Session 18

Condensed matter

Dr. Samuel Atarah

Physics Innovations Centre
for Excellence in Learning and Teaching

πCETL (Leicester)

Department of Physics and Astronomy

University of Leicester

Contents

Welcome

Welcome to session 18.

In this session we'll look at certain macroscopic properties of solids that result from the quantum mechanical behaviour of electrons. This field of physics initially concerned just the behaviour of solids so was referred to as solid state physics. It has been called condensed matter physics since the late 1960s, when it was realised that the type of collective behaviour extended beyond that of electrons in solids to many other systems such as, for example, superfluids.

Session Author

Dr. Samuel Atarah , University of Leicester.

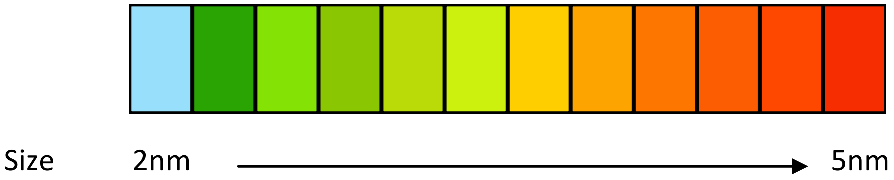
Session Editor – Tim Puchtler

Learning Objectives

- Show knowledge of the free electron model of metals and the Fermi distribution
- Show a knowledge of the origin and significance of band theory
- Classify solids by their energy bands structure
- Discuss examples of semiconductor devices
- Define positive and negative (p- & n-type) semiconductors
- Use the Uncertainty Principle to explain the special properties of nanoparticles

The Problem

The picture shows the range of colours that can be produced using the photoluminescence of Cadmium Selenide (CdSe) nanoparticles. The range in sizes of the nanoparticles are shown:



The particles fluoresce when stimulated, for example by light. By emitting a range of colours, nanoparticles, also called quantum dots, behave differently from the bulk material. The different colours arise from particles of different sizes. They can be used as tags in a variety of situations (for example as biomarkers) or as sources of light (for example in displays). One condition for this to be possible is that the colours are stable to changes in temperature. For example if we wanted to use a large number of markers how close could they be in size and wavelength? So our problem is to investigate the changes in wavelength we might expect from a suspension of nanoparticles as the temperature changes. Is this also different from the behaviour of the bulk material?

Learning Issues

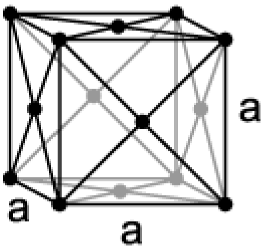
- What is a nanoparticle?
- What type of material is CdSe?
- What is the difference in structure between metals, insulators and semiconductors?
- Why does CdSe emit light?
- Why do nanoparticles emit differently from the bulk material?
- What properties of a material change with temperature?

Free Electron Model

Crystalline solids

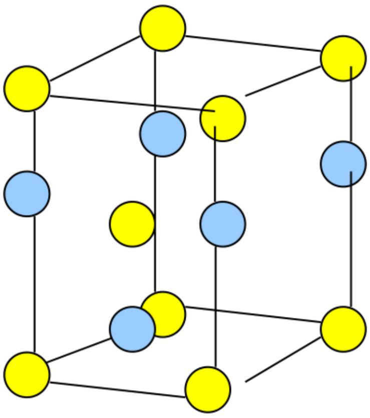
Ionically bonded solids have a crystal structure with the atoms arranged in a regular pattern. For example:

Face centred cubic crystal (e.g Copper)



Image[1]

"Wurzite" crystal structrure. eg CdSe:



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[1] Cubic, face-centered en:crystal structure, Daniel Mayer, DrBob, as posted on commons.wikimedia.org, Creative Commons Licensed

Free electron Model

When atoms are brought together to form a metallic solid, we think of the outer electrons as no longer attached to individual atoms, but free to move through the crystal lattice. The simplest assumption is that the electrons are entirely free and interact neither with each other nor with the atoms of the crystal lattice. This is the free electron model.

This is therefore the “particle in a box” picture that we met in quantum mechanics.

To illustrate the model and introduce some important ideas we shall calculate the specific heat of the electrons, and their electrical and thermal conductivity.

We begin by recalling the number of quantum states available to an electron in phase space, where phase space is the 6-dimensional space comprising 3 spatial dimensions and three momentum dimensions. In one space dimension (and one momentum dimension) we found one state in an area h of phase space, where h is Planck’s constant. In three dimensions there is one state in every h^3 of phase space.

Fermi Energy

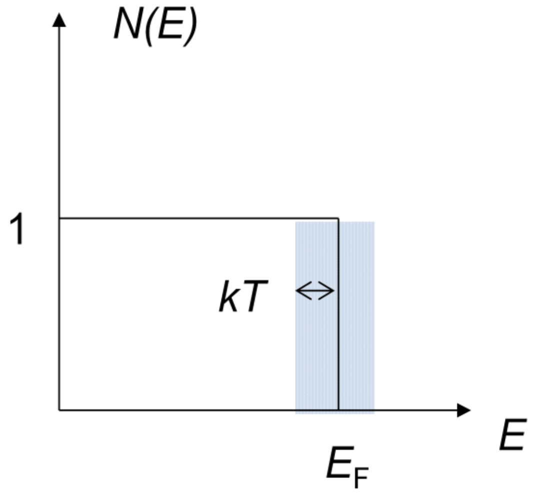
We’ll see that at normal temperatures the electrons in a metal cannot be treated as classical point masses: we have to consider them quantum mechanically. So next we look at the distribution of electrons amongst the possible quantum states.

$$N = 2 \times \frac{V \times \frac{4}{3}\pi p^3}{h^3} = \frac{8\pi}{3} V \frac{(2mE)^{3/2}}{h^3} \qquad (1)$$

$$E = \frac{p^2}{2m}$$

Equation 1 tells us the number of electron states in a volume V of physical space and a volume $4/3\ \pi\ p^3$ of momentum space. So it gives us the number of states with a momentum less than or equal to p in the volume V of the crystal. The initial factor of 2 arises from a property of electrons called spin. Other things being equal, an electron can have 2 spin states. In the final expression in equation 1 we’ve replaced momentum by energy using $E=p^2/2m$, where m is the electron mass.

How are the electrons actually distributed amongst these states? At the absolute zero of temperature the answer turns out to be straightforward: the states are filled by electrons from the lowest energy upwards with no two electrons in the same state. The fact that no more than one electron can be in a given state is the Pauli Exclusion Principle which we met when we were considering the structure of atoms.



Filling up the states one at a time we eventually run out of electrons. The energy of the last electron is called the Fermi energy, E_F. Actually the electrons are indistinguishable, so the "last electron" is a convenient fiction here. The value of E_F for a given density of electrons can be calculated by rearranging equation 1. The result is shown as equation 2.

The energy of the last electron in it's ground state is given by the Fermi energy:

Fermi Energy $$E_F = \frac{1}{2m}\left(\frac{3h^3}{8\pi}\frac{N}{V}\right)^{2/3} \qquad (2)$$

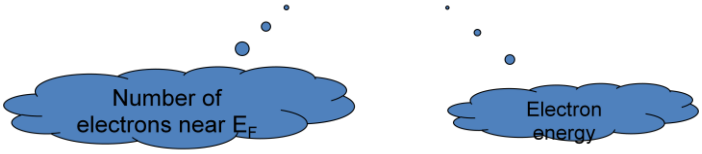
Pauli Exclusion Principle: no two electrons can occupy the same quantum state

Specific heat of free electrons

Here we estimate the contribution of electrons to the specific heat of a metal in the free electron model.

Equation (1) gives the estimate of the thermal energy of the free electrons at temperature T.

$$U \approx \left(\frac{kT}{E_F} \times N \right) \times kT \qquad \text{(1) (Energy of electrons)}$$



valid if $kT \ll E_F$ *i.e.* $T \ll E_F/k$

Let's explain how we get this: Most of the electrons cannot change their energy because there are no unfilled states for them to go to. So these electrons do not in effect contribute to changes in thermal energy. Only electrons near the Fermi level can contribute. A typical energy for an electron at a temperature T would be 3/2 kT. We don't need to worry about the factor of 3/2 if we're just estimating orders of magnitude, which is the best we can do here. So let's say the mean thermal energy of an electron is kT. Thus only those with an energy within kT of the Fermi energy can be excited into a vacant level, and of course they each contribute kT to the thermal energy. The thermal energy of the electron gas is therefore kT (for the energy of the electron) times kT/E_F which is the fraction of the total number of electrons that can be affected by the addition of heat, times the total number of electrons N.

Finally, equation 2 gives an approximation for the specific heat of the metal up to a numerical factor of $\pi^2/2$, which of course we cannot obtain from an order of magnitude estimate.

$$C = \frac{dU}{dT} \approx Nk \frac{kT}{E_F} \propto T \qquad \text{(2) (Specific heat of electrons)}$$

(+ cubic term from lattice vibrations)

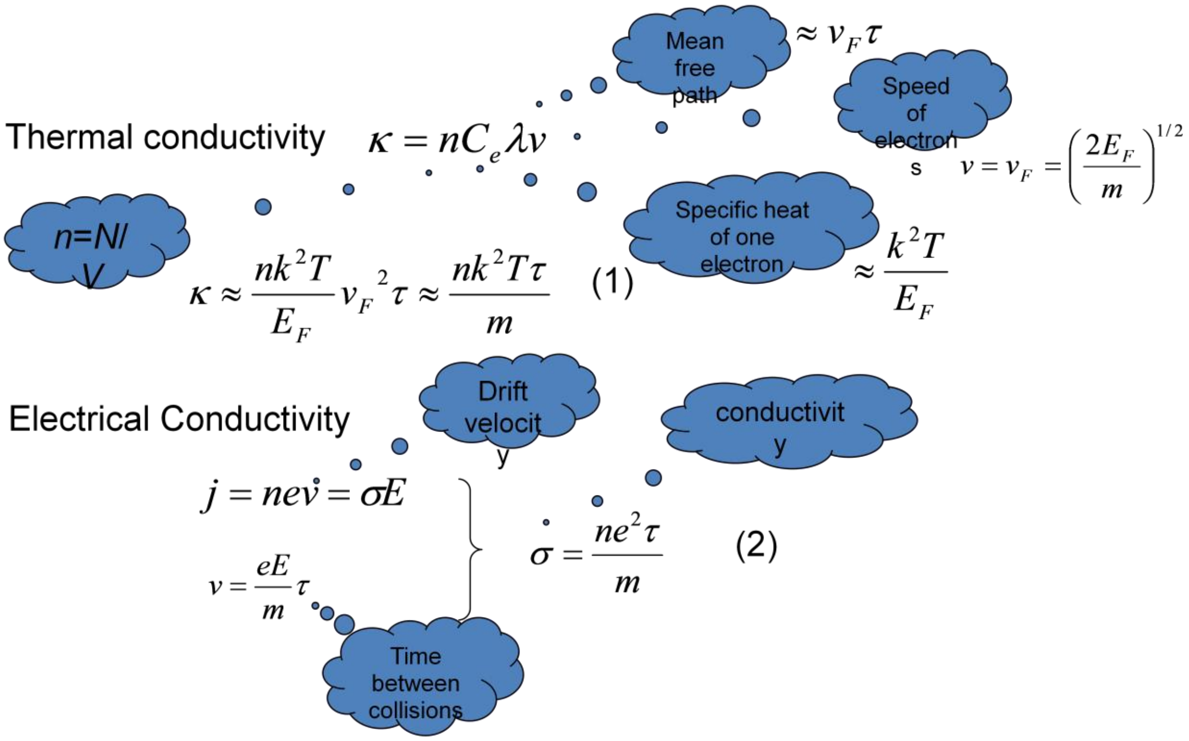
Equation 1 is valid only for temperatures such that kT is much less than the Fermi energy, E_F, since the fraction of electrons contributing to the specific heat cannot be greater than 1. At higher temperatures classical physics gives a constant specific heat of 3/2Nk for the electrons. For these purposes, low temperature means anything below the Fermi energy divided by Boltzman's constant. This is typically around 40 000K for a metal, so in practice the electrons in a metal must always be treated quantum mechanically.

At low temperatures the specific heat is proportional to temperature. In fact, we've simplified this somewhat. The quantised vibrations of the atoms of the crystal lattice (called phonons) contribute to the specific heat a T^3 term. But this can be neglected at low enough temperatures compared with the free electron gas term proportional to T. This predication is one of the big successes of the free electron model.

Transport properties

Turning now to transport properties we'll work out the thermal conductivity and the electrical conductivity in the free electron model. The thermal conductivity can be guessed from session 17 where we considered diffusion: thermal conduction is just the rate of diffusion of heat, so the conductivity is just the diffusion constant times the specific heat per unit volume of electrons. The diffusion constant is the mean free path λ times the mean speed v. And the specific heat per unit volume is just the number of electrons per unit volume, n, times the specific heat per electron Ce, which we found in the previous section.

However, just as we found for the specific heat, only the electrons near the Fermi level can change their state, so only these electrons can transport heat. Thus the appropriate mean speed is not the speed corresponding to a thermal energy kT, but the speed of an electron at the Fermi energy. This is also the case for the mean free path – only electrons at the Fermi energy can collide so the mean free path is the collision time τ multiplied by the speed of electrons at the Fermi energy. We end up with equation (1) for the thermal conductivity. Notice that the derivation involves quantum mechanics, which gives rise to the Fermi level, in an essential way. Also, it's only valid for metals: for insulators it's the vibrations of the atomic lattice that transport heat by conduction, whereas in metals this contribution is relatively small.



Thermal conductivity $\kappa = nC_e\lambda v$

$$\lambda \approx v_F\tau \qquad v = v_F = \left(\frac{2E_F}{m}\right)^{1/2} \qquad C_e \approx \frac{k^2T}{E_F}$$

$$\kappa \approx \frac{nk^2T}{E_F}v_F{}^2\tau \approx \frac{nk^2T\tau}{m} \qquad (1)$$

Electrical Conductivity

$$j = nev = \sigma E$$

$$v = \frac{eE}{m}\tau$$

$$\sigma = \frac{ne^2\tau}{m} \qquad (2)$$

The electrical conductivity σ is defined by the equation j, the current density, equals sigma times the electric field E. The current density is j = nev, where n is the number of electrons per unit volume and v their speed. The speed of an electron can be estimated as the acceleration times time; the force on an electron in an electric field E is its charge times E, so the acceleration is eE/m. Putting this together gives us equation (2). From (1) and (2) we can derive the Wiedermann- Franz law that the ratio of thermal to electrical conductivity is proportional to temperature.

Derive the Wiedermann-Franz law: κ/σT = constant

Estimates for sodium

In this section we've put together some numerical values for the metal sodium. Sodium crystallises as a cubic structure with an additional central atom. This cube has side 42 nm and contains two atoms – one in the centre and one made up from the atoms at the corners of the cube. Each atom contributes one free electron. So the number of electrons per unit volume is $N/V = 2/(0.42\text{nm})^3 = 3 \times 10^{28}\ \text{m}^{-3}$.

The Fermi energy ($E_F = \frac{1}{2m}\left(\frac{3h^3}{8\pi}\frac{N}{V}\right)^{2/3}$) is 3.5 eV and the speed of electrons with this energy, from the usual 1/2mv^2 for kinetic energy (so $v=(2E_F/m)^{1/2}$), is 10^6 metres per second. This is much faster than the thermal average of root 3 kT/m at room temperature.

Compare this speed with $\sqrt{\frac{3kT}{m}}$ the thermal speed at room temperature.

Summary

- The free electron theory of metals accounts for their specific heats (proportional to temperature at low temperatures), their conductivities and the Wiedermann-Franz law
- It does not account for the distinction between metals and insulators or the existence of semi-conductors

SAQs

1. The lattice can be ignored in the free electron model because

   (a) The electron mfp is many lattice spacings

   (b) The electron mfp is less than a lattice spacing

   (c) It is electrically neutral

2. The Fermi energy in a metal is

   (a) The mean energy of the free electrons

   (b) The total energy per unit volume of the free electrons

   (c) The maximum energy of a free electron

   (d) The energy required to liberate a valence electron from an atom

3. The specific heat of a metal is less than kT per atom because

   (a) the atoms are fixed in the crystal lattice

   (b) the EP means that only electrons near the Fermi level can be excited

   (c) the EP means that electrons are excluded from sharing energy

The answers appear on the following page

Answers

1. (a) correct: the electron mfp is much larger than the spacing of atoms in the crystal lattice, so electrons interact only with the constant average potential, which corresponds to zero electric field.

   (b) Incorrect: if the mfp were less than a lattice spacing the electron would be subject to a highly variable filed.

   (c) Incorrect: the overall structure is neutral but negatively charged electrons interact (in principle) with positively charged ions in the lattice

2. (a) Incorrect: the Fermi energy is related to the mean energy, but is in fact the maximum energy of the occupied states

   (b) Incorrect: the Fermi energy is related to the total energy, but is in fact the maximum energy of the occupied states

   (c) Correct: the available quantum state are filled from that with the lowest energy up to that with the Fermi energy

   (d) Incorrect: this would be the ionisation energy

3. (a) Incorrect: the vibrations of the crystal lattice contribute a quantity proportional to T^3 which is small compared to kT at low temperatures

   (b) Correct: electrons can interact only if their energies can change. (Swapping energy would make no difference since the electrons are indistinguishable.) If all the available levels are filled therefore, electrons cannot interact. Near the Fermi energy there are unfilled states available.

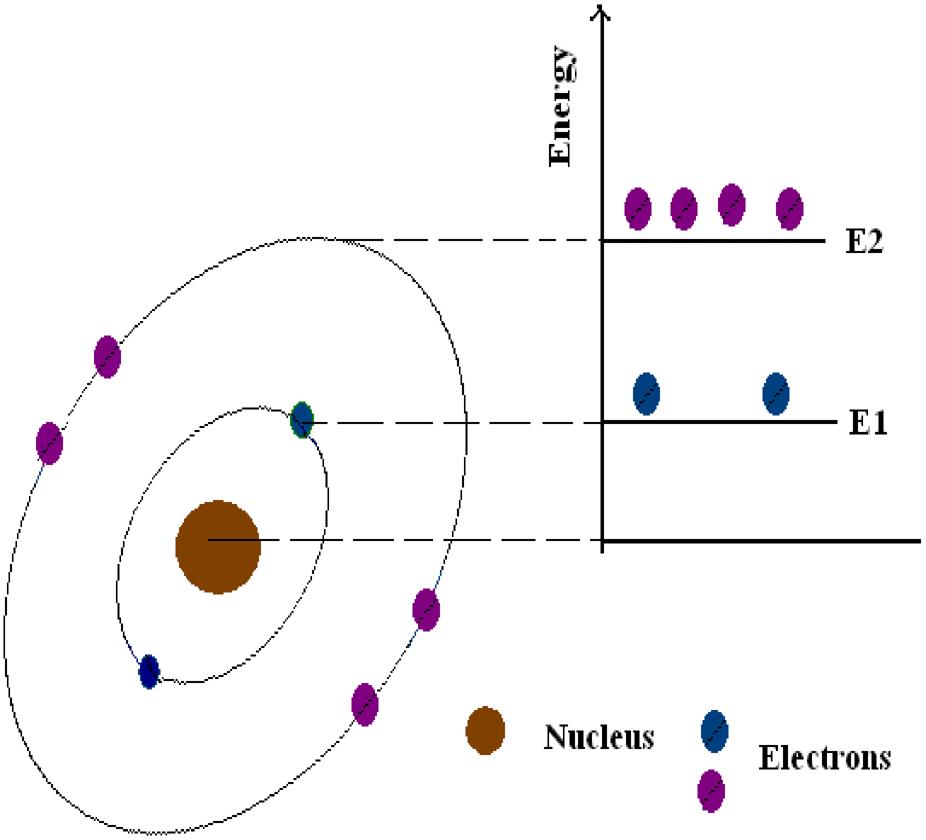
   (c) Incorrect: electrons can share energy provided there are unfilled states available.

Band Theory

Here we study the affect of the interaction between the atoms of a solid. We'll see that it leads to bands of allowed energies for the electrons in the solid, in contrast to the free electron model which put no restrictions on the allowed energies. This has profound effects on the macroscopic properties of non-metals.

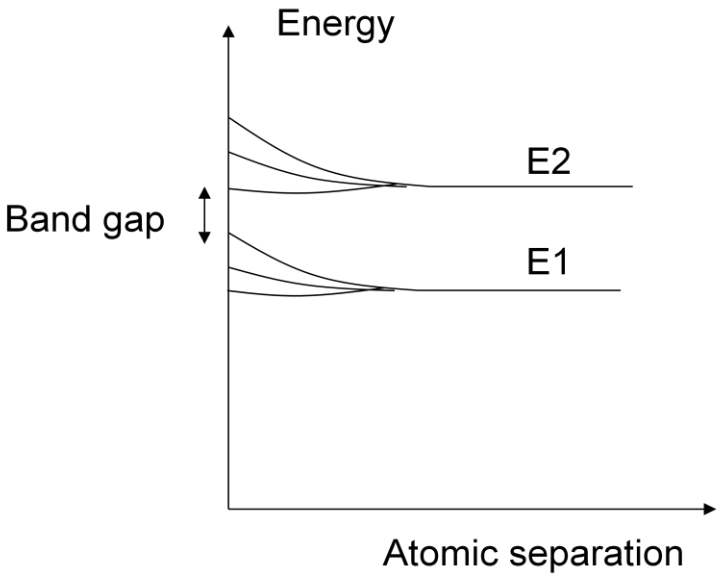
Electrons and energy levels

Electrons in an isolated atom are arranged in discrete energy levels. Energies between the levels are not allowed states for the atomic electrons.



When two atoms are close on the atomic scale, they perturb each other's energy levels. The energy levels each split: in a collection of N atoms each level in the isolated atom splits into N sublevels. The sublevels can be considered to be continuous bands.

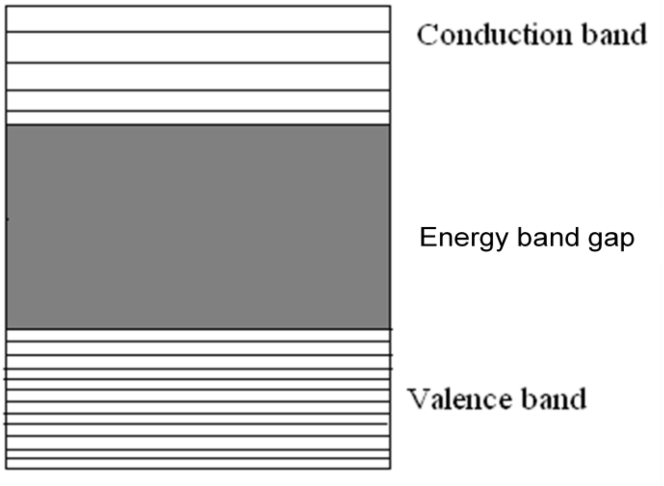
In a crystalline solid, discrete energy levels of the isolated atoms become bands of closely spaced levels. The perturbation of the energy levels of the inner electrons is small so these bands are narrow and the gaps between them are large. The energy levels of the outermost electrons form broader bands separated by narrower gaps. These are the band gaps.



The allowed bands of energy levels may overlap or be some way apart in energy, so the energy band gaps can range from zero to relatively large: it is this difference that defines the properties of the solid as conducting or non-conducting.

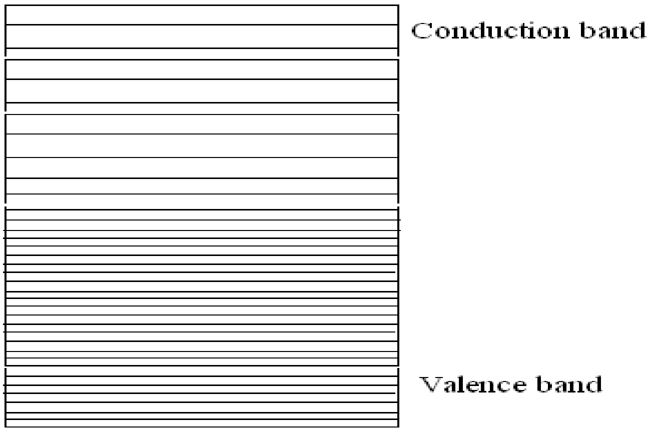
Energy bands

The energy levels of electrons in solids are divided into bands separated by gaps. The lowest energy bands are filled with electrons that would otherwise occupy the lower energy levels in the isolated atom. More energetic electrons occupy higher energy bands available from splitting of the next higher energy level. The outermost electrons in a solid are thus separated into two bands: ‘low’ and ‘high’ bands. The highest energy level that can be unoccupied by electrons in the lower band is the top of the **valence** band. The lowest energy level that can be occupied by electrons in the higher band is called the base of the **conduction** band. As its name implies, electrons in this band contribute to conduction. The separation between the valence and the conduction band is known as the forbidden **energy band gap**. Electrons cannot have energies in this energy gap.



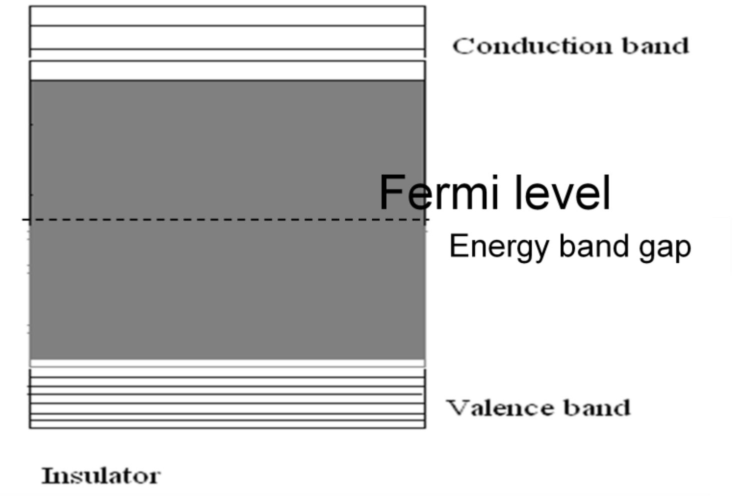
Conductors, insulators, semiconductors

In some solids, the valence and conduction bands virtually overlap and there is no forbidden energy gap. This means that at least some of the valence electrons are free to move through the material and hence to conduct electricity and heat. This type of solid is therefore a good conductor.

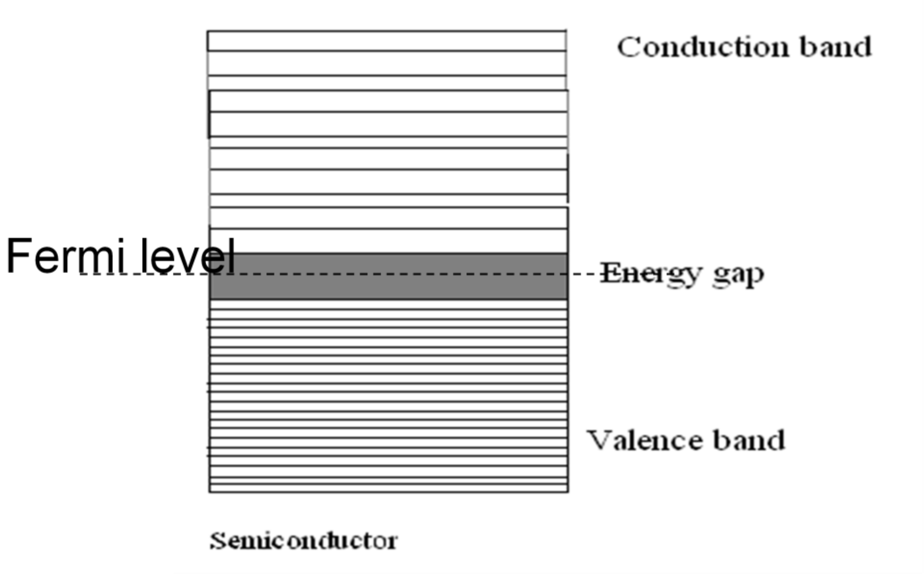


Conducor (Metal)

In other solids however, the valence band is completely filled with electrons and a large energy gap separates the valence and conduction bands. The Fermi level lays mid way between the two bands. To be promoted to the higher band an electron in the valence band has to acquire the band gap energy. In these solids the band gap energy is larger than the thermal energy of the electrons at ordinary temperatures, so few, if any, electrons are promoted. This type of solid is a bad conductor or an insulator.



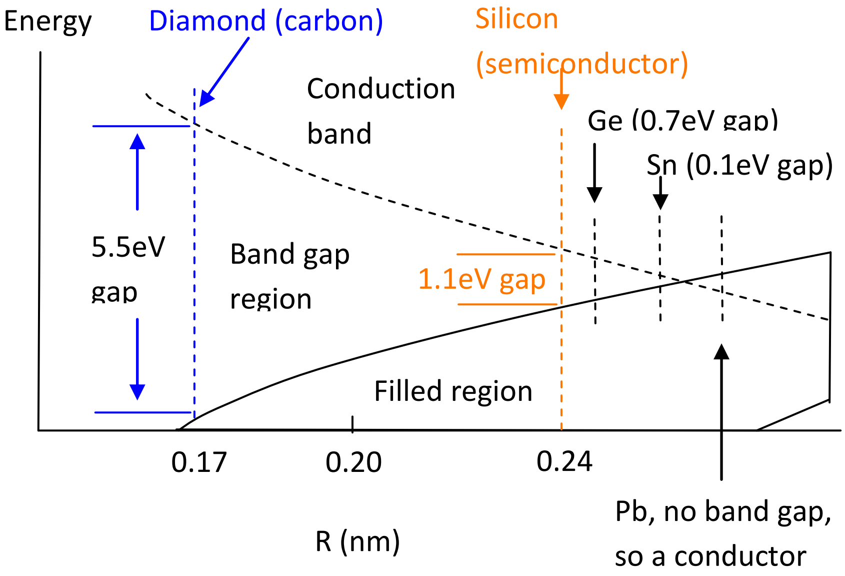
In contrast to insulators and conductors, a third class of solids have a completely filled valence band and a small energy gap between the valence band and the empty conduction band. With an energy of the order of 1 eV, electrons can make transitions to the conduction band where they contribute to conduction. At T= 0 K there are no electrons in the conduction band and the material is an insulator. At room temperature some electrons are excited into the conduction band and the material can conduct electricity. These solids are called semiconductors.



Semiconductors are termed **intrinsic** semiconductors if they are pure substances and **extrinsic** if they are mixed, or doped, with elements from group 3 or group 5 of the periodic table. Intrinsic semiconductors are very poor conductors because the band gap is of order 1 electron volts, which is significantly greater than the thermal energy at room temperature of around 0.25 electron volts.

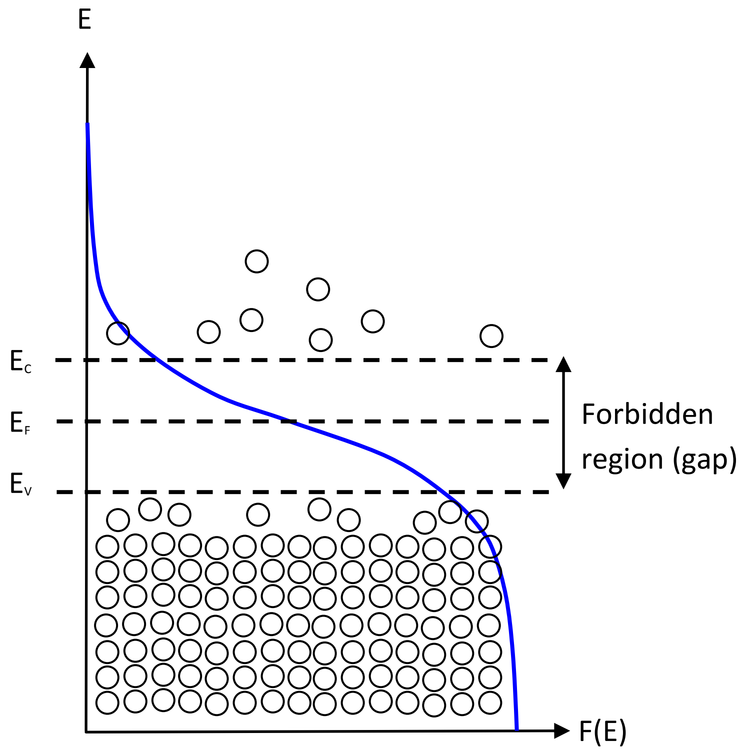
The change in band gap with interatomic spacing

Here we show some examples of the change in width of the band gap as a function of interatomic spacing. Again we see how semiconductors lie between conductors and insulators. Note that when elements can take on different crystalline forms the band gaps can be different for the different structures.

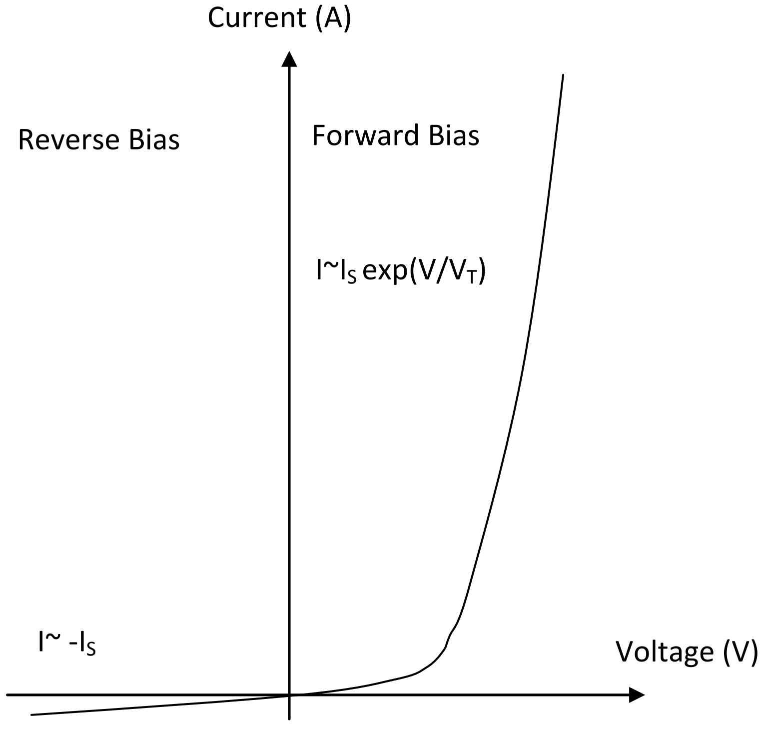


At temperatures above absolute zero some electrons in a semiconductor are excited above the band gap into the conduction band. The electrical conductivity therefore increases with temperature.

Since there are now vacant states in the valence band, the electrons in this band can also interact with an applied field and thereby contribute to the electrical conductivity. It turns out to be easier to think of this contribution in terms of the minority vacant states. Promoting an electron into the conduction band leaves a vacancy or 'hole' in the valence band. Since the absence of a negative charge is a positive charge the holes are positively charged. Thus, as we'll see, the behaviour of a semiconductor is usually described in terms of the excited electrons and their partner holes.



The number of electrons in the conduction band also increases exponentially with applied voltage. Since the change in the number of charge carriers affects the conductivity, a semiconductor does not obey Ohm's law. A graph of current versus applied voltage for a semiconductor is shown below.



Summary

- The discrete energy levels of isolated atoms form bands when atoms are brought together in bulk
- The number of states in a band equals the number of atoms in the solid. For macroscopic materials therefore the bands can be considered as a continuum
- The bands do not in general overlap and are separated by energy gaps.
- The width of the band gap determines the behaviour of the material i.e. whether it is a conductor, insulator or semiconductor.
- In a semiconductor electrons can be thermally excited from the valence to the conduction band leaving a hole in the valence band which behaves as a positively charged particle.

SAQs

Answer (a) True or (b) false?

In an insulator:

1. The electrons remain attached to their parent atoms
2. The electron energies all lie below the Fermi level
3. The gap between the conduction and valence bands exceeds the Fermi energy

In a semiconductor:

4. The gap between the conduction and valence bands is less than the Fermi energy
5. The Fermi energy lies half way between the valence and conduction bands
6. Electrons can be promoted to the conduction band by the introduction of positively charged protons

7. Diamond is a good conductor of heat.

The answers appear on the following page

Answers

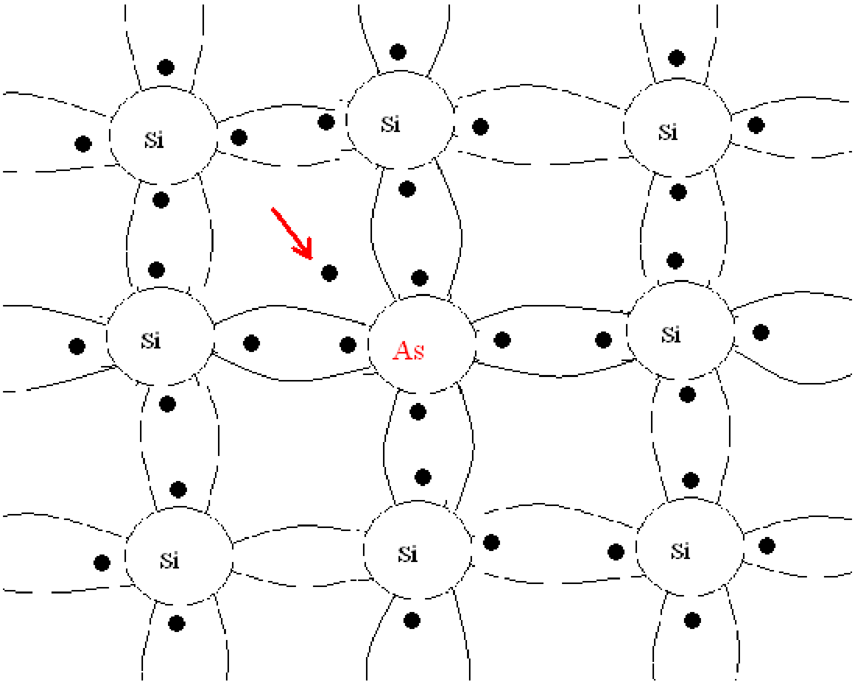
1. (b). An insulator has a band structure: this arises because of the splitting of levels as a result of interactions between the atoms
2. (a) the Fermi level lies mid way between the valence and conduction bands; in an insulator the conduction band is empty
3. (b) The gap exceeds the thermal energy at room temperature but the Fermi energy is generally much larger and bears no relation to the size of the band gap.
4. (b) This is generally untrue: the band gap is greater than the thermal energy which is *less than* the Fermi energy, so there is no single order
5. (a) True
6. (b) A positively charged hole is created in the valence band when an electron is promoted thermally to the conduction band.
7. False: the large band gap (as shown in a previous diagram) means that there are few electrons in the conduction band to conduct either heat or electricity.

Semiconductors

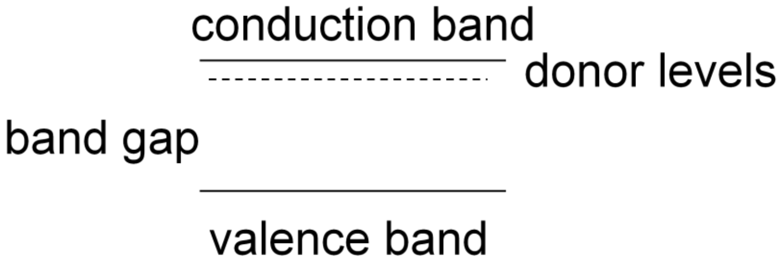
Our problem concerns the properties of cadmium selenide or CdSe. CdSe is an n-type semiconductor: in this section we'll find out what that means. We'll also see how semiconductors can emit light and at what wavelength. As a useful digression from the main problem we'll look at some semiconductor applications. We'll begin with some semiconductor basics.

n-type semiconductors

N-type semiconductors are created by introduction of an impurity atom with more (surplus) outer electrons than the intrinsic semiconductor: A silicon atom has 4 electrons in its outer shell. In a silicon crystal, it shares these in bonds with its neighbouring silicon atoms. If an atom, say of arsenic, with 5 outer electrons replaces a silicon atom in the crystal, it shares 4 of its outer electrons in bonding (with its 4 new silicon neighbours). This leaves an extra electron loosely bound to its parent in the lattice: it occupies an energy level just below the conduction band so can easily be excited into the conduction band. This extra electron has an energy in the band gap just below the conduction band so it is easily excited into the conduction band. This surplus electron increases the conductivity of the material relative to its intrinsic form.



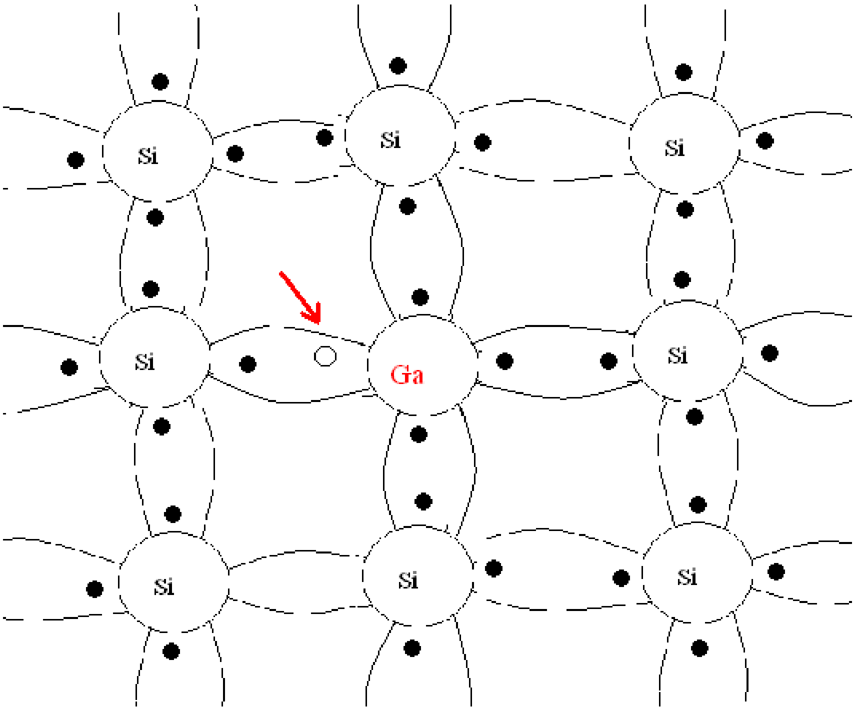
The net result of substituting some silicon atoms with arsenic atoms (or any other atoms from group V of the periodic table) is the availability of more free electrons in the semiconductor lattice at a given temperature. The process of adding impurities to a semiconductor is called **doping.** A semiconductor doped with electron rich atoms is termed a negative type, **n-type**, semiconductor.



In n-type material, majority charge carriers are electrons.

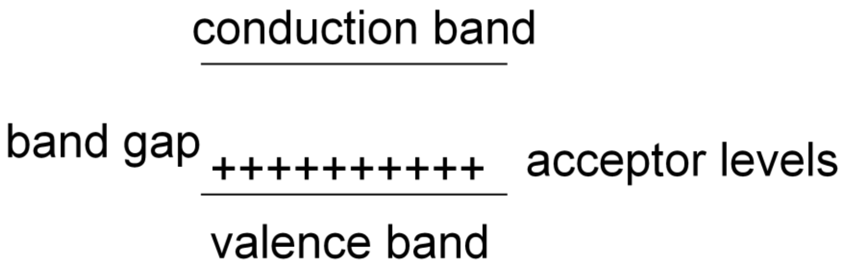
p-type semiconductors

p-type semiconductors are created by introduction of an impurity atom with less outer electrons than the intrinsic semiconductor: If an atom, say of Gallium, with 3 outer electrons, replaces a Si atom, it shares the 3 outer electrons in bonding leaving a vacancy. The bonding is completed by accepting an electron from the valence band. This leaves a hole in the band. The hole occupies an energy state just above the top of the valence band, called an acceptor level. Excess holes participate in the conductivity of the material. The net result off substituting Silicon atoms with Gallium atoms (or any other group III elements) is the availability of more holes in the semiconductor. The semiconductor is now termed a positive type, **p-type**, semiconductor.



Note that the type, n or p, refers to the majority carriers. Cadmium selenide is an intrinsic semiconductor so there are the same number of holes in the valence band as electrons in the conduction band. To say it is n-type means that the majority carriers are electrons because they are more mobile than the holes. Cadmium selenide is in fact also more easily doped to be an n-type semiconductor.

In p-type material, the majority charge carriers are holes.


conduction band
band gap
+++++++++++
acceptor levels
valence band

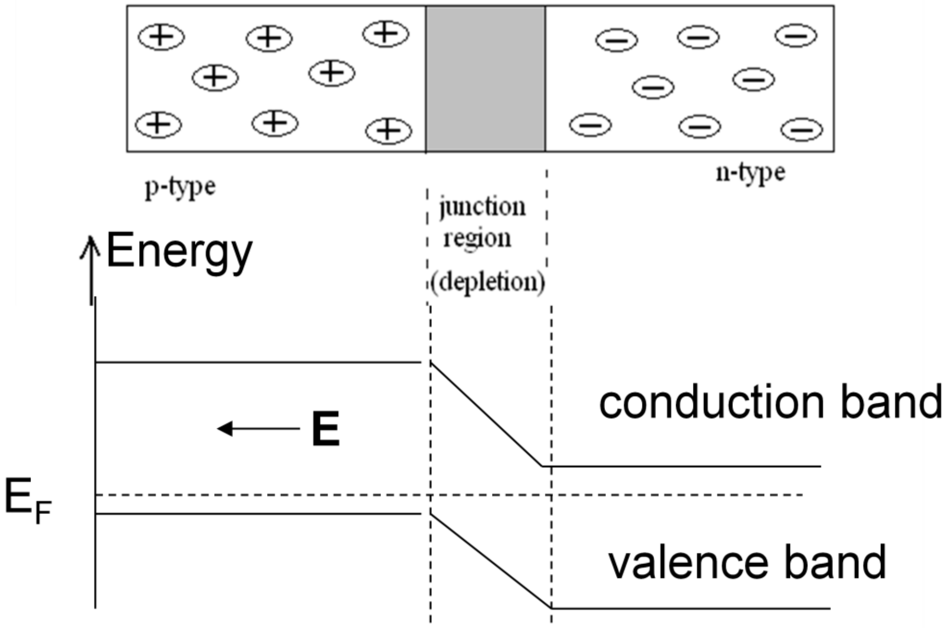
p-n junction

The applications we are going to discuss involve putting a p-type and an n-type semiconductor together to form a p-n junction. At the p-n junction electrons diffuse from the n-side to the p-side while holes from the p-side diffuse to the n-side of the material. The flow of carriers to opposite sides soon creates a region where all vacancies are occupied by electrons. This region is then empty of any carrier type and is known as the **depletion** region.

A p-n junction is created by doping one side of the material positively and the other negatively.

On either side of the depletion region is a layer of charges of opposite polarity and so there is a potential difference across the depletion region. Any further carrier movement across the depletion region is countered by the potential barrier. However, if an external potential is connected to the p- and n- sides, it can aid or further impede the movement of carriers across the depletion region depending on its sense.

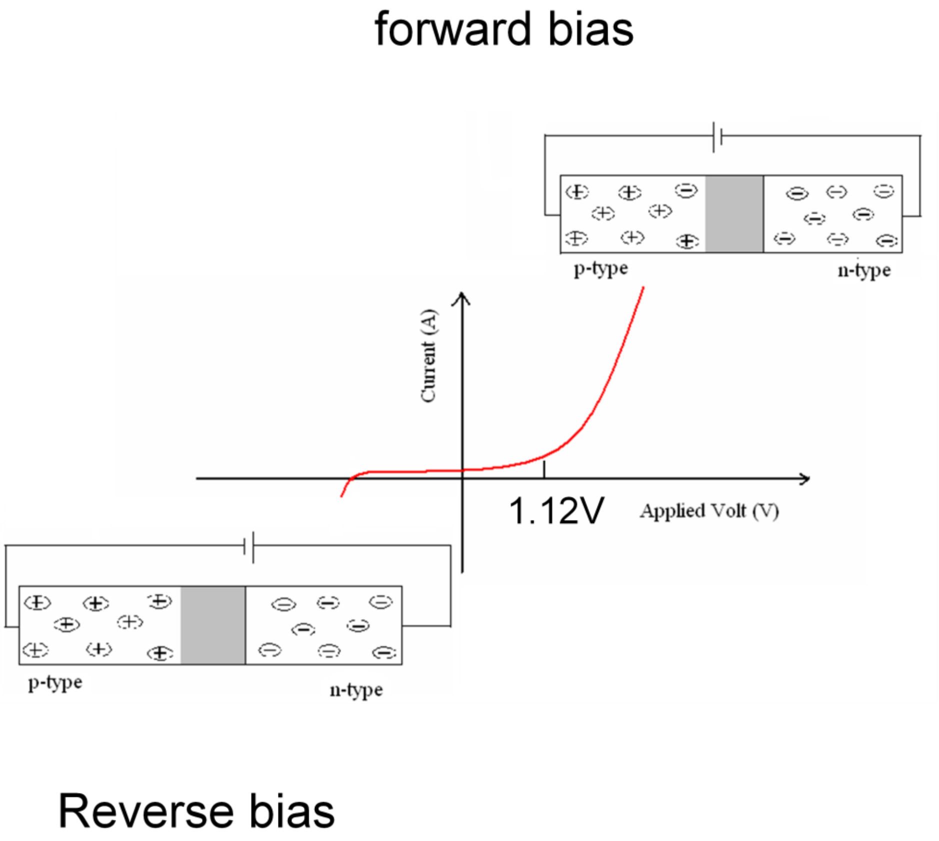
The Fermi energy is the same on both sides. Holes have diffused to the n region so there is an excess positive charge on the right and an excess negative charge on the left. This results in an electric field in the direction shown.



Application 1: Diodes

A p-n junction allows flow of charges in one bias mode and allows very little flow in a reverse bias mode.

See the diagram below. Suppose that the positive pole of a battery is connected to the p-side of a p-n junction and the negative pole to the n-side. As the voltage is increased from zero, at first the current flow is negligible until the reverse bias of 1.12 volts is reached. Then, as the figure shows, the current grows exponentially with voltage. This is because the electrons are attracted to the positive polarity on the p-side whilst holes are also attracted to the negative polarity at the n-side. The junction is said to be **forward biased**, when connected this way.



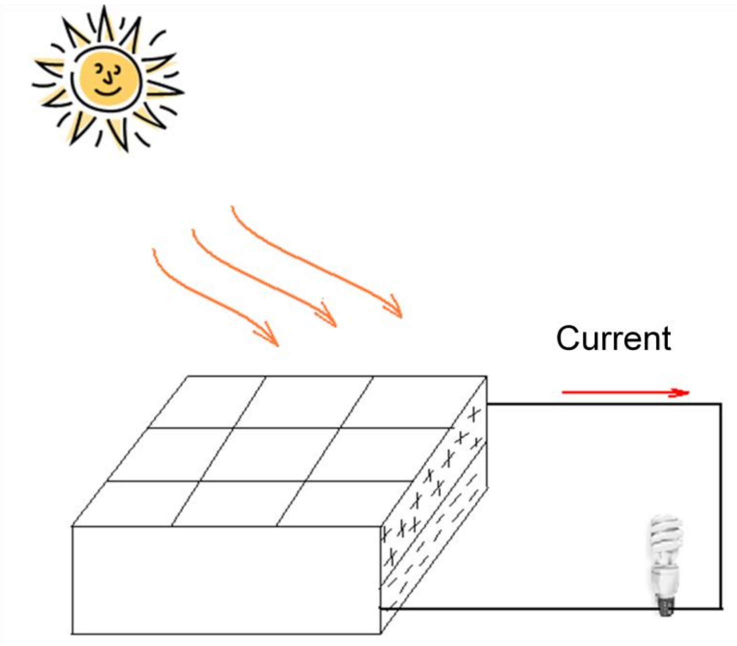
However, when the positive pole of the battery is connected to the n-side and the negative pole to the p-side, the junction is said to be **reverse biased**. In reverse mode very little charge flows across the junction because the barrier potential is actually increased. The p-n junction therefore acts as a rectifier.

A p-n junction is a diode

Diodes are used for rectifying AC current

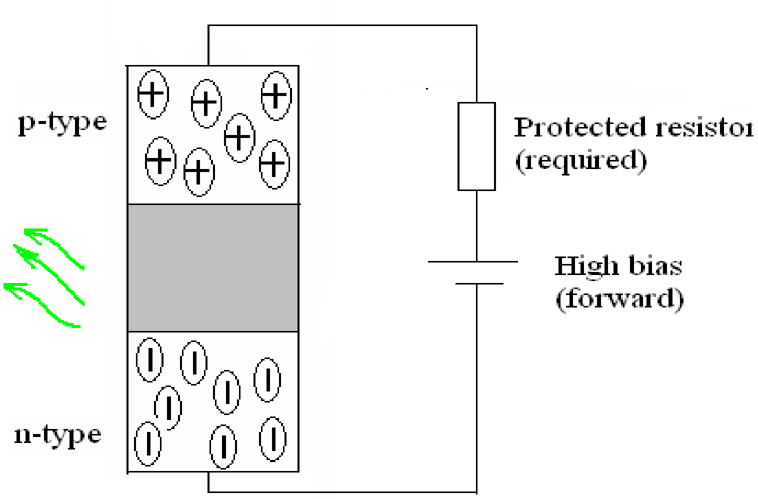
Application 2: Solar cells & LEDs

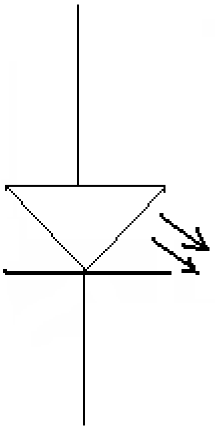
A solar cell converts light energy to electrical energy. When the light falls on the p-side of a p-n structure, free carriers (electron-hole pairs) can be created. The redistribution of the excess carriers causes a potential difference between the two regions. If an external circuit connects the two sides of the diode, the carriers flow across it so as to restore the equilibrium potential. The flow of carriers constitutes a current in the external circuit.



Application 3: Light Emitting Diodes

Light Emitting Diodes, or LEDs for short, are forward biased diodes that produce large numbers of holes on the n-side and electrons on the p-side of the junction. Under this circumstance light is emitted when the carriers recombine across the junction. The energy of the photons is equal to the energy across the band gap, and hence the band gap determines the colour of the diode. LEDs are used in many digital display panels and even traffic lights.





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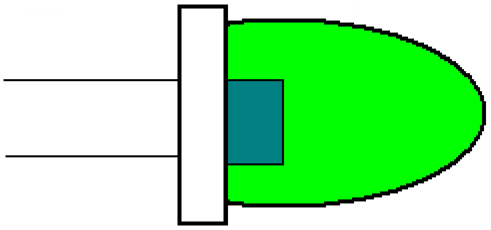


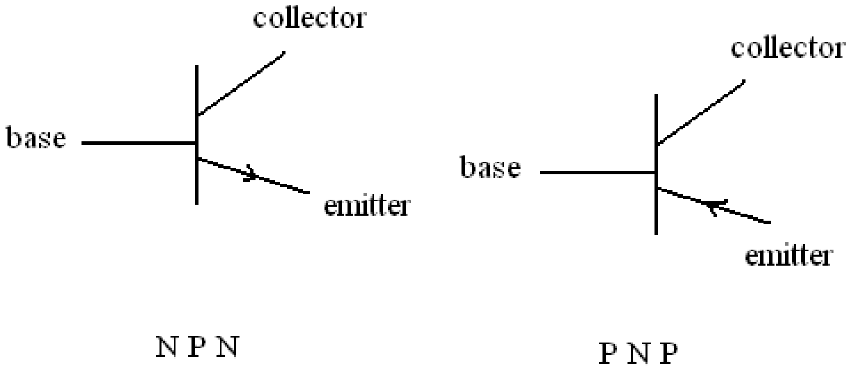
LED lamp

Light Emitting Diodes (LEDs) are forward biased p-n junctions (diodes).

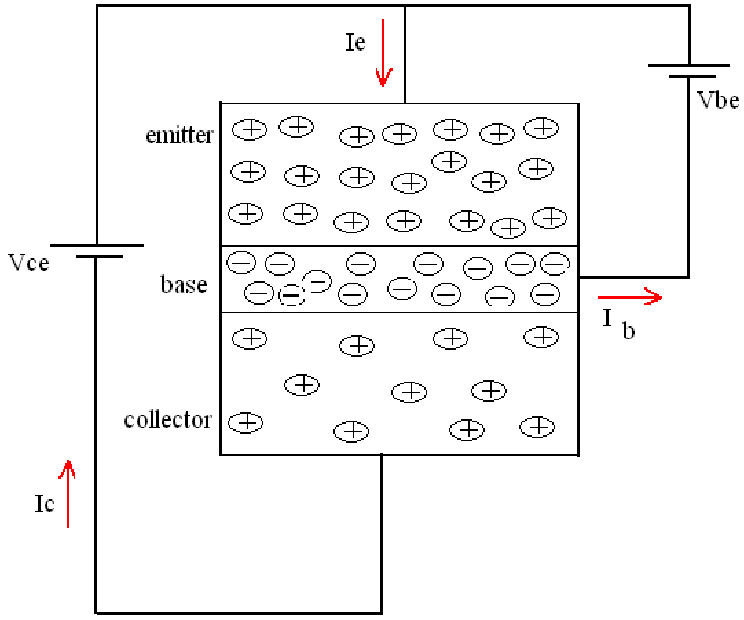
Application 4: Transistors

A transistor is an important part of modern electronics. One type of transistor, a bipolar junction transistor (BJT), acts an amplifier.

A bipolar junction transistor, or BJT, is made by sandwiching a p-type semiconductor between an n-type one or vice versa. As the name suggests therefore, a BJT is composed of two semiconductor junctions (p-n and n-p junctions) but with each biased differently.



In a BJT structure, the mid 'belt' called the base is normally thin. One of the regions at the end, called the emitter, is heavily doped whilst the other end, called the collector normally has the same lower concentration of dopant as the base. The essence of heavily doping the emitter is to enable carriers to be easily emitted across the junction under a suitable bias, labelled Vce in the diagram.



The BJT example shown here is the pnp transistor. It can be seen that the emitter/ base junction is forward biased whilst the base/collector junction is reverse biased. In this circumstance, holes are emitted from the p-side, the emitter region, into the base, so an emitter current (Ie) flows. Because the base region is thin, most of the holes flow into the collector region so a collector current, Ic, flows into the collector. The bias potential, Vbe, extracts any holes in the base that do not cross into the collector. Thus the bias Vbe causes a flow of base current, Ib.

$I_c = \beta I_b$. β is called the current gain of the transistor

Ib is smaller than both Ie and Ic. We can put Ic equal to (beta) times Ib. Beta is then called the current **gain** of the transistor, analogous to the gain of an operational amplifier.

This illustrates how transistors are used as digital signal boosters in modern electronic, power (step up) transformers.

Summary

- Intrinsic semiconductors may be doped so that the majority carriers are either holes (p-type) or electrons (n-type)
- A p-n junction acts as a diode or rectifier
- Applications include solar cells and LEDs
- A transistor is a pnp or npn layered structure

SAQs

1. CdSe has a bandgap at 300K of 1.74 eV. to 2 s.f. What is the wavelength of the peak of the emission spectrum?

2. (a) True or (b) False:
   (i) In a p=type semiconductor a hole occupies a level in the conduction band.
   (ii) In an n-type semiconductor the donor levels lie just below the conduction band.

3. The Fermi energy on each side of a p-n junction is
   (a) the same
   (b) separated by the band gap energy
   (c) does not exist

4. The total electric current in an intrinsic semiconductor at temperature T > 0 is equal to
   (a) $i_e + i_h$
   (b) $i_e - i_h$
   (c) i_e

The answers appear on the following page

Answers

1. 710 (accept 700 to 720) Feedback: the peak wavelength is given by hc/E with h = 4.1 x 10^{-15} eV s and c = 3.0 x 10^{8} m s^{-1}. So the wavelength is 1230/1.74 nm = 706 nm

2. (i) False: the holes are in the valence band.

   (ii) True

3. (a) Correct: otherwise the total energy of the system would be reduced by a flow of electrons.

   (b) Incorrect: the Fermi energy and band gap are independent concepts

   (c) Incorrect: The Fermi energy is a theoretical construct that depends only on the density of electrons.

4. (a) correct: the holes flow in a direction opposite to the electrons so add to the current

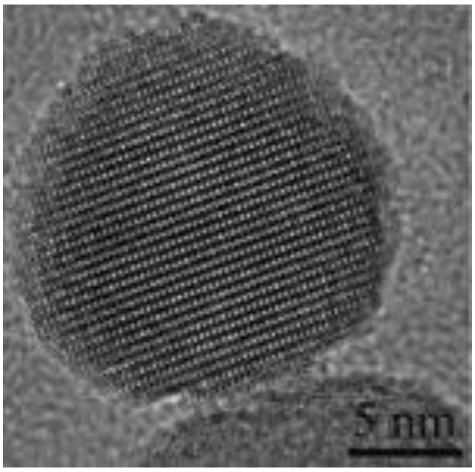
   (b), (c) Incorrect: the holes flow in a direction opposite to the electrons so add to the current

Nanoparticles

In this section we'll look at the distinctive properties of semiconducting nanoparticles which will enable us to address our original problem.

What is a nanoparticle (or quantum dot)?

A nanoparticle, also called a quantum dot, is a structure consisting of a few to a few hundred atoms with a size on the scale of nanometres, that is 10^{-9} metres. On this scale surface effects become important and give rise to properties that are different from those of the bulk material. This distinctive behaviour of nanoparticles, compared to the same bulk material, arises from quantum mechanics.



Image[2]

To see how, consider an electron that has been excited into the conduction band leaving a hole in the valence band. The electron and the hole attract one another, rather like the electron and the proton in the hydrogen atom, to form what is called an exciton.

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[2] TEM image of Fe3O4 nanoparticle, Yobmod, as posted on commons.wikimedia.org. Creative Commons Licensed.

Exciton Bohr Radius

The slight difference is that the electron and hole have similar masses, so they orbit a common centre, in contrast to the hydrogen atom in which the more massive proton remains almost at rest. The other difference is the presence of all the other atoms in the solid, so the electron and hole cannot be considered to be in empty space! Instead, we think of the crystal as providing medium with a dielectric constant ε. Thus the usual Bohr radius of the hydrogen atom, $4\pi\varepsilon_0 h^2/(e^2m)$, is replaced by $4\pi\varepsilon_0\varepsilon h^2/(e^2\mu)$, where μ is the so-called reduced mass, one half of the harmonic mean of the electron and hole masses.

Material	Bandgap, eV	Exciton Bohr radius, nm	Lattice spacing
CdSe	1.84	4.9	0.55 nm

$$4\pi\varepsilon_0\,\varepsilon\,h^2/\mu e^2 \quad \text{where} \quad \frac{1}{\mu}=\frac{1}{m_e}+\frac{1}{m_h}$$

Compare H atom: $a = 4\pi\varepsilon_0 h^2/me^2$

A nanoparticle is smaller than the exciton Bohr radius

Let's take a structure like CdSe. This has a lattice constant, the distance between atoms, of 0.55 nm. The radius of an exciton, the analogue of the Bohr radius, is 4.9 nm for CdSe, much larger than the lattice spacing and larger than a cluster of up to a few hundred atoms. Of course, the electron-hole pair must be confined to the cluster, so in a nanoparticle their behaviour must be altered in some way. Therefore the properties of a nanoscale crystal of CdSe containing up to a few hundred atoms, will be influenced by the size of the nanoparticle.

Energy of confinement

We can obtain an estimate of the effect of confining the exciton to a nanoparticle from the Uncertainty Principle. The spread in momentum can be determined from the spread of the wavefunction over the size of the particle, R say. Then the spread of Δp is of order Planck's constant/R. Since the average momentum is zero for a nanoparticle at rest, this is also the momentum of the exciton. We get its energy, from $p^2/2m$, to be $h^2/2mR^2$. This is the extra energy that the exciton acquires as a result of confinement to a nanoparticle of size R. The change in energy is reflected in a change in the band gap and hence in the colour of light emitted when an excited electron-hole pair recombine. Nanoparticles of different sizes emit different colours: this is the explanation for the range of colours obtained from cadmium selenide.

Confinement energy:

$$\Delta x \Delta p = h \qquad \Delta p = \frac{h}{R}$$

$$E_C = \frac{\Delta p^2}{2m} = \frac{h^2}{2mR^2} \Rightarrow \frac{\Delta E_C}{E_C} = 2\frac{\Delta R}{R}$$

- explains difference in colour from the bulk

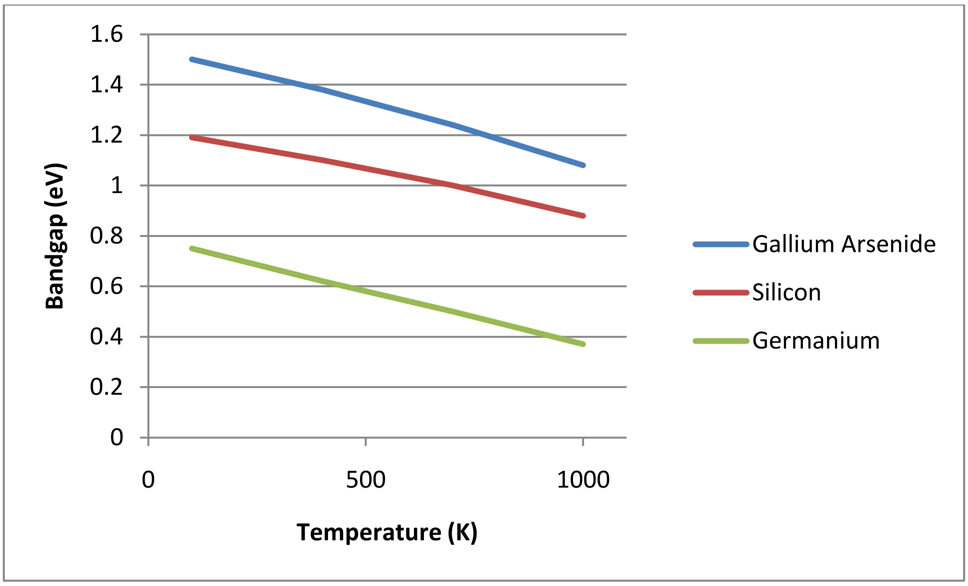
$$E_c = \frac{hc}{\lambda} \Rightarrow \frac{\Delta E_C}{E_C} = -\frac{\Delta \lambda}{\lambda} = -2\frac{\Delta R}{R}$$

- explains large change in colour

What about the stability of these colours with temperature? If we want to use many different markers how close could they be in size and hence wavelength under conditions in which the temperature might vary?

Temperature dependence of band gaps

First we look at the change in band gap energy with temperature of the bulk material for some typical semiconductors. Over a large enough range these changes are significant, but over a small range near room temperature the change in bandgap energy is unlikely to change the colour of light emitted.



But the problem we started with does not concern bulk materials: instead we want to know the effect of temperature on nanoparticles.

Change in confinement energy with expansion

The change in band gap with temperature is complicated. But one thing we can check is the change in the confinement energy with thermal expansion of the nanoparticle. In outline we have just found the dependence of energy E on the size R of the nanoparticle, and the coefficient of thermal expansion tells us the change in R with temperature. So applying the chain rule gives us equation (1).

$$\frac{dE}{dT} = \frac{dE}{dR}\frac{dR}{dT} = \frac{dE}{dR}\alpha R \qquad (1)$$

$$= -\frac{h^2}{R^3 m}\alpha R \qquad \text{since } E = E_C = \frac{h^2}{2mR^2}$$

$$= -\frac{1}{2}\alpha E \qquad (2)$$

Where α is the coefficient of thermal expansion

Simple differentiation and substitution leads to equation 2. The wavelength of the emitted light is related to the band gap energy by the usual relation between energy and wavelength for a photon, $E = hc/\lambda$ and again some simple algebra leads to the final relation in equation 3. This is negligible.

$$E = \frac{hc}{\lambda} \Rightarrow \Delta\lambda = \Delta\frac{hc}{E} = -\frac{hc}{E^2}\Delta E = \alpha\frac{hc}{2E}\Delta T = \frac{\alpha}{2}\lambda\Delta T \qquad (3)$$

$\alpha = 0.33 \times 10^{-5}\ \mathrm{K}^{-1}$ - explains colour stability

Therefore we expect the changes in wavelength to be the same as for the bulk material. For CdSe this is 0.11nm per degree. If we take 500nm as a typical wavelength this translates to a change of .02% per degree, so we would need to use markers that differ by significantly more than this in radius. In practice this would not be a concern.

Show that for red light at around 600 nm $\Delta\lambda \cong .001$ nm

Summary

- An excited electron and hole form an exciton
- In a nanoparticle the exciton Bohr radius is larger than the particle
- Confinement effects can be estimated from the uncertainty principle and explain the dependence of nanoparticle properties on their sizes

SAQs

1. In a nanoparticle the exciton Bohr radius is (a) larger (b) smaller than the spacing of atoms in the crystal lattice

2. As the radius of the nanoparticle increases

   (a) the emitted wavelength approaches the radius of the nanoparticle

   (b) the emitted wavelength approaches the lattice spacing

   (c) the emitted energy approaches the Fermi energy

   (d) the emitted energy approaches the bulk band gap energy

The answers appear on the following page

Answers

1. (a) Correct: the exciton Bohr radius must be comparable to the nanoparticle size for confinement effects to be important, hence it must be much larger than the lattice constant

   (b) Incorrect: the exciton Bohr radius must be comparable to the nanoparticle size for confinement effects to be important, hence it must be much larger than the lattice constant

2. (a) Incorrect: the emission arises from recombination of electrons and holes so the wavelength depends only on the excitation energy i.e. the band gap. This is influenced by the radius of the particle, but is not directly related to it.

   (b) Incorrect: the emission arises from recombination of electrons and holes so the wavelength depends only on the excitation energy i.e. the band gap. This is influenced by the lattice spacing, but is not directly related to it.

   (c) Incorrect: the emission arises from recombination of electrons and holes so the wavelength depends only on the excitation energy i.e. the band gap. The Fermi energy lies in the band gap, but is unrelated to its width.

   (d) Correct: the emission arises from recombination of electrons and holes so the wavelength depends only on the excitation energy i.e. the band gap

Overall Summary

- The free electron model of metals at ‘low’ temperatures predicts the linear dependence of specific heats on temperature
- Band theory accounts for the different behaviour of conductors insulators and semiconductors
- Intrinsic seniconductors can be doped n or p to increase the number of charge carriers
- The properties of nanoscale particles differ from the bulk material as a result of the confinement energy

Meta tags

Author: Samuel Atarah.

Owner: University of Leicester

Title: Enhancing Physics Knowledge for Teaching – Condensed matter

Keywords: Nanoparticles; Band Theory; Superfluids; Semiconductors; sfsoer; ukoer

Description: In this session we'll look at certain macroscopic properties of solids that result from the quantum mechanical behaviour of electrons. This field of physics initially concerned just the behaviour of solids so was referred to as solid state physics. It has been called condensed matter physics since the late 1960s, when it was realised that the type of collective behaviour extended beyond that of electrons in solids to many other systems such as, for example, superfluids.

Language: English

Version: 1.0

Additional Information

This pack is the Version 1.0 release of the module. Additional information can be obtained by contacting the Centre for Interdisciplinary Science at the University of Leicester. http://www.le.ac.uk/iscience