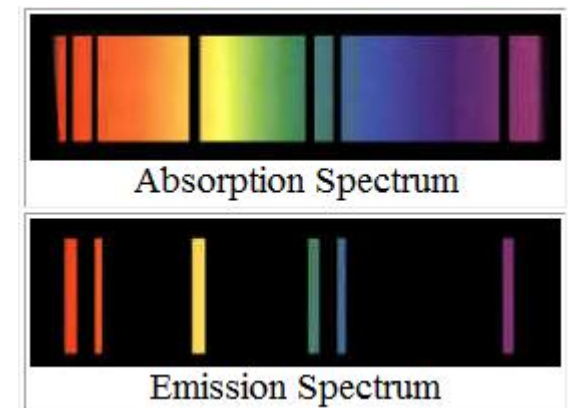
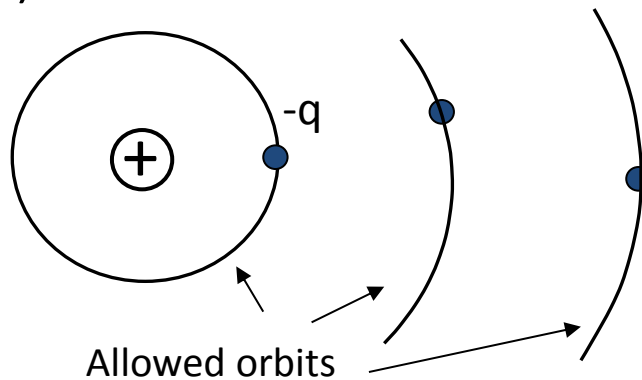


Chapter 1

Introduction to Energy Band Theory in Crystalline Solids

Introduction to Energy Band Theory

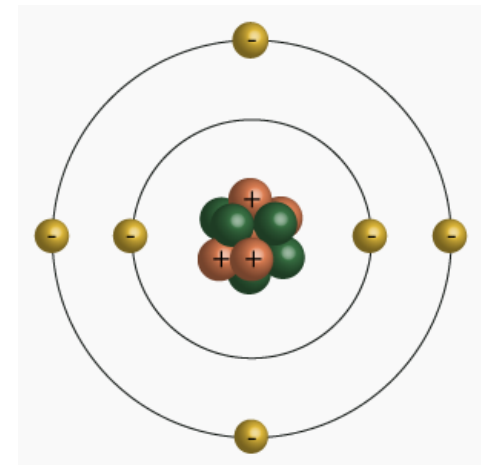
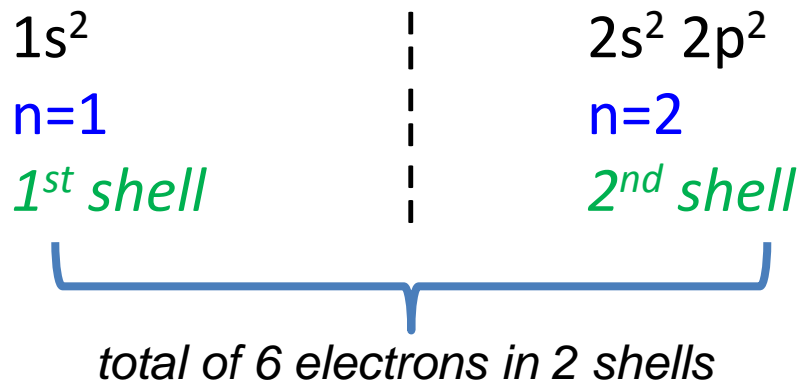
- In 1913, in order to explain spectral emissions from hydrogen, Neils Bohr proposed that for the electrons in an atom, certain dynamical parameters are “quantised” i.e. they are allowed to have only certain well-defined (or “discrete”) values.



- The associated defined (or “discrete”) values for the energy are called “energy levels”.
- In this view, the electrons may be imagined as arranged in space such that they occupy “shells”, concentric with the nucleus. Quantum Mechanics shows that each shell may have a further complex “sub-shell” structure. The sub-shells are described using the letters (s, p, d, f ...)

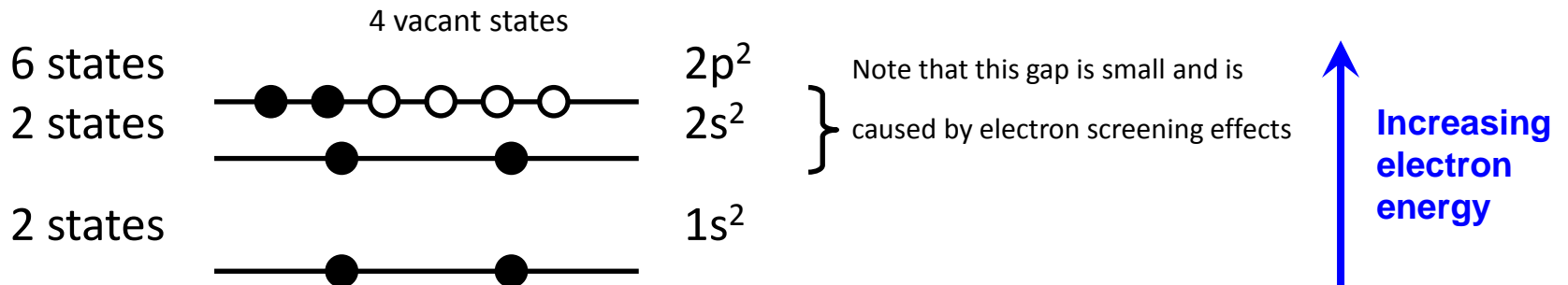
Introduction to Energy Band Theory

- As an example of the Bohr model of an atom we will choose an important element from Group IV of the periodic table:
Carbon (Chemical symbol C) ${}_6\text{C}^{12}$
 - › 6 protons + 6 neutrons in the nucleus (Atomic Number =6)
 - › 6 electrons
- In the case of carbon we can write the electron configuration as:



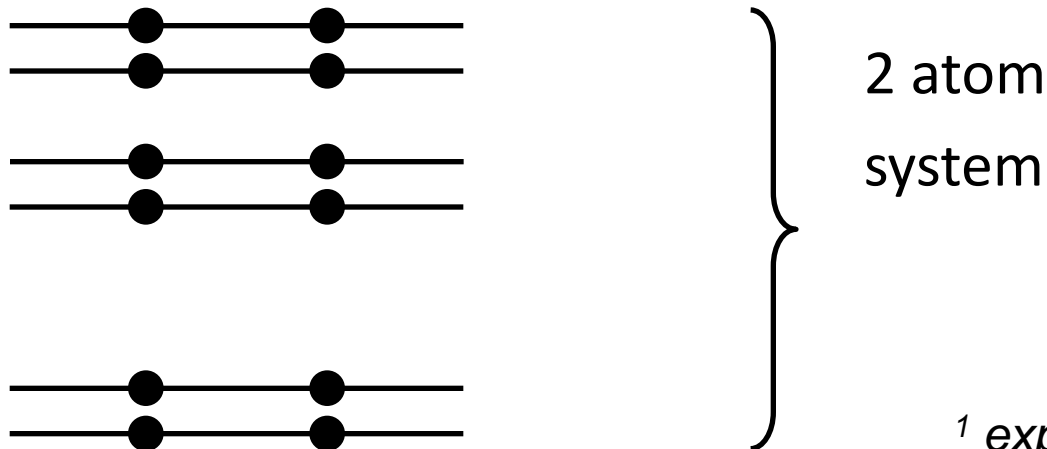
Introduction to Energy Band Theory

- The “s” sub-shells can have up to 2 electrons, each with the same energy
- The “p” sub-shell can have up to 6 electrons (made up of 3 p-orbitals – p_x , p_y , p_z – each occupied by up to 2 electrons)
- Starting from the bottom we get the pattern shown for Carbon on the previous page. Note that 4 more electrons are required to complete the outermost sub-shell.
- We could picture the energy levels in an isolated Carbon atom as follows:



Introduction to Energy Band Theory

- Now bring TWO Carbon atoms close enough for their electron distributions to interact. Constructive and destructive interference of the electron waves¹ leads to a splitting of the discrete energy levels in the isolated atom.
- Why don't all the electrons occupy the lowest energy level? This is prohibited by the *Pauli Exclusion Principle*



¹ explained
further in SSE2

Introduction to Energy Band Theory

Pauli Exclusion Principle:

no energy level or orbital (in a single- (or multi-) atom system) can have more than 2 electrons.

i.e. s : max. =2 electrons, p_x : max =2 electrons, p_y : =max 2 electrons... etc.

We now extend to “N” = number of Carbon atoms (N large) spread out uniformly in a regular spatial pattern in 3D space (i.e. In a *crystal* structure). Suppose we assume operation at *absolute zero temperature*, i.e. T (temperature) = 0K.

Let “d” be a measure of inter-atomic spacing in the regular spatial pattern of the crystal.

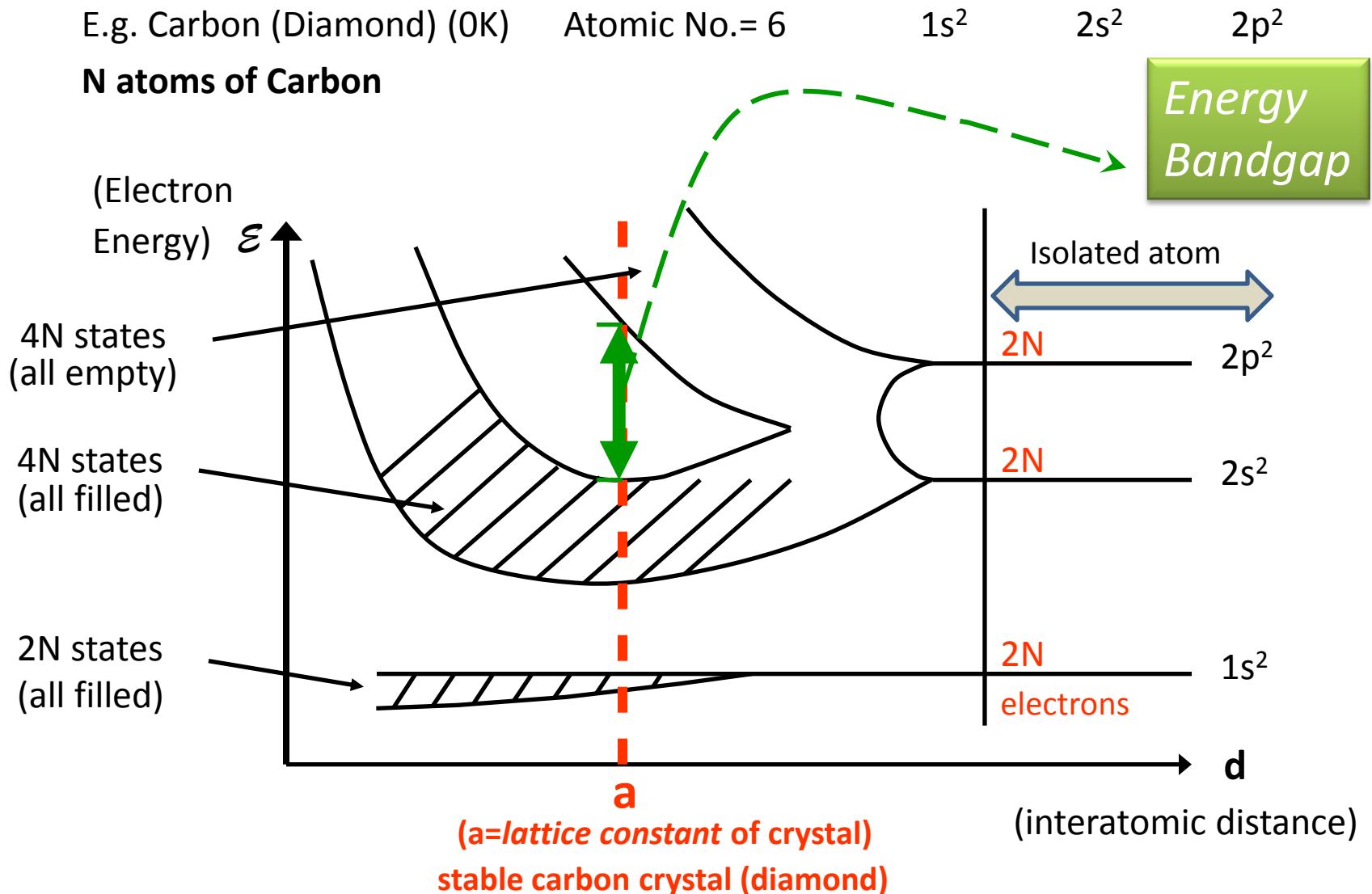
Introduction to Energy Band Theory

What happens to the distribution of allowed electron energies as we shrink “d”?

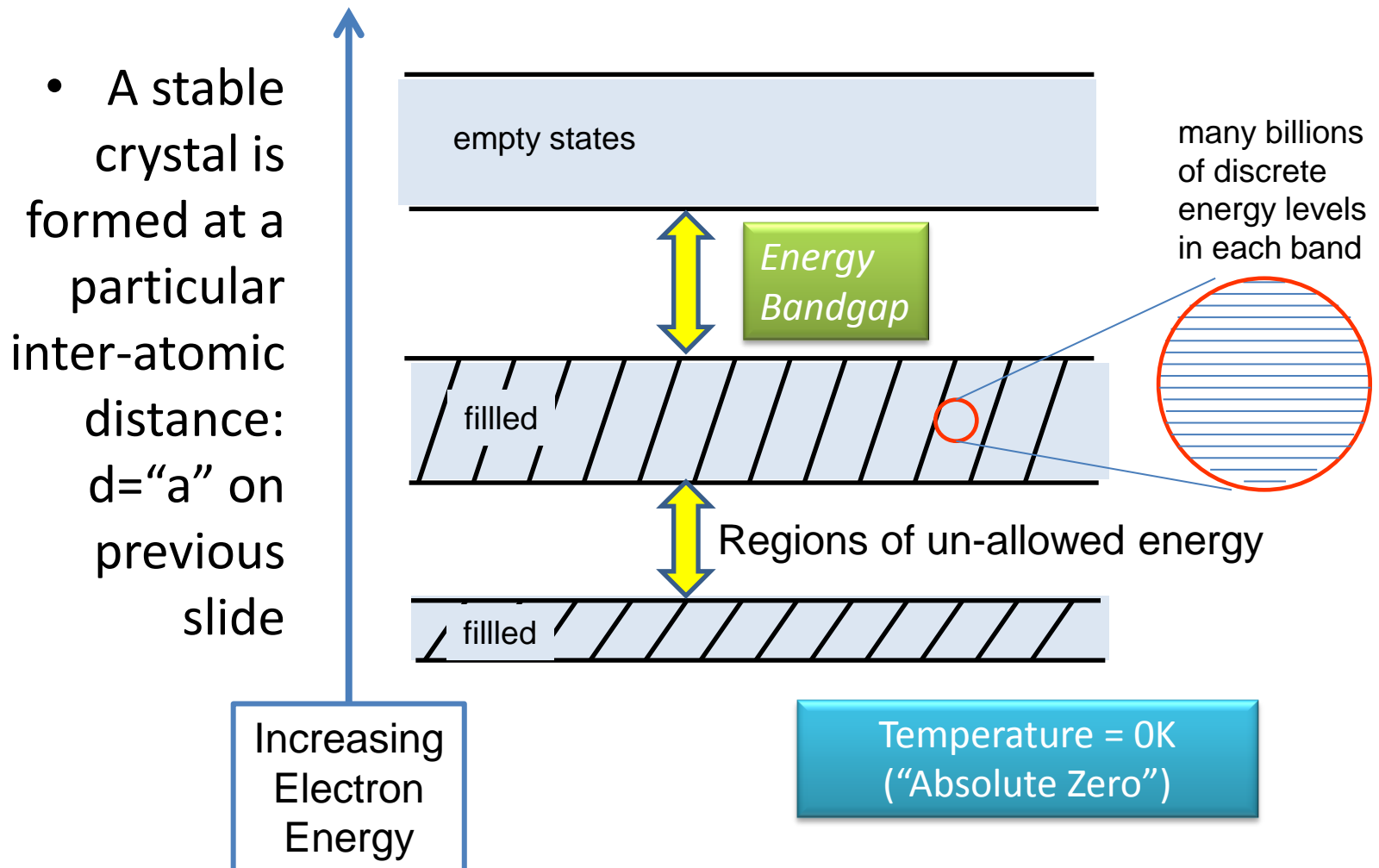
Multiple interference patterns, multiple splitting of energy levels occur.

The **discrete** energy levels of the **isolated atoms** **broaden** into **bands** of (still discrete) but extremely closely-spaced energy levels as “d” becomes small (assuming “N” is large).

Introduction to Energy Band Theory



Resulting *Band Structure* of Carbon (Diamond)



Energy Bands and Electric Current

- The flow of electric current arises from the ability of electrons to **move** in response to an applied **electric field** (or voltage)
- This requires that the electrons involved can **acquire energy** from the field.
- This is only possible if there are **some immediately-available energy states** within the bands that these now higher-energy electrons can occupy.
- In the case of C at 0K, we see that in the ideal case **no such states exist** (each band is either completely full or completely empty, with a large energy bandgap between them).
- Carbon (as a diamond crystal) is therefore ideally a **perfect non-conductor** of electricity (or **INSULATOR**) at 0K.

Definitions

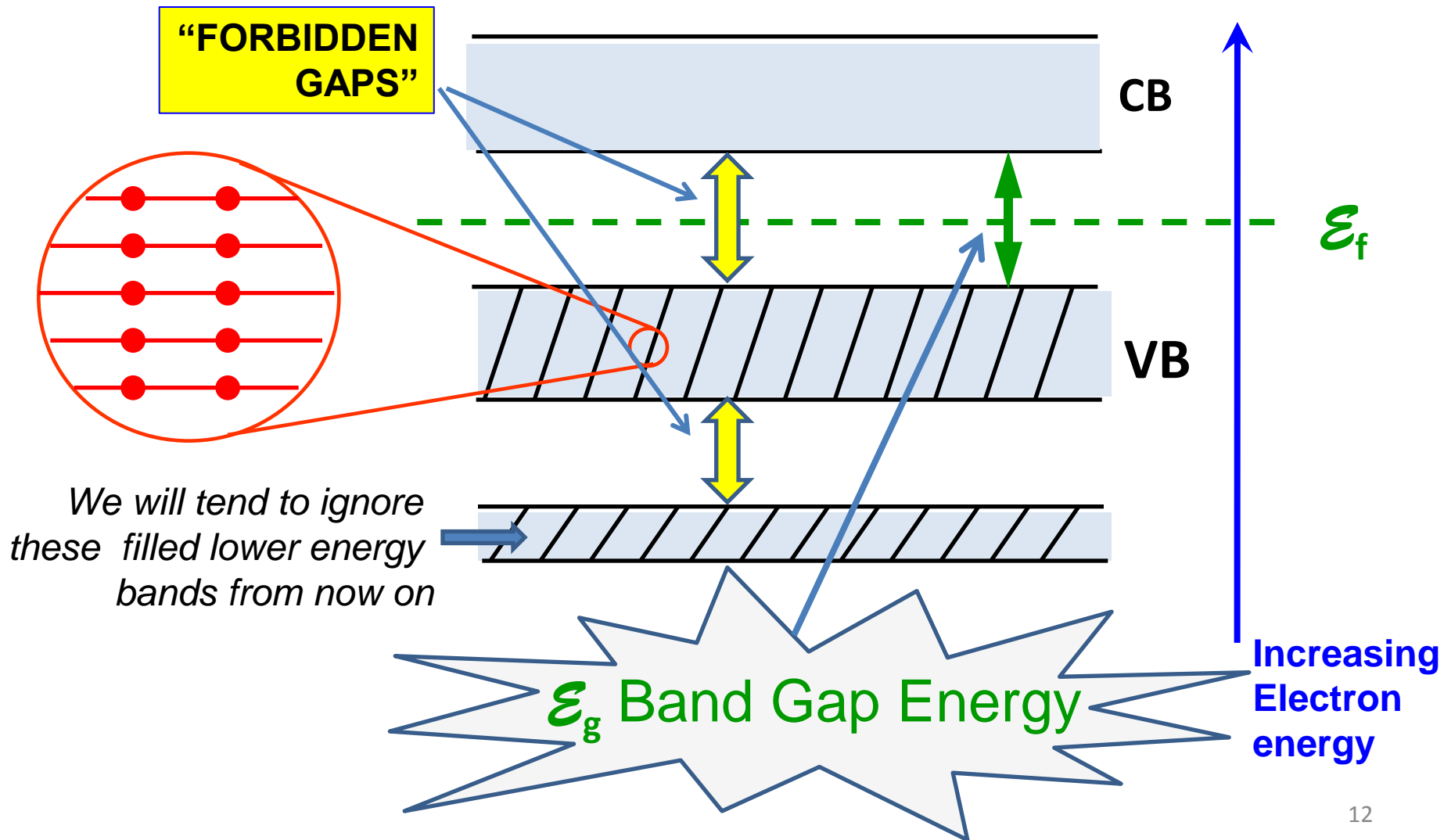
The Conduction Band (CB): The lowest energy band in a crystalline solid with *empty* states at 0 K

The Valence Band (VB): The highest energy band with *filled* states at 0 K

The Energy Bandgap (\mathcal{E}_g): A measure of the size of the “forbidden gap” separating the top of the VB and bottom of the CB.

The Fermi Energy Level \mathcal{E}_f : For now, we will just use as a definition of the Fermi level the statement that no electron can have an energy greater than \mathcal{E}_f at 0K.

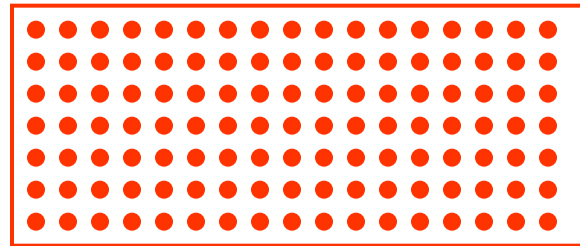
Energy Bands: Example of Carbon in Diamond Crystal Form at 0K



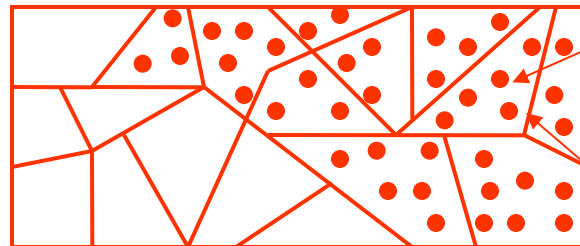
Arrangements of Atoms in a Solid

- The previous example describes a regular arrangement of Carbon atoms in space (“crystal”). 3 common situations:

- Single Crystal



- Polycrystalline
small regions of
regularity

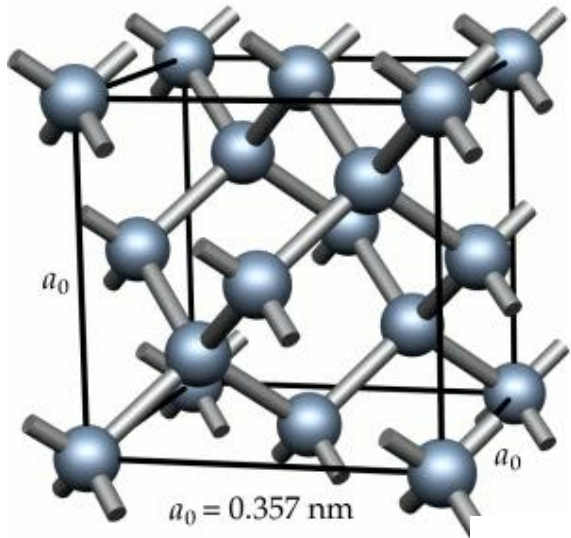


Single crystal in
each zone

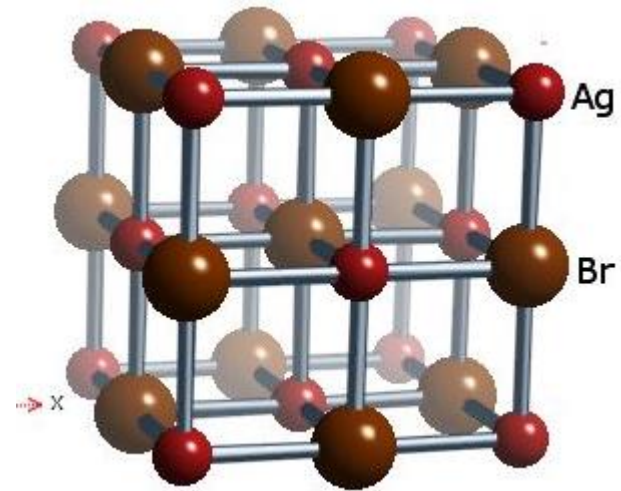
Grain boundary

- Amorphous
no regular pattern

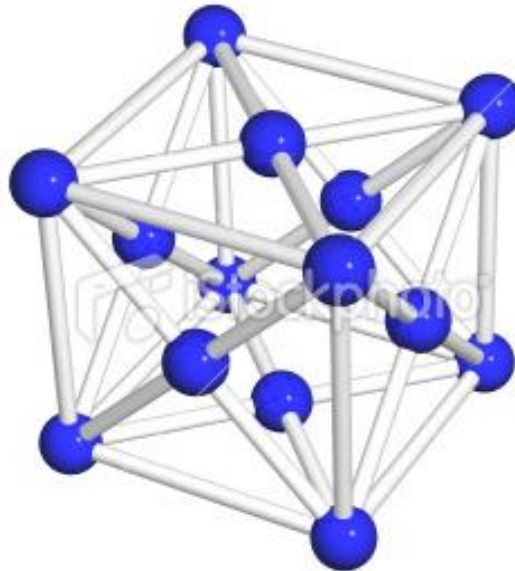
Examples of Crystal Structures in 3D



Diamond
(covalent)



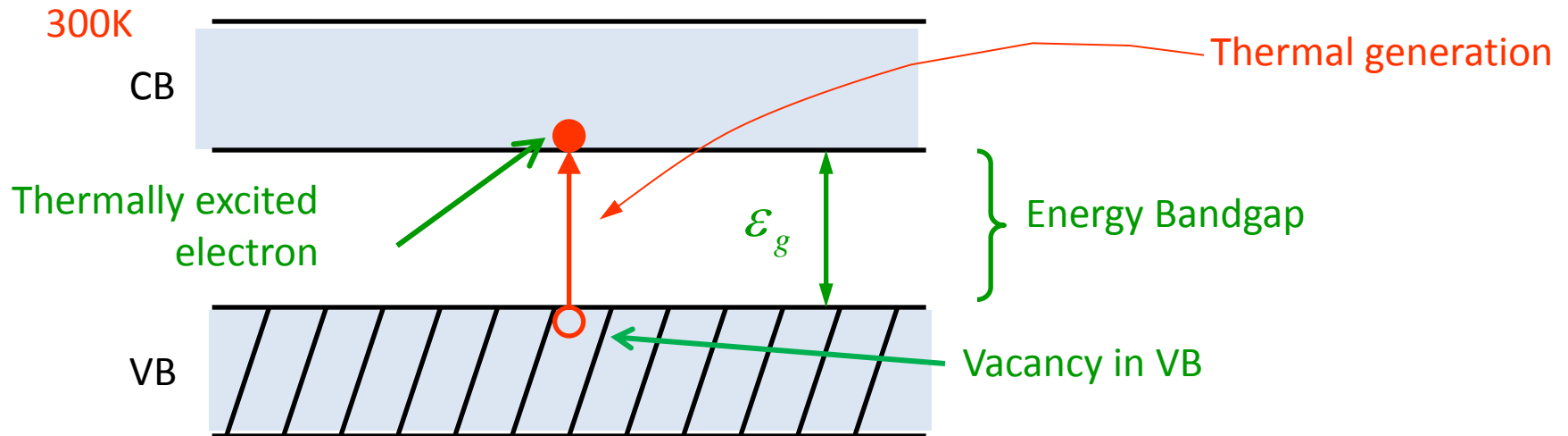
AgBr (or NaCl...)
(ionic)



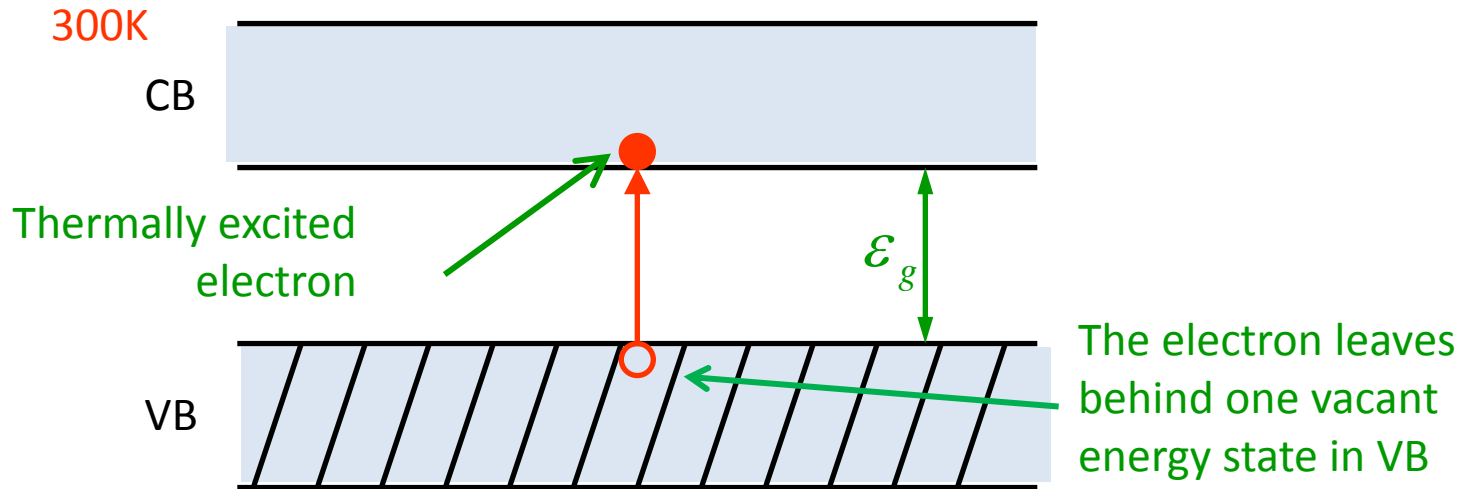
Fe
(FCC - metallic)

Energy Bands at Higher Temperature

Now increase temperature T to 300K. It is then possible that (on a statistical basis) some VB electrons could acquire enough **thermal** energy to cross the “forbidden gap” to the CB.



Electrons and Holes



The negatively charged electron excited into the CB has plenty of available energy states into which to move (i.e. it can contribute readily to electric current if a voltage were applied to the crystal)

However the fact that an energy level has been vacated in the VB is also significant: this means that a VB electron can **acquire** energy and move into this free state: detailed analysis shows that this is equivalent to supposing that a positively charged particle (+q) or **HOLE** has been created in the VB

Electron-Hole Pair Formation

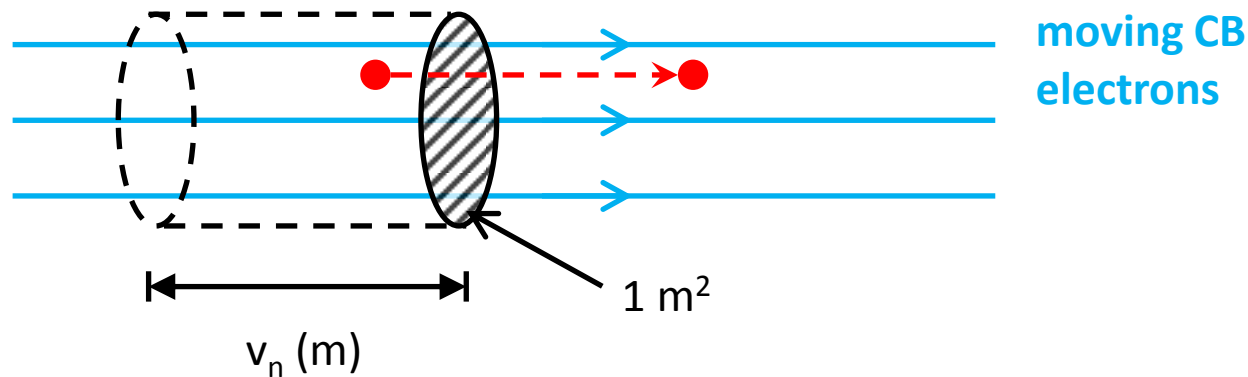
- As we have just seen, when an electron is excited across the forbidden gap (i.e. if it acquires an energy $\geq \mathcal{E}_g$), a **hole** is automatically created in the VB
- We refer to this as **Electron-Hole Pair** or **EHP formation**
- In the above case this was caused by thermal energy, but other mechanisms are possible (e.g. light photons can cause **optical generation** of EHPs)
- It is important to understand that electrons and holes can make separate and additive contributions to electric current in such materials.
- Note that “q” denotes the magnitude of the charge on both the electron and the hole (i.e. it is un-signed in this Course)

Energy Bands and Electron Current Flow

- Apply a voltage across a crystal sample of the kind just discussed, leading to the creation of an internal electric field (E). What current will flow (at, say $T=300\text{K}$, or “room temperature”)?
- First, we just consider electrons in CB (produced by thermal EHPs)
- Let n = average no. of CB electrons per unit volume ($/\text{m}^3$): the **“electron concentration”**
- Let v_n = average speed with which each CB electron moves in response to E (m/sec). As we will see later, the acceleration action of the E field is opposed by collision forces in the crystal, making the concept of an average or “drift” speed meaningful.

Energy Bands and Electron Current Flow

- We assume 1-Dimensional CB electron flow from right-to-left.
- Imagine a cylinder of unit cross-sectional area (in m^2), and a length equal to the numerical value of v_n (in m)



- Then the number of electrons in this cylinder at a given instant in time = (concentration of electrons, or the number per unit volume) \times (volume) = $(n) \cdot (v_n \cdot 1) = n \cdot v_n$

Energy Bands and Electron Current Flow

- This means that in one second all the electrons in the cylinder move through the hatched area. But each electron carries a charge of magnitude “q”. Hence the total charge passing through the hatched area in each second is:

$$= q.n.v_n \text{ (Coul/sec)/m}^2$$

- By definition, this is the (electron) current density J_n .

$$\boxed{J_n = q.n.v_n} \text{ Amp/m}^2$$

- Directions



Electrons move this way



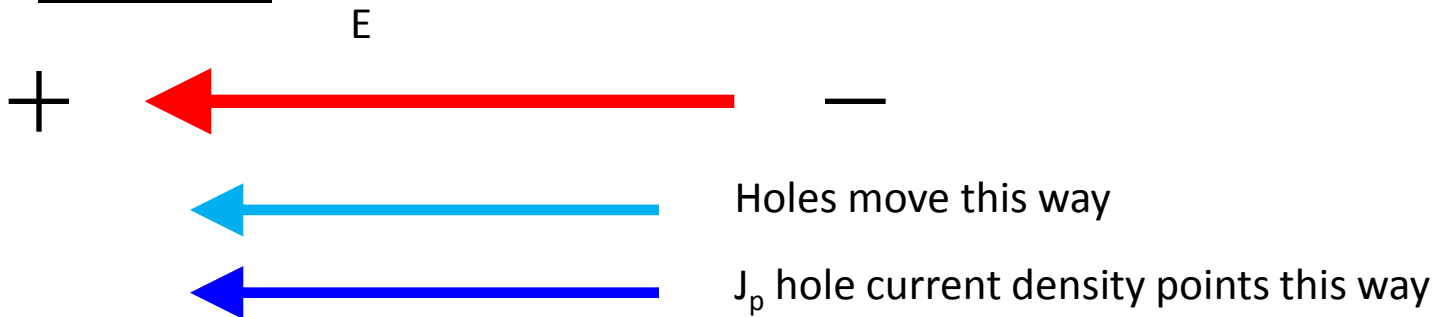
J_n electron current density points this way

Energy Bands and Hole Current Flow

- Now consider the contribution to current of **holes in the VB**
- Let p = (average) no. of holes in VB per unit volume of “**hole concentration**”.
- Let v_p = average speed of a hole in response to E
- Then, using similar arguments as before, the hole current density is:

$$J_p = q.p.v_p \quad (\text{Amp/m}^2)$$

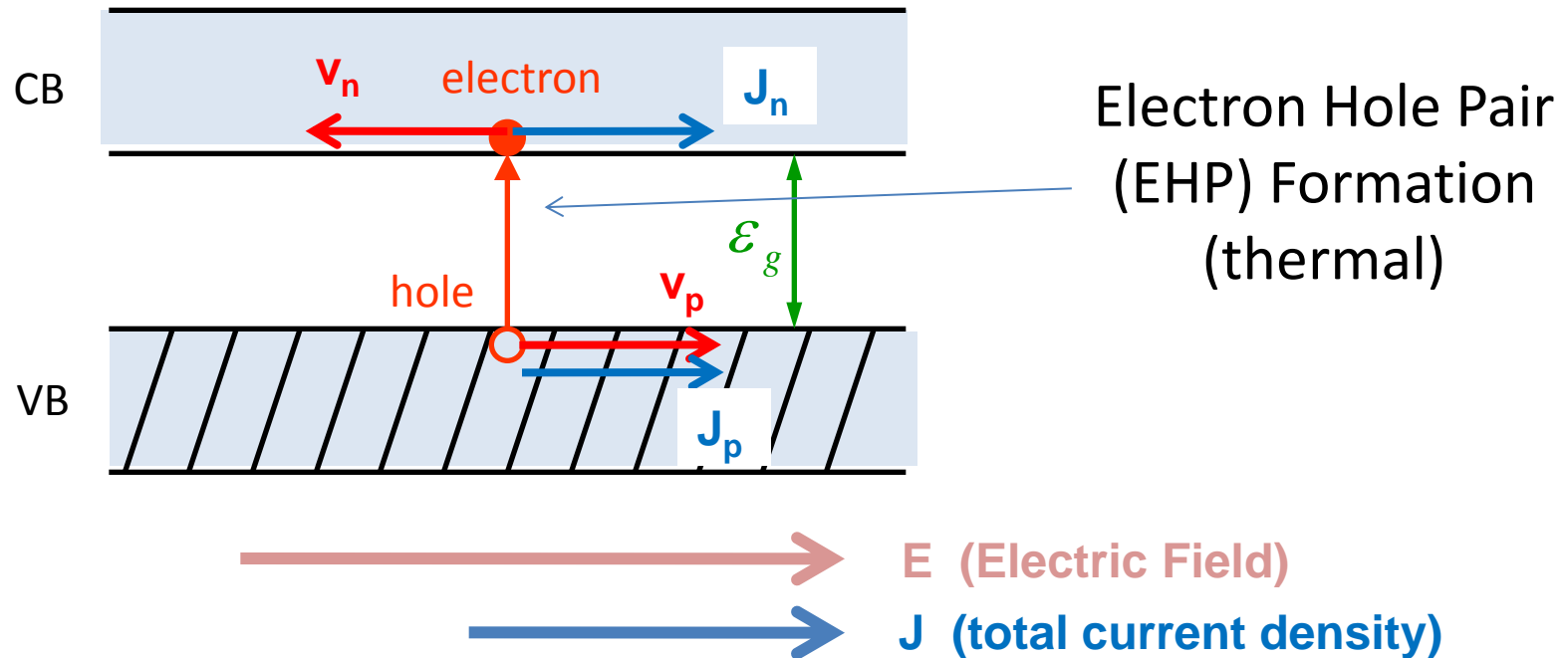
- Directions:



Energy Bands and Total Current Flow

- The total current density is thus:

$$J = J_n + J_p = q.n.v_n + q.p.v_p$$



Example 1.1

The Energy Bandgap

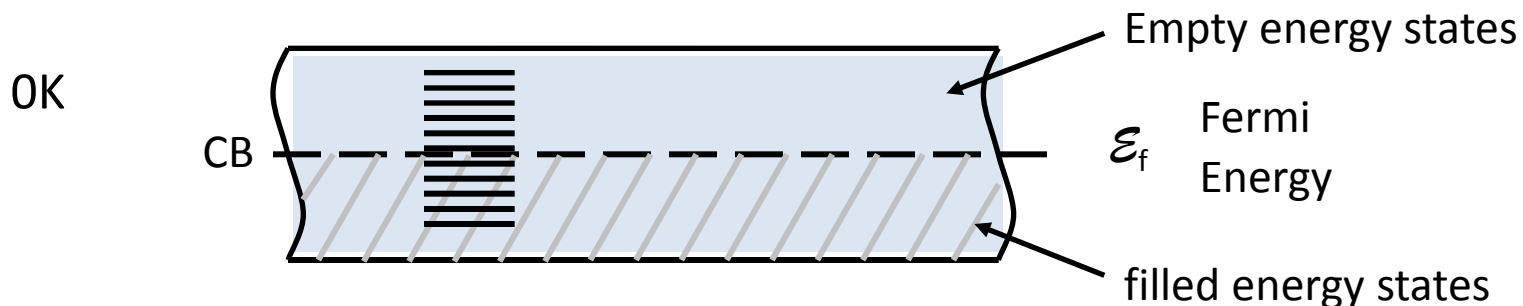
- In a given material, the thermal EHP generation rate is a sensitive (increasing) function of temperature
- In different crystalline materials (but similar to Carbon) the **bandgap energy** is a critical quantity that has an enormous influence on the electrical behaviour of the material.
- If we compare different materials of this kind at a fixed temperature T , then **as \mathcal{E}_g increases** the no. of thermally generated EHPs **falls** very quickly
- In Carbon (diamond), with a band-gap energy of 5.4eV, the number of thermal EHPs is actually very small around room temperature, and so we may expect electrical current flow to be vanishingly small.

INSULATORS

- Crystalline materials with relatively large bandgaps ($\sim 5\text{eV} - 10\text{eV}$ or more) tend to be extremely poor conductors of electricity. Such materials are called (electrical) **insulators**
- Solid-state examples include glass, diamond, sapphire, quartz etc
- In practice, it is found that such materials do pass a minute electric current when voltage is applied, but the “ohmic” component of this current due to thermally-generated EHPs is normally negligible: any current flowing is mainly due to **surface leakage**

METALS

- In many crystalline materials, the distribution of energy levels into bands is quite different to that observed for Carbon
- In these cases when we combine atoms to form a crystal, it is found that the VB and CB merge or overlap to form a **single partially-filled band** conventionally called the **Conduction Band (CB)**
- It is very easy for carriers to find higher energy levels in such cases: such materials are therefore good-to-excellent **CONDUCTORS** of electricity. They are called **metals** (e.g. Copper (Cu), Aluminium (Al), Gold (Au), Silver (Ag) etc)
- Note that holes do not contribute to conduction in a metal.



Electrical Conduction in Metals

- Let n be the number of CB electrons per unit volume (the “electron concentration”)
- Let v_e be electron velocity in metal at a particular electric field E .
- Remember that no holes contribute to the electric current in a metal, it is **just carried by electrons**.
- A similar analysis to that carried out for semiconductors shows that the **total current density** in a metal at the given value of electric field is:

Total current density (metal) = $J = J_e = q n v_e$

Example 1.2

SEMICONDUCTORS

- A class of crystalline material of enormous practical interest in electronics can be thought of as arising as **special case** of the insulator energy band structure considered earlier. Once again there is a VB and a CB separated by an energy bandgap and the material is a perfect insulator at 0K
- The crucial difference is that the **bandgap energy \mathcal{E}_g is relatively small, i.e. only approx 1eV.**
- At room temperature, a reasonably **significant number of thermally generated EHPs** can therefore be produced in such a material.
- The material is thus not a great conductor at room temperature, but it is equally not a good insulator: it is somewhere in-between, and is called a **SEMICONDUCTOR**

Semiconductors

- Important examples of semiconductors include Silicon (Si), Gallium Arsenide (GaAs), Gallium Nitride (GaN) etc.
- Generally, semiconductors are found in and around Group IV of the Periodic Table (see next slide – also, more later on)
- The total current density in a semiconductor at a given electric field is still given by the same formula as developed earlier for an insulator:

$$J = J_n + J_p = q \cdot n \cdot v_n + q \cdot p \cdot v_p$$

- The difference is that in a semiconductor the carrier concentrations **n** and **p** are relatively **large compared to an insulator**. However, the electron concentration **n** is **very much less than that found in a metal**.

Example 1.3

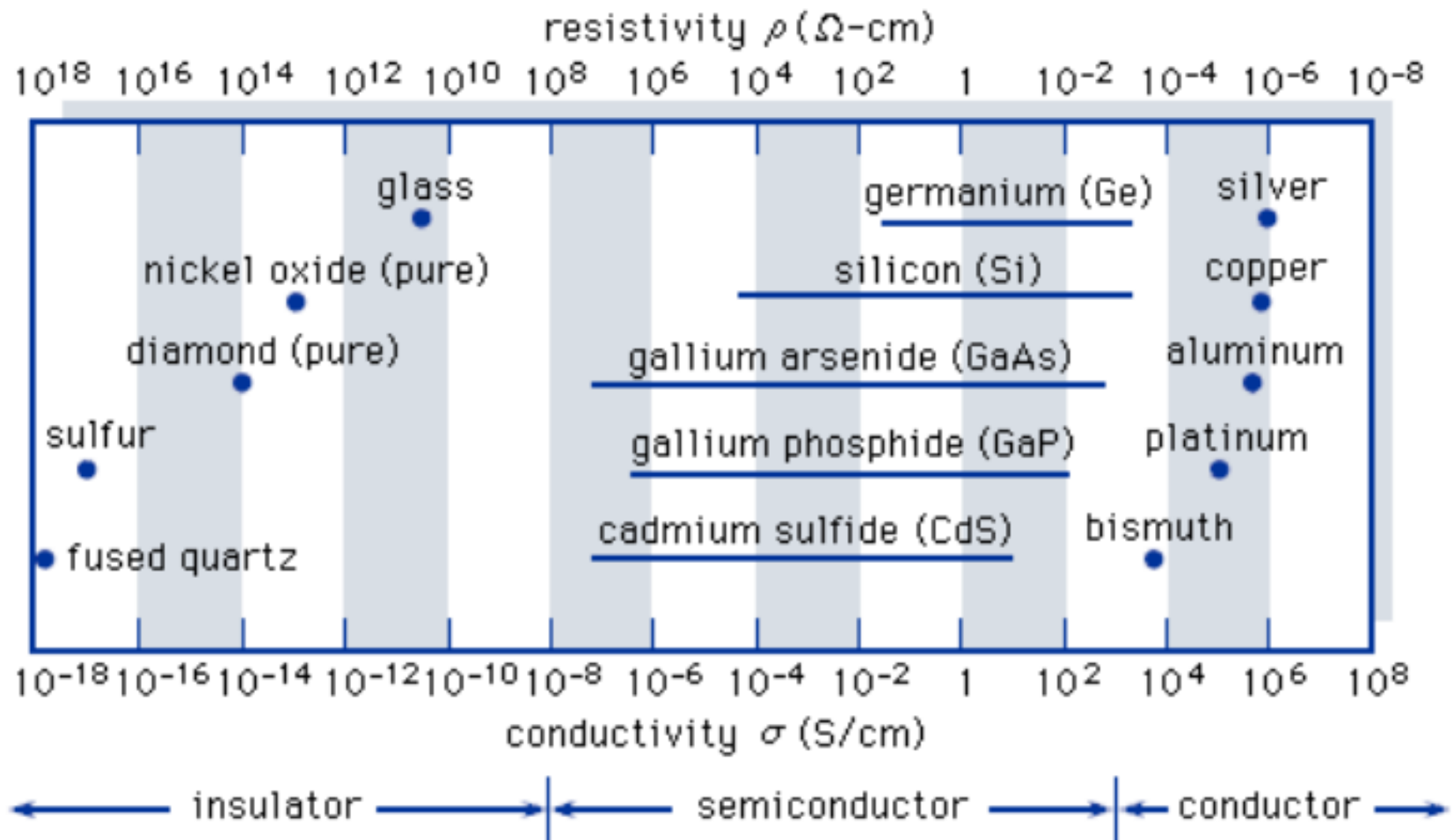
- A rod of pure Silicon at 300K has 1.5×10^{10} electrons/cm³ in the CB and the same concentration of holes in the VB. Assume that the CB electrons move at 3 m/sec while the VB holes move at 1 m/sec in response to an applied voltage. Find the current flowing through a cylindrical rod of pure silicon of cross-sectional area 1mm².

$$J = J_n + J_p = q \cdot n \cdot v_n + q \cdot p \cdot v_p$$

The Periodic Table of Elements

IA																		VIII																	
hydrogen 1 H 1.0079																		helium 2 He 4.0026																	
II A																		III A		IV A	V A	VIA	VII A												
lithium 3 Li 6.941		beryllium 4 Be 9.0122																boron 5 B 10.811		carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180											
sodium 11 Na 22.990		magnesium 12 Mg 24.305																aluminum 13 Al 26.982		silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948											
				Transition Elements																															
				III B	IV B	V B	VI B	VII B		I B	II B																								
potassium 19 K 39.098		calcium 20 Ca 40.078		scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80																
rubidium 37 Rb 85.468		strontium 38 Sr 87.62		yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29																
caesium 55 Cs 132.91		barium 56 Ba 137.33		lanthanum 57-70 Lu 174.97	hafnium 71 Hf 178.49	tantalum 72 Ta 180.95	tungsten 73 W 183.84	rhenium 74 Re 186.21	osmium 75 Os 190.23	iridium 76 Ir 192.22	platinum 77 Pt 195.08	gold 78 Au 196.97	mercury 79 Hg 200.59	thallium 80 Tl 204.38	lead 81 Pb 207.2	bismuth 82 Bi 208.98	polonium 83 Po [209]	astatine 84 At [210]	radon 85 Rn [222]																
francium 87 Fr [223]		radium 88 Ra [226]		actinium 89-102 Lr [262]	rutherfordium 103 Rf [261]	dubnium 104 Db [262]	seaborgium 105 Sg [266]	bohrium 106 Bh [264]	hassium 107 Hs [269]	meitnerium 108 Mt [268]	unnilium 109 Uun [271]	ununium 110 Uuu [272]	unbibium 111 Uub [277]		ununquadium 112 Uuq [289]																				

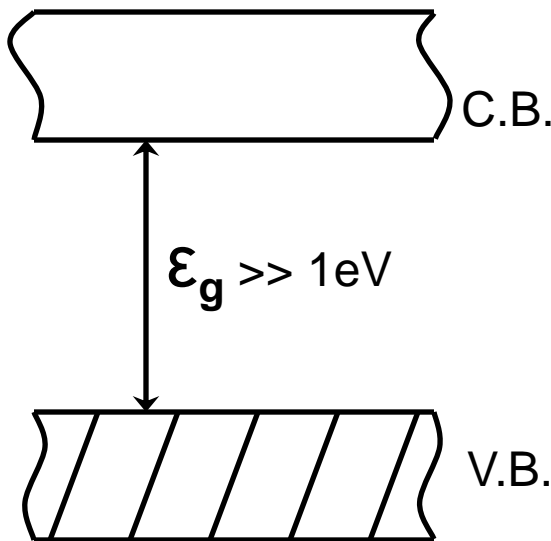
Range of Electrical Conductivity in Nature



Summary of Band Picture of Solid-State Crystalline Materials

3 categories of solid-state crystalline materials based on energy band properties:

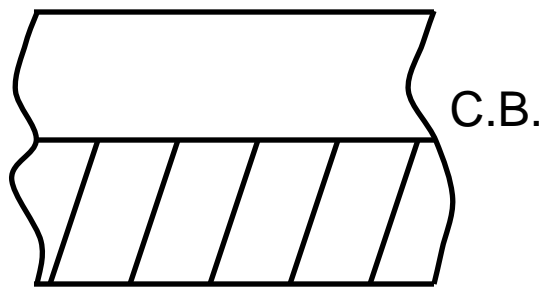
(1)



INSULATORS

- Large Band-Gap Energy;
- $J_n \approx 0$ and $J_p \approx 0$ - approx. zero current;
- Insulators are very poor conductors of electricity.

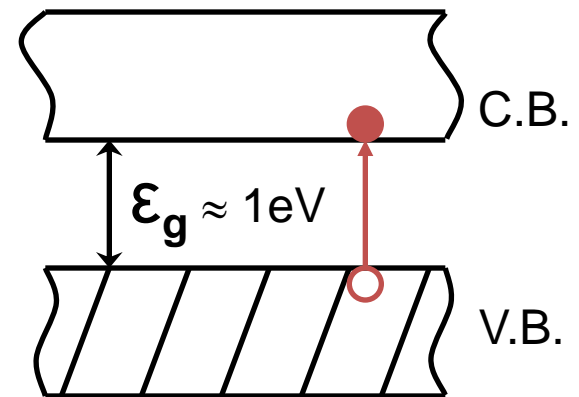
(2)



METALS

- No bandgap, no holes;
- Current due to CB electrons only;
- Large concentration of CB electrons;
- Metals are excellent conductors of electric current.

(3)



SEMICONDUCTORS

- Small Band-Gap Energy;
- Both holes and electrons contribute to current flow;
- Small J_n and J_p in pure material –relatively poor conductors of electricity.