Lecture 1 - 4

Introduction, Atomic Bonding & Crystal Structure: metallic bond, unit cell, atomic packing, interstitial sites, Miller indices, crystal orientation, stereographic projection:

Question:

1. What are the three primary bonds in materials? Which is the strongest? Why?
2. What is the electronic configuration of silicon atom? What type of bond do you expect here?
3. Inert gases have completely filled outer cell yet the boiling point of these increases with the atomic number. Explain why it is so.
4. Find out from Handbook the melting points of metals in the 4th row of the periodic table (K-Zn). Which has the highest melting point? Explain this in terms of their electronic configurations.
5. Stiffness of C-C bond is around 200N/m. Estimate its elastic modulus assuming the distance between the atoms to be 2×10^{-10}m. Which form of carbon has such a modulus?
6. Sketch an unit cell and show the following planes (a) (112) (b) (101) (c) ($\bar{1}11$) (d) (123)
7. Find out the indices of the direction joining following points in a cubic lattice: (a) 1,1,1 with 1,1,2 (b) -1,1,1 with -3, 2, 1 (c) 1,1,2 with 3,2,-1
8. Show the atomic arrangements in (111) plane of face centre cubic structure and show the following directions $[1\bar{1}0], [\bar{1}01], [01\bar{1}], [\bar{2}11], [1\bar{2}1], [11\bar{2}]$
9. Estimate the density of platinum and lead from their lattice parameters at room temperature. Both are FCC. Compare the theoretical density with experimental values. Which is closer? Why?
10. What is the basic difference between engineering & stereographic projections? Show with the help of a neat sketch the relation between a plane and a pole drawn on a projection plane.
11. Draw a standard (001) projection of cubic crystal showing poles of low indices planes: (100), (110) and (111). List the [112] poles lying on plane (111)
12. You are given a standard 001 projection of a cubic crystal. Comment on the size of the crystal.
13. Why do you need to bring the two poles of stereographic projection on a longitude of the Wulff net by rotating it about its centre to measure the angle between the two?
14. The potential energy of a pair of atoms due to attractive force is (-A/x) and that due to repulsive force is (B/x^n) giving the net potential energy U = (-A/x)+(B/x^n). Use this to find out the minimum distance of separation of the two atoms & the corresponding binding energy.
15. If the strength of an atomic bond in a solid is given by $f = f_{max} \, sin\left\{\frac{\pi(x-a_0)}{a}\right\}$ where f represents force needed to stretch a bond as a function of the distance of separation between two atoms (x), a_0 denotes lattice parameter and a is measure of distance over which effect of inter-atomic forces can be felt find out an expression for strength of solid in terms of its elastic modulus, lattice parameters and surface energy.
16. Use the expression derived in problem 15 to show that the surface energy necessary to cause fracture is given by $\gamma = \frac{E}{a_0}\left(\frac{a}{\pi}\right)^2$ and estimate the same for iron. Given elastic modulus along <100> = 132 GPa , lattice parameter = 0.286 nm and $a = a_0$.
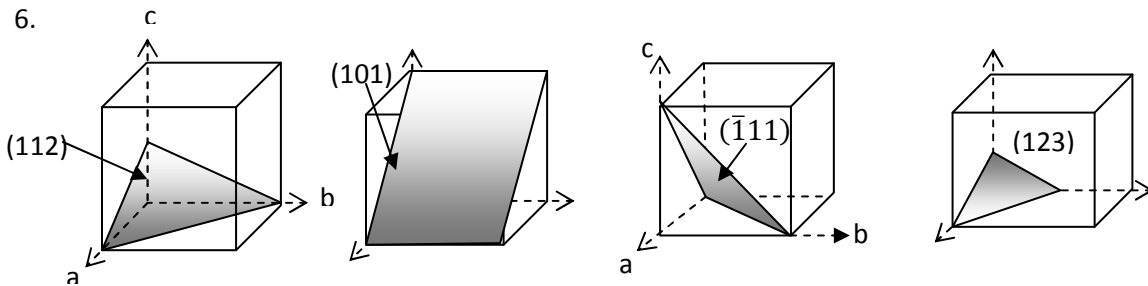
Answer:

1. Three primary bonds are covalent, ionic and metallic. Boiling or melting points of material are indicators of the strength of the bond. C-C bond (covalent) in diamond is possibly the strongest

bond. Its melting point is ~3700°C. Its atomic diameter is small. It is verified by x-ray diffraction data.

2. Atomic number of Si is 14. Its electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^2$. It has four atoms in the outer cell like carbon. It also forms covalent bond. Its atomic diameter is larger. The bond is not as strong as C-C bond. Its melting pint is 1410°C.

3. Inert gases have completely filled outer cell. As you go down the group (from He to Xe) the diameter increases as more orbits are added. As the diameter increases the centre of orbital electrons will no longer coincide with the nucleus. The deviation increases with the increase in diameter. The atoms will therefore behave like dipoles & promote bonding due to van der waal force. Boiling point of He (Z=2) & Xe (Z=54) are 4.2°K & 165°K respectively.

4. The fourth row of periodic table has several metals with atomic numbers varying from 19 (K) to 30(Zn). Their melting points are given in the following table. Electronic configuration of Ar (18) is $1s^2 2s^2 2p^6 3s^2 3p^6$. K atom has one more electron. Its preferred site is 4s. The next atom Ca has 2 electron in 4s cell. Thereafter electrons occupy 3d cell. Unpaired 3d electrons too participate in bond formation. If the number of such electron increases the cohesive energy and hence melting point increases. (Mn: exception?). In Zn all 3d electrons are paired & do not take part in bonding. In this case number of electrons that take part in bond formation is less. Therefore its melting point is low.

K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn25	Fe26	Co27	Ni28	Cu29	Zn30
64	833	1539	1668	1900	1875	1245	1539	1495	1453	1083	419

5. The bond is often visualized as a stiff spring which breaks without deformation. Relation between the force (F) needed to snap a bond and the stiffness (strength) of the bond (S) is given by $F = S\delta$ where δ is the minimum distance of separation at which bond breaks. Note that dimension of stiffness is N/m. The cross sectional area is of the order of a^2. Therefore stress $\sigma = F/a^2 = (S/a)(\delta/a) = E\varepsilon$ where E is modulus & ε is strain. Thus E = S/a. If $\boldsymbol{a}$ is of the order of inter atomic distance (a~0.2nm). $E = 200/(0.2 \times 10^{-9}) = 10^{12}$ N/m^2 = 1000 GPa.

6.

7.

If the coordinate of first point is u1, v1, w1 & the second point is u2, v2, w2 the indices of the line joining the two points can easily be shown with the help of the diagram on the left is [u2-u1, v2-v1, w2-w1]. Line joining point 111 with 112 is shown try others.

[001]
112
111

8.

[$\bar{1}$10]
[$\bar{2}$11]
[$\bar{1}$01]
[2$\bar{1}\bar{1}$]
[1$\bar{2}$1] [0$\bar{1}$1]

In a cubic crystal a direction [uvw] lies on a plane (hkl) then hu+kv+lw=0. Using this three close packed direction lying on (111) are [-110], [-101] & {0-11}. These are shown by firm line. Three [112] directions are [11-2], [-211] & [1-21]. These are shown as dotted lines.

9. The relation between density (ρ) & lattice parameter (a) is given by $\rho = \frac{An}{Na^3}$ where n= number of atom /unit cell, A = atomic weight & N=Avogrado number. For platinum A=192.09, n=4 fcc, N=6.02x10^{23} & a=3.9239 Angstrom. On substitution ρ = 21.45 gm/cc. Experimental density of Pt = 21.47. For lead A=207.2, n=4 fcc, a=4.9502Angstrom. On substitution in the expression for density ρ= 11.35 Experimental density =11.34. The estimation of x-ray density in based on assumptions that all sites are occupied and atoms are hard. If there are vacancies in the lattice real density should be less than x-ray density. If atoms are soft the density should be higher.

10. In engineering projection is a distance true projection where as stereographic projection is an angle true projection.

Plane
Pole
90^0

11.

$\bar{1}$00
$\bar{1}\bar{1}$0
$1\bar{1}$0
$\bar{1}$11
0$\bar{1}$0
010
1$\bar{1}$1
111
1$\bar{1}$0
110
100

12. The crystal (dimension) is assumed to be a point to construct a stereographic projection of a crystal. All planes in the crystal would therefore pass through the centre of the reference sphere. Crystal planes like (100), (200), (300) etc are all coincident.

13. A pole hkl in a stereographic projection represents a normal to the plane (hkl). It is therefore a direction in 3D. The angle measurement is done on plane passing through the two directions. A great circle in a Wulff net represents a plane. Therefore to measure the angle the two poles the Wulff net in so kept that both the poles lie on a great circle.

14. At equilibrium du/dx is zero & potential energy u is the minimum. If $u = -\frac{A}{x} + \frac{B}{x^n}$ or, $\frac{du}{dx} = \frac{A}{x^2} - \frac{nB}{x^{n+1}} = 0$. Therefore the minimum distance between two ions is given by: $x = \left(\frac{nB}{A}\right)^{1/(n-1)}$.

Therefore binding energy u is given by:

$$u = -A\left(\frac{A}{nB}\right)^{1/(n-1)} + B\left(\frac{A}{nB}\right)^{n/(n-1)} = A^n\left(\frac{A}{nB}\right)^{\frac{1}{n-1}}\left(\left(\frac{1}{n}\right)^n - 1\right)$$

15. The following sketch shows the nature of the force as a function of distance for this solid. If n is the number of bonds per unit area of the solid its strength $\sigma = nf_{max}\ sin\left\{\frac{\pi(x-a_0)}{a}\right\}$. If the bond stretches by a small distance dx the corresponding strain is $d\varepsilon = dx/a_0$. The elastic modulus (E) should therefore be given by the slope of the curve at $x = a_0$. Thus $E = a_0\left(\frac{d\sigma}{dx}\right)_{x=a_0} = \pi nf_{max}\frac{a_0}{a}$. Thus $nf_{max} = E\frac{a}{\pi a_0}$. The strong solids must have high elastic modulus, smaller atomic spacing and high surface energy.
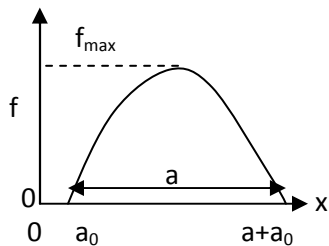
The area under the curve in the adjoining sketch is a measure of the energy creating two free surfaces whose net energy is $2\gamma = \int_{a_0}^{a+a_0}\frac{Ea}{\pi a_0}Sin\frac{\pi(x-a_0)}{a}dx$

$=\frac{Ea}{\pi a_0}\frac{a}{\pi}\left[-Cos\frac{\pi(x-a_0)}{a}\right]_{a_0}^{a+a_0} = 2\frac{a^2}{\pi^2 a_0}E$. Or $a = \pi\sqrt{\frac{\gamma a_0}{E}}$.

Thus strength $\sigma_{max} = nf_{max} = E\frac{a}{\pi a_0} = \sqrt{\frac{E\gamma}{a_0}}$

16. Rearrange the terms in the following equation derived in the problem 15 $a = \pi\sqrt{\frac{\gamma a_0}{E}}$ to get

$$\gamma = \left(\frac{E}{a_0}\right)\left(\frac{a}{\pi}\right)^2 \approx \frac{E}{10}a_0 = 132\times 10^9 \times 0.286 \times \frac{10^{-9}}{10} = 3.78\ J/m^2$$