1.3

Solution

a. Consider the *PE* of the whole arrangement of charges shown in the figure. In evaluating the *PE* of all the charges, we must avoid double counting of interactions between the same pair of charges. The total *PE* is the sum of the following:

> Electron 1 interacting with the proton at a distance r_o on the left, with the proton at r_o on the right and with electron 2 at a distance $2r_o$
>
> \+ Electron 2 on the far left interacting with a proton at r_o and another proton at $3r_o$
>
> \+ Two protons, separated by $2r_o$, interacting with each other

$$PE = -\frac{e^2}{4\pi\varepsilon_o r_o} - \frac{e^2}{4\pi\varepsilon_o r_o} + \frac{e^2}{4\pi\varepsilon_o (2r_o)} - \frac{e^2}{4\pi\varepsilon_o r_o} - \frac{e^2}{4\pi\varepsilon_o 3r_o} + \frac{e^2}{4\pi\varepsilon_o 2r_o}$$

Substituting and calculating, we find ***PE*** = -1.0176×10^{-17} J or **-63.52 eV**

The negative *PE* for this particular arrangement indicates that this arrangement of charges is indeed energetically favorable compared with all the charges infinitely separated (*PE* is then zero).

b. The potential energy of an isolated H-atom is -2× 13.6 eV or -27.2 eV. The difference between the *PE* of the H_2 molecule and two isolated H-atoms is,

$$\Delta PE = \ - (63.52)\text{ eV} - 2(-27.2)\text{ eV}=9.12\text{eV}$$

We can write the last expression above as the change in the total energy.

$$\Delta\overline{E} = \frac{1}{2}\Delta\overline{PE} = \frac{1}{2}(-9.12\text{eV}) = -4.56\text{eV}$$

This change in the total energy is negative. The H_2 molecule has lower energy than two H-atoms by 4.56 eV which is the bonding energy. This is very close to the experimental value of 4.51 eV. (Note: We used a r_o value from quantum mechanics - so the calculation was not totally classical).

1.4

Solution

Bonding will occur when potential energy $E(r)$ is minimum at $r = r_0$ corresponding to the equilibrium separation between Cs^+ and Cl^- ions. Thus, differentiating $E(r)$ and setting it equal to zero at $r = r_o$ we have

$$\left[\frac{dE(r)}{dr}\right]_{r=r_o} = \frac{d}{dr}\left[-\frac{e^2M}{4\pi\varepsilon_o r} + \frac{B}{r^m}\right]_{r=r_o} = 0$$

$$\therefore \qquad \left[\frac{e^2M}{4\pi\varepsilon_o r^2} - m\frac{B}{r^{m+1}}\right]_{r=r_o} = 0$$

$$\therefore \qquad \frac{e^2M}{4\pi\varepsilon_o r_o^2} - m\frac{B}{r_o^{m+1}} = 0$$

$$\therefore \qquad r_o = \left[\frac{4\pi\varepsilon_o mB}{e^2M}\right]^{\frac{1}{m-1}}$$

Thus substituting the appropriate values we have

$$r_0 = \left[\frac{4\pi(8.8542\times 10^{-12}\,\mathrm{Fm^{-1}})\times 9\times(1.192\times 10^{-104}\,\mathrm{J\,m^9})}{1.763\times\left(1.6\times 10-19\mathrm{C}\right)^2}\right]^{\frac{1}{8}}$$

$\boldsymbol{r_o = 3.57\times 10^{-10}}$ **m** or **0.357 nm**.

The minimum energy is the energy at $r = r_o$, that is

$$E_{\min} = -\frac{e^2M}{4\pi\varepsilon_o r_o} + \frac{B}{r_o^m}$$

which in terms of eV is

$$E_{\min}(\mathrm{eV}) = -\frac{eM}{4\pi\varepsilon_o r_o} + \frac{B(\mathrm{eV\,nm^9})}{r_o(\mathrm{nm})^9}$$

$$= -\frac{(1.6\times 10^{-19}\mathrm{C})^2(1.763)}{4\pi(8.8542\times 10^{-12}\,\mathrm{Fm^{-1}})(3.57\times 10^{-10}\mathrm{m})} + \frac{7.442\times 10^{-4}\,\mathrm{eV\,nm^9}}{(0.357\,\mathrm{nm})^9}$$

= − 6.32 eV per ion pair, or 3.16 eV per ion.

The amount of energy required to break up Cs^+-Cl^- pair into Cs^+ and Cl^- ions = 6.32 eV per pair of ions.

The corresponding *ionic cohesive energy* is

$E_{\mathrm{cohesive}} = (6.32\ \mathrm{eV})(1.6\times 10^{-19}\ \mathrm{J\,eV^{-1}})(6.022\times 10^{-23}\ \mathrm{mol^{-1}})$

= **610 kJ mol**$\boldsymbol{^{-1}}$ **of** $\boldsymbol{Cs^+Cl^-}$ **ion pairs or 610 kJ mol**$\boldsymbol{^{-1}}$ **of** $\boldsymbol{Cs^+}$ **ions and** $\boldsymbol{Cl^-}$ **ions.**

(Not far out from the experimental value given the large numbers and the high index, $m = 9$, involved in the calculations.)

The amount of energy required to remove an electron from Cl^- ion = 3.61 eV.
The amount of energy released when an electron is put into the Cs^+ ion = 3.89 eV.
Bond Energy per pair of Cs-Cl atoms = 6.32 eV + 3.61 eV – 3.89 eV = **6.04 eV**
Atomic cohesive energy in kJ/mol is,

$$E_{\text{cohesive}} = (6.04\text{ eV})(1.6 \times 10^{-19}\text{ J eV}^{-1})(6.022\times 10^{23}\text{ mol}^{-1})$$

= 582 kJ mol^{-1} of Cs or Cl atom (*i.e.* per mole of Cs-Cl atom pairs)

= 291 kJ mol^{-1} of atoms

Author's Note: There is a *selected topic* entitled "Bonding" in the Chapter 1 folder in the textbook's CD where the bonding energy is calculated more accurately by taking a more realistic energy curve. The above calculation is similar to that given in Alan Walton, *Three Phases of Matter* (2nd Edition), Oxford University Press, 1983 (pp. 258-259)

Author's Note to the Instructors: Various books and articles report different values for B and m, which obviously affect the calculated energy; r_o is less affected because it requires the $(m-1)^{\text{th}}$ root of mB. Richard Christman (*Introduction to Solid State Physics*, Wiley, 1988) in Table 5-1 gives, m = 10.65 and $B = 3.44 \times 10^{120}$, quite different than values here, which are closer to values in Alan Walton's book. The experimental value of 657 kJ mol^{-1} for the ionic cohesive energy (the ionic lattice energy) is from
T. Moeller et al, *Chemistry with Inorganic Qualitative Analysis,* Second Edition, Academic Press, 1984) p. 413, Table 13.5.

Some authors use the term molecular cohesive energy to indicate that the crystal is taken apart to molecular units e.g. Cs^+Cl^-, which would correspond to the ionic cohesive energy here. Further, most chemists use "energy per mole" to imply energy per chemical unit, and hence the atomic cohesive energy per mole would usually refer to energy be per Cs and Cl atom pairs. Some authors refer to the atomic cohesive energy per mole as cohesive energy per mole of atoms, independent of chemical formula.

1.6

Solution

a. Interatomic separation $r = r_0$ is the distance at minimum $E(r)$, Therefore we differentiate $E(r)$ and set it equal to zero. *i.e.*

$$\left[\frac{dE(r)}{dr}\right]_{r=r_0} = \frac{d}{dr}\left[-\frac{A}{r^n} + \frac{B}{r^m}\right]_{r=r_0} = 0$$

$$\therefore \qquad \left[\frac{An}{r^{n+1}} - \frac{mB}{r^{m+1}}\right]_{r=r_0} = 0$$

$$\therefore \qquad \frac{An}{r_0^{\;n+1}} - \frac{mB}{r_0^{\;m+1}} = 0$$

$$\therefore \qquad \frac{r_0^{m+1}}{r_0^{\;n+1}} = \frac{mB}{nA} \qquad \text{or} \qquad r_0^{m-n} = \frac{mB}{nA}$$

$$\therefore \qquad r_0 = \left[\frac{mB}{nA}\right]^{\frac{1}{m-n}}$$

The potential energy is minimum at $r = r_0$ and is related with bonding energy $E(r_0) = -E_{\text{bond}}$. From the equation for r_0 we have

$$r_0^{\;m-n} = \frac{Bm}{An} \quad \text{and isolate for } B,$$

$$B = \frac{Anr_0^{m-n}}{m}$$

Substitute for B in the energy relation

$$E(r) = -\frac{A}{r_0^n} + \frac{B}{r_0^m} = -\frac{A}{r_0^n} + \frac{1}{r_0^m}\left(\frac{Anr_0^{m-n}}{m}\right)$$

$$= -\frac{A}{r_0^n} + \frac{Anr_0^{m-n-m}}{m} = -\frac{A}{r_0^n} + \frac{Anr_0^{-n}}{m} = -\frac{A}{r_0^n} + \frac{An}{mr_0^n}$$

$$\therefore \qquad E_{\text{bond}} = -E(r) = -\left[-\frac{A}{r_0^n}\left(1 - \frac{n}{m}\right)\right]$$

$$\therefore \qquad E_{\text{bond}} = \frac{A}{r_0^n}\left(1 - \frac{n}{m}\right)$$

b. Show that the bulk modulus is given by

$$K = \frac{An}{9cr_o^{n+3}}(m-n) \qquad \text{or} \qquad K = \frac{mnE_{\text{bond}}}{9cr_o^3}$$

From the definition of Bulk modulus mentioned in the problem statement above

$$K = \frac{1}{9cr_0}\left[\frac{d^2E}{dr^2}\right]_{r=r_0}$$

First we find $\dfrac{d^2E}{dr^2}$

$$\frac{dE(r)}{dr} = \frac{d}{dr}\left(-\frac{A}{r^n} + \frac{B}{r^m}\right) = \frac{An}{r^{n+1}} - \frac{mB}{r^{m+1}}$$

$$\therefore \qquad \left[\frac{dE^2(r)}{dr^2}\right]_{r=r_0} = \left[\frac{d}{dr}\left(\frac{An}{r^{n+1}} - \frac{mB}{r^{m+1}}\right)\right]_{r=r_0}$$

$$= \left[\frac{-n(n+1)A}{r^{n+2}} + \frac{m(m+1)B}{r^{m+2}} \right]_{r=r_0} = \frac{-n(n+1)A}{r_0^{\;n+2}} + \frac{m(m+1)B}{r_0^{\;m+2}}$$

Again substituting the value of *B* in the above relation, *i.e.* $B = \dfrac{Anr_0^{m-n}}{m}$ we have

$$\left[\frac{dE^2(r)}{dr^2} \right]_{r=r_0} = \frac{-n(n+1)A}{r_0^{\;n+2}} + \frac{m(m+1)}{r_0^{\;m+2}} \frac{Anr_0^{m-n}}{m} = \frac{-n(n+1)A}{r_0^{\;n+2}} + \frac{An(m+1)}{r_0^{\;m+2-m+n}}$$

$$= \frac{-n(n+1)A}{r_0^{\;n+2}} + \frac{An(m+1)}{r_0^{\;n+2}} = \frac{An}{r_0^{\;n+2}}\left(-n-1+m+1\right) = \frac{An(m-n)}{r_0^{\;n+2}}$$

Not substitute for the second derivative in the equation for the Bulk modulus

$$K = \frac{1}{9cr_0}\left[\frac{d^2E}{dr^2} \right]_{r=r_0} = \frac{1}{9cr_0}\left(\frac{An(m-n)}{r_0^{n+2}} \right)$$

or $$K = \frac{An(m-n)}{9cr_0^{n+3}}$$

From the relationship for bonding energy,

$$E_{\text{bond}} = -\frac{A}{r_0^n}\left(1 - \frac{n}{m}\right) = -\frac{A(m-n)}{r_0^n m}$$

$\therefore$ $$K = \frac{A(m-n)}{r_0^n m} \frac{mn}{9cr_0^3}$$

or $$K = E_{\text{bond}} \frac{mn}{9cr_0^3}$$

c. From Example 1.3, the bonding energy for NaCl is $M = 1.748$, $n = 1$, $m = 8$, $r_0 = 0.281 \times 10^{-9}$ m, $c = 2$. Therefore,

$$A = \frac{e^2M}{4\pi\varepsilon_0} = \frac{(1.6\times10^{-19}\,\text{C})^2(1.748)}{4\pi(8.85\times10^{-12}\,\text{F}\,\text{m}^{-1})} = 4.022 \times 10^{-28}.$$

Substitute *A* in expression for *K* we have

$$K = \frac{An(m-n)}{9cr_0^{n+3}} = \frac{(4.022\times10^{-28})(1)(8-1)}{9\cdot(2)(0.281\times10^{-9})^{1+3}} = \mathbf{25.1 \times 10^9\ Pa\ or\ 25.1\ GPa}$$

Author's Note: Experimental value is roughly 2.4×10^{10} Pa or 24 GPa. The calculated value is quite close.

1.22

Solution

a. Since molybdenum has BCC crystal structure, there are 2 atoms in the unit cell. The density is

$$\rho = \frac{\text{Mass of atoms in unit cell}}{\text{Volume of unit cell}} = \frac{(\text{Number of atoms in unit cell}) \times (\text{Mass of one atom})}{\text{Volume of unit cell}}$$

that is, $$\rho = \frac{2\left(\dfrac{M_{at}}{N_A}\right)}{a^3}$$

Solving for the lattice parameter *a* we receive

$$a = \sqrt[3]{\frac{2M_{at}}{\rho N_A}} = \sqrt[3]{\frac{2(95.94 \times 10^{-3}\text{kg mol}^{-1})}{(10.22 \times 10^3\text{kg m}^{-3})(6.022 \times 10^{23}\text{ mol}^{-1})}}$$ = **3.147 × 10^{-10} m = 0.3147 nm**

The Atomic concentration is 2 atoms in a cube of volume a^3, *i.e.*

$$n_{at} = \frac{2}{a^3} = \frac{2}{(3.147 \times 10^{-10}\text{m})^3}$$ = **6.415 × 10^{22} cm^{-3} = 6.415 × 10^{28} m^{-3}**

For a BCC cell, the lattice parameter *a* and the radius of the atom *R* are in the following relation (listed in Table 1.3):

$$R = \frac{a\sqrt{3}}{4} = \frac{(3.147 \times 10^{-10}\text{m})\sqrt{3}}{4}$$ = **1.363 × 10^{-10} m 0.1363 nm**

b. Gold has the FCC crystal structure, hence, there are 4 atoms in the unit cell (as shown in Table 1.3).

The lattice parameter *a* is

$$a = \left[\frac{4M_{at}}{\rho N_A}\right]^{1/3} = \left[\frac{4(196.97 \times 10^{-3}\text{kg mol}^{-1})}{(19.3 \times 10^3\text{kg m}^{-3})(6.022 \times 10^{23}\text{ mol}^{-1})}\right]^{1/3}$$ = **4.077 × 10^{-10} m = 0.4077 nm**

The atomic concentration is

$$n_{at} = \frac{4}{a^3} = \frac{4}{(4.077 \times 10^{-10}\text{m})^3}$$ = **5.901 × 10^{22} cm^{-3} = 5.901 × 10^{28} m^{-3}**

For an FCC cell, the lattice parameter *a* and the radius of the atom *R* are in the following relation (shown in Table 1.3):

$$R = \frac{a\sqrt{3}}{4} = \frac{(4.077 \times 10^{-10}m)\sqrt{2}}{4}$$ = **1.442 × 10^{-10} m = 0.1442 nm**

1.24

Solution

Planar concentration (or density) is the number of atoms per unit area on a given plane in the crystal. It is the surface concentration of atoms on a given plane. To calculate the planar concentration $n_{(hkl)}$ on a given (*hkl*) plane, we consider a bound area *A*. Only atoms whose centers lie on *A* are involved in the calculation of $n_{(hkl)}$. For each atom, we then evaluate what portion of the atomic cross section cut by the plane (*hkl*) is contained within *A*.

For the BCC crystalline structure the planes (100), (110) and (111) are drawn in Figure 1Q24-1.

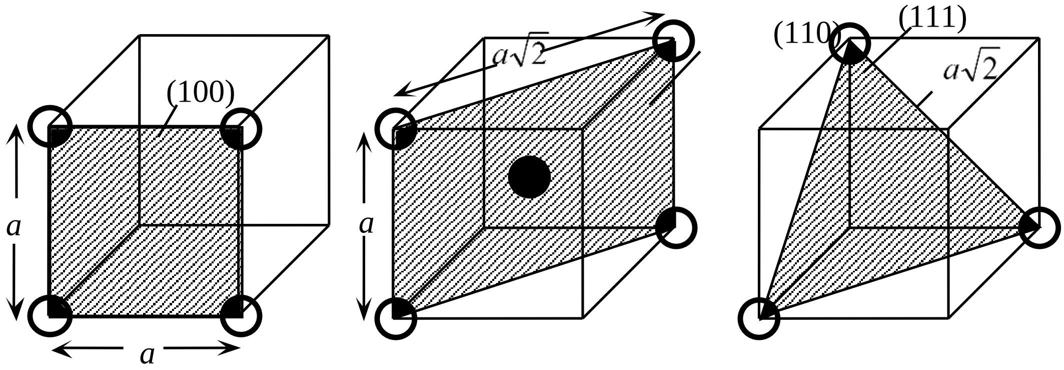

Figure 1Q24-1: (100), (110), (111) planes in the BCC crystal

Consider the (100) plane.

Number of atoms in the area a × a, which is the cube face = (4 corners) × (1/4th atom at corner) = 1.

Planar concentration is

$$n_{(100)} = \frac{4\left(\frac{1}{4}\right)}{a^2} = \frac{1}{\left(3.294\times10^{-10}\text{m}\right)^2} \quad \mathbf{= 9.216 \times 10^{18}\ atoms\ m^{-2}}$$

The most populated plane for BCC structure is (110).

Number of atoms in the area $a \times a\sqrt{2}$ defined by two face-diagonals and two cube-sides

= (4 corners) × (1/4th atom at corner) + 1 atom at face center = 2

Planar concentration is

$$n_{(110)} = \frac{4\left(\frac{1}{4}\right)+1}{a^2\sqrt{2}} = \frac{2}{\left(3.294\times10^{-10}\text{m}\right)^2\sqrt{2}} \quad \mathbf{= 1.303 \times 10^{19}\ atoms\ m^{-2}}$$

The plane (111) for the BCC structure is the one with rarest population. The area of interest is an equilateral triangle defined by face diagonals of length $a\sqrt{2}$ (see Figure 1Q24-1). The height of the triangle is $a\sqrt{\frac{3}{2}}$ so that the triangular area is $\frac{1}{2}\times a\sqrt{2}\times a\sqrt{\frac{3}{2}}=\frac{a^2\sqrt{3}}{2}$. An atom at a corner only contributes a fraction (60°/360°=1/6) to this area.

So, the planar concentration is

$$n_{(111)}=\frac{\frac{1}{6}(3)}{\frac{a^2\sqrt{3}}{2}}=\frac{1}{a^2\sqrt{3}}=\frac{1}{\left(3.294\times10^{-10}\text{m}\right)^2\sqrt{3}}\quad \mathbf{= 5.321 \times 10^{18}\ atoms\ m^{-2}}$$

For the BCC structure there are two atoms in unit cell and the bulk atomic concentration is

$$n_{bulk}=\frac{\text{number of atoms in unit cell}}{vo\text{volume of the cell}}=\frac{2}{a^3}=\frac{2}{\left(3.294\times10^{-10}\text{m}\right)^3}$$

$$\mathbf{= 5.596 \times 10^{28}\ atoms\ m^{-3}}$$

and the surface concentration is

$$n_{surface}=\left(n_{bulk}\right)^{\frac{2}{3}}=\left(5.596\times10^{28}m^{-3}\right)^{\frac{2}{3}}\quad \mathbf{= 1.463 \times 10^{19}\ atoms\ m^{-2}}$$

1.27

Solution

This problem assumes that students are familiar with three dimensional geometry and vector products.

Figure 1Q27-1(a) shows a typical [*hkl*] line, labeled as **ON**, and a (*hkl*) plane in a cubic crystal. $\mathbf{u}_x$, $\mathbf{u}_y$ and $\mathbf{u}_z$ are the unit vectors along the *x*, *y*, *z* coordinates. This is a cubic lattice so we have Cartesian coordinates and $\mathbf{u_x}\cdot\mathbf{u_x}$ = 1 and $\mathbf{u}_x\cdot\mathbf{u}_y$ = 0 etc.

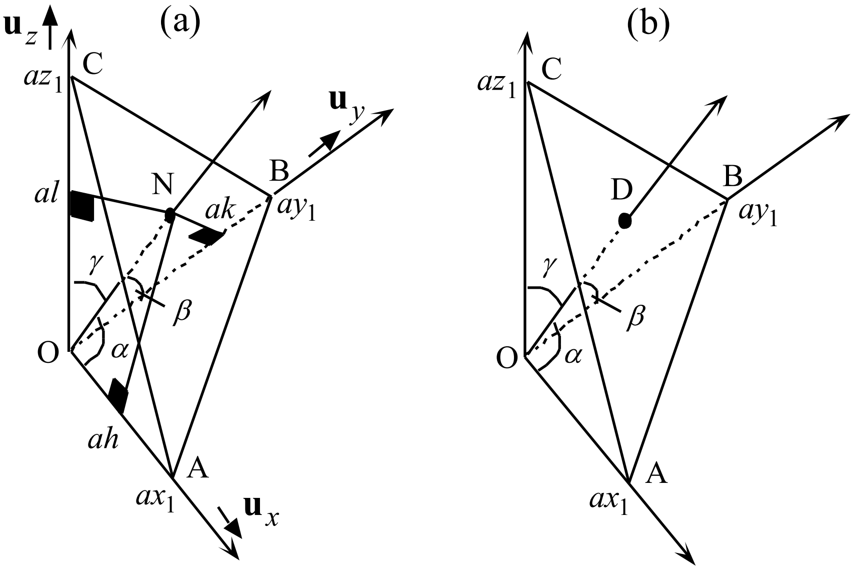

Figure 1Q27-1: Crystallographic directions and planes

a. Given a = lattice parameter, then from the definition of Miller indices ($h = 1/x_1$, $k = 1/y_1$ and $l = 1/z_1$), the plane has intercepts: $x_o = ax_1 = a/h$; $y_o = ay_1 = a/k$; $z_o = az_1 = a/l$.

The vector **ON** = $ah\mathbf{u}_x + ak\mathbf{u}_y + al\mathbf{u}_z$

If **ON** is perpendicular to the (hkl) plane then the product of this vector with any vector in the (hkl) plane will be zero. We only have to choose 2 non-parallel vectors (such as **AB** and **BC**) in the plane and show that the dot product of these with **ON** is zero.

AB = **OB** – **OA** = $(a/k)\mathbf{u}_y - (a/h)\mathbf{u}_x$

ON•AB = $(ah\mathbf{u}_x + ak\mathbf{u}_y + al\mathbf{u}_z) \bullet ((a/k)\mathbf{u}_y - (a/h)\mathbf{u}_x) = a^2 - a^2 = 0$

Recall that $\mathbf{u}_x\mathbf{u}_x = \mathbf{u}_y\mathbf{u}_y = 1$ and $\mathbf{u}_x\mathbf{u}_y = \mathbf{u}_x\mathbf{u}_z = \mathbf{u}_y\mathbf{u}_z = 0$

Similarly, **ON•BC** = $(ah\mathbf{u}_x + ak\mathbf{u}_y + al\mathbf{u}_z) \bullet ((a/l)\mathbf{u}_z - (a/k)\mathbf{u}_y) = 0$

Therefore **ON** or [hkl] is normal to the (hkl) plane.

b. Suppose that **OD** is the normal from the plane to the origin as shown in Figure 1Q27-1(b). Shifting a plane by multiples of lattice parameters does not change the miller indices. We can therefore assume the adjacent plane passes through O. The separation between the adjacent planes is then simply the distance **OD** in Figure 1Q27-1(b).

Let α, β and γ be the angles of **OD** with the x, y and z axes. Consider the direction cosines of the line **OD**: $\cos\alpha = d/(ax_1) = dh/a$; $\cos\beta = d/(ay_1) = dk/a$; $\cos\gamma = d/(az_1) = dl/a$

But, in 3 dimensions, $(\cos\alpha)^2 + (\cos\beta)^2 + (\cos\gamma)^2 = 1$

Thus, $(d^2h^2/a^2) + (d^2k^2/a^2) + (d^2l^2/a^2) = 1$

Rearranging, $d^2 = a^2 / [h^2 + k^2 + l^2]$

or, $\boldsymbol{d = a / [h^2 + k^2 + l^2]^{1/2}}$

1.28

Solution

a. Si has the diamond crystal structure with 8 atoms in the unit cell, and we are given the lattice parameter $a = 0.543 \times 10^{-9}$ m and atomic mass $M_{at} = 28.09 \times 10^{-3}$ kg/mol. The concentration of atoms per unit volume (n) in nm^{-3} is therefore:

$$n = \frac{8}{a^3}\frac{1}{\left(10^9\ \text{nm/m}\right)^3} = \frac{8}{\left(0.543\times10^{-9}\ \text{m}\right)^3}\frac{1}{\left(10^9\ \text{nm/m}\right)^3} = \mathbf{50.0\ atoms/nm^3}$$

If desired, the density ρ can be found as follows:

$$\rho = \frac{8\dfrac{M_{at}}{N_A}}{a^3} = \frac{8\dfrac{28.09\times10^{-3}\ \text{kg/mol}}{6.022\times10^{23}\ \text{mol}^{-1}}}{\left(0.543\times10^{-9}\ \text{m}\right)^3} = \mathbf{2331\ kg\ m^{-3}} \text{ or } \mathbf{2.33\ g\ cm^{-3}}$$

b. The (100) plane has 4 shared atoms at the corners and 1 unshared atom at the center. The corner atom is shared by 4 (100) type planes. Number of atoms per square nm of (100) plane area (n) is shown in Fig. 1Q28-1:

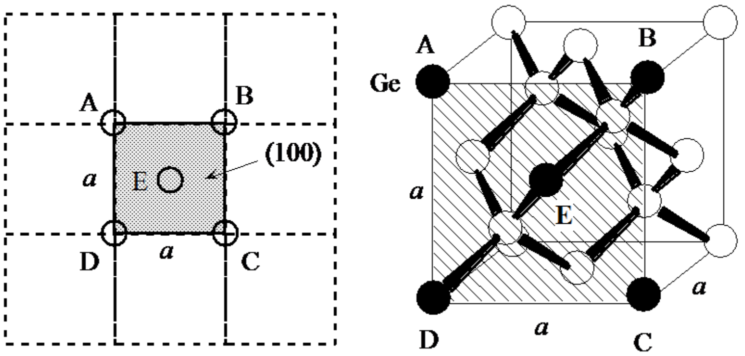

Figure 1Q28-1: The (100) plane of the diamond crystal structure.

The number of atoms per nm^2, n_{100}, is therefore:

$$n_{100} = \frac{4\left(\frac{1}{4}\right)+1}{a^2}\frac{1}{\left(10^9\ \text{nm/m}\right)^2} = \frac{4\left(\frac{1}{4}\right)+1}{\left(0.543\times10^{-9}\ \text{m}\right)^2}\frac{1}{\left(10^9\ \text{nm/m}\right)^2}$$

$\therefore$ $\mathbf{n_{100} = 6.78\ atoms/nm^2}$ or $\mathbf{6.78 \times 10^{18}\ atoms/m^2}$

The (110) plane is shown below in Fig. 1Q28-2. There are 4 atoms at the corners and shared with neighboring planes (hence each contributing a quarter), 2 atoms on upper and lower sides shared with upper and lower planes (hence each atom contributing 1/2) and 2 atoms wholly within the plane.

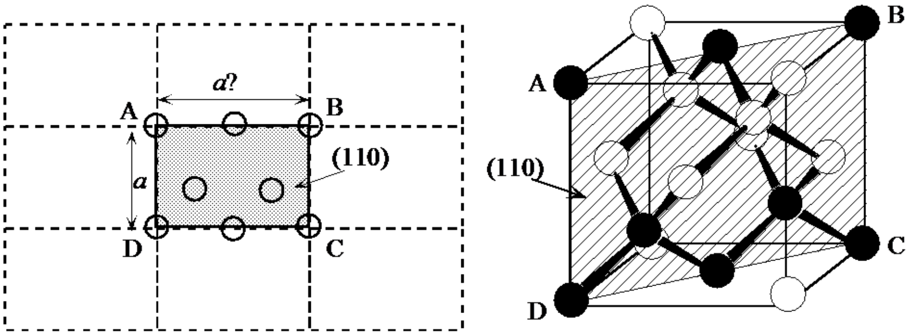

Figure 1Q28-2: The (110) plane of the diamond crystal structure.

The number of atoms per nm^2, n_{110}, is therefore:

$$n_{110} = \frac{4\left(\frac{1}{4}\right) + 2\left(\frac{1}{2}\right) + 2}{a\left(a\sqrt{2}\right)}\left(\frac{1}{\left(10^9 \text{ nm/m}\right)^2}\right)$$

$\therefore$

$$n_{110} = \frac{4\left(\frac{1}{4}\right) + 2\left(\frac{1}{2}\right) + 2}{\left[\left(0.543\times10^{-9}\text{ m}\right)\left(\left(0.543\times10^{-9}\text{ m}\right)\sqrt{2}\right)\right]}\left(\frac{1}{\left(10^9 \text{ nm/m}\right)^2}\right)$$

$\therefore$ **n_{110} = 9.59 atoms/nm^2** or **9.59 × 10^{18} atoms/m^2**

This is the most crowded plane with the most number of atoms per unit area.

The (111) plane is shown below in Fig. 1Q28-3:

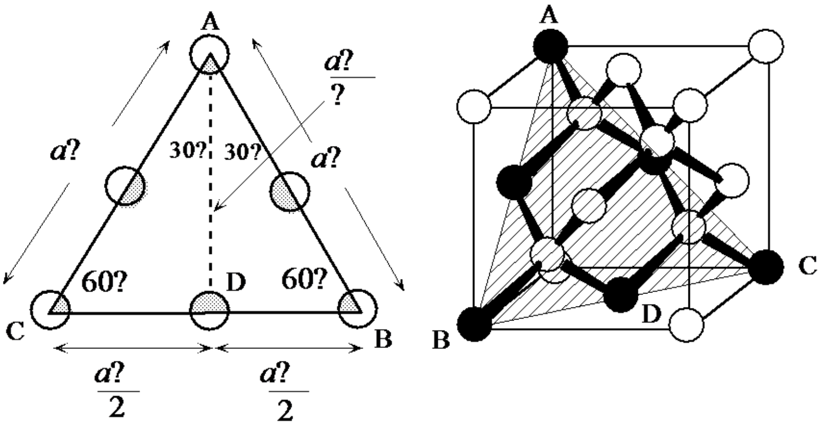

Figure 1Q28-3: The (111) plane of the diamond crystal structure

The number of atoms per nm^2, n_{111}, is therefore:

$$n_{111} = \frac{3\left(\frac{60}{360}\right) + 3\left(\frac{1}{2}\right)}{\left[2\left(\frac{1}{2}\right)\left(a\frac{\sqrt{2}}{2}\right)\left(a\frac{\sqrt{3}}{\sqrt{2}}\right)\right]}\left(\frac{1}{\left(10^9 \text{ nm/m}\right)^2}\right)$$

∴ $$n_{111} = \frac{3\left(\frac{60}{360}\right) + 3\left(\frac{1}{2}\right)}{\left[2\left(\frac{1}{2}\right)\left((0.543\times10^{-9}\text{ m})\frac{\sqrt{2}}{2}\right)\left((0.543\times10^{-9}\text{ m})\frac{\sqrt{3}}{\sqrt{2}}\right)\right]}\left(\frac{1}{(10^9\text{ nm/m})^2}\right)$$

∴ **n_{111} = 7.83 atoms/nm^2** or **7.83 × 10^{18} atoms/m^2**

c. Given:

Molar mass of SiO$_2$: M_{at} = 28.09 × 10^{-3} kg/mol + 2 × 16 × 10^{-3} kg/mol = 60.09 × 10^{-3} kg/mol

Density of SiO$_2$: ρ = 2.27 × 10^3 kg m^{-3}

Let n be the number of SiO$_2$ molecules per unit volume, then:

$$\rho = n\frac{M_{at}}{N_A}$$

∴ $$n = \frac{N_A\rho}{M_{at}} = \frac{(6.022\times10^{23}\text{ mol}^{-1})(2.27\times10^3\text{ kg m}^{-3})}{(60.09\times10^{-3}\text{ kg/mol})}$$ = 2.27 × 10^{28} molecules per m^3

Or, converting to molecules per nm^3:

$$\boldsymbol{n} = \frac{2.27\times10^{28}\text{ molecules/m}^3}{(10^9\text{ nm/m})^3} = \textbf{22.7 moleculesper nm}^{\mathbf{3}}$$

Oxide has less dense packing so it has a more open structure. For every 1 micron of oxide formed on the crystal surface, only about 0.5 micron of the Si crystal is consumed.

2.3

Solution

The drift mobility of electrons can be obtained by using the conductivity relation $\sigma = en\mu_d$.

Resistivity of pure gold from Table 2.1 at 0°C (273 K) is ρ_0 = 22.8 nΩ m. Resistivity at 20 °C can be calculated by using Eq. 2.19.

$$\rho = \rho_0[1+\alpha_0(T-T_0)]$$

The TCR α_0 for Au from Table 2.1 is 1/251 K^{-1}. Therefore the resistivity for Au at 22°C is

ρ(22°C)=22.8 nΩ m [1 + 1/251 K^{-1}(293K – 273K)] = 24.62 nΩ m

Since one Au atom donates one conduction electron, the electron concentration is

$$n = \frac{dN_A}{M_{at}}$$

where for gold d = density = 19300 kg m^{-3}, atomic mass M_{at} = 196.67 g mol^{-1}. Substituting for d, N_A, and M_{at}, we have $n = 5.91 \times 10^{28}$ m^{-3}, or 5.91×10^{22} cm^{-3}.

$$\mu_d = \frac{\sigma}{en} = \frac{(24.62\times10^{-9}\Omega m)^{-1}}{(1.6\times10^{-19}C)(5.91\times10^{28}m^{-3})}$$

$$\mathbf{= 4.26\times10^{-3}\ m^2\ V^{-1}\ s^{-1} = 42.6\ cm^2\ V^{-1}\ s^{-1}.}$$

Given the mean speed of electron is u = 1.4×10^6 m s^{-1}, mean free path from Equation 2.10 is

$$l = \frac{\mu_d m_e u}{e} = \frac{(4.26\times10^{-3}m^2V^{-1}s^{-1})(9.1\times10^{-31}kg)(1.4\times10^6 ms^{-1})}{1.6\times10^{-19}C}$$

$$= 3.39 \times 10^{-8}\ \text{m} = 33.9\ \text{nm}.$$

2.4

Solution

a. Electron concentration can be calculated from the conductivity of Sn, $\sigma = en\mu_d$.

$$n_e = \frac{\sigma}{e\mu_d} = \frac{(110\times10^{-9}\Omega m)^{-1}}{(1.6\times10^{-19}C)(3.9\times10^{-4}m^2V^{-1}s^{-1})}$$

$$= 1.46\times10^{29}\ \text{electrons m}^3.$$

The atomic concentration, i.e. number of Sn atoms per unit volume is

$$n_{at} = \frac{dN_A}{M_{at}} = \frac{(7.3\times10^3 kg)(6.022\times10^{23}mol^{-1})}{(118.69\times10^{-3}kg\,mol^{-1})}$$

$$= 3.70 \times 10^{28}\ \text{Sn atoms m}^{-3}.$$

Hence the number of electrons donated by each atom is (n_e/n_{at}) = 3.94 or **4** electrons per Sn atom. This is in good agreement with the position of the Sn in the Periodic Table (IVB) and its valency of 4.

b. Using the same method used above, the number of electrons donated by each atom of the element are calculated and tabulated as follows:

Metal	Periodic Group	Valency	Atomic Concentration n_{at} (m^{-3})	Electron Concentration n_e (m^{-3})	Number of electrons n_e/n_{at}	Integer (n_e/n_{at})
Na	IA	1	2.541×10^{28}	2.808×10^{28}	1.105	1
Mg	IIA	2	4.311×10^{28}	8.262×10^{28}	1.916	2
Ag	IB	1	5.862×10^{28}	7.019×10^{28}	1.197	1
Zn	IIB	2	6.575×10^{28}	1.320×10^{29}	2.007	2
Al	IIIB	3	6.026×10^{28}	1.965×10^{29}	3.262	3
Sn	IVB	4	3.703×10^{28}	1.457×10^{29}	3.934	4
Pb	IVB	4	3.313×10^{28}	1.319×10^{29}	3.981	4

Table 2Q4-1: Number of electrons donated by various elements

As evident from the above table, the calculated number of electrons donated by one atom of the element is the same as the valency of that element and the position in the periodic table.

2.12

Solution

a. Atomic concentration n_{at} is

$$n_{\mathrm{at}} = \frac{dN_A}{M_{\mathrm{at}}} = \frac{(10.50\times10^{3}\ \mathrm{kg\ m^{-3}})(6.022\times10^{23}\ \mathrm{mol^{-1}}}{(107.87\times10^{-3}\ \mathrm{kg\ mol^{-1}})} \quad = 5.862 \times 1028 \text{ m-3}$$

If we assume there is one conduction electron per Ag atom, the concentration of conduction electrons (n) is 5.862×10^{28} m^{-3}, and the conductivity is therefore:

$\sigma = en\mu_d = (1.602 \times 10^{-19}\ \mathrm{C})(5.862 \times 10^{28}\ \mathrm{m^{-3}})(56 \times 10^{-4}\ \mathrm{m^2\ V^{-1}s^{-1}}) = 5.259 \times 10^{7}\ \Omega^{-1}\ \mathrm{m^{-1}}$

and the resistivity, $\rho = 1/\sigma = 19.0$ nΩ m

The experimental value of ρ is 16 nΩ m. We assumed that exactly 1 "free" electron per Ag atom contributes to conduction. This is not necessarily true. We need to use energy bands to describe conduction more accurately and this is addressed in Chapter 4.

b. From the Wiedemann-Franz-Lorenz law at 27 °C,

$$\kappa = \sigma T C_{\mathrm{WFL}} = (5.259 \times 10^{7}\ \Omega^{-1}\ \mathrm{m^{-1}})(27 + 273\ \mathrm{K})(2.44 \times 10^{-8}\ \mathrm{W\ \Omega\ K^{-2}})$$

i.e. $\boldsymbol{\kappa = 385\ \mathrm{W\ m^{-1}\ K^{-1}}}$

For pure metals such as Ag this is nearly independent of temperature (same at 0 °C).

2.20

Solution

a. The Hall coefficient, R_H, is related to the electron concentration, *n*, by $R_H = -1 / (en)$, and is defined by $R_H = E_y / (JB)$, where E_y is the electric field in the *y*-direction, *J* is the current density and *B* is the magnetic field. Equating these two equations:

$$-\frac{1}{en} = \frac{E_y}{JB}$$

$$\therefore \qquad E_y = -\frac{JB}{en}$$

This electric field is in the opposite direction of the Hall field (E_H) and therefore:

$$E_H = -E_y = \frac{JB}{en} \qquad (1)$$

The current density perpendicular (going through) the plane $W \times D$ (width by depth) is:

$$J = \frac{I}{WD}$$

$$\therefore \qquad W = \frac{I}{JD} \qquad (2)$$

The Hall voltage (V_H) across *W* is:

$$V_H = WE_H$$

If we substitute expressions (1) and (2) into this equation, the following will be obtained:

$$V_H = \frac{IB}{Den}$$

Note: this expression only depends on the thickness and not on the length of the sample.

In general, the Hall voltage will depend on the specimen shape. In the elementary treatment here, the current flow lines were assumed to be nearly parallel from one end to the other end of the sample. In an irregularly shaped sample, one has to consider the current flow lines. However, if the specimen thickness is uniform, it is then possible to carry out meaningful Hall effect measurements using the van der Pauw technique as discussed in advanced textbooks.

b. We are given the depth of the film D = 1 micron = 1 μm and the current through the film I = 100 mA = 0.1 A. The Hall voltage can be taken to be V_H = 1 μV, since we are looking for the magnetic field *B* per μV of Hall voltage. To be able to use the equation for Hall voltage in part (*a*), we must find the electron concentration of gold. Appendix *B* in the textbook contains values for gold's atomic mass (M_{at} =196.97 g mol^{-1}) and density (d = 19.3 g/cm^3 = 19300 kg/m^3). Since gold has a valency of 1 electron, the concentration of free electrons is equal to the concentration of Au atoms.

$$\therefore \qquad n = \frac{dN_A}{M_{at}} = \frac{(19300\ \text{kg m}^{-3})(6.022\times10^{23}\ \text{mol}^{-1})}{(196.97\times10^{-3}\ \text{kg mol}^{-1})} = 5.901\times10^{28}\ \text{m}^{-3}$$

Now the magnetic field B can be found using the equation for Hall voltage:

$$V_H = \frac{IB}{Den}$$

$$\therefore \qquad B = \frac{V_H Den}{I} = \frac{\left(1\times10^{-6}\ \mathrm{V}\right)\left(1\times10^{-6}\ \mathrm{m}\right)\left(1.602\times10^{-19}\ \mathrm{C}\right)\left(5.901\times10^{28}\ \mathrm{m}^{-3}\right)}{\left(0.1\,\mathrm{A}\right)}$$

$\therefore$ **B = 0.0945 T**

As a side note, the power (P) dissipated in the film could be found very easily. Using the value for resistivity of Au at T = 273 K, ρ = 22.8 nΩ m, the resistance of the film is:

$$R = \frac{\rho L}{A} = \frac{\rho L}{WD} = \frac{\left(22.8\times10^{-9}\ \Omega\,\mathrm{m}\right)\left(0.001\,\mathrm{m}\right)}{\left(0.0001\,\mathrm{m}\right)\left(1\times10^{-6}\ \mathrm{m}\right)} = 0.228\,\Omega$$

The power dissipated is then:

$$P = I^2R = (0.1\ \mathrm{A})^2(0.228\ \Omega) = 0.00228\ \mathrm{W}$$