

23 The solid state

Solutions to exercises

Discussion questions

E23.1(b) We can use the Debye–Scherrer powder diffraction method, follow the procedure of Example 23.3, and in particular look for systematic absences in the diffraction patterns. We can proceed through the following sequence

1. Measure distances of the lines in the diffraction pattern from the centre.
2. From the known radius of the camera, convert the distances to angles.
3. Calculate $\sin^2 \theta$.
4. Find the common factor $A = \lambda^2/4a^2$ in $\sin^2 \theta = (\lambda^2/4a^2)(h^2 + k^2 + l^2)$.
5. Index the lines using $\sin^2 \theta/A = h^2 + k^2 + l^2$.
6. Look for the systematic absences in (hkl) . See Fig. 23.22 of the text. For body-centred cubic, diffraction lines corresponding to $h + k + l$ that are odd will be absent. For face-centred cubic, only lines for which h, k , and l are either all even or all odd will be present, other will be absent.
7. Solve $A = \lambda^2/4a^2$ for a .

E23.2(b) The phase problem arises with the analysis of data in X-ray diffraction when seeking to perform a Fourier synthesis of the electron density. In order to carry out the sum it is necessary to know the signs of the structure factors; however, because diffraction intensities are proportional to the square of the structure factors, the intensities do not provide information on the sign. For non-centrosymmetric crystals, the structure factors may be complex, and the phase α in the expression $F_{hkl} = |F_{hkl}|e^{i\alpha}$ is indeterminate. The phase problem may be evaded by the use of a Patterson synthesis or tackled directly by using the so-called direct methods of phase allocation.

The Patterson synthesis is a technique of data analysis in X-ray diffraction which helps to circumvent the phase problem. In it, a function P is formed by calculating the Fourier transform of the squares of the structure factors (which are proportional to the intensities):

$$P(r) = \frac{1}{V} \sum_{hkl} |F_{hkl}|^2 e^{-2\pi i(hx+ky+lz)}$$

The outcome is a map of the *separations* of the atoms in the unit cell of the crystal. If some atoms are heavy (perhaps because they have been introduced by isomorphous replacement), they dominate the Patterson function, and their locations can be deduced quite simply. Their locations can then be used in the determination of the locations of lighter atoms.

E23.3(b) In a face-centred cubic close-packed lattice, there is an octahedral hole in the centre. The rock-salt structure can be thought of as being derived from an fcc structure of Cl^- ions in which Na^+ ions have filled the octahedral holes.

The caesium-chloride structure can be considered to be derived from the ccp structure by having Cl^- ions occupy all the primitive lattice points and octahedral sites, with all tetrahedral sites occupied by Cs^+ ions. This is exceedingly difficult to visualize and describe without carefully constructed figures or models. Refer to S.-M. Ho and B. E. Douglas, *J. Chem. Educ.* **46**, 208, 1969, for the appropriate diagrams.

E23.4(b) A metallic conductor is a substance with a conductivity that decreases as the temperature is raised. A semiconductor is a substance with a conductivity that increases as the temperature is raised. A

semiconductor generally has a lower conductivity than that typical of metals, but the magnitude of the conductivity is not the criterion of the distinction. It is conventional to classify semiconductors with very low electrical conductivities, such as most synthetic polymers, as insulators. We shall use this term. But it should be appreciated that it is one of convenience rather than one of fundamental significance.

The conductivity of these three kinds of materials is explained by band theory. When each of N atoms of a metallic element contributes one atomic orbital to the formation of molecular orbitals, the resulting N molecular orbitals form an almost continuous band of levels. The orbital at the bottom of the band is fully bonding between all neighbours, and the orbital at the top of the band is fully antibonding between all immediate neighbours. If the atomic orbitals are s -orbitals, then the resulting band is called an s -band; if the original orbitals are p -orbitals, then they form a p -band. In a typical case, there is so large an energy difference between the s and p atomic orbitals that the resulting s - and p -bands are separated by a region of energy in which there are no orbitals. This region is called the band gap, and its width is denoted E_g .

When electrons occupy the orbitals in the bands, they do so in accord with the Pauli principle. If insufficient electrons are present to fill the band, the electrons close to the top of the band are mobile and the solid is a metallic conductor. An unfilled band is called a conduction band and the energy of the highest occupied orbital at $T = 0$ K is called the Fermi level. Only the electrons close to the Fermi level can contribute to conduction and to the heat capacity of a metal. If the band is full, then the electrons cannot transport a current readily, and the solid is an insulator; more formally, it is a species of semiconductor with a large band gap. A full band is called a valence band. The detailed population of the levels in a band taking into account the role of temperature is expressed by the Fermi–Dirac distribution.

The distinction between metallic conductors and semiconductors can be traced to their band structure: a metallic conductor has an incomplete band, its conduction band, and a semiconductor has full bands, and hence lacks a conduction band. The decreasing conductance of a metallic conductor with temperature stems from the scattering of electrons by the vibrating atoms of the metal lattice. The increasing conductance of a semiconductor arises from the increasing population of an upper empty band as the temperature is increased. Many substances, however, have such large band gaps that their ability to conduct an electric current remains very low at all temperatures: it is conventional to refer to such solids as insulators. The ability of a semiconductor to transport charge is enhanced by doping it, or adding substances in controlled quantities. If the dopant provides additional electrons, then the semiconductor is classified as n -type. If it removes electrons from the valence band and thereby increases the number of positive holes, it is classified as p -type.

E23.5(b) The Fermi–Dirac distribution is a version of the Boltzmann distribution that takes into account the effect of the Pauli exclusion principle. It can therefore be used to calculate the population, P , of a state of given energy in a many-electron system at a temperature T :

$$P = \frac{1}{e^{(E-\mu)/kT} + 1}$$

In this expression, μ is the Fermi energy, or chemical potential, the energy of the level for which $P = 1/2$. The Fermi energy should be distinguished from the Fermi level, which is the energy of the highest occupied state at $T = 0$. See Fig. 23.53 of the text.

From thermodynamics (Chapter 5) we know that $dU = -p dV + T dS + \mu dn$ for a one-component system. This may also be written $dU = -p dV + T dS + \mu dN$, and this μ is the chemical potential per particle that appears in the F–D distribution law. The term in dU containing μ is the chemical work and gives the change in internal energy with change in the number of particles. Thus, μ has a wider significance than its interpretation as a partial molar Gibbs energy and it is not surprising that

it occurs in the F–D expression in comparison to the energy of the particle. The Helmholtz energy, A , and μ are related through $dA = -p dV - S dT + \mu dN$, and so μ also gives the change in the Helmholtz energy with change in number of particles. To fully understand how the chemical potential μ enters into the F–D expression for P , we must examine its derivation (see *Further reading*) which makes use of the relation between μ and A and of that between A and the partition function for F–D particles.

Numerical exercises

E23.6(b) $(\frac{1}{2}, 0, \frac{1}{2})$ is the midpoint of a face. All face midpoints are alike, including $(\frac{1}{2}, \frac{1}{2}, 0)$ and $(0, \frac{1}{2}, \frac{1}{2})$.

There are six faces to each cube, but each face is shared by two cubes. So other face midpoints can be described by one of these three sets of coordinates on an adjacent unit cell.

E23.7(b) Taking reciprocals of the coordinates yields $(1, \frac{1}{3}, -1)$ and $(\frac{1}{2}, \frac{1}{3}, \frac{1}{4})$ respectively. Clearing the fractions yields the Miller indices $(31\bar{3})$ and (643)

E23.8(b) The distance between planes in a cubic lattice is

$$d_{hkl} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}}$$

This is the distance between the origin and the plane which intersects coordinate axes at $(h/a, k/a, l/a)$.

$$d_{121} = \frac{523 \text{ pm}}{(1 + 2^2 + 1)^{1/2}} = 214 \text{ pm}$$

$$d_{221} = \frac{523 \text{ pm}}{(2^2 + 2^2 + 1)^{1/2}} = 174 \text{ pm}$$

$$d_{244} = \frac{523 \text{ pm}}{(2^2 + 4^2 + 4^2)^{1/2}} = 87.2 \text{ pm}$$

E23.9(b) The Bragg law is

$$n\lambda = 2d \sin \theta$$

Assuming the angle given is for a first-order reflection, the wavelength must be

$$\lambda = 2(128.2 \text{ pm}) \sin 19.76^\circ = 86.7 \text{ pm}$$

E23.10(b) Combining the Bragg law with Miller indices yields, for a cubic cell

$$\sin \theta_{hkl} = \frac{\lambda}{2a} (h^2 + k^2 + l^2)^{1/2}$$

In a face-centred cubic lattice, h , k , and l must be all odd or all even. So the first three reflections would be from the (111) , (200) , and (220) planes. In an fcc cell, the face diagonal of the cube is

$4R$, where R is the atomic radius. The relationship of the side of the unit cell to R is therefore

$$(4R)^2 = a^2 + a^2 = 2a^2 \quad \text{so} \quad a = \frac{4R}{\sqrt{2}}$$

Now we evaluate

$$\frac{\lambda}{2a} = \frac{\lambda}{4\sqrt{2}R} = \frac{154 \text{ pm}}{4\sqrt{2}(144 \text{ pm})} = 0.189$$

We set up the following table

hkl	$\sin \theta$	$\theta / ^\circ$	$2\theta / ^\circ$
111	0.327	19.1	38.2
200	0.378	22.2	44.4
220	0.535	32.3	64.6

E23.11(b) In a circular camera, the distance between adjacent lines is $D = R\Delta(2\theta)$, where R is the radius of the camera (distance from sample to film) and θ is the diffraction angle. Combining these quantities with the Bragg law ($\lambda = 2d \sin \theta$, relating the glancing angle to the wavelength and separation of planes), we get

$$\begin{aligned} D &= 2R\Delta\theta = 2R\Delta\left(\sin^{-1} \frac{\lambda}{2d}\right) \\ &= 2(5.74 \text{ cm}) \times \left(\sin^{-1} \frac{96.035}{2(82.3 \text{ pm})} - \sin^{-1} \frac{95.401 \text{ pm}}{2(82.3 \text{ pm})}\right) = \boxed{0.054 \text{ cm}} \end{aligned}$$

E23.12(b) The volume of a hexagonal unit cell is the area of the base times the height c . The base is equivalent to two equilateral triangles of side a . The altitude of such a triangle is $a \sin 60^\circ$. So the volume is

$$\begin{aligned} V &= 2\left(\frac{1}{2}a \times a \sin 60^\circ\right)c = a^2c \sin 60^\circ = (1692.9 \text{ pm})^2 \times (506.96 \text{ pm}) \times \sin 60^\circ \\ &= 1.2582 \times 10^9 \text{ pm}^3 = \boxed{1.2582 \text{ nm}^3} \end{aligned}$$

E23.13(b) The volume of an orthorhombic unit cell is

$$V = abc = (589 \text{ pm}) \times (822 \text{ pm}) \times (798 \text{ pm}) = \frac{3.86 \times 10^8 \text{ pm}^3}{(10^{10} \text{ pm cm}^{-1})^3} = 3.86 \times 10^{-22} \text{ cm}^3$$

The mass per formula unit is

$$m = \frac{135.01 \text{ g mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 2.24 \times 10^{-22} \text{ g}$$

The density is related to the mass m per formula unit, the volume V of the unit cell, and the number N of formula units per unit cell as follows

$$d = \frac{Nm}{V} \quad \text{so} \quad N = \frac{dV}{m} = \frac{(2.9 \text{ g cm}^{-3}) \times (3.86 \times 10^{-22} \text{ cm}^3)}{2.24 \times 10^{-22} \text{ g}} = \boxed{5}$$

A more accurate density, then, is

$$d = \frac{5(2.24 \times 10^{-22} \text{ g})}{3.86 \times 10^{-22} \text{ cm}^3} = \boxed{2.90 \text{ g cm}^{-3}}$$

E23.14(b) The distance between the origin and the plane which intersects coordinate axes at $(h/a, k/b, l/c)$ is given by

$$d_{hkl} = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)^{-1/2} = \left(\frac{3^2}{(679 \text{ pm})^2} + \frac{2^2}{(879 \text{ pm})^2} + \frac{2^2}{(860 \text{ pm})^2} \right)^{-1/2}$$

$$d_{322} = \boxed{182 \text{ pm}}$$

E23.15(b) The fact that the 111 reflection is the third one implies that the cubic lattice is simple, where all indices give reflections. The 111 reflection would be the first reflection in a face-centred cubic cell and would be absent from a body-centred cubic

The Bragg law

$$\sin \theta_{hkl} = \frac{\lambda}{2a} (h^2 + k^2 + l^2)^{1/2}$$

can be used to compute the cell length

$$a = \frac{\lambda}{2 \sin \theta_{hkl}} (h^2 + k^2 + l^2)^{1/2} = \frac{137 \text{ pm}}{2 \sin 17.7^\circ} (1^2 + 1^2 + 1^2)^{1/2} = 390 \text{ pm}$$

With the cell length, we can predict the glancing angles for the other reflections expected from a simple cubic

$$\theta_{hkl} = \sin^{-1} \left(\frac{\lambda}{2a} (h^2 + k^2 + l^2)^{1/2} \right) = \sin^{-1} (0.176 (h^2 + k^2 + l^2)^{1/2})$$

$$\theta_{100} = \sin^{-1} (0.176 (1^2 + 0 + 0)^{1/2}) = 10.1^\circ \text{ (checks)}$$

$$\theta_{110} = \sin^{-1} (0.176 (1^2 + 1^2 + 0)^{1/2}) = 14.4^\circ \text{ (checks)}$$

$$\theta_{200} = \sin^{-1} (0.176 (2^2 + 0 + 0)^{1/2}) = 20.6^\circ \text{ (checks)}$$

These angles predicted for a simple cubic fit those observed, confirming the hypothesis of a simple lattice; the reflections are due to the $\boxed{(100), (110), (111), \text{ and } (200)}$ planes.

E23.16(b) The Bragg law relates the glancing angle to the separation of planes and the wavelength of radiation

$$\lambda = 2d \sin \theta \quad \text{so} \quad \theta = \sin^{-1} \frac{\lambda}{2d}$$

The distance between the origin and plane which intersects coordinate axes at $(h/a, k/b, l/c)$ is given by

$$d_{hkl} = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)^{-1/2}$$

So we can draw up the following table

hkl	d_{hkl}/pm	$\theta_{hkl}/^\circ$
100	574.1	4.166
010	796.8	3.000
111	339.5	7.057

E23.17(b) All of the reflections present have $h + k + l$ even, and all of the even $h + k + l$ are present. The unit cell, then, is body-centred cubic.

E23.18(b) The structure factor is given by

$$F_{hkl} = \sum_i f_i e^{i\phi_i} \quad \text{where} \quad \phi_i = 2\pi(hx_i + ky_i + lz_i)$$

All eight of the vertices of the cube are shared by eight cubes, so each vertex has a scattering factor of $f/8$.

The coordinates of all vertices are integers, so the phase ϕ is a multiple of 2π and $e^{i\phi} = 1$. The body-centre point belongs exclusively to one unit cell, so its scattering factor is f . The phase is

$$\phi = 2\pi \left(\frac{1}{2}h + \frac{1}{2}k + \frac{1}{2}l \right) = \pi(h + k + l)$$

When $h + k + l$ is even, ϕ is a multiple of 2π and $e^{i\phi} = 1$; when $h + k + l$ is odd, ϕ is $\pi + a$ multiple of 2π and $e^{i\phi} = -1$. So $e^{i\phi} = (-1)^{h+k+l}$ and

$$F_{hkl} = 8(f/8)(1) + f(-1)^{h+k+l}$$

$$= \boxed{2f \text{ for } h + k + l \text{ even} \quad \text{and} \quad 0 \text{ for } h + k + l \text{ odd}}$$

E23.19(b) There are two smaller (white) triangles to each larger (grey) triangle. Let the area of the larger triangle be A and the area of the smaller triangle be a . Since $b = \frac{1}{2}B$ (base) and $h = \frac{1}{2}H$ (height), $a = \frac{1}{4}A$. The white space is then $2NA/4$, for N of the larger triangles. The total space is then $(NA + \frac{NA}{2}) = 3NA/2$. Therefore the fraction filled is $NA/(3NA/2) = \boxed{\frac{2}{3}}$

E23.20(b) See Fig. 23.1.

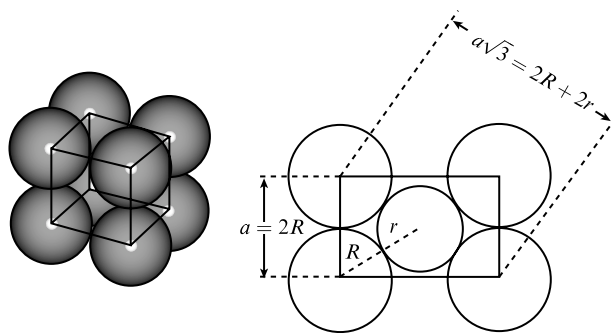


Figure 23.1

The body diagonal of a cube is $a\sqrt{3}$. Hence

$$a\sqrt{3} = 2R + 2r \quad \text{or} \quad \sqrt{3}R = R + r \quad [a = 2R]$$

$$\frac{r}{R} = \boxed{0.732}$$

E23.21(b) The ionic radius of K^+ is 138 pm when it is 6-fold coordinated, 151 pm when it is 8-fold coordinated.

(a) The smallest ion that can have 6-fold coordination with it has a radius of $(\sqrt{2} - 1) \times (138 \text{ pm}) =$
 $\boxed{57 \text{ pm}}$.

(b) The smallest ion that can have 8-fold coordination with it has a radius of $(\sqrt{3} - 1) \times (151 \text{ pm}) =$
 $\boxed{111 \text{ pm}}$.

E23.22(b) The diagonal of the face that has a lattice point in its centre is equal to $4r$, where r is the radius of the atom. The relationship between this diagonal and the edge length a is

$$4r = a\sqrt{2} \quad \text{so} \quad a = 2\sqrt{2}r$$

The volume of the unit cell is a^3 , and each cell contains 2 atoms. (Each of the 8 vertices is shared among 8 cells; each of the 2 face points is shared by 2 cells.) So the packing fraction is

$$\frac{2V_{\text{atom}}}{V_{\text{cell}}} = \frac{2(4/3)\pi r^3}{(2\sqrt{2}r)^3} = \frac{\pi}{3(2)^{3/2}} = \boxed{0.370}$$

E23.23(b) The volume of an atomic crystal is proportional to the cube of the atomic radius divided by the packing fraction. The packing fractions for hcp, a close-packed structure, is 0.740; for bcc, it is 0.680. So for titanium

$$\frac{V_{\text{bcc}}}{V_{\text{hcp}}} = \frac{0.740}{0.680} \left(\frac{122 \text{ pm}}{126 \text{ pm}} \right)^3 = 0.99$$

The bcc structure has a smaller volume, so the transition involves a $\boxed{\text{contraction}}$. (Actually, the data are not precise enough to be sure of this. 122 could mean 122.49 and 126 could mean 125.51, in which case an expansion would occur.)

E23.24(b) Draw points corresponding to the vectors joining each pair of atoms. Heavier atoms give more intense contributions than light atoms. Remember that there are two vectors joining any pair of atoms (\overrightarrow{AB} and \overleftarrow{AB}); don't forget the AA zero vectors for the centre point of the diagram. See Fig. 23.2 for C_6H_6 .

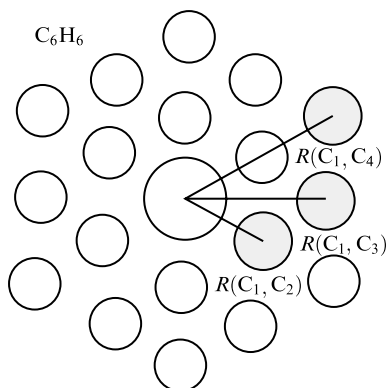


Figure 23.2

E23.25(b) Combine $E = \frac{1}{2}kT$ and $E = \frac{1}{2}mv^2 = \frac{h^2}{2m\lambda^2}$, to obtain

$$\lambda = \frac{h}{(mkT)^{1/2}} = \frac{6.626 \times 10^{-34} \text{ J s}}{[(1.675 \times 10^{-27} \text{ kg}) \times (1.381 \times 10^{-23} \text{ JK}^{-1}) \times (300 \text{ K})]^{1/2}} = \boxed{252 \text{ pm}}$$

E23.26(b) $\lambda = \frac{h}{p} = \frac{h}{m_e v}$

$$\frac{1}{2}m_e v^2 = e\Delta\phi \quad \text{so} \quad v = \left(\frac{2e\Delta\phi}{m_e}\right)^{1/2}$$

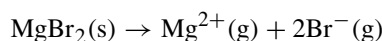
$$\begin{aligned} \text{and } \lambda &= \left(\frac{h^2}{2m_e e \Delta\phi}\right)^{1/2} = \frac{6.626 \times 10^{-34} \text{ J s}}{[(2) \times (9.109 \times 10^{-31} \text{ kg}) \times (1.602 \times 10^{-19} \text{ C}) \times (\Delta\phi)]^{1/2}} \\ &= \frac{1.227 \text{ nm}}{(\Delta\phi/V)^{1/2}} \end{aligned}$$

$$\text{(a) } \Delta\phi = 1.0 \text{ kV}, \quad \lambda = \frac{1.227 \text{ nm}}{(1.0 \times 10^3)^{1/2}} = \boxed{39 \text{ pm}}$$

$$\text{(b) } \Delta\phi = 10 \text{ KV}, \quad \lambda = \frac{1.227 \text{ nm}}{(1.0 \times 10^4)^{1/2}} = \boxed{12 \text{ pm}}$$

$$\text{(c) } \Delta\phi = 40 \text{ KV}, \quad \lambda = \frac{1.227 \text{ nm}}{(4.0 \times 10^4)^{1/2}} = \boxed{6.1 \text{ pm}}$$

E23.27(b) The lattice enthalpy is the difference in enthalpy between an ionic solid and the corresponding isolated ions. In this exercise, it is the enthalpy corresponding to the process



The standard lattice enthalpy can be computed from the standard enthalpies given in the exercise by considering the formation of $\text{MgBr}_2(\text{s})$ from its elements as occurring through the following steps: sublimation of $\text{Mg}(\text{s})$, removing two electrons from $\text{Mg}(\text{g})$, vaporization of $\text{Br}_2(\text{l})$, atomization of $\text{Br}_2(\text{g})$, electron attachment to $\text{Br}(\text{g})$, and formation of the solid MgBr_2 lattice from gaseous ions

$$\begin{aligned} \Delta_f H^\ominus(\text{MgBr}_2, \text{s}) &= \Delta_{\text{sub}} H^\ominus(\text{Mg}, \text{s}) + \Delta_{\text{ion}} H^\ominus(\text{Mg}, \text{g}) + \Delta_{\text{vap}} H^\ominus(\text{Br}_2, \text{l}) \\ &\quad + \Delta_{\text{at}} H^\ominus(\text{Br}_2, \text{g}) + 2\Delta_{\text{eg}} H^\ominus(\text{Br}, \text{g}) - \Delta_L H^\ominus(\text{MgBr}_2, \text{s}) \end{aligned}$$

So the lattice enthalpy is

$$\begin{aligned} \Delta_L H^\ominus(\text{MgBr}_2, \text{s}) &= \Delta_{\text{sub}} H^\ominus(\text{Mg}, \text{s}) + \Delta_{\text{ion}} H^\ominus(\text{Mg}, \text{g}) + \Delta_{\text{vap}} H^\ominus(\text{Br}_2, \text{l}) \\ &\quad + \Delta_{\text{at}} H^\ominus(\text{Br}_2, \text{g}) + 2\Delta_{\text{eg}} H^\ominus(\text{Br}, \text{g}) - \Delta_f H^\ominus(\text{MgBr}_2, \text{s}) \end{aligned}$$

$$\Delta_L H^\ominus(\text{MgBr}_2, \text{s}) = [148 + 2187 + 31 + 193 - 2(331) + 524] \text{ kJ mol}^{-1} = \boxed{2421 \text{ kJ mol}^{-1}}$$

E23.28(b) Tension reduces the disorder in the rubber chains; hence, if the rubber is sufficiently stretched, crystallization may occur at temperatures above the normal crystallization temperature. In unstretched rubber the random thermal motion of the chain segments prevents crystallization. In stretched rubber these random thermal motions are drastically reduced. At higher temperatures the random motions may still have been sufficient to prevent crystallization even in the stretched rubber, but lowering the

temperature to 0°C may have resulted in a transition to the crystalline form. Since it is random motion of the chains that resists the stretching force and allows the rubber to respond to forced dimensional changes, this ability ceases when the motion ceases. Hence, the seals failed.

Comment. The solution to the problem of the cause of the Challenger disaster was the final achievement, just before his death, of Richard Feynman, a Nobel prize winner in physics and a person who loved to solve problems. He was an outspoken person who abhorred sham, especially in science and technology. Feynman concluded his personal report on the disaster by saying, 'For a successful technology, reality must take precedence over public relations, for nature cannot be fooled' (James Gleick, *Genius: the life and science of Richard Feynman*. Pantheon Books, New York (1992).)

E23.29(b) Young's modulus is defined as:

$$E = \frac{\text{normal stress}}{\text{normal strain}}$$

where stress is deforming force per unit area and strain is a fractional deformation. Here the deforming force is gravitational, mg , acting across the cross-sectional area of the wire, πr^2 . So the strain induced in the exercise is

$$\text{strain} = \frac{\text{stress}}{E} = \frac{mg}{\pi(d/2)^2 E} = \frac{4mg}{\pi d^2 E} = \frac{4(10.0 \text{ kg})(9.8 \text{ m s}^{-2})}{\pi(0.10 \times 10^{-3} \text{ m})^2(215 \times 10^9 \text{ Pa})} = \boxed{5.8 \times 10^{-2}}$$

The wire would stretch by 5.8%.

E23.30(b) Poisson's ratio is defined as:

$$\nu_P = \frac{\text{transverse strain}}{\text{normal strain}}$$

where normal strain is the fractional deformation along the direction of the deforming force and transverse strain is the fractional deformation in the directions transverse to the deforming force. Here the length of a cube of lead is stretched by 2.0 per cent, resulting in a contraction by 0.41×2.0 per cent, or 0.82 per cent, in the width and height of the cube. The relative change in volume is:

$$\frac{V + \Delta V}{V} = (1.020)(0.9918)(0.9918) = 1.003$$

and the absolute change is:

$$\Delta V = (1.003 - 1)(1.0 \text{ dm}^3) = \boxed{0.003 \text{ dm}^3}$$

E23.31(b) $m = g_e \{S(S + 1)\}^{1/2} \mu_B$ [23.34, with S in place of s]

Therefore, since $m = 4.00 \mu_B$

$$S(S + 1) = \left(\frac{1}{4}\right) \times (4.00)^2 = 4.00, \quad \text{implying that } S = 1.56$$

Since $S \approx \frac{3}{2}$, implying three unpaired spins.

In actuality most Mn^{2+} compounds have $\boxed{5}$ unpaired spins.

$$\begin{aligned} \text{E23.32(b)} \quad \chi_m &= \chi V_m = \frac{\chi M}{\rho} = \frac{(-7.9 \times 10^{-6}) \times (84.15 \text{ g mol}^{-1})}{0.811 \text{ g cm}^{-3}} \\ &= \boxed{-8.2 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1}} \end{aligned}$$

E23.33(b) The molar susceptibility is given by

$$\chi_m = \frac{N_A g_e^2 \mu_0 \mu_B^2 S(S+1)}{3kT}$$

NO₂ is an odd-electron species, so it must contain at least one unpaired spin; in its ground state it has one unpaired spin, so $S = \frac{1}{2}$. Therefore,

$$\begin{aligned} \chi_m &= (6.022 \times 10^{23} \text{ mol}^{-1}) \times (2.0023)^2 \times (4\pi \times 10^{-7} \text{ T}^2 \text{ J}^{-1} \text{ m}^3) \\ &\quad \times \frac{(9.274 \times 10^{-24} \text{ J T}^{-1})^2 \times \left(\frac{1}{2}\right) \times \left(\frac{1}{2} + 1\right)}{3(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})} \\ &= \boxed{1.58 \times 10^{-8} \text{ m}^3 \text{ mol}^{-1}} \end{aligned}$$

The expression above does not indicate any pressure-dependence in the molar susceptibility. However, the observed decrease in susceptibility with increased pressure is consistent with the fact that NO₂ has a tendency to dimerize, and that dimerization is favoured by higher pressure. The dimer has no unpaired electrons, so the dimerization reaction effectively reduced the number of paramagnetic species.

E23.34(b) The molar susceptibility is given by

$$\chi_m = \frac{N_A g_e^2 \mu_0 \mu_B^2 S(S+1)}{3kT} \quad \text{so} \quad S(S+1) = \frac{3kT \chi_m}{N_A g_e^2 \mu_0 \mu_B^2}$$

$$\begin{aligned} S(S+1) &= \frac{3(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})}{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (2.0023)^2} \\ &\quad \times \frac{(6.00 \times 10^{-8} \text{ m}^3 \text{ mol}^{-1})}{(4\pi \times 10^{-7} \text{ T}^2 \text{ J}^{-1} \text{ m}^3) \times (9.274 \times 10^{-24} \text{ J T}^{-1})^2} \\ &= 2.84 \quad \text{so} \quad S = \frac{-1 + \sqrt{1 + 4(2.84)}}{2} = 1.26 \end{aligned}$$

corresponding to $\boxed{2.52}$ effective unpaired spins. The theoretical number is $\boxed{2}$. The magnetic moments in a crystal are close together, and the interact rather strongly. The discrepancy is most likely due to an interaction among the magnetic moments.

E23.35(b) The molar susceptibility is given by

$$\chi_m = \frac{N_A g_e^2 \mu_0 \mu_B^2 S(S+1)}{3kT}$$

Mn^{2+} has five unpaired spins, so $S = 2.5$ and

$$\begin{aligned}\chi_m &= \frac{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (2.0023)^2 \times (4\pi \times 10^{-7} \text{ T}^2 \text{ J}^{-1} \text{ m}^3)}{3(1.381 \times 10^{-23} \text{ J K}^{-1})} \\ &\quad \times \frac{(9.274 \times 10^{-24} \text{ J T}^{-1})^2 \times (2.5) \times (2.5 + 1)}{(298 \text{ K})} \\ &= \boxed{1.85 \times 10^{-7} \text{ m}^3 \text{ mol}^{-1}}\end{aligned}$$

E23.36(b) The orientational energy of an electron spin system in a magnetic field is

$$E = g_e \mu_B M_S B$$

The Boltzmann distribution says that the population ratio r of the various states is proportional to

$$r = \exp\left(\frac{-\Delta E}{kT}\right)$$

where ΔE is the difference between them. For a system with $S = 1$, the M_S states are 0 and ± 1 . So between adjacent states

$$\begin{aligned}r &= \exp\left(\frac{-g_e \mu_B M_S B}{kT}\right) = \exp\left(\frac{-(2.0023) \times (9.274 \times 10^{-24} \text{ J T}^{-1}) \times (1) \times (15.0 \text{ T})}{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})}\right) \\ &= \boxed{0.935}\end{aligned}$$

The population of the highest-energy state is r^2 times that of the lowest; $r^2 = \boxed{0.873}$

Solutions to problems

Solutions to numerical problems

P23.1 $\lambda = 2d_{hkl} \sin \theta_{hkl} = \frac{2a \sin \theta_{hkl}}{(h^2 + k^2 + l^2)^{1/2}}$ [eqn 23.5, inserting eqn 23.2] = $2a \sin 6.0^\circ = 0.209a$

In an NaCl unit cell (Fig. 23.3) the number of formula units is 4 (each corner ion is shared by 8 cells, each edge ion by 4, and each face ion by 2).

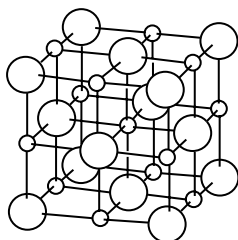


Figure 23.3

Therefore,

$$\rho = \frac{NM}{VN_A} = \frac{4M}{a^3 N_A}, \quad \text{implying that } a = \left(\frac{4M}{\rho N_A} \right)^{1/3} \quad [\text{Exercise 23.13(a)}]$$

$$a = \left(\frac{(4) \times (58.44 \text{ g mol}^{-1})}{(2.17 \times 10^{16} \text{ g m}^{-3}) \times (6.022 \times 10^{23} \text{ mol}^{-1})} \right)^{1/3} = 563.5 \text{ pm}$$

and hence $\lambda = (0.209) \times (563.5 \text{ pm}) = \boxed{118 \text{ pm}}$

P23.4 Note that since $R = 28.7 \text{ mm}$, $\theta/\text{deg} = \left(\frac{D}{2R} \right) \times \left(\frac{180}{\pi} \right) = D/\text{mm}$. Then proceed through the following sequence:

1. Measure the distances from the figure.
2. Convert from distances to angle using $\theta/\text{deg} = D/\text{mm}$.
3. Calculate $\sin^2 \theta$.
4. Find the common factor $A = \frac{\lambda^2}{4a^2}$ in $\sin^2 \theta = \left(\frac{\lambda^2}{4a^2} \right) (h^2 + k^2 + l^2)$.
5. Index the lines using $\frac{\sin^2 \theta}{A} = h^2 + k^2 + l^2$.
6. Solve $A = \frac{\lambda^2}{4a^2}$ for a .

(a)

D/mm	22	30	36	44	50	58	67	77
θ/deg	22	30	36	44	50	58	67	77
$10^3 \sin^2 \theta$	140	250	345	482	587	719	847	949

Analysis of face-centred cubic possibility								
(hkl)	(1 1 1)	(2 0 0)	(2 1 1)	(3 1 1)	(2 2 2)	(4 0 0)	(3 3 1)	(4 2 0)
$10^4 A$	467	625	431	438	489	449	446	475

Analysis of body-centred cubic possibility								
(hkl)	(1 1 0)	(2 0 0)	(2 1 1)	(2 2 0)	(3 1 0)	(2 2 2)	(3 2 1)	(4 0 0)
$10^4 A$	700	625	575	603	587	599	605	593

Begin by performing steps 1–3 in order to determine D , θ , and $\sin^2 \theta$ and place them in tabular form as above. It is now possible to reject the primitive (simple) cubic cell possibility immediately because the separation between the sixth and seventh lines is not significantly larger than the separation between the fifth and sixth lines (see Problem 23.2 and Fig. 23.22).

The relatively large uncertainties of the separation measurements force the modification of steps 4 and 5 for the identification of the unit cell as being either face-centred cubic or body-centred cubic. We analyse both possibilities by calculating the common factor $A = \sin^2 \theta / (h^2 + k^2 + l^2)$ for each datum in each case. Comparison of the standard deviations of the average of A determines the unit cell type.

The analysis of both the face-centred cubic and body-centred cubic possibilities is found in the above table. Successive reflective planes are determined with the rules found in Fig. 23.22.

$$\text{fcc possibility: } A_{\text{av.}} = 0.0478, \quad \sigma_A = 0.0063 \text{ (13 per cent)}$$

$$\text{bcc possibility: } A_{\text{av.}} = 0.0611, \quad \sigma_A = 0.0016 \text{ (6 per cent)}$$

These standard deviations (σ_A) indicate that the cell type is body-centred cubic

The Q test of the (1 1 0) reflection datum for A yields $Q = 0.6$. Consequently this datum may be rejected with better than 95 per cent confidence. This yields a better average value for A .

$$A_{\text{av.}} = 0.0598, \quad \sigma_A = 0.0016 \text{ (3 per cent)}$$

$$\text{Then } a = \frac{\lambda}{2A^{1/2}} = \frac{154 \text{ pm}}{(2) \times (0.0598)^{1/2}} = \boxed{315 \text{ pm}}$$

$$4R = \sqrt{3}a, \quad \text{so } \boxed{R = 136 \text{ pm}} \text{ [Fig. 23.1 above with } r = R]$$

(b)

D/mm	21	25	37	45	47	59	67	72
θ/deg	21	25	37	45	47	59	67	72
$10^3 \sin^2 \theta$	128	179	362	500	535	735	847	905

Analysis of face-centred cubic possibility								
(hkl)	(1 1 1)	(2 0 0)	(2 2 0)	(3 1 1)	(2 2 2)	(4 0 0)	(3 3 1)	(4 2 0)
$10^4 A$	427	448	453	455	446	459	446	453

Analysis of body-centred cubic possibility								
(hkl)	(1 1 0)	(2 0 0)	(2 1 1)	(2 2 0)	(3 1 0)	(2 2 2)	(3 2 1)	(4 0 0)
$10^4 A$	640	448	603	625	535	613	605	566

Following the procedure established in part (a), the above table is constructed.

$$\text{fcc possibility: } A_{\text{av.}} = 0.0448, \quad \sigma_A = 0.0010 \text{ (2 per cent)}$$

$$\text{bcc possibility: } A_{\text{av.}} = 0.0579, \quad \sigma_A = 0.0063 \text{ (11 per cent)}$$

The standard deviations indicate that the cell type is face-centred cubic

$$\text{Then } a = \frac{\lambda}{2A^{1/2}} = \frac{154 \text{ pm}}{(2) \times (0.0448)^{1/2}} = \boxed{364 \text{ pm}}$$

$$4R = \sqrt{2}a, \quad \text{so } R = \boxed{129 \text{ pm}}$$

P23.6

When a very narrow X-ray beam (with a spread of wavelenths) is directed on the centre of a genuine pearl, all the crystallites are irradiated parallel to a trigonal axis and the result is a Laue photograph with sixfold symmetry. In a cultured pearl the narrow beam will have an arbitrary orientation with respect to the crystallite axes (of the central core) and an unsymmetrical Laue photograph will result. (See J. Bijvoet *et al.*, *X-ray analysis of crystals*. Butterworth (1951).)

P23.8 $V = abc \sin \beta$

and the information given tells us that $a = 1.377b$, $c = 1.436b$, and $\beta = 122^\circ 49'$; hence

$$V = (1.377) \times (1.436b^3) \sin 122^\circ 49' = 1.662b^3$$

Since $\rho = \frac{NM}{VN_A} = \frac{2M}{1.662b^3 N_A}$ we find that

$$b = \left(\frac{2M}{1.662\rho N_A} \right)^{1/3} \\ = \left(\frac{(2) \times (128.18 \text{ g mol}^{-1})}{(1.662) \times (1.152 \times 10^6 \text{ g m}^{-3}) \times (6.022 \times 10^{23} \text{ mol}^{-1})} \right)^{1/3} = 605.8 \text{ pm}$$

Therefore, $a = \boxed{834 \text{ pm}}$, $b = \boxed{606 \text{ pm}}$, $c = \boxed{870 \text{ pm}}$

P23.10 In a monoclinic cell, the area of parallelogram faces whose sides are a and c is

$$A = ca \cos(\beta - 90^\circ)$$

so the volume of the unit cell is

$$V = abc \cos(\beta - 90^\circ) = (1.0427 \text{ nm}) \times (0.8876 \text{ nm}) \times (1.3777 \text{ nm}) \times \cos(93.254^\circ - 90^\circ) \\ = 1.2730 \text{ nm}^3$$

The mass per unit cell is

$$m = \rho V = (2.024 \text{ g cm}^{-3}) \times (1.2730 \text{ nm}^3) \times (10^{-7} \text{ cm nm}^{-1})^3 = 2.577 \times 10^{-21} \text{ g}$$

The monomer is $\text{CuC}_7\text{H}_{13}\text{N}_5\text{O}_8\text{S}$, so its molar mass is

$$M = 63.546 + 7(12.011) + 13(1.008) + 5(14.007) + 8(15.999) + 32.066 \text{ g mol}^{-1} \\ = 390.82 \text{ g mol}^{-1}$$

The number of monomer units, then, is the mass of the unit cell divided by the mass of the monomer

$$N = \frac{mN_A}{M} = \frac{(2.577 \times 10^{-21} \text{ g}) \times (6.022 \times 10^{23} \text{ mol}^{-1})}{390.82 \text{ g mol}^{-1}} = 3.97 \quad \text{or} \quad \boxed{4}$$

P23.12 The problem asks for an estimate of $\Delta_f H^\ominus(\text{CaCl})$. A Born–Haber cycle would envision formation of $\text{CaCl}(\text{s})$ from its elements as sublimation of $\text{Ca}(\text{s})$, ionization of $\text{Ca}(\text{g})$, atomization of $\text{Cl}_2(\text{g})$, electron gain of $\text{Cl}(\text{g})$, and formation of $\text{CaCl}(\text{s})$ from gaseous ions. Therefore

$$\Delta_f H^\ominus(\text{CaCl}, \text{s}) = \Delta_{\text{sub}} H^\ominus(\text{Ca}, \text{s}) + \Delta_{\text{ion}} H^\ominus(\text{Ca}, \text{g}) + 2\Delta_f H^\ominus(\text{Cl}, \text{g}) \\ + 2\Delta_{\text{eg}} H^\ominus(\text{Cl}, \text{g}) - \Delta_L H^\ominus(\text{CaCl}, \text{s})$$

Before we can estimate the lattice enthalpy of CaCl , we select a lattice with the aid of the radius-ratio rule. The ionic radius for Cl^- is 181 pm; use the ionic radius of K^+ (138 pm) for Ca^+

$$\gamma = \frac{138 \text{ pm}}{181 \text{ pm}} = 0.762$$

suggesting the CsCl structure. We can interpret the Born–Mayer equation (eqn 23.15) as giving the negative of the lattice enthalpy

$$\Delta_L H^\ominus \approx \frac{A|z_1 z_2| N_A e^2}{4\pi \epsilon_0 d} \left(1 - \frac{d^*}{d} \right)$$

The distance d is

$$d = 138 + 181 \text{ pm} = 319 \text{ pm}$$

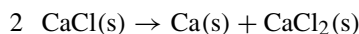
$$\text{so } \Delta_{\text{L}}H^{\ominus} \approx \frac{(1.763)(1)(-1)(6.022 \times 10^{23} \text{ mol}^{-1})(1.602 \times 10^{-19} \text{ C})^2}{4\pi(8.854 \times 10^{-12} \text{ J}^{-1}\text{C}^2 \text{ m}^{-1})(319 \times 10^{-12} \text{ m})} \left(1 - \frac{34.5 \text{ pm}}{319 \text{ pm}}\right)$$

$$\Delta_{\text{L}}H^{\ominus} \approx 6.85 \times 10^5 \text{ J mol}^{-1} = 685 \text{ kJ mol}^{-1}$$

The enthalpy of formation, then, is

$$\Delta_{\text{f}}H^{\ominus}(\text{CaCl}, \text{s}) \approx [176 + 589.7 + 2(121.7 - 348.7) - 685] \text{ kJ mol}^{-1} = \boxed{-373 \text{ kJ mol}^{-1}}.$$

Although formation of $\text{CaCl}(\text{s})$ from its elements is exothermic, formation of $\text{CaCl}_2(\text{s})$ is still more favoured energetically. Consider the reaction



$$\text{for which } \Delta H^{\ominus} = \Delta_{\text{f}}H^{\ominus}(\text{Ca}) + \Delta_{\text{f}}H^{\ominus}(\text{CaCl}_2) - 2\Delta_{\text{f}}H^{\ominus}(\text{CaCl})$$

$$\approx [0 - 795.8 - 2(-373)] \text{ kJ mol}^{-1}$$

$$\Delta H^{\ominus} \approx -50 \text{ kJ mol}^{-1}$$

Note: Using the tabulated ionic radius of Ca (i.e., that of Ca^{2+}) would be less valid than using the atomic radius of a neighbouring monovalent ion, for the problem asks about a hypothetical compound of monovalent calcium. Predictions with the smaller Ca^{2+} radius (100 pm) differ substantially from those listed above: the expected structure changes to rock-salt, the lattice enthalpy to 758 kJ mol^{-1} , $\Delta_{\text{f}}H^{\ominus}(\text{CaCl})$ to -446 kJ mol^{-1} and the final reaction enthalpy to $+96 \text{ kJ mol}^{-1}$.

Solutions to theoretical problems

P23.15 If the sides of the unit cell define the vectors \mathbf{a} , \mathbf{b} , and \mathbf{c} , then its volume is $V = \mathbf{a} \cdot \mathbf{b} \times \mathbf{c}$ [given]. Introduce the orthogonal set of unit vectors $\hat{i}, \hat{j}, \hat{k}$ so that

$$\mathbf{a} = a_x \hat{i} + a_y \hat{j} + a_z \hat{k}$$

$$\mathbf{b} = b_x \hat{i} + b_y \hat{j} + b_z \hat{k}$$

$$\mathbf{c} = c_x \hat{i} + c_y \hat{j} + c_z \hat{k}$$

$$\text{Then } V = \mathbf{a} \cdot \mathbf{b} \times \mathbf{c} = \begin{vmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{vmatrix}$$

Therefore

$$V^2 = \begin{vmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{vmatrix} \begin{vmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{vmatrix}$$

$$= \begin{vmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{vmatrix} \begin{vmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{vmatrix}$$

[interchange rows and columns, no change in value]

$$\begin{aligned}
&= \begin{vmatrix} a_x a_x + a_y a_y + a_z a_z & a_x b_x + a_y b_y + a_z b_z & a_x c_x + a_y c_y + a_z c_z \\ b_x a_x + b_y a_y + b_z a_z & b_y b_x + b_y b_y + b_z b_z & b_x c_x + b_y c_y + b_z c_z \\ c_x a_x + c_y a_y + c_z a_z & c_x b_x + c_y b_y + c_z b_z & c_x c_x + c_y c_y + c_z c_z \end{vmatrix} \\
&= \begin{vmatrix} a^2 & \mathbf{a} \cdot \mathbf{b} & \mathbf{a} \cdot \mathbf{c} \\ \mathbf{b} \cdot \mathbf{a} & b^2 & \mathbf{b} \cdot \mathbf{c} \\ \mathbf{c} \cdot \mathbf{a} & \mathbf{c} \cdot \mathbf{b} & c^2 \end{vmatrix} = \begin{vmatrix} a^2 & ab \cos \gamma & ac \cos \beta \\ ab \cos \gamma & b^2 & bc \cos \alpha \\ ac \cos \beta & bc \cos \alpha & c^2 \end{vmatrix} \\
&= a^2 b^2 c^2 (1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)^{1/2}
\end{aligned}$$

Hence $V = abc(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)^{1/2}$

For a monoclinic cell, $\alpha = \gamma = 90^\circ$

$$V = abc(1 - \cos^2 \beta)^{1/2} = abc \sin \beta$$

For an orthorhombic cell, $\alpha = \beta = \gamma = 90^\circ$, and

$$V = abc$$

P23.18 $F_{hkl} = \sum_i f_i e^{2\pi i(hx_i + ky_i + lz_i)}$ [23.7]

For each A atom use $\frac{1}{8} f_A$ (each A atom shared by eight cells) but use f_B for the central atom (since it contributes solely to the cell).

$$\begin{aligned}
F_{hkl} &= \frac{1}{8} f_A \{1 + e^{2\pi i h} + e^{2\pi i k} + e^{2\pi i l} + e^{2\pi i(h+k)} + e^{2\pi i(h+l)} + e^{2\pi i(k+l)} + e^{2\pi i(h+k+l)}\} \\
&\quad + f_B e^{2\pi i(h+k+l)} \\
&= f_A + (-1)^{(h+k+l)} f_B \quad [h, k, l \text{ are all integers, } e^{i\pi} = -1]
\end{aligned}$$

(a) $f_A = f$, $f_B = 0$; $F_{hkl} = f$ [no systematic absences]

(b) $f_B = \frac{1}{2} f_A$; $F_{hkl} = f_A \left[1 + \frac{1}{2} (-1)^{(h+k+l)}\right]$

Therefore, when $h + k + l$ is odd, $F_{hkl} = f_A \left(1 - \frac{1}{2}\right) = \frac{1}{2} f_A$, and when $h + k + l$ is even, $F_{hkl} = \frac{3}{2} f_A$.

That is, there is an alternation of intensity ($I \propto F^2$) according to whether $h + k + l$ is odd or even.

(c) $f_A = f_B = f$; $F_{h+k+l} = f \left\{1 + (-1)^{h+k+l}\right\} = 0$ if $h + k + l$ is odd.

Thus, all $h + k + l$ odd lines are missing.

P23.20 Write $t = aT$, then

$$\left(\frac{\partial t}{\partial T}\right)_l = a, \quad \left(\frac{\partial U}{\partial l}\right)_T = t - aT \text{ [Problem 23.19]} = 0$$

and the internal energy is independent of the extension. Therefore

$$t = -T \left(\frac{\partial S}{\partial l}\right)_T \text{ [Problem 23.19]}$$

and the tension is proportional to the variation of entropy with extension. The extension reduces the disorder of the chains, and they tend to revert to their disorderly (nonextended) state.

P23.22 (a) The density of energy levels is:

$$\rho(E) = \frac{dk}{dE} = \left(\frac{dE}{dk} \right)^{-1}$$

$$\text{where } \frac{dE}{dk} = \frac{d}{dk} \left(\alpha + 2\beta \cos \frac{k\pi}{N+1} \right) = -\frac{2\pi\beta}{N+1} \sin \frac{k\pi}{N+1}$$

$$\text{so } \rho(E) = -\frac{N+1}{2\pi\beta} \left(\sin \frac{k\pi}{N+1} \right)^{-1}$$

Unlike the expression just derived, the relationship the problem asks us to derive has no trigonometric functions and it contains E and α within a square root. This comparison suggests that the trigonometric identity $\sin^2 \theta + \cos^2 \theta = 1$ will be of use here. Let $\theta = k\pi/(N+1)$; then

$$\sin \theta = 1(1 - \cos^2 \theta)^{1/2}$$

however, $\cos \theta$ is related to the energy

$$E = \alpha + 2\beta \cos \theta \quad \text{so} \quad \cos \theta = \frac{E - \alpha}{2\beta}$$

$$\text{and } \sin \theta = \left[1 - \left(\frac{E - \alpha}{2\beta} \right)^2 \right]^{1/2}$$

$$\text{Finally, } \rho(E) = \frac{-\frac{N+1}{2\pi\beta}}{\left[1 - \left(\frac{E - \alpha}{2\beta} \right)^2 \right]^{1/2}}$$

(b) The denominator of this expression vanishes as the energy approaches $\alpha \pm 2\beta$. Near those limits, $E - \alpha$ becomes $\pm 2\beta$, making the quantity under the square root zero, and $\rho(E)$ approach infinity.

P23.23

$$\xi = \frac{-e^2}{6m_e} \langle r^2 \rangle$$

$$\begin{aligned} \langle r^2 \rangle &= \int_0^\infty r^2 \psi^2 d\tau \quad \text{with } \psi = \left(\frac{1}{\pi a_0^3} \right)^{1/2} e^{-r/a_0} \\ &= 4\pi \int_0^\infty r^4 \psi^2 dr \quad [d\tau = 4\pi r^2 dr] \\ &= \frac{4}{a_0^3} \int_0^\infty r^4 e^{-2r/a_0} dr = 3a_0^2 \left[\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}} \right] \end{aligned}$$

$$\text{Therefore, } \xi = \frac{-e^2 a_0^2}{2m_e}$$

Then, since $\chi_m = N_A \mu_0 \xi$ [23.32, $m = 0$]

$$\chi_m = \frac{-N_A \mu_0 e^2 a_0^2}{2m_e}$$

P23.25 If the proportion of molecules in the upper level is P , where they have a magnetic moment of $2\mu_B$ (which replaces $\{S(S+1)\}^{1/2}\mu_B$ in eqn 23.35), the molar susceptibility

$$\chi_m = \frac{(6.3001) \times [S(S+1)]}{T/K} \text{ cm}^3 \text{ mol}^{-1} \text{ [Illustration 23.1]}$$

is changed to

$$\chi_m = \frac{(6.3001) \times (4) \times P}{T/K} \text{ cm}^3 \text{ mol}^{-1} [2^2 \text{ replaces } S(S+1)] = \frac{25.2P}{T/K} \text{ cm}^3 \text{ mol}^{-1}$$

The proportion of molecules in the upper state is

$$P = \frac{e^{-hc\tilde{\nu}/kT}}{1 + e^{-hc\tilde{\nu}/kT}} \text{ [Boltzmann distribution]} = \frac{1}{1 + e^{hc\tilde{\nu}/kT}}$$

$$\text{and } \frac{hc\tilde{\nu}}{kT} = \frac{(1.4388 \text{ cm K}) \times (121 \text{ cm}^{-1})}{T} = \frac{174}{T/K}$$

$$\text{Therefore, } \chi_m = \frac{25.2 \text{ cm}^3 \text{ mol}^{-1}}{(T/K) \times (1 + e^{174/(T/K)})}$$

This function is plotted in Fig. 23.4

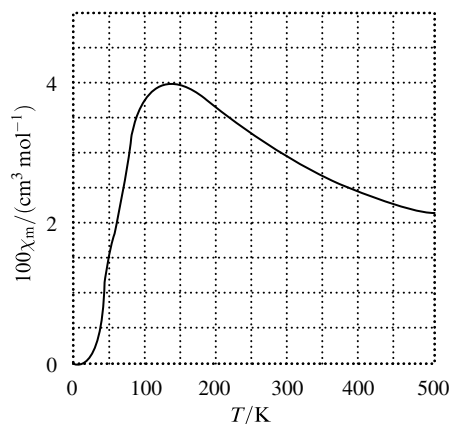


Figure 23.4

Comment. The explanation of the magnetic properties of NO is more complicated and subtle than indicated by the solution here. In fact the full solution for this case was one of the important triumphs of the quantum theory of magnetism which was developed about 1930. See J. H. van Vleck, *The theory of electric and magnetic susceptibilities*. Oxford University Press (1932).

Solutions to applications

P23.29 $\theta(100 \text{ K}) = 22^\circ 2' 25''$, $\theta(300 \text{ K}) = 21^\circ 57' 59''$

$$\sin \theta(100 \text{ K}) = 0.37526, \quad \sin \theta(300 \text{ K}) = 0.37406$$

$$\frac{\sin \theta(300 \text{ K})}{\sin \theta(100 \text{ K})} = 0.99681 = \frac{a(100 \text{ K})}{a(300 \text{ K})} \text{ [see Problem 21.7]}$$

$$a(300 \text{ K}) = \frac{\lambda\sqrt{3}}{2 \sin \theta} = \frac{(154.062 \text{ pm}) \times \sqrt{3}}{(2) \times (0.37406)} = 356.67 \text{ pm}$$

$$a(100 \text{ K}) = (0.99681) \times (356.67 \text{ pm}) = 355.53 \text{ pm}$$

$$\frac{\delta a}{a} = \frac{356.67 - 355.53}{355.53} = 3.206 \times 10^{-3}$$

$$\frac{\delta V}{V} = \frac{356.67^3 - 355.53^3}{355.53^3} = 9.650 \times 10^{-3}$$

$$\alpha_{\text{volume}} = \frac{1}{V} \frac{\delta V}{\delta T} = \frac{9.650 \times 10^{-3}}{200 \text{ K}} = \boxed{4.8 \times 10^{-5} \text{ K}^{-1}}$$

$$\alpha_{\text{volume}} = \frac{1}{a} \frac{\delta a}{\delta T} = \frac{3.206 \times 10^{-3}}{200 \text{ K}} = \boxed{1.6 \times 10^{-5} \text{ K}^{-1}}$$