable
- High conductivity
- Non toxic compared to conventional electrode used in bionic device

Protective Coating

- It is resistant to acids, alkalis etc.
- Being impermeable
- Coating of containers, Jars etc
- Paints for car body, steel structure

Solar Cell

- It is super capacitor
- With high recharge rate and a normal discharge rate

Flexible Mobilephone

- It can be used to make flexible LED screen that can be used in mobile phones.

Obstacles

- Conventional production method still in search
- Cost $100,000,000/cm^2 2008
  $100/cm^2 2009
- Availability of low Quality
- No band Gap

The Strongest

The Lightest

Flexible

Transparent

Electrical Conductive

Thermal Conductive