PYL102 Course Lecture-9 on 26-08-2021

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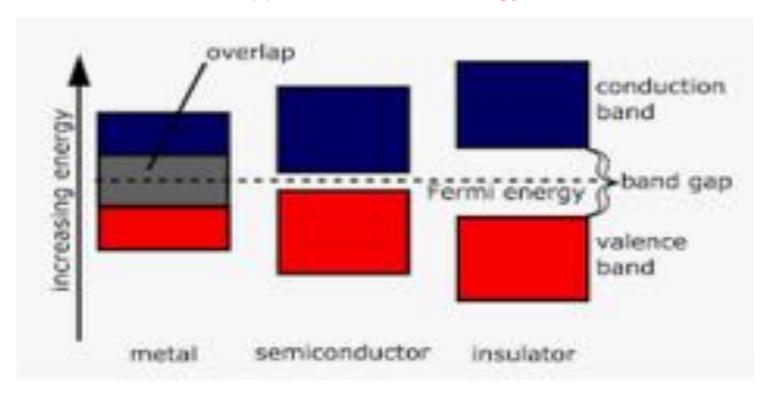
PYL102:

Principles of Electronic Materials

- > Formation of energy bands.....
- > Energy bands in solids.....
- Classification of electronic materials......
- Understanding metal, semiconductor and insulator....

Metals, insulators, and semiconductors:

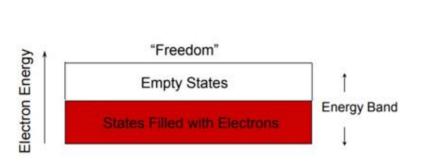
- ❖ The band scheme of a semiconductor is essentially similar to that of the insulator; the highest band is completely full of electrons...
- ❖ However, in a semiconductor the energy gap E_g is small and electrons in the VB can potentially acquire enough energy to surmount this energy gap and make it to the conduction band. These electrons will, therefore, become free and available for conduction in the presence of an electric field across the semiconductor.
- ❖ Generally, in a semiconductor this energy E_g required to raise the electron to the conduction band can be supplied as thermal energy.

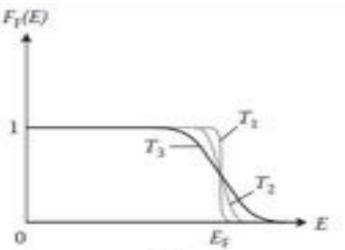


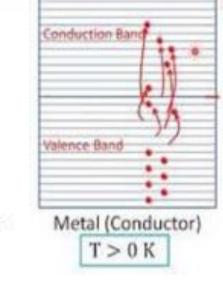
Metals:

As the levels are closely spaced to each other in energy and there is an overlap between the bands, generally the energy provided by the electric field or temperature is

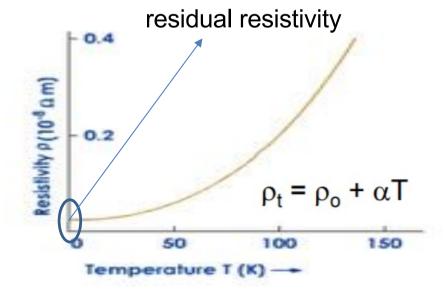
sufficient to stimulate an electrons to any empty states







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- Problem Resistivity typically increases linearly with temperature, where ρ_o and α are constants for a specific material....
- The number of electrons in the CB does not vary with temperature.
- But increase in temperature increases the scattering events.

Insulators:

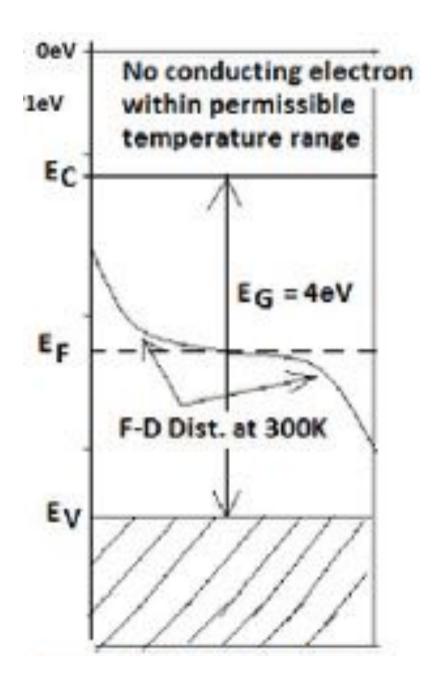
- Insulators are the materials which don't allow the flow of electrons through them!!
- Insulators possess a high resistivity and low conductivity.
- ❖ Their atoms have tightly bound electrons that do not move throughout the material. Because the electrons are static and not freely roaming, the current cannot pass through easily.
- High resistance, breakdown voltage and air permeability are the basic properties of insulators..
- ❖ The valence band and conduction band are separated by a large (> 4eV) energy gap, which is a "forbidden" range of energies.
- Electrons must be promoted across the energy gap to conduct, but the energy gap is large, here.
- Diamond is an insulator with a band gap of about 6eV!!!!!







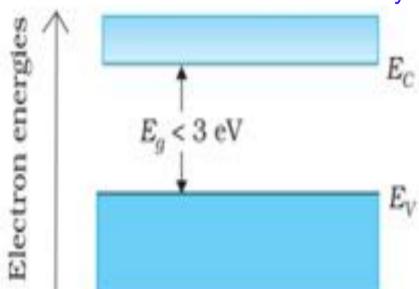
Insulators:



- □ At T = 0, lower valence band is filled with electrons and upper conduction band is empty, leading to zero conductivity.
- □ Fermi level E_F is at midpoint of large energy gap (2-10 eV) between conduction and valence bands.
- □ At T > 0, electrons are usually NOT thermally "excited" from valence to conduction band, leading to zero conductivity

Semiconductors:

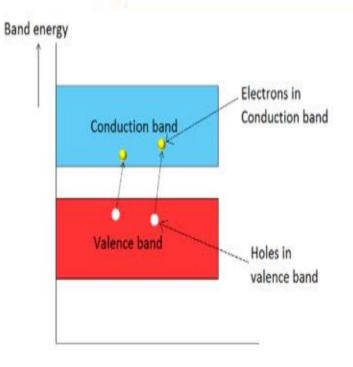
Band scheme for intrinsic conductivity in a semiconductor



A finite but small band gap (Eg < 3 eV) exists

At 0 K the conductivity is zero because all states in the VB are filled and all states in the CB are vacant

As the temperature is increased, there is a finite probability that an electron is thermally excited from the VB to the CB, where they become mobile. Such carriers are called "intrinsic."



When an electron is excited to CB from a VB it leaves behind an unoccupied state known as hole.

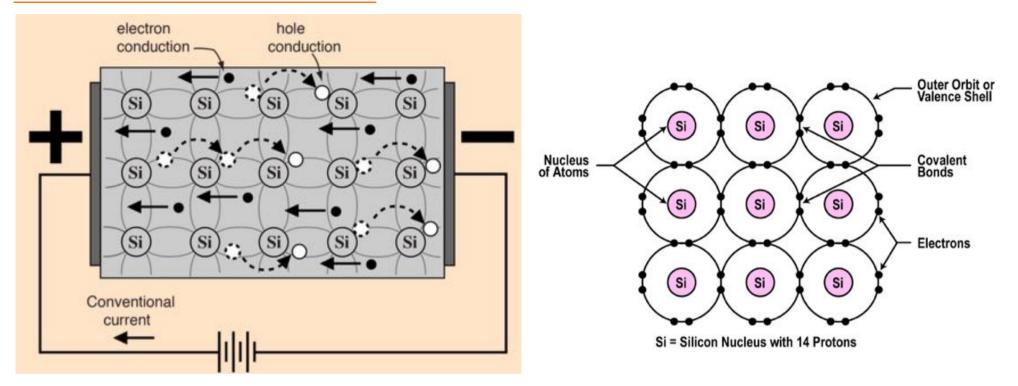
Holes are therefore absence/deficiency of an electron...

Hole is a positively charged carrier and has a charge equal to that of an electron but with an opposite polarity

Holes also participate in total conduction.

Holes in a semiconductor can move in crystal lattice like electrons and play an important role in conduction.

Semiconductors:



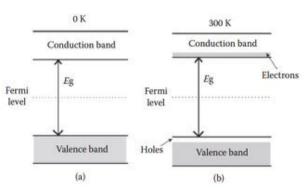
- The total current in the semiconductor on the application of voltage will be consisting of contributions from both the holes and electrons.
- Movement of the holes will be due to the jumping of neighboring electrons into the holes. Holes will move in opposite directions to the electrons and contribute positively to the current as they posses a positive charge.
- Holes have effective mass higher compared to their electron counterparts meaning that they are less mobile compared to electrons.

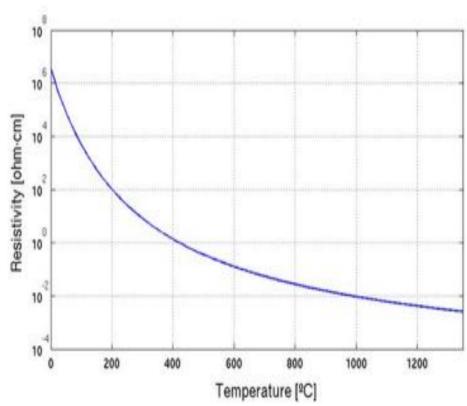
Semiconductors:

In an intrinsic semiconductor, the number of free electrons equals the number of holes.

As the temperature is increased the number of free electrons in the conduction band and holes in valance band increases.

Number of free charge carriers at a fixed temperature also depends on the energy gap of the semiconductor.





Resistivity behavior of intrinsic silicon material with the temperature.

- ➤ For large gap materials number of free electron and holes will lower compared to the material with small band gap at fixed temperature
- Light can also generate free electrons and holes in a semiconductor. Optical: The energy of the photons (hv) must equal or exceed the energy gap of the semiconductor (Eg).
- ➤ If hv > Eg , a photon can be absorbed, creating a free electron and left behind a hole.

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PYL102 Course Lecture-10 on 01-09-2021

Course coordinator: Rajendra S. Dhaka (Rajen)

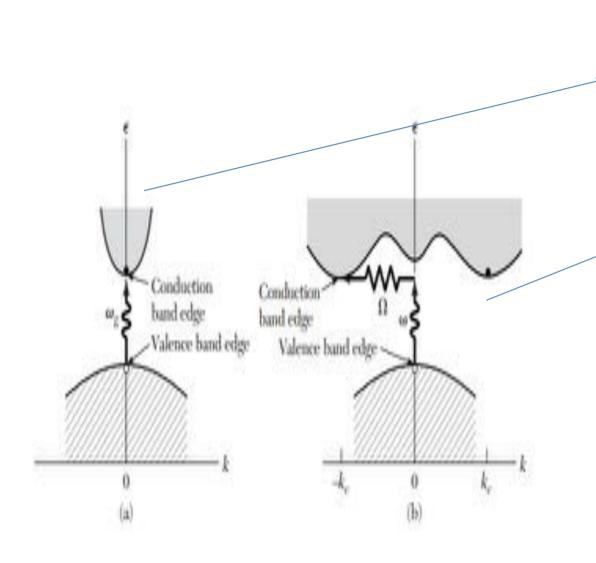
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PYL102:

Principles of Electronic Materials

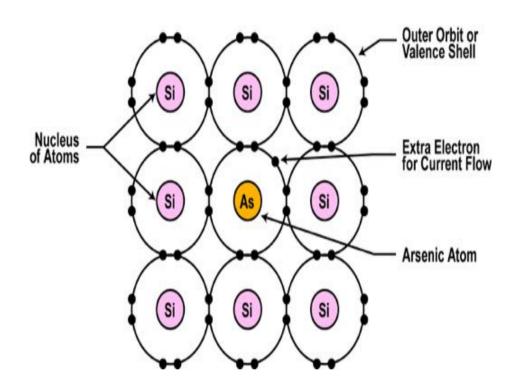
- > Energy bands in solids.....
- > Classification of electronic materials......
- > Understanding metal, semiconductor and insulator...
- Effective mass of charge carrier....

Direct and indirect band gap semiconductors:



- ➤ In the direct band gap semiconductors, the lowest point of the conduction band occurs at the same value of k as the highest point of the valence band.
- In indirect band gap
 semiconductors, the lowest of the conduction band and highest point of the valance band both exist at different values of K.
- ➤ The indirect transition involves both a photon and a phonon because the band edges of the conduction and valence bands are widely separated in k space as shown in (b)

Semiconductors can become conductor:



Bandgap Value	es of Several					
Common Semiconducting Materials						
Semiconducting	$E_{\rm g}$					
Material	Туре	(eV)				
Si	Elemental	1.12				
Ge	Elemental	0.67				
GaP	III-V compound	2.25				
GaAs	III-V compound	1.42				
CdS	II-VI compound	2.40				
ZnTe	II-VI compound	2.26				

- An impurity, or element like arsenic, has 5 valence electrons.
- Adding arsenic (doping) will allow four of the arsenic valence electrons to bond with the neighboring silicon atoms.
- The one electron left over for each arsenic atom becomes available to conduct current flow.

If an electron is travelling through a vacuum and being accelerated by an electric field, its motion can be described by Newton's laws of motion.

Newton's laws can also describe the motion of a free electron that is being accelerated within a crystal by the electric field produced by an applied voltage.

When an electric field E_x is applied to a metal, an electron near the Fermi level can gain energy from the field and move to higher energy levels.

The external force $F_{ext} = eEx$ is in the x direction, and it drives the electron along x.

The acceleration of the electron is still given by a = Fext/me, where m_e is the mass of the electron in vacuum.

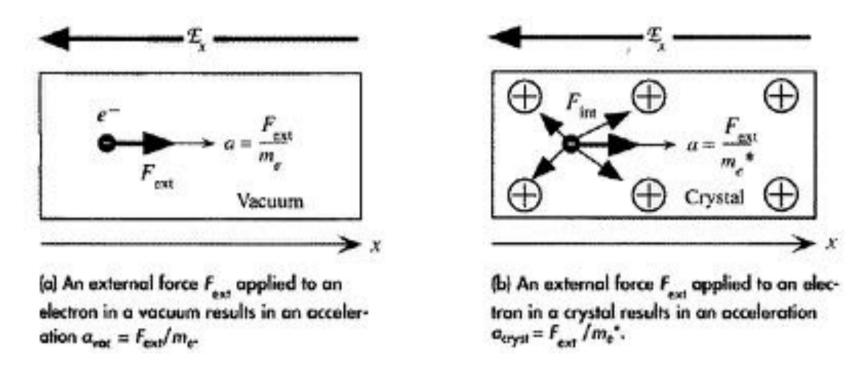
However, as the electrons are interacting with different potentials as they make their way through the lattice, in order for the simple Newtonian physics to work, the normal mass of the electron, m_e, must be replaced by the effective mass, m_e*.

An electron in crystal behaves as if it had a mass different from the free electron mass m_e, i.e., electron in a periodic potential is accelerated relative to the lattice in an applied electric or magnetic field as if its mass is equal to what is called an effective mass...

There are crystals in which the effective mass of the carriers is much larger or much smaller than m_e.

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The law $F_{ext} = m_e a$ cannot strictly be valid for the electron inside a solid, bcz the e-interacts with the host ions and experiences internal forces F_{int} as it moves around.....



The electron therefore has a PE that varies with distance.

Recall that we interpret mass as inertial resistance against acceleration per unit applied force. When an external force F_{ext} , is applied to an electron in the vacuum level, the electron will accelerate by an amount

 $a_{\rm vac} = \frac{r_{\rm ext}}{m_e} \qquad ----(1)$

as determined by its mass m_e, in vacuum...

When the same force F_{ext} , is applied to the electron inside a crystal, the acceleration of the electron will be different, because it will also experience internal forces, its acceleration in the crystal will be

$$a_{\text{cryst}} = \frac{F_{\text{ext}} + F_{\text{int}}}{m_e} \qquad ----(2)$$

where F_{int} is the sum of all the internal forces acting on the electron.....

To the outside agent applying the force F_{ext} the electron will appear to be exhibiting a different inertial mass, since its acceleration will be different.

It would be most useful for the external agent if the effect of the internal forces in F_{int} could be accounted for in a simple way, and if the acceleration could be calculated from the external force F_{ext} , this is indeed possible. How?

In a crystalline solid, the atoms are arranged periodically, and the variation of F_{int} , and hence the PE, or V (x), of the electron with distance along x, is also periodic.

In fact, when we solve the Schrodinger equation with the periodic PE, or V(x), we essentially obtain the effect of these internal forces on the electron motion.

It has been found that when the electron is in a band that is not full, we can still use eq.1 but we must use the effective mass m_e^* of the electron in that particular crystal....

The effective mass is a quantum mechanical quantity that behaves in the same way as the inertial mass in classical mechanics.

The acceleration of the electron in the crystal is then simply

$$a_{\text{cryst}} = \frac{F_{\text{ext}}}{m_e^*} \qquad -----(3)$$

The effects of all internal forces are incorporated into m_e*. It should be emphasized that m_e* can be obtained theoretically from the solution of the Schrodinger equation for the electron in a particular crystal. However, the effective mass can be readily measured....

	T		Bi							
$\frac{m_e^*}{m_e}$	0.99	1.10	0.047	1.01	1.12	1.28	1.2	28	13	0.85

The effective mass takes all of the complex interactions between the e⁻s and the lattice into account, & adjusts the classical equations enough for them to still be adequate...

In fact, when we look at the energy-wavevector relation $E = h^2k^2/2m$ for free electrons, we see that the coefficient of k^2 determines the curvature of E-k plot. This means we can say that 1/m, the reciprocal mass, determines the curvature.

For electrons in a band there can be regions of unusually high curvature near the band gap at the zone boundary, will discuss later...

PYL102 Course Lecture-11 on 02-09-2021

Course coordinator: Rajendra S. Dhaka (Rajen)

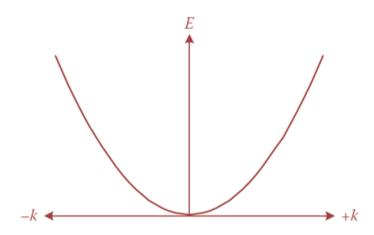
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PYL102:

Principles of Electronic Materials

- Classification of electronic materials....
- > Understanding metal, semiconductor and insulator...
- Effective mass of charge carrier.....
- Concept of phonons....

Let's see the example of free electron...



$$E = \frac{\hbar^2 k^2}{2m}$$

 $\frac{dE}{dk}$ = the slope of the curved line

 $\frac{d^2E}{dk^2}$ = the rate of change of the slope.

So, the mass of electron is inversely proportional to the curvature of band structure (rate of change of slope).

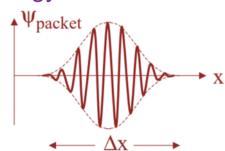
We shall now attempt to find an expression for the effective mass.

For this, we shall compare the acceleration of an electron in an electric field calculated by classical as well as by quantum mechanical means.

At first, we write an expression for the velocity of an electron in an energy band.

I hope you know the group velocity concept, the group velocity, i.e., the velocity with which a wave packet moves.

Let ω be the angular frequency and $|\mathbf{k}| = 2\pi/\lambda$ the wave number of the electron wave..



Then the group velocity can be written as:

$$v_{\rm g} = \frac{d\omega}{dk} = \frac{d(2\pi v)}{dk} = \frac{d(2\pi E/h)}{dk} = \frac{1}{\hbar} \frac{dE}{dk}$$

From the above equation, we can calculate the acceleration:

$$a = \frac{dv_{\rm g}}{dt} = \frac{1}{\hbar} \frac{d^2 E}{dk^2} \frac{dk}{dt}$$

As we know, $p = \hbar k$, we can write:

$$\frac{dp}{dt} = \hbar \frac{dk}{dt}$$

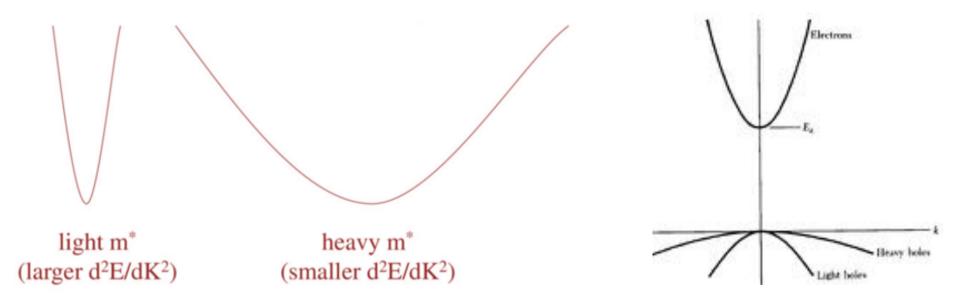
Now we can combine above two equations:

$$a = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2} \frac{dp}{dt} = \frac{1}{\hbar^2} \cdot \frac{d^2 E}{dk^2} \cdot \frac{d(mv)}{dt} = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2} F$$

where F is the force on the electron,

As we know,
$$F=ma$$
, we can write $m^*=\hbar^2\left(\frac{d^2E}{dk^2}\right)^{-1}$

- The effective mass depends on the curvature of band structure.
- > So, the velocity of the electron within a crystal strongly dependent on how the slope of the energy wave vector diagram changes.
- The effective mass is inversely proportional to the curvature of an electron band
- Now let's consider two different E-k diagram having different curvatures:



So now let's revise what information can we get from the band diagrams?

- 1) Allowed and forbidden bands. Identification of the gap energy.
- 2) Slope of the bands group velocity.
- 3) Curvature of bands effective mass.

Now let's inspect the band structures, we shall demonstrate the k-dependence of the effective mass for a simple case...

So, let's take an ideal electron band within the first BZ...

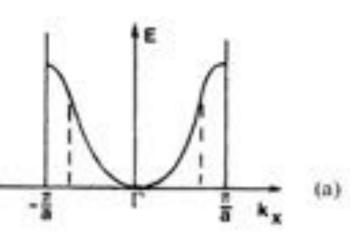
It is of importance to note that beyond a point the velocity decreases with energy, a feature which is altogether different from the behavior of free electrons..

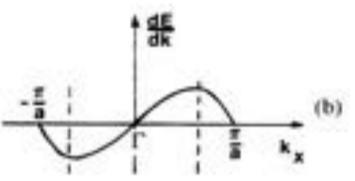
Point A represents an electron (with positive mass and negative charge)

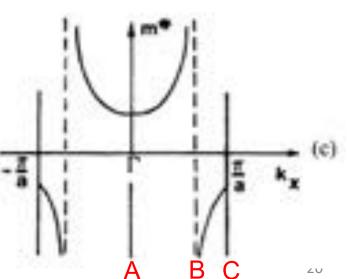
A particle near point B that has an infinite mass would be so heavy it could not move at all...

At point C, a negative effective mass means that the "particle" travels in the opposite direction to an applied electric force (and opposite to an electron.)...

This represents a particle known as a "hole" which can be thought of as having a positive mass and positive charge (equal in magnitude to the charge on the electron)







So far, when we have considered the atoms in a crystal lattice, we have assumed that they are stationary.

But, actually atoms never sit completely still. They always have some motion about their lattice point.

In fact if they did not, they would violate Heisenberg's uncertainty principle, which states that if the position of a particle is known exactly, its momentum cannot be known as well, and vice versa.

So although diffraction reveals the positions of the atoms in a crystal, it only in fact reveals the positions of the atoms at the instant they reflect the radiation being used in the diffraction experiment.

An instant later, their positions will have changed. However, this change in position is incredibly small, so it makes no difference to identifying a structure by diffraction.

Although the structure of a particular crystal may look the same when different diffraction patterns from it are analysed, there are other properties of crystals that are affected much more by the motion of the atoms about their lattice positions.

In particular the thermal properties of solids are entirely due to atomic motion.

Also, the electrical properties of solids are influenced by the vibrations of their atoms. ²¹

Since atoms in solids do not remain still at their lattice positions, they need some form of energy in order to be able to move.

This energy is either heat energy or mechanical energy. For example, the hotter a solid is, the more the atoms vibrate about their positions in the lattice.

Although atoms move much less at low temperatures than at high temperatures, they still move even at absolute zero, otherwise, it would violate Heisenberg's uncertainty principle for the atoms in crystals to be totally still.

This movement is known as zero-point motion, and the kinetic energy possessed by atoms with zero-point motion is termed "zero-point energy".

If an atom is considered individually, its motion about its own lattice point is approx. the same as that of simple harmonic motion (SHM).

However, atoms cannot vibrate independently of each other because they are connected together by bonds.

So any vibration in one atom gets passed on to its neighbours, which in turn pass the vibration on to their neighbours, and so on,

And, producing a vibratory wave that passes through the solid.

PYL102 Course Lecture-12 on 04-09-2021

Course coordinator: Rajendra S. Dhaka (Rajen)

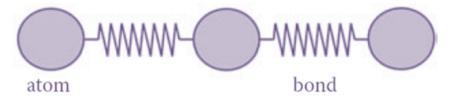
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PYL102:

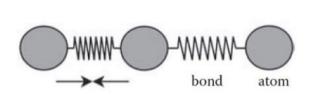
Principles of Electronic Materials

- Understanding metal, semiconductor and insulator....
- Effective mass of charge carrier......
- Concept of phonons......
- Thermoelectricity....

One way of thinking about the atoms in a crystal is as a collection of balls linked by springs, where the balls represent the atoms and the springs represent the bonds...



There are two ways in which an elastic wave—in other words, a wave that travels along because of the vibration of the particles of the material...



WWWW bond atom

an acoustic (longitudinal) wave

an optical (transverse) wave

Two representations of a wave travelling along a one-dimensional chain of atoms linked by atomic bonds.

Let's first talk about longitudinal waves, these are actually sound waves, although that does not mean sound waves in solids are audible.

They are sound waves simply because sound waves are longitudinal vibrational waves; that is, vibrational waves moving along the same direction as the vibration making up the wave?

So audible sound waves in air are produced by the same mechanism as sound waves in solids, but to avoid confusion, sound waves in solids tend to be referred to as "acoustic" waves...

The other way in which a wave can be set up in a solid is for the atoms to start oscillating in a vertical direction.

This sets up a transverse wave, in which the wave travels in a direction perpendicular to the direction of motion of the particles making it up, and since light is a transverse wave, these waves are known as "optical" waves.

In the same way that light can be regarded as either a wave or a stream of particles known as photons, vibrations in solids can be thought of either as waves or particles known as phonons.

This means that, as with other quantum mechanical particles, phonons can only have certain values of energy. In fact a phonon vibrating at a frequency ω can only have values of energy that are $\hbar\omega$ apart from one another.

If a phonon is thought of as a quantized packet of vibratory energy, a region of a solid containing larger amplitude atomic vibrations than another area can be said to contain more phonons. Equally, if a solid is considered as a whole, the greater the atomic vibrations are throughout the solid, the more phonons are said to be in the solid....

The particle nature of phonons means they can be considered to "move" through solids, and many properties of solids that are affected by temperature can be explained in terms of phonons being scattered.

This scattering can either be by point defects or dislocations, by one another, or by the surface of the solid. In each case there will be a mean free path, I, which represents how far a phonon travels on average before being scattered...

Phonons have a wavelength associated with them, that depends on the temperature of the solid... and the extent to which phonons are scattered by lattice defects....

There is actually a range of phonon wavelengths at all temperatures, but on average the phonon wavelength is longer at low temperatures and shorter at high temperatures.

In fact as a very rough guide, the dominant phonon wavelength can be considered to be in the order of a few hundred atomic spacings just above absolute zero, while at room temperature and above it is around twice the value of the lattice parameter, a.

This means that at low temperatures, the phonon wavelength is much larger than any point defect, so the defect is unable to scatter the wave.

Therefore, the amount of scattering is much less at low temperatures than that at higher temperatures, where the phonon wavelength is of a comparable size to that of the defects.

As higher temperatures mean a larger amount of movement of the atoms, and the larger the amplitude of any two waves the greater the chance of them interacting, the scattering of phonons by one another is also greater at higher temperatures.

Earlier we did not consider phonons, but still could get satisfactory results of many physical properties of solids, why?

The reason for this success is that the internal energy U of the solid can be written as

 $U = E_{\text{static}} + E_{\text{vib}}$, where E_{static} is the electronic ground state energy with a fixed lattice (on which we have focused so far) and E_{vib} is the additional energy due to lattice motion.

In general (and we will substantiate this below), $E_{\text{static}} >> E_{\text{vib}}$ and thus many properties are correctly obtained, even when simply neglecting E_{vib} .

Application/contribution of phonons:

- Lattice contribution to specific heat and thermal conductivity
- Elastic properties and structural phase transitions
- BCS theory of superconductivity

Home assignment:

Find the dispersion relation for phonons in solid?

Phonons are quantized lattice waves; these are quasi-particles associated to the lattice vibration...

Phonons are characterized by a frequency ω and a wavevector k with a dispersion relation, basically phonons are bosons, described by symmetric wavefunction...

PYL102 Course Lecture-13 on 06-09-2021

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PYL102:

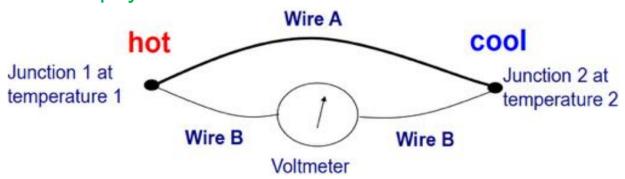
Principles of Electronic Materials

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- > Thermoelectricity....

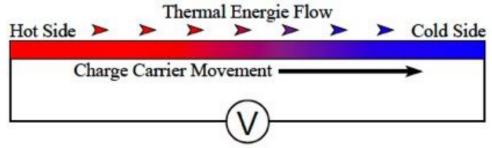
The word **thermoelectric** means the production of the electricity by the means of the temperature difference...

The Seebeck effect: In 1820-21, German physicist discovered that when two dissimilar

metals, Cu and Bi are joined at the ends to form a loop, a voltage is developed in the circuit if the two junctions are kept at the different temperatures.



The pair of metals forming the circuit is called a thermocouple.



As energy flows from the higher energy to the lower energy, the heat will flow from the hot surface to the cold surface.

The conduction of the heat inside the material can be transferred by the various routes:

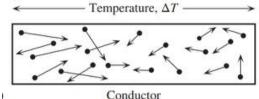
- Phonons
- Ionic conductors i.e. ions
- Mobile carriers: electrons and holes

Creation of thermal emf (electromotive force) by temperature gradient

The Seebeck Effect is relevant to the operation of thermocouples for temperature measurements.......

Electrons at the hot end being more energetic, have higher velocities than the electrons in the cold end.

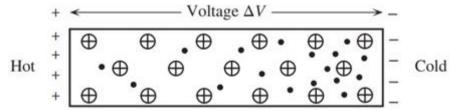
Net diffusion of the electrons from the hot end to the cold end



Positive ions at the hot end and the electrons accumulates at the cold end

This situation prevails until the electric field developed between the positive ions in the hot region and electrons in the cold end prevent the electronic motion at both ends.

❖ A voltage is developed between both the ends, with the hot end at the +ve potential.

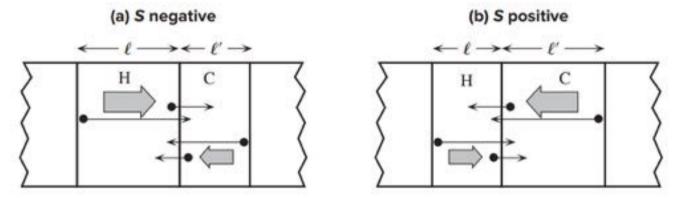


- **...** The potential difference ΔV across the piece of metal as a result of the temperature difference ΔT is called the **Seebeck Effect.**
- The magnitude of Seebeck effect is defined by the coefficient, which is the potential difference ΔV per unit temperature difference;
- ❖ S = Seebeck Coefficient or Thermoelectric Power

By convention,

the sign of *S* represents the potential of the cold side with respect to the hot side. If electrons diffuse from the hot end to the cold end, then the cold side is negative with respect to the hot side and the Seebeck coefficient is negative (as for aluminum)...

However, copper has positive Seebeck coefficient... how to understand this?



The net diffusion process depends on how the mean free path ℓ and the mean free time (due to scattering from lattice vibrations) change with the electron energy.

Consider a hot region (H) and cold region (C) with the widths proportional to the mean free path lengths \(\ell\) and \(\ell'\) in the hot and cold regions. The electron concentration (n) in the hot and cold regions is roughly the same.

- ✓ Half of the electrons move in the +x direction and other half move in the -x direction
- ✓ Half of the electrons in H therefore cross into C, and half in C cross into H
- ✓ No. of electrons travelling from H to C is (1/2)nℓ and the no. of electrons travelling from C to H is (1/2)nℓ and the no. of electrons travelling from C to H is (1/2)nℓ has been determined by the control of the co

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Net diffusion from H to C
$$\propto \frac{1}{2}n(\ell - \ell')$$

For $\ell > \ell'$, as in Fig. (a), scattering of electrons is such that ℓ increases strongly with the electron energy. Then electrons in H, which are more energetic, have a longer mean free path.

This implies that the net migration is from the hot region to the cold region and S is –ve..

For metals such as Cu, ℓ decreases strongly with the energy, electrons in the cold region have a longer mean free path, $\ell' > \ell$ as in Fig. (b).

The net migration of the electrons is from the cold region to the hot region and S is +ve.

Seebeck effect arises from the diffusion of the electrons via different scattering processes alongwith a temperature gradient, called as electron diffusion contribution.

The other driving force is the thermal vibrations that setup the lattice waves which travel inside the crystal, called as phonons.

- Lattice waves will flow from the hot to the cold region.
- Lattice waves will collide with the electron, scatter them and push them along the temperature gradient
- Collision of the phonons with the electrons drags them along with the phonons and creates potential difference, this contribution is called as phonon drag contribution.32.

Seebeck coefficient is not constant, but dependent on the temperature!!!

S is a material property, a function of temperature, S =S(T)

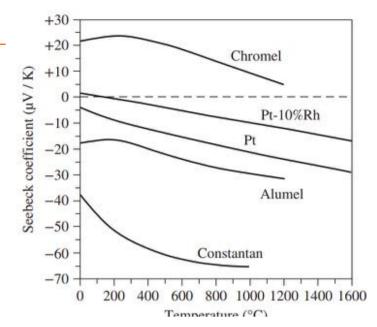
From eqn.1, given the Seebeck coefficient S(T), the voltage difference between the two temperatures T_o and T is given as:

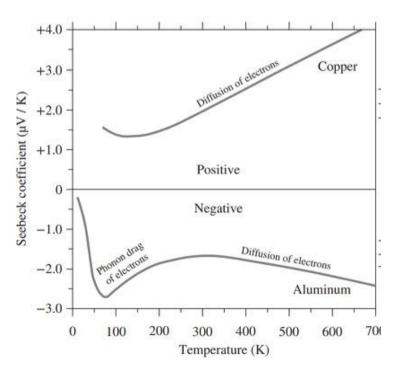
 $\Delta V = \int_{T_o}^{T} S \, dT$

S is positive for Copper and negative for Aluminium.

In both cases, around and above room temperature, the magnitude of *S* increases almost linearly with the temperature.

For pure metal AI, S arises from the diffusion of the electrons and phonon drag (collision of phonons with the electrons causes the electrons to be dragged with the phonons) $S \approx aT + \frac{b}{T}$





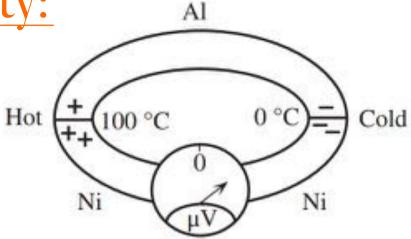
Seebeck Effect is utilized in the thermocouple.

Thermocouple uses two different metals with one junction maintained at a reference temperature T_o and the other used to sense the temperature T.

- The voltage across each metal element depends on the Seebeck Coefficient.
- The potential difference between the two wires will depend on the S_A – S_B
- The electromotive force between the two wires is given as:

$$V_{AB} = \Delta V_A - \Delta V_B$$

$$V_{AB} = \int_{T_o}^{T} (S_A - S_B) dT = \int_{T_o}^{T} S_{AB} dT$$





connected to multimeter



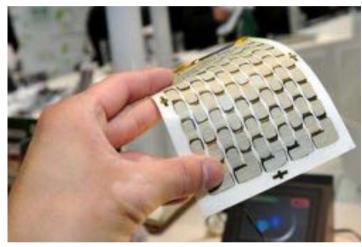
Here $S_A - S_B$ is defined as the **thermoelectric power for the thermocouple pair** $A\!-\!B$.

Applications of thermoelectricity:

- Temperature difference across a solid produces thermally generated emf which can drive current through a load (power generation)....
- Driving current through the same solid results in heating in one contact and cooling in another (refrigeration)...



RTG converts heat from the natural radioactive decay of plutonium into electricity.



Mars Science Laboratory



Thermoelectric converter module

TEGs can be used to harvest 100s of W ₃₅

Applications of thermoelectricity:

Energy Harvesting from Waste Heat

- Almost everything we do wastes heat
- Power generation
- Transportation (engine + friction)
- Computing

TEs could play a big role in waste heat recovery

- Cooling in small size applications (e.g. lasers, seats, cup holders)
- What matters is not just efficiency, but cost per Watt
- Many groups are looking at polymer TEs even though efficiency is lower than traditional semiconductors, paralleling work in solar cell community
- Power generation in communities without power plants and electric grid
- TE modules in cooking stoves and solar thermal systems

In fact, body heat powered watches already demonstrated.. usable power from the body

thermoelectrics could be a solution