
1.1 Virial theorem The Li atom has a nucleus with a +3*e* positive charge, which is surrounded by a full 1*s* shell with two electrons, and a single valence electron in the outer 2*s* subshell. The atomic radius of the Li atom is about 0.17 nm. Using the Virial theorem, and assuming that the valence electron sees the nuclear +3*e* shielded by the two 1s electrons, that is, a net charge of +*e*, estimate the ionization energy of Li (the energy required to free the 2*s* electron). Compare this value with the experimental value of 5.39 eV. Suppose that the actual nuclear charge seen by the valence electron is not +*e* but a little higher, say +1.25*e*, due to the imperfect shielding provided by the closed 1*s* shell. What would be the new ionization energy? What is your conclusion?

Solution

First we consider the case when the outermost valence electron can see a net charge of +e. From Coulomb's law we have the potential energy

$$PE = \frac{Q_1 Q_2}{4\pi\varepsilon_0 r_0} = \frac{(+e)(-e)}{4\pi\varepsilon_0 r_0}$$

$$= -\frac{(1.6\times10^{-19}\ \text{C})^2}{4\pi(8.85\times10^{-12}\ \text{Fm}^{-1})(0.17\times10^{-9}\ \text{m})} = 1.354 \times 10^{-18}\ \text{J or } -8.46\ \text{eV}$$

Virial theorem relates the overall energy, the average kinetic energy $\overline{KE}$, and average potential energy $\overline{PE}$ through the relations

$$\overline{E} = \overline{PE} + \overline{KE} \qquad \text{and} \qquad \overline{KE} = -\frac{1}{2}\overline{PE}$$

Thus using Virial theorem, the total energy is

$$\overline{E} = \frac{1}{2}\overline{PE} = 0.5 \times -8.46\text{eV} = -4.23\ \text{eV}$$

The ionization energy is therefore **4.23 eV.** Now we consider the second case where electron the sees +1.25*e* due to imperfect shielding. Again the Coulombic *PE* between +*e* and +1.25*e* will be

$$PE = \frac{Q_1 Q_2}{4\pi\varepsilon_0 r_0} = \frac{(+1.25e)(-e)}{4\pi\varepsilon_0 r_0}$$

$$= -\frac{1.25\cdot(1.6\times10^{-19}\ \text{C})^2}{4\pi(85\times10^{-12}\ \text{Fm}^{-1})(0.17\times10^{-9}\ \text{m})} = -1.692 \times 10^{-18}\ \text{J or } -10.58\ \text{eV}$$

The total energy is,

$$\overline{E} = \frac{1}{2}\overline{PE} = 5.29\text{eV}$$

The ionization energy, considering imperfect shielding, is **5.29 eV**. This value is in closer agreement with the experimental value. Hence the second assumption seems to be more realistic

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1.5 The covalent bond Consider the H_2 molecule in a simple way as two touching H atoms as depicted in Figure 1.77. Does this arrangement have a lower energy than two separated H atoms? Suppose that electrons totally correlate their motions so that they move to avoid each other as in the snapshot in Figure 1.77. The radius r_o of the hydrogen atom is 0.0529 nm. The electrostatic potential energy *PE* of two charges Q_1 and Q_2 separated by a distance r is given by $Q_1Q_2/(4\pi\varepsilon_o r)$. Using the Virial Theorem as in Example 1.1, consider the following:

a. Calculate the total electrostatic potential energy (*PE*) of all the charges when they are arranged as shown in Figure 1.77. In evaluating the *PE* of the whole collection of charges you must consider all pairs of charges and, at the same time, 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, proton at r_o on the right, and electron 2 at a distance $2r_o$ + electron 2 interacting with a proton at r_o and another proton at $3r_o$ + two protons, separated by $2r_o$, interacting with each other. Is this configuration energetically favorable?

b. Given that in the isolated H-atom the *PE* is 2 ×(-13.6 eV), calculate the change in *PE* in going from two isolated H-atoms to the H_2 molecule. Using the Virial theorem, find the change in the total energy and hence the covalent bond energy. How does this compare with the experimental value of 4.51 eV?

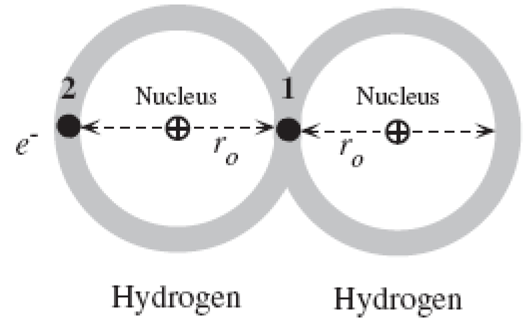

Figure 1.77

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)

1.6 Ionic bonding and CsCl The potential energy *E* per Cs^+-Cl^- pair within the CsCl crystal depends on the interionic separation *r* in the same fashion as in the NaCl crystal,

$$E(r) = -\frac{e^2 M}{4\pi\varepsilon_o r} + \frac{B}{r^m}$$

Energy per ion pair in ionic crystals [1.50]

where for CsCl, $M = 1.763$, $B = 1.192\times10^{-104}$ J m^9 or 7.442×10^{-5} eV (nm)^9 and $m = 9$. Find the equilibrium separation (r_o) of the ions in the crystal and the ionic bonding energy, that is, the ionic cohesive energy; and compare the latter value to the experimental value of 657 kJ mol^{-1}. Given the *ionization energy* of Cs is 3.89 eV and the *electron affinity* of Cl (energy released when an electron is added) is 3.61 eV, calculate the atomic cohesive energy of the CsCl crystal as joules per mole.

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

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

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

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

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

Thus substituting the appropriate values we have

$$r_0 = \left[\frac{4\pi(8.8542\times10^{-12}\,\mathrm{Fm^{-1}})\times 9\times(1.192\times10^{-104}\,\mathrm{J\,m^9})}{1.763\times(1.6\times10-19\mathrm{C})^2}\right]^{\frac{1}{8}}$$

r_o = 3.57 × 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

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

$$= -\frac{(1.6\times10^{-19}\,\mathrm{C})^2(1.763)}{4\pi(8.8542\times10^{-12}\,\mathrm{Fm^{-1}})(3.57\times10^{-10}\,\mathrm{m})} + \frac{7.442\times10^{-4}\,\mathrm{eV\,nm^9}}{(0.357\,\mathrm{nm})^9}$$

= − 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_{cohesive} = (6.32 eV)(1.6 × 10^{-19} J eV^{-1})(6.022× 10^{-23} mol^{-1})

= 610 kJ mol^{-1} of Cs$^+$Cl$^-$ ion pairs or 610 kJ mol^{-1} of Cs$^+$ ions and 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_{cohesive} = (6.04 eV)(1.6 × 10^{-19} J eV^{-1})(6.022× 10^{23} 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.

1.10 Van der Waals bonding Below 24.5 K, Ne is a crystalline solid with an FCC structure. The interatomic interaction energy per atom can be written as

$$E(r) = -2\varepsilon\left[14.45\left(\frac{\sigma}{r}\right)^6 - 12.13\left(\frac{\sigma}{r}\right)^{12}\right] \qquad \text{(eV/atom)}$$

where ε and σ are constants that depend on the polarizability, the mean dipole moment, and the extent of overlap of core electrons. For crystalline Ne, $\varepsilon = 3.121 \times 10^{-3}$ eV and $\sigma = 0.274$ nm.

a. Show that the equilibrium separation between the atoms in an inert gas crystal is given by $r_o = (1.090)\sigma$. What is the equilibrium interatomic separation in the Ne crystal?

b. Find the bonding energy per atom in solid Ne.

c. Calculate the density of solid Ne (atomic mass = 20.18).

Solution

a. Let E = potential energy and x = distance variable between the atoms. The energy E is given by

$$E(x) = -2\varepsilon\left[14.45\left(\frac{\sigma}{x}\right)^6 - 12.13\left(\frac{\sigma}{x}\right)^{12}\right]$$

The force F on each atom is given by

$$F(x) = -\frac{dE(x)}{dx} = 2\varepsilon\left[145.56\frac{\sigma\left(\frac{\sigma}{x}\right)^{11}}{x^2} - 86.7\frac{\sigma\left(\frac{\sigma}{x}\right)^{5}}{x^2}\right]$$

$\therefore$ $$F(x) = 2\varepsilon\left[145.56\frac{\sigma^{12}}{x^{13}} - 86.7\frac{\sigma^6}{x^7}\right]$$

When the atoms are in equilibrium, this net force must be zero. Using r_o to denote equilibrium separation,

$$F(r_o) = 0$$

$\therefore$ $$2\varepsilon\left[145.56\frac{\sigma^{12}}{r_o^{13}} - 86.7\frac{\sigma^6}{r_o^7}\right] = 0$$

$\therefore$ $$145.56\frac{\sigma^{12}}{r_o^{13}} = 86.7\frac{\sigma^6}{r_o^7}$$

$\therefore$ $$\frac{r_o^{13}}{r_o^7} = \left(\frac{145.56}{86.7}\right)\frac{\sigma^{12}}{\sigma^6}$$

$\therefore$ $\boldsymbol{r_o = 1.090\sigma}$

For the Ne crystal, $\sigma = 2.74 \times 10^{-10}$ m and $\varepsilon = 0.003121$ eV. Therefore,

$r_o = 1.090(2.74 \times 10^{-10}\text{ m}) = \mathbf{2.99 \times 10^{-10}\text{ m for Ne.}}$

b. Calculate energy per atom at equilibrium:

$$E(r_o) = -2\varepsilon\left[14.45\left(\frac{\sigma}{r_o}\right)^6 - 12.13\left(\frac{\sigma}{r_o}\right)^{12}\right]$$

$\therefore$

$$E(r_o) = -2(0.003121\,\text{eV})(1.602\times10^{-19}\text{ J/eV})\left[14.45\left(\frac{2.74\times10^{-10}\text{ m}}{2.99\times10^{-10}\text{ m}}\right)^6 - 12.13\left(\frac{2.74\times10^{-10}\text{ m}}{2.99\times10^{-10}\text{ m}}\right)^{12}\right]$$

$\therefore$ $\boldsymbol{E(r_o) = -\,4.30 \times 10^{-21}}$ **or —0 .0269 eV**

Therefore the bonding energy in solid Ne is 0.027 eV per atom.

c. To calculate the density, remember that the unit cell is FCC, and density = (mass of atoms in the unit cell) / (volume of unit cell). There are 4 atoms per FCC unit cell, and the atomic mass of Ne is 20.18 g/mol. (See Figure 1Q7-1)

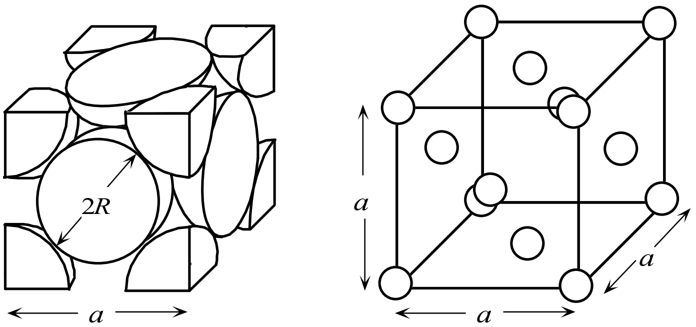

Figure 1Q7-1: Left: An FCC unit cell with close-packed spheres. Right: Reduced-sphere representation of the FCC unit cell. Examples: Ag, Al, Au, Ca, Cu, γ-Fe (>912 °C), Ni, Pd, Pt, Rh.

Since it is an FCC crystal structure, let a = lattice parameter (side of cubic cell) and R = radius of atom. The shortest interatomic separation is $r_o = 2R$ (atoms in contact means nucleus to nucleus separation is $2R$ (see Figure 1Q7-1).

$$R = r_o/2$$

and $$2a^2 = (4R)^2$$

$$\therefore \quad a = 2\sqrt{2}R = 2\sqrt{2}\left(\frac{r_o}{2}\right) = \sqrt{2}\left(2.99\times10^{-10}\ \text{m}\right)$$

$$\therefore \quad a = 4.228 \times 10^{-10}\ \text{m or } \mathbf{0.423\ nm}$$

Therefore, the volume (V) of the unit cell is:

$$V = a^3 = (4.228 \times 10^{-10}\ \text{m})^3 = 7.558 \times 10^{-29}\ \text{m}^3$$

The mass (m) of 1 Ne atom in grams is the atomic mass (M_{at}) divided by N_A, because N_A number of atoms have a mass of M_{at}.

$$m = M_{at} / N_A$$

$$\therefore \quad m = \frac{(20.18\ \text{g/mol})(0.001\ \text{kg/g})}{6.022\times10^{23}\ \text{mol}^{-1}} = 3.351\times10^{-26}\ \text{kg}$$

There are 4 atoms per unit cell in the FCC cell. The density (ρ) can then be found by:

$$\rho = (4m) / V = [4 \times (3.351 \times 10^{-26}\ \text{kg})] / (7.558 \times 10^{-29}\ \text{m}^3)$$

$$\therefore \quad \boldsymbol{\rho} = \mathbf{1774\ kg/m^3}$$

In g/cm^3 this density is:

$$\boldsymbol{\rho} = \frac{1774\ \text{kg/m}^3}{(100\ \text{cm/m})^3} \times (1000\ \text{g/kg}) = \mathbf{1.77\ g/cm^3}$$

The density of solid Ne is 1.77 g cm^{-3}.

Author's Note: The experimental value for a at 4 K is 0.44 nm. The calculated value is close.

1.31 BCC and FCC crystals

a. Molybdenum has the BCC crystal structure, has a density of 10.22 g cm^{-3} and an atomic mass of 95.94 g mol^{-1}. What is the atomic concentration, lattice parameter a, and atomic radius of molybdenum?

b. Gold has the FCC crystal structure, a density of 19.3 g cm^{-3} and an atomic mass of 196.97 g mol^{-1}. What is the atomic concentration, lattice parameter a, and atomic radius of gold?

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

$$a = \sqrt[3]{\frac{2M_{at}}{\rho N_A}} = \sqrt[3]{\frac{2(95.94\times10^{-3}\,\text{kg mol}^{-1})}{(10.22\times10^{3}\,\text{kg m}^{-3})(6.022\times10^{23}\ \text{mol}^{-1})}}$$ = **3.147 × 10^{-10} m = 0.3147 nm**

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

$$n_{at} = \frac{2}{a^3} = \frac{2}{(3.147\times10^{-10}\text{m})^3}$$ = **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):

$$R = \frac{a\sqrt{3}}{4} = \frac{(3.147\times10^{-10}\text{m})\sqrt{3}}{4}$$ = **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

$$a = \left[\frac{4M_{at}}{\rho N_A}\right]^{1/3} = \left[\frac{4(196.97\times10^{-3}\,\text{kg mol}^{-1})}{(19.3\times10^{3}\,\text{kg m}^{-3})(6.022\times10^{23}\ \text{mol}^{-1})}\right]^{1/3}$$ = **4.077 × 10^{-10} m = 0.4077 nm**

The atomic concentration is

$$n_{at} = \frac{4}{a^3} = \frac{4}{(4.077\times10^{-10}\text{m})^3}$$ = **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):

$$R = \frac{a\sqrt{3}}{4} = \frac{\left(4.077\times10^{-10}m\right)\sqrt{2}}{4} \quad = \mathbf{1.442\times10^{-10}\ m = 0.1442\ nm}$$

1.33 Planar and surface concentrations Niobium (Nb) has the BCC crystal with a lattice parameter $a = 0.3294$ nm. Find the planar concentrations as the number of atoms per nm^2 of the (100), (110) and (111) planes. Which plane has the most concentration of atoms per unit area? Sometimes the number of atoms per unit area n_{surface} on the surface of a crystal is estimated by using the relation $n_{\text{surface}} = n_{\text{bulk}}^{2/3}$ where n_{bulk} is the concentration of atoms in the bulk. Compare n_{surface} values with the planar concentrations that you calculated and comment on the difference. [*Note:* The BCC (111) plane does not cut through the center atom and the (111) has one-sixth of an atom at each corner.]

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.

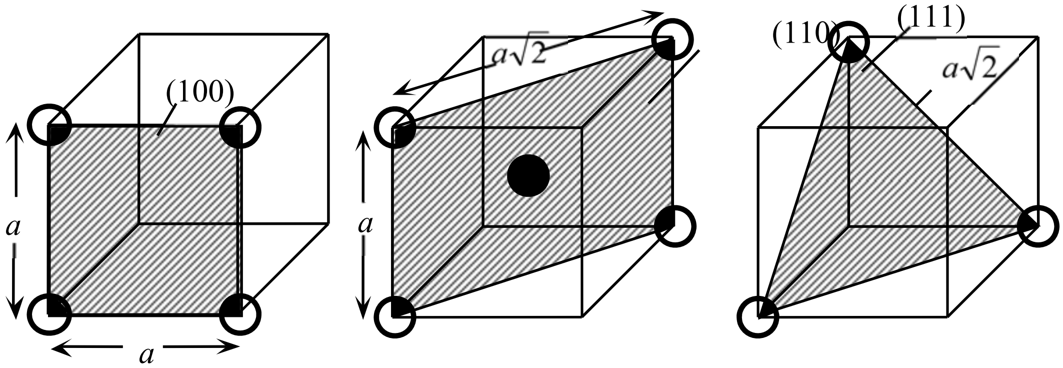

Figure 1Q24-1: (100), (110), (111) planes in the BCC crystal

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

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

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

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

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

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

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

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

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

and the surface concentration is

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

1.34 Diamond and zinc blende Si has the diamond and GaAs has the zinc blende crystal structure. Given the lattice parameters of Si and GaAs, *a* = 0.543 nm and *a* = 0.565 nm, respectively, and the atomic masses of Si, Ga, and As as 28.08, 69.73 g/mol, and 74.92, respectively, calculate the density of Si and GaAs. What is the atomic concentration (atoms per unit volume) in each crystal?

Solution

Referring to the diamond crystal structure in Figure 1Q25-1, we can identify the following types of atoms

8 corner atoms labeled C,

6 face center atoms (labeled FC) and

4 inside atoms labeled 1,2,3,4.

The effective number of atoms within the unit cell is:

(8 Corners) × ($^1/_8$ C-atom) + (6 Faces) × ($^1/_2$ FC-atom) + 4 atoms within the cell (1, 2, 3, 4) = 8

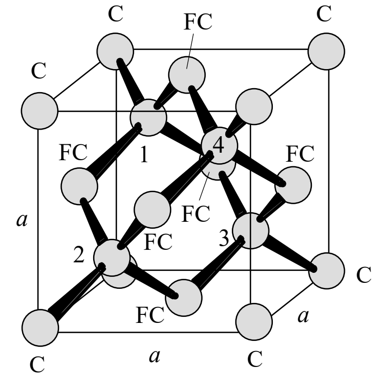

Figure 1Q25-1: The diamond crystal structure.

The lattice parameter (lengths of the sides of the unit cell) of the unit cell is *a*. Thus the atomic concentration in the Si crystal (n_{Si}) is

$$\boldsymbol{n}_{\text{Si}} = \frac{8}{a^3} = \frac{8}{(0.543\times10^{-9}\text{m})^3} = \mathbf{5.0 \times 10^{28}\ atoms\ per\ m^{-3}}$$

If M_{at} is the atomic mass in the Periodic Table then the mass of the atom (m_{at}) in kg is

$$m_{at} = (10^{-3}\text{ kg/g})M_{at}/N_A \qquad (1)$$

where N_A is Avogadro's number. For Si, $M_{at} = M_{Si} = 28.09$ g/mol, so then the density of Si is

$$\rho = (\text{number of atoms per unit volume}) \times (\text{mass per atom}) = n_{Si}\, m_{at}$$

or

$$\rho = \left(\frac{8}{a^3}\right)\left[\frac{(10^{-3}\text{ kg/g})M_{\text{Si}}}{N_A}\right]$$

i.e.

$$\rho = \left[\frac{8}{\left(0.543\times10^{-9}\text{ m}\right)^3}\right]\left[\frac{(10^{-3}\text{ kg/g})\left(28.09\text{ g mol}^{-1}\right)}{6.022\times10^{23}\text{ mol}^{-1}}\right] = \mathbf{2.33 \times 10^3\ kg\ m^{-3}} \text{ or}$$

$\mathbf{2.33\ g\ cm^{-3}}$

In the case of GaAs, it is apparent that there are 4 Ga and 4 As atoms in the unit cell. The concentration of Ga (or As) atoms per unit volume (n_{Ga}) is

$$n_{\text{Ga}} = \frac{4}{a^3} = \frac{4}{(0.565\times10^{-9}\text{m})^3} = \mathbf{2.22 \times 10^{28}\ m^{-3}}$$

Total atomic concentration (counting both Ga and As atoms) is twice n_{Ga}.

$$\boldsymbol{n}_{\textbf{Total}} = 2n_{Ga} = \mathbf{4.44 \times 10^{28}\ m^{-3}}$$

There are 2.22 × 10^{28} Ga-As pairs per m^3. We can calculate the mass of the Ga and As atoms from their relative atomic masses in the Periodic Table using Equation (1) with $M_{at} = M_{Ga} = 69.72$ g/mol for Ga and $M_{at} = M_{As} = 74.92$ g/mol for As. Thus,

$$\rho = \left(\frac{4}{a^3}\right)\left[\frac{(10^{-3}\text{ kg/g})(M_{\text{Ga}} + M_{\text{As}})}{N_A}\right]$$

or $$\rho = \left[\frac{4}{(0.565\times10^{-9}\text{ m})^3}\right]\left[\frac{(10^{-3}\text{ kg/g})(69.72\text{ g/mol}+74.92\text{ g/mol})}{6.022\times10^{23}\text{ mol}^{-1}}\right]$$

i.e. ρ **= 5.33 × 10^3 kg m^{-3}** or **5.33 g cm^{-3}**

1.37 Si and SiO$_2$

a. Given the Si lattice parameter $a = 0.543$ nm, calculate the number of Si atoms per unit volume, in nm^{-3}.

b. Calculate the number of atoms per m^2 and per nm^2 on the (100), (110) and (111) planes in the Si crystal as shown on Figure 1.75. Which plane has the most number of atoms per unit area?

c. The density of SiO$_2$ is 2.27 g cm^{-3}. Given that its structure is amorphous, calculate the number of molecules per unit volume, in nm^{-3}. Compare your result with (a) and comment on what happens when the surface of an Si crystal oxidizes. The atomic masses of Si and O are 28.09 and 16, respectively.

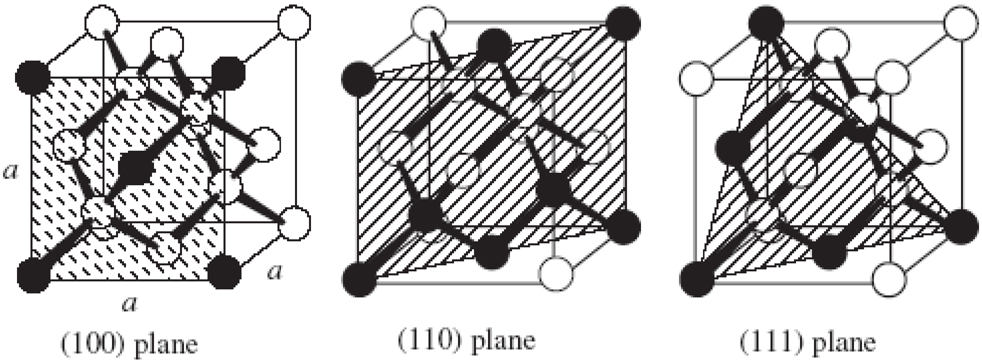

Figure 1.75: Diamond cubic crystal structure and planes. Determine what portion of a black-colored atom belongs to the plane that is hatched.

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:

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

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

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

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:

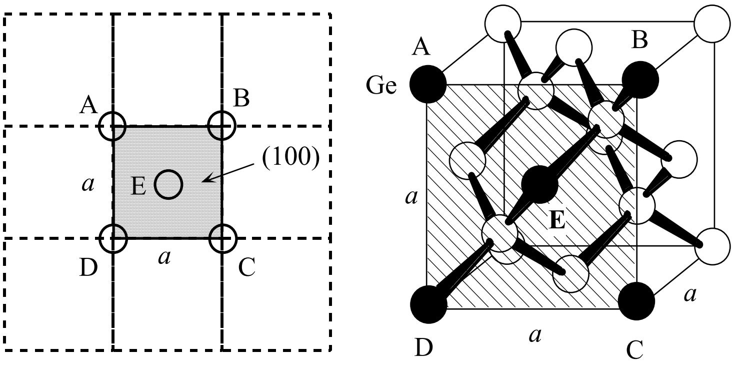

Figure 1Q28-1: The (100) plane of the diamond crystal structure.

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

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

$\therefore$ **n_{100} = 6.78 atoms/nm^2** or **6.78 × 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.

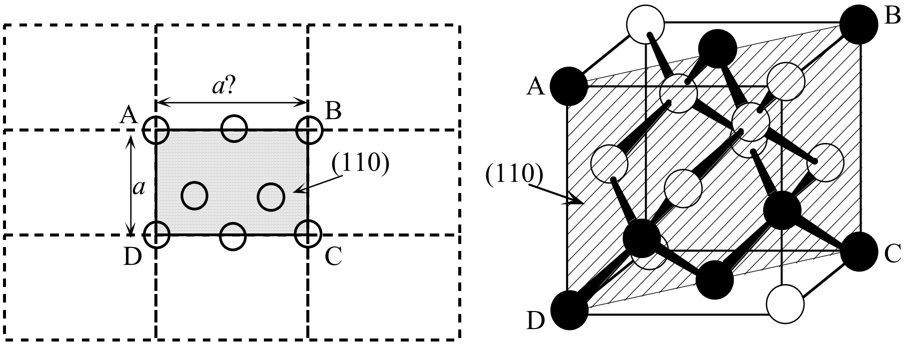

Figure 1Q28-2: The (110) plane of the diamond crystal structure.

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

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

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

$\therefore$ **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:

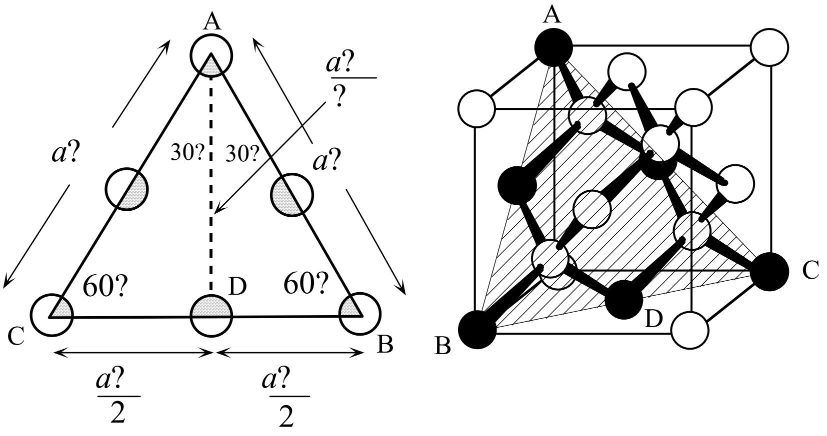

Figure 1Q28-3: The (111) plane of the diamond crystal structure

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

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

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

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

c. Given:

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

Density of SiO$_2$: $\rho = 2.27 \times 10^3$ kg m^{-3}

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

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

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

Or, converting to molecules per nm^3:

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

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