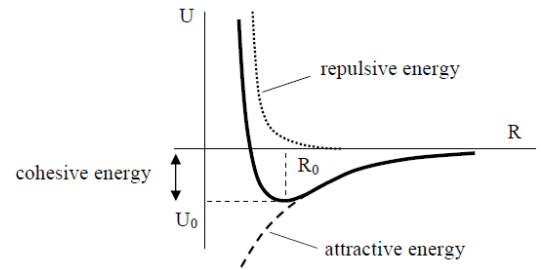




(Each question = 16 Marks)

1. Crystal binding

- a. Plot and explain the variation of (i) attractive potential energy (ii) repulsive potential energy (iii) resultant potential energy with interatomic distance, when two atoms are brought near.



The answer:

- The energy of the crystal is lower than that of the free atoms by an amount equal to the energy required to pull the crystal apart into a set of free atoms. This is called the binding (cohesive) energy of the crystal.
 - NaCl is more stable than a collection of free Na and Cl.
 - Ge crystal is more stable than a collection of free Ge.

This typical curve has a minimum at equilibrium distance R_0

$R > R_0$;

Potential increases gradually, approaching 0 as $R \rightarrow \infty$ the force is attractive

$R < R_0$;

Potential increases very rapidly, approaching ∞ at small separation.
 the force is repulsive.

- Force between the atoms is the negative of the slope of this curve. At equilibrium, repulsive force becomes equals to the attractive part.

The potential energy of either atom will be given by:

$$V = \text{decrease in potential energy (due to attraction)} + \text{increase in potential energy (due to repulsion)}$$

or simply: $F(r) = -\frac{\partial V(r)}{\partial r}$ and

$$V(r) = \frac{-a}{r^m} + \frac{b}{r^n}$$

- $V(r)$: the net potential energy of interaction as function of r
- r : the distance between atoms, ions, or molecules
- a, b : proportionality constant of attraction and repulsion, respectively
- m, n : constant characteristics of each type of bond and type of structure

- b. Explain the various types of bonding in crystals. Illustrate with examples.

Answer:

It is conventional to classify the bonds between atoms into different types as Ionic, Covalent, Metallic, Van der Waals and Hydrogen.

All bonding is a consequence of the electrostatic interaction between nuclei and electrons obeying Schrödinger's equation.

1. ionic

- Ionic bonding is the electrostatic force of attraction between positively and negatively charged ions (between non-metals and metals).



- These ions have been produced as a result of a transfer of electrons between two atoms with a large difference in electro negativities.
- All ionic compounds are crystalline solids at room temperature.
- NaCl is a typical example of ionic bonding.

2. Covalent

- Covalent bonding takes place between atoms with small differences in electronegativity which are close to each other in periodic table (*between non-metals and non-metals*).
- The covalent bonding is formed by sharing of outer shell electrons (i.e., s and p electrons) between atoms rather than by electron transfer.
- This bonding can be attained if the two atoms each share one of the other's electrons.
- So the noble gas electron configuration can be attained.

3. Metallic

- Metallic bonding is the type of bonding found in metal elements. This is the electrostatic force of attraction between positively charged ions and delocalized outer electrons.
- The metallic bond is weaker than the ionic and the covalent bonds.
- Metallic structures are typically rather empty (having large internuclear spacings) and prefer lattice arrangements in which each atom has many nearest neighbors.
- The weakness of the individual bonding actions in a metal is due to the enlargement of the internuclear spacing.

4- Van Der Waals

- It is a weak bond, with a typical strength of 0.2 eV/atom.
- It occurs between neutral atoms and molecules.
- The explanation of these weak forces of attraction is that there are natural fluctuation in the electron density of all molecules and these cause small temporary dipoles within the molecules. It is these temporary dipoles that attract one molecule to another. They are called van der Waals' forces.
- The bigger a molecule is, the easier it is to polarize (to form a dipole), and so the van der Waal's forces get stronger, so bigger molecules exist as liquids or solids rather than gases.
- The **shape** of a molecule influences its ability to form temporary dipoles. Long thin molecules can pack closer to each other than molecules that are more spherical. The bigger the 'surface area' of a molecule, the greater the van der Waal's forces will be and the higher the melting and boiling points of the compound will be.
- Van der Waal's forces are of the order of 1% of the strength of a covalent bond.

2. Crystal Structure and X-ray diffraction

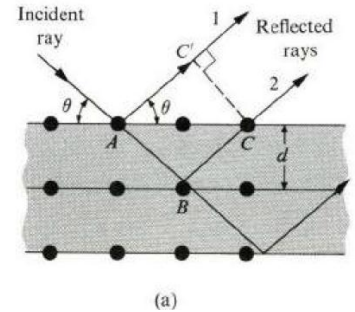
- a. Define or explain: crystal lattice, lattice vector, unit cell, primitive cell, Miller indices and packing ratio?

Answer

- Crystal lattice is geometrical pattern, or simply the lattice; all the atomic sites have been replaced by lattice sites.
- The lattice has a translational symmetry under all displacements specified by the lattice vectors R_n .
- The area of the parallelogram whose sides are the basis vectors a and b is called a unit cell of the lattice
- Primitive cell is unit cell has only one lattice point.
- Packing ration is defined as the fraction of the total volume of the cell that is filled by atoms



- Miller indices: The orientation of a plane in a lattice is specified by giving its Miller indices, which are defined as the reciprocal of intercepts with the axes along the basis vectors a , b , and c .



- b. In tetragonal lattice, $a = b = 0.25$ nm and $c = 0.18$ nm, deduce the spacing between (111) planes.

Answer:

$$d_{hkl} = \frac{1}{\sqrt{\frac{a^2}{h^2} + \frac{b^2}{k^2} + \frac{c^2}{l^2}}} = \frac{1}{\sqrt{\frac{(0.25)^2}{1^2} + \frac{(0.25)^2}{1^2} + \frac{(0.18)^2}{1^2}}} = \frac{1}{\sqrt{0.28254}} = \frac{1}{0.5314} \text{ nm} = 1.881 \text{ nm}$$

- c. Derive Bragg's law of X-ray diffraction.

Answer:

The incident beam is reflected partially at each of these planes, which act as mirrors, and the reflected rays are then collected simultaneously at a distant detector. The reflected rays interfere at the detector and, according to physical optics, the interference is constructive only if the difference between the paths of any two consecutive rays is an integral multiple of the wavelength. That is, $\text{Path difference}(\Delta) = n\lambda$, $n = 1, 2, 3, \dots$ where λ is the wavelength and n is a positive integer. The path difference Δ between rays 1 and 2 in the figure is $\Delta = \overline{AB} + \overline{BC} - \overline{AC'}$ when the angles of incidence equal the angles of reflection. When the interplanar distance is denoted by d , it follows from the figure that

$$\overline{AB} = d / \sin \theta \text{ and } \overline{AC'} = \overline{AC} \cos \theta = (2d / \tan \theta) \times \cos \theta$$

where θ is the glancing angle between the incident beam and the reflecting planes. Substituting these into (1) and performing some trigonometric manipulation, we arrive at the following condition for constructive interference: $2d \sin \theta = n\lambda$

- d. A beam X-rays of wavelength 0.071 nm is diffracted by (110) plane of rock salt with lattice constant of 0.28 nm. Find the glancing angle for the second order diffraction.

Answer:

$$2d \sin \theta = n\lambda \rightarrow \sin \theta = \frac{n\lambda}{2d} \rightarrow \theta = \sin^{-1} \left(\frac{n\lambda}{2d_{110}} \right) = \sin^{-1}(0.36) \rightarrow \theta = 21.12$$

3. Free electron theory

- a. Derive the electrical conductivity in metals.

Answer:

$$I = \frac{V}{R}, J = \frac{I}{A} \cdot \varepsilon = \frac{V}{L}, R = \frac{L\rho}{A}, J = \sigma \varepsilon \text{ and } \sigma = \frac{1}{\rho}$$

$$m^* \frac{dv}{dt} = -e\varepsilon - m^* \frac{v}{\tau} \rightarrow v = -\frac{e\tau}{m^*} \varepsilon$$

$$J = (-Ne) v_d = (-Ne) \left(-\frac{e\tau}{m^*} \varepsilon \right) = \frac{Ne^2\tau}{m^*} \varepsilon.$$

$$\sigma = \frac{Ne^2\tau}{m^*},$$



- b. Explain the assumptions made in quantum theory to overcome the drawbacks in heat capacity of free electron theory of metals.

Answer

$$\langle \bar{E} \rangle = N_A \left(\frac{3}{2} kT \right) = \frac{3}{2} RT,$$

$$C_e = \frac{3}{2} R \approx 3 \text{ cal/mole } ^\circ\text{K}.$$

$$C = C_{ph} + C_e,$$

$$C = 3R + \frac{3}{2} R = 4.5R \approx 9 \text{ cal/mole } ^\circ\text{K}.$$

$$f(E) = \frac{1}{e^{(E-E_F)/kT} + 1} \quad f(E) = \begin{cases} 1, & E < E_F \\ 0, & E > E_F \end{cases}$$

$$\bar{E} = \frac{N_A (kT)^2}{E_F},$$

$$C_e = 2R \frac{kT}{E_F} \rightarrow C_e = 2R \frac{T}{T_F}.$$

$$C_e = \frac{\pi^2}{2} R \frac{kT}{E_F},$$

4. Lattice dynamics

- a. Define or explain the following terms: 1) Dispersion Relation, 2) Phonon, 3) Harmonic Oscillators, 4) Zero Point Energy

Answer

- Dispersion relation is the relation connecting the frequency and wavenumber $\omega = v_s q$
- Phonon is the particle-like entity which carries the unit energy of the elastic field in a particular mode.
- Harmonic oscillators is reached when the solid is heated, the atoms vibrate around their sites.
- Zero point energy: Actually the exact expression is $\varepsilon_n = \left(n + \frac{1}{2} \right) \hbar \omega$. The lowest state, $n = 0$, is the ground state, while the higher states are the excited states. This shows that the oscillator executes some motion even in the lowest possible state. This is referred to as zero-point motion, and its energy as zero-point energy.

1. Consider the model one-dimensional diatomic lattice. A diatomic lattice in which the unit cell is composed of two atoms of masses M_1 and M_2 , and, the distance between two neighboring atoms is a . The force constant coupling each atom to its nearest-neighbors is α . We discussed in class that the normal mode vibrational frequency $\omega(\mathbf{q})$ of a mode with wavevector \mathbf{q} for this model is:



$$\omega^2 = \alpha \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \mp \alpha \sqrt{\left(\frac{1}{M_1} + \frac{1}{M_2} \right)^2 - \frac{4 \sin^2(qa)}{M_1 M_2}} \quad [-(\pi/a) \leq q \leq (\pi/a)]$$

- Plot and describe the relation between ω and q .
- How the diatomic lattice acts as a band-pass mechanical filter?

With my best wishes &