CHAPTER TWENTY

THE SOLID STATE

We consider four more or less distinct aspects of the physical chemistry of the solid state. The emphasis is on crystalline as opposed to glassy phases, and the first topic is that of the perfect crystal as a regular, infinitely repeating structure. A special field of geometry informs us that only certain symmetry properties are possible if space is to be filled by a repeating structure or lattice. We then introduce some very simple examples of such lattices, involving the ways in which spherical atoms or ions can pack. This leads us to the structure of alkali metal halide and other ionic crystals and, in the Special Topics section, to calculations of the total cohesive energy of a crystal, called the lattice energy.

We consider next the use of x-ray diffraction as a means of determining the symmetry class of a crystal, and then its actual structure. Modern x-ray crystallography is a rather specialized subject and only the introductory aspects of it will be presented. Most crystal structures of interest today are rather complex ones, and a few examples of this type are described in the Commentary and Notes section. The main part of the chapter concludes with some material on imperfect crystals. Actual crystals have defects and dislocations, the presence of which can be quite important to their physical properties.

20-1 Space-Filling Lattices

There is an interesting history to the development of the awareness that the external regularity of crystals implies an inner regularity of structure. A beautifully perceptive intuition on this subject was that of Johannes Kepler. In a presentation to his benefactor, Counsellor Wackher, Kepler (1611) ponders the questions: Why should a snowflake have just six sides? Is it because this is a two-dimensional space-filling geometry? Is it significant that spheres on a flat surface pack to give a hexagonal pattern?

Topologists have since greatly developed the subject of mosaics, or infinitely repeating two-dimensional patterns; as illustrated in Fig. 20-1, the hexagonal unit is but one of many possibilities. The possibilities have restrictions, however. They can be shown to be limited by asking what symmetry operations can be applied
at a point that will generate a lattice. It turns out that the only types possible are
(a) mirror reflections across a line and (b) one-, two-, three-, four-, or sixfold axes. A square lattice has a fourfold axis and mirror plane along each axis. An oblique lattice, such as shown in Fig. 20-2(a), has only a twofold rotation axis. There are in fact only five possible area-filling lattices: oblique, rectangular, centered rectangular, square, and hexagonal. These are known as Bravais lattices, after A. Bravais (1848), or just as plane lattices or plane nets.

A Bravais lattice is not in itself a crystal or, in two dimensions, a mosaic. It is a geometric construct—a repeating frame of reference. It can be described by the various symmetry operations which put the lattice into an equivalent configuration. These will be point symmetry operations since one given lattice point remains unchanged. The unit cell of a lattice is the smallest portion of it exhibiting the symmetry features of the whole.

![FIG. 20-1. Mosaics of (a) modified triangles and (b) modified squares. (From M. Kraitchik, “Mathematical Recreations.” Dover, New York, 1942.)](image)

![FIG. 20-2. (a) Two-dimensional oblique lattice having $C_1$ symmetry. (b) The same, but with $C_3$ symmetry as indicated by the symbols for a twofold axis (lens). (c) Lattice plus basis belonging to $C_1$ point group. (d) Lattice plus basis belonging to $C_3$ point group.](image)
Not all of the point groups mentioned in Chapter 17 are possible for lattices. In the case of a two-dimensional lattice, we are restricted to just principal axes and vertical symmetry planes; further, as mentioned before, the order of the principal axes can only be 1, 2, 3, 4, or 6. This leaves the 10 point groups $C_1$, $C_2$, $C_3$, $C_4$, $C_6$, $C_{3v}$, $C_{4v}$, $C_{6v}$, and $C_{6v}$. (The corresponding designations in the international crystallographic notation are 1, 2, 3, 4, 6, m, 2mm, 3m, 4mm, and 6mm—see Section 20-ST-1.)

The unit cell of a Bravais lattice may have certain but not all of these point group symmetries. The unit cell of a two-dimensional oblique lattice may have $C_1$ or $C_2$ symmetry but not others, for example. The former is illustrated in Fig. 20-2(a) and the latter in Fig. 20-2(b), where a lens denotes a twofold rotation axis.

As an exercise the reader might convince himself that the presence of one twofold axis at a lattice corner implies the presence of all of the others shown. For example, place an asymmetric object near one corner and carry out the twofold rotation—this places a second object in the adjacent cell. The existence of the lattice implies, however, that the object can be moved about by unit translations along the lattice directions; the object produced in the adjacent cell must also appear in the original cell.

The various possible combinations of the ten point group symmetries with the five Bravais lattices generate 12 lattice types, two of which are shown in Fig. 20-2(a,b). However, because one is dealing with a lattice rather than with a single object such as a molecule, some additional symmetry operations are possible which combine rotation or reflection with translation (see Section 20-ST-1). On inclusion of possible combinations of these new operations, a final total of 17 two-dimensional lattice types are possible. These are called plane groups. The space group designations for the lattices of Fig. 20-2(a,b) are oblique, $PC_1$ and $PC_2$ or, in crystallographic symmetry notation, $P1$ and $P2$, where $P$ denotes a primitive as opposed to a face-centered lattice.

In any actual crystal (or mosaic) some pattern of atoms is superimposed on a particular Bravais lattice. This pattern is called the basis and repeats with the unit cell of the lattice. Another way of seeing how the various space groups come about is as follows. The basis will have its own symmetry properties; if it is asymmetric, then the only symmetry of the repeating pattern is that of the lattice framework itself, as illustrated in Fig. 20-2(c). If, however, the basis has a higher symmetry, then it may conform to a more symmetric space group. Thus in Fig. 20-2(d) the basis consists of paired triangles, the pair having a $C_3$ axis. The presence of this axis then generates the pattern shown in the figure. The same higher lattice symmetry would be present if the basis were still more symmetric, as, for example, if it consisted of just an atom at each lattice point. Thus the space group designation implies a certain minimum symmetry for the basis or, conversely, one can determine the space group if the lattice and the basis are known.

The analysis of the situation in three dimensions is similar to that for two dimensions. There are 14 Bravais lattices, however, as summarized in Table 20-1. The possible point groups now include those with secondary axes and $\sigma_h$ planes, but are still restricted to $C_1$, $C_2$, $C_3$, $C_4$, and $C_6$ principal axes. The various combinations of symmetry elements consistent with each Bravais lattice give rise to 32 lattice types or lattice point groups. If combined rotation–translation and reflection–translation operations are included, then a total of 230 space groups are obtained. A three-dimensional crystal must belong to one of these space groups.
TABLE 20-1. The Bravais Lattices

<table>
<thead>
<tr>
<th>System</th>
<th>Number of lattices</th>
<th>Lattice symbol</th>
<th>Unit cell axes and angles</th>
<th>Symmetry designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>3</td>
<td>P I F</td>
<td>(a = b = c) (\alpha = \beta = \gamma = 90^\circ)</td>
<td>m3m</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>2</td>
<td>P I F</td>
<td>(a = b \neq c) (\alpha = \beta = \gamma = 90^\circ)</td>
<td>4/mmm</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>4</td>
<td>P C I F</td>
<td>(a \neq b \neq c) (\alpha = \beta = \gamma = 90^\circ)</td>
<td>mmm</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>2</td>
<td>P C I F</td>
<td>(a = b = c) (\alpha = \gamma = 90^\circ \neq \beta)</td>
<td>2/m</td>
</tr>
<tr>
<td>Rhombohedral</td>
<td>1</td>
<td>P</td>
<td>(a = b = c) (\alpha = \beta = \gamma \neq 90^\circ)</td>
<td>3m</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>1</td>
<td>P</td>
<td>(a = b \neq c) (\alpha = \beta = 90^\circ; \gamma = 120^\circ)</td>
<td>6/mmm</td>
</tr>
<tr>
<td>Triclinic</td>
<td>1</td>
<td>P</td>
<td>(a \neq b \neq c) (\alpha \neq \beta \neq \gamma \neq 90^\circ)</td>
<td>m3m</td>
</tr>
</tbody>
</table>

* The symbols stand for: P, primitive, with lattice points only at the corners of the unit cell; C, base centered; I, interior or body centered; F, centered on all faces, or face-centered.

Clearly, the detailed treatment of all of these symmetry combinations is too long to be practical here, and we will confine ourselves almost entirely to some important examples in the cubic system.

We will, in fact, deal mainly with rather simple crystals—ones having atoms or ions at lattice corners or in lattice faces. Figure 20-3 shows the unit cell for a simple cubic lattice whose basis consists of an atom at each lattice point. A distinction to emphasize is that the unit cell is not necessarily the repeating unit. In Fig. 20-3 each corner atom is shared with eight adjacent unit cells and an attempt to generate the complete crystal by translations of this unit would superimpose atoms on each other. The repeating unit is in this case just the atom at the origin,
that is, at position (0, 0, 0). If this atom is translated by all possible combinations of the unit lattice distance \(a\), then the crystal is generated.

The number of atoms or ions in a unit cell is, of course, just the number present in the repeating unit. The same answer can be obtained from a diagram of the unit cell provided that corner atoms are counted as one-eighth of an atom each, face atoms as one-half, and so on. That is, each atom or ion is weighted according to the number of adjacent unit cells which share it.

Figure 20-4 shows the unit cells for the 14 Bravais lattices. These can be described by specifying the unit lengths \(a\), \(b\), and \(c\) and the angles \(\alpha\), \(\beta\), and \(\gamma\) as indicated in Fig. 20-5. The positions of the lattice points are then given in terms of this coordinate system. Thus the simple cubic unit cell has points (or atoms in the
corresponding simplest possible crystal) at (0, 0, 0), (1, 0, 0), (0, 1, 0), (1, 1, 0),
(0, 0, 1), (1, 0, 1), (0, 1, 1), and (1, 1, 1), the numbers giving positions in terms of
(a, b, c); similar coordinates would likewise locate the atoms in the primitive
tetragonal, orthorhombic, hexagonal, and triclinic lattices, measured in units
of (a, b, c) and along the required axis directions. The body-centered cubic lattice
has the same positions as does the simple cubic lattice plus one at (1/2, 1/2, 1/2); the
face-centered cubic lattice has the additional points (1/2, 1/2, 0), (0, 1/2, 1/2),
(1/2, 0, 1/2), (1/2, 1/2, 1/2), and (1/2, 1/2, 1/2). In these last two cases the repeating units consist
of the points (0, 0, 0) and (1/2, 1/2, 1/2), and (0, 0, 0), (1/2, 1/2, 0), (0, 1/2, 1/2), and (1/2, 0, 1/2),
respectively. Thus the body-centered cubic repeating unit has two points and the
face-centered unit has four points. The same numbers would result if the unit cell
points shown in Fig. 20-4 were counted as one-eighth if at a corner, one-half if on
a face, and full weight if in the interior.

It is to be remembered that there will be actual crystals such that each point in
Fig. 20-4 is occupied by a single atom, as just assumed, but many other crystals
where each point is occupied by some molecule or grouping of atoms—a grouping
whose symmetry is reduced from that of a sphere. Thus the lattice of crystalline
carbon dioxide is face-centered cubic, but the basis consists of variously oriented
CO₂ molecules, as illustrated in Fig. 20-6.

20-2 Crystal Planes; Miller Indices

Any actual crystal is finite in extent and its surfaces are made up of planes that
pass through lattice points. Thus ideal physical crystals are bounded by planes
which are lattice or rational planes; the inverse reasoning was made by Hauy in
1784, namely that the regular shapes of crystals imply an inner regularity. How­
ever, the appearance of a crystal is very dependent on which planes bound it, as
illustrated in Fig. 20-7 for a crystal whose lattice is cubic. As we truncate the corners
of a simple cube progressively, surfaces corresponding to planes of the type indi­
cated in Fig. 20-8(a) increase in extent until the crystal is bounded only by such
planes. These different appearances are called crystal habits. It was gradually appreciated that it is not the crystal habit that is in itself fundamental, but rather its symmetry, especially the angles between crystal faces, and hence between crystal planes. One may often determine the point group to which a crystal belongs just from its external symmetry.

A system for characterizing rational planes was developed by W. H. Miller in 1839, using what are now called Miller indices. If we locate an origin at some lattice point, then any crystal plane must intercept the crystal axes originating from this point, as illustrated in Fig. 20-9. A theorem which we will not prove is that the three intercepts of any rational plane must be in the ratio of integers. This is known as the law of rational intercepts, due to Haüy. Parallel to any such plane there is a whole set of planes which may be generated from it by application of unit translations along the axes of the lattice. If we now consider that plane of the set which is closest to the origin (without actually containing it), then the Miller indices \((hkl)\) are the reciprocals of the intercepts, expressed in units of the lattice distances. In practice the indices \((hkl)\) may refer either to this particular plane or to the whole set of equivalent ones.

\[\text{FIG. 20-7. Some crystal habits for a cubic crystal.}\]

\[\text{FIG. 20-8. (a) The (111) plane of a cubic lattice. (b) The (11\bar{1}) plane of a cubic lattice.}\]
To illustrate, the plane shown in Fig. 20-8(a) is the closest of its set to the origin and has the intercepts \( (1, 1, 1) \), expressed in units of \( a \). The Miller indices are therefore the reciprocals, or \((111)\). Other orientations are possible. Thus the plane shown in Fig. 20-8(b) has the intercepts \((1, 1, -1)\), and corresponding indices \((11\bar{1})\). Similarly, the planes \((1\bar{1}1), (1\bar{1}1)\), and so on exist. We will class all of these as just \((111)\) planes in dealing with crystals in the cubic system.

Figure 20-10(a) shows a nearest-origin plane whose intercepts are \((1, 1, \infty)\) and corresponding Miller indices, \((110)\). Planes parallel to one of the axes are more easily shown by means of a projection down that axis, as illustrated in Fig. 20-10(b), where the \((110)\) planes now appear as set I. The intercepts for the nearest-origin plane of set II are \((1, \frac{1}{2}, \infty)\), giving the indices \((120)\). Those for the planes of set III are left for the reader to determine. Note, incidentally, that the equation \(hx + ky + lz = 1\) is that of the plane nearest to the origin.
20-3 Some Simple Crystal Structures

A. Close Packing of Spheres

Many of the elements assume a crystal structure which corresponds to the closest possible packing of spheres. As illustrated in Fig. 20-11(a), a single layer of spheres forms a pattern having triangular pockets. There are two equivalent ways of locating the second layer, namely by placing the spheres either in the set of first layer pockets labeled A or in the set labeled B. If the A set is used, as in Fig. 20-11(b), then the B set is excluded. The second layer again has two kinds of triangular pockets, those labeled B, which lie above the B pockets of the first layer, and those labeled C, which lie above the centers of the first-layer spheres.

There are now two distinguishable ways of placing a third layer. If the spheres are put in the set of C-type pockets, they will lie directly above the first-layer spheres. The structure then repeats, the types of pockets in which successive layers rest being in the sequence ACACAC..., as shown in Fig. 20-12. The resulting symmetry is easier to visualize if the spheres are replaced by points at their centers, as in Fig. 20-13(a); the structure can now be seen to have hexagonal symmetry. This arrangement is, accordingly, called hexagonal close packing, or hcp.

Returning to Fig. 20-11(b), if the third-layer spheres are placed in the B-type pockets, this third layer will now have pockets of the A and C types. The next simplest repeating unit is then obtained by placing the fourth layer in the C pockets,

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figs/20-11}
\caption{Close packing of spheres. (a) First layer. (b) Second layer located with centers above A-type pockets of the first layer.}
\end{figure}
so as to be directly above the first layer (Fig. 20-12). The symmetry of the ABCABC arrangement is somewhat difficult to see. As shown in Fig. 20-13(b), we can trace the pattern of a face-centered cube by connecting points between the successive layers. Figure 20-14 shows the cube in a normal orientation; we now see more clearly that the successive layers of Figs. 20-12 and 20-13 correspond to (111) planes of a face-centered cubic lattice. The ABCABC arrangement is for this reason called cubic close packing, or ccp. Alternatively, of course, the structure is face-centered cubic, or fcc.

It must be remembered that it is the symmetry and not the density of packing that differs between the hcp and ccp structures. In both cases (but most easily seen in the hcp symmetry), each sphere in a close-packed plane has six neighbors which are touching. There is a triangle of three nearest neighbors above and one below, to give 12 neighbors in all. In the hcp structure the above and below triangles are

FIG. 20-12. Perspective view of (a) hexagonal and (b) cubic close packing of spheres.

FIG. 20-13. Perspective view of the positions of sphere centers in (a) hexagonal close packing, ACACAC sequence, and (b) cubic close packing, ABCABC sequences. Note in (b) the pattern that forms a face-centered cube with axes x', y', and z'.
FIG. 20-14. Cubic close packing drawn so as to show the face-centered cubic lattice.

oriented in the same way, while in the ccp structure they are rotated 120° relative to each other. It may be shown, incidentally, that the close packing of spheres leaves 26% void space.

Many metals crystallize in either the hcp or the ccp structure, the choice apparently being determined by relatively weak directional preferences in the metal–metal bonding. Metals having the hcp structure include γ-Ca, Cd, α-Co, β-Cr, Mg, and Zn, while those having the ccp structure are Cu, Ag, Au, Al, Pb, β-Ni, and γ-Fe. The rare gases Ar, Ne, and Xe also crystallize in the ccp structure.

A definite tendency toward directed bonding appears with Zn and Cd; although the structure is approximately hcp, the axial ratio \( c/a \) is 1.856 for Zn and 1.885 for Cd, as compared to 1.633 for closest packing. In other metals, this tendency leads to some other crystal structure, often body-centered cubic, or bcc. Metals showing bcc structures include Ba, α-Cr, Cs, α-Fe, δ-Fe, K, Li, Mo, Na, and β-W. Notice that a given element may show more than one crystal modification, as in the case of Cr and Fe.

While hcp and ccp structures both represent the closest packing of spheres, the physical properties of metals can be sharply dependent on which structure is present. Thus ccp metals tend to be much more ductile than hcp ones. The reason is as follows. For crystals in general it is those planes that are the most closely packed which slip past each other most easily [note Eq. (20-5)]. There is only one such set of planes in the hcp structure—namely the basal or hexagonal planes shown in Fig. 20-13(a). In the ccp structure, however, the close-packed planes are the (111) planes, and there are four of these, that is, there is a set of (111) planes, one normal to each of the four cube diagonals. In practice, one deals with metals which are polycrystalline, or have randomly oriented and mutually reinforcing crystal domains. As a consequence, the hcp metals tend to resist distortion in any given direction since most of the crystallites will not be properly oriented for slip to occur. A much smaller fraction will be able to oppose slip in the case of a ccp metal.

B. Alkali Metal Halide and Other MX Structures

One of the early triumphs of x-ray diffraction was the determination of the crystal structure of sodium chloride. It consists of two interpenetrating fcc lattices, as shown in Fig. 20-15, where, for clarity, the spherical ions are located by points
marking their centers. It must be remembered, however, that in any lattice whose positions are occupied by spheres, nearest neighbors are in contact (see Special Topics section). Thus Na\(^+\) and Cl\(^-\) ions are touching along the \(a\) axes, and the sum of the two ionic radii \(r_{Na^+} + r_{Cl^-}\) is \(a/2\).

The NaCl type of structure is a fairly common one for MX-type salts. It is the structure of most of the other alkali halides (M = Na\(^+\), K\(^+\), and Rb\(^+\), and \(X = F^-, Cl^-, Br^-,\) and I\(^-\), and CsF), as well as for compounds such as BaO, BaS, CaO, CaS, CdO, FeO, and other divalent metal oxides and sulfides. Ammonium ion acts like a spherical ion and NH\(_4\)I also has the NaCl structure.

The figure gives the unit cell for NaCl; this is not, however, the repeating unit, which consists of four Na\(^+\) ions, at \((0, 0, 0), (\frac{1}{2}, 0, \frac{1}{2}), (\frac{1}{2}, \frac{1}{2}, 0),\) and \((0, \frac{1}{2}, \frac{1}{2})\), and four Cl\(^-\) ions, at \((\frac{1}{2}, 0, 0), (0, \frac{1}{2}, 0), (0, 0, \frac{1}{2}),\) and \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\). If this set is translated by all possible combinations of multiples of \(a\) in the \(x, y,\) and \(z\) directions, the entire crystal is generated. The same count of ions can be obtained from Fig. 20-15.

\[
\begin{align*}
\text{Na}^+ \text{ ions:} & \quad (8 \text{ corner}) \frac{1}{8} = 1 \\
& \quad (6 \text{ face}) \frac{1}{2} = 3 \\
& \quad \quad = 4 \\
\text{Cl}^- \text{ ions:} & \quad (12 \text{ edge}) \frac{1}{4} = 3 \\
& \quad (1 \text{ interior}) \frac{1}{1} = 1 \\
& \quad \quad = 4
\end{align*}
\]

As a check in the counting of atoms, the proportion of each kind must always
correspond to the stoichiometry of the formula of the compound. Notice also, as one characteristic of the NaCl structure, that each ion has six nearest neighbors, in an octahedral arrangement.

A second, and quite common, structure for MX salts is that of two interpenetrating simple cubic lattices, as illustrated in Fig. 20-16 for the best-known case, CsCl. The CsCl structure is also found for CsBr and CsI, as well as for other MX compounds, such as NH$_4$Cl and NH$_4$Br, and various intermetallic compounds, such as AgCd, AuZn, and CuZn. Each ion or atom has eight nearest neighbors, in square symmetry.

The NaCl and CsCl structures are only two of a number that MX compounds have been found to exhibit. Most such compounds, however, crystallize in one or the other of the structures shown in Fig. 20-17, each labeled according to its most prominent example. Notice that not all of the structures are cubic and that the number of nearest neighbors to a given kind of atom, or its coordination number, diminishes in the sequence:

<table>
<thead>
<tr>
<th>lattice type</th>
<th>CsCl</th>
<th>NaCl</th>
<th>ZnO</th>
<th>ZnS</th>
<th>BN</th>
</tr>
</thead>
<tbody>
<tr>
<td>coordination number</td>
<td>8</td>
<td>6</td>
<td>4</td>
<td>4</td>
<td>3</td>
</tr>
</tbody>
</table>

It should be apparent at this point that crystal structure does not correlate with the chemistry of a compound, nor with the atomic weights of the constituents per se. V. Goldschmidt, who determined many of the simple crystal structures around 1925, concluded that the structure of such crystals is determined by the stoichiometry of the compound, the ratio of atomic radii, and the polarizability of the units.

C. MX$_2$ Structures

Two of the important structures for MX$_2$ compounds are shown in Fig. 20-18. For example, the form of TiO$_2$ known as rutile crystallizes in the tetragonal system, with $c = 4.58$ Å and $a = b = 2.98$ Å. The unit cell contains two Ti atoms and four O atoms and is thus consistent with the formula of the compound. Each Ti has six O nearest neighbors and each O has three Ti nearest neighbors. If $C$ denotes the coordination number in an $M_aX_b$ compound, a useful rule of stoichiometry is that

$$C_{Ma} = C_Xb.$$  \hspace{1cm} (20-1)
D. Covalent Crystals. Diamond and Graphite

We next consider briefly two examples of covalent crystals, diamond and graphite. In the case of diamond, the C—C bonds are of the covalent, sigma-bonded type, and show the tetrahedral bond angle of 109°28'. In a sense a diamond crystal is a single large molecule; the crystal structure, however, has a cubic unit cell, displayed in Fig. 20-19. As one way of visualizing the structure, notice that there is an atom at each corner, in the center of each face, and in the centers of alternate small cubes; one set of bonds is shown (the bond distance is 1.542 Å). Germanium, silicon, and gray tin have the same structure.

The diamond structure may also occur with covalent AB-type compounds, such as ZnS (zincblende) (see Fig. 20-17), AgI, CuBr, and BN. The atoms alternate in type, so each A and B atom has four tetrahedrally disposed nearest neighbors. Again, it is not the chemistry of the compound but primarily the relative size of the atoms and the geometry of their bonding that determine crystal structures in these cases.

Graphite serves as an example of a layer crystal. The structure is shown in Fig. 20-20 and is seen to consist of layers having a hexagonal tile pattern. The layers are aromatic in character; the C—C distance is 1.42 Å, or not much greater than the value of 1.397 Å for benzene. The distance between layers is relatively large, 3.40 Å, and the layer–layer bonds are consequently rather weak.

The high electrical conductivity of graphite can be regarded as due to the conjugation or aromaticity of the planes, which permits electrons to move through the crystal easily. The lubricating property has been thought to stem from the ease of slippage of one layer over the next, but the actual situation has been found to be somewhat more complex. If graphite is thoroughly
degassed, its coefficient of friction rises about sixfold, and it appears that gases adsorbed between layers are responsible for the very low friction ordinarily observed. The same may be true for a useful modern lubricant, MoS$_2$, whose structure is analogous to that of graphite, as well as for other layer crystals, such as talc.

**E. Molecular Crystals**

The substances considered so far—metals, alkali metal halides and other ionic crystals, and covalent crystals—all have high melting points. This is a reflection of the strong bonds—metallic, ionic, or covalent—between the atoms of the lattice.
A rather different situation exists in the case of crystals whose basis consists of stable molecules and which are therefore held together by secondary or van der Waals forces (note Table 8-8). Figure 20-21 shows the structure of crystalline benzene. This is a low-melting (6°C) white solid; it is soft and is not electrically conducting and clearly is made up of only weakly interacting benzene molecules.

The crystals of most simple molecules, such as O\textsubscript{2}, N\textsubscript{2}, CO, CO\textsubscript{2}, CH\textsubscript{4}, are of this type. Most nonionic organic substances also crystallize by virtue of van der Waals forces only, except where hydrogen bonding is involved.

**F. Hydrogen-Bonded Crystals. Ice**

We conclude this section with a brief discussion of a remaining type of crystal structure, namely that in which hydrogen bonding is present. The most important example is undoubtedly that of ice, whose ordinary structure is shown in Fig. 20-22. It will be recalled from Fig. 8-8(b) that ice exhibits a number of crystal modifications, but only two, tetrahedral and hexagonal ice, are stable under atmospheric pressure. It is the latter modification that is shown in Fig. 20-22. The basic structure is determined by the positions of the oxygen atoms; each is surrounded tetrahedrally by four nearest neighbors at a distance of 2.67 Å. Only recently have advanced techniques using neutron diffraction (see Section 20-CN-1) established that the hydrogen atoms are located on the lines between oxygen atoms but asymmetrically placed; each oxygen is coordinated to two close hydrogen atoms and to two that are further away. The assignment of close versus far hydrogens is random, however, and in this respect the structure is disordered.

Hydrogen bonding is important in molecular crystals in which electronegative atoms, such as fluorine, oxygen, and nitrogen, can interact with an acidic proton of a neighboring molecule. This type of interaction becomes extremely important in crystals of biologically important substances, such as proteins and nucleic acids.
20-4 Some Geometric Calculations

The following types of calculations can be performed on any crystal but the geometric expressions rapidly become complicated as one departs from the cubic system. The general expression for the density of a crystal is, for example,

\[ \rho = \frac{\sum n_i M_i}{N \cdot V_c}, \]  

(20-2)

where \( n_i \) is the number of the \( i \)th kind of atom (or molecule) of molecular weight \( M_i \) in the unit cell, and \( V_c \) is the cell volume. In the case of a cubic crystal \( V_c \) is just \( a^3 \), while for a tetragonal unit cell \( V_c \) is \( a^2c \), and so on.

Two illustrations of the use of Eq. (20-2) follow. Iron (\( \alpha \)-Fe) crystallizes in the bcc system with \( a = 2.861 \, \text{Å} \); the eight corner and one interior atom in the unit cell give a net of two atoms, so

\[ \rho = \frac{2(55.85)}{6.02 \times 10^{23}(2.861 \times 10^{-8})^3} = 7.92 \, \text{g cm}^{-3}. \]

Reference to Fig. 20-4 shows that each atom in a body-centered cubic lattice has eight nearest neighbors; the center atom, for example, must therefore be in contact with the eight corner ones and the body diagonal of the cube must equal two atomic diameters. The radius of each Fe atom is therefore

\[ r_{Fe} = \frac{1}{4} \sqrt{3} (2.861 \times 10^{-8}) = 1.24 \, \text{Å}. \]

Iron also crystallizes in the fcc structure, and a reasonable assumption is that the radius of the atom does not change. In the cubic close-packed arrangement each atom has twelve nearest neighbors, and examination of either Fig. 20-4 or Fig. 20-14 shows that for a face-centered atom four of these neighbors consist of the atoms at the corners of the face. The face diagonal now contains two atomic diameters, or \( r_{Fe} = \frac{1}{4} \sqrt{2} a \). On setting \( r_{Fe} = 1.24 \, \text{Å} \), we obtain \( a = 3.50 \, \text{Å} \) for the fcc structure. The unit cell has eight corner and six face atoms, or a net of four atoms, so the density of fcc iron should be

\[ \rho = \frac{4(55.85)}{6.02 \times 10^{23}(3.50 \times 10^{-8})^3} = 8.66 \, \text{g cm}^{-3}. \]

As a second illustration, the density of NaCl is 2.165 g cm\(^{-3}\). There are four Na\(^+\) and four Cl\(^-\) ions per unit cell, so we have

\[ 2.165 = \frac{4(22.99) + 4(35.45)}{6.02 \times 10^{23}a^3}, \]

whence \( a = 5.64 \, \text{Å} \). Reference to Fig. 20-15 shows that the closest distance between ions is that along a cube edge, so that \( a = 2r_{Na^+} + 2r_{Cl^-}. \) The sum of the two ionic radii is then \( a/2 = 2.82 \, \text{Å} \). As discussed in the Special Topics section, only sums of ionic radii may be determined from a crystal structure, but there are various schemes whereby individual ionic radii can be assigned.

Another important type of calculation is that of the interplanar distances in a crystal. In the case of a two-dimensional, square lattice, illustrated in Fig. 20-23, it is obvious that (10) and (01) planes are spaced just \( a \) units apart, or that \( d_{10} = d_{01} = a \), and likewise that \( d_{11} = \frac{1}{2} \sqrt{2} a = 0.707a \). The direction perpendi-
cicular to (12) planes is evidently that of the diagonal of a rectangle of sides 1 and 2 in the \( \chi \) and \( \psi \) directions, respectively. The particular diagonal shown is of length \( \sqrt{3} a \) and spans five interplanar distances, so \( d_{12} = (1/\sqrt{3})a \). The general formula is \( d_{hk} = a/(h^2 + k^2)^{1/2} \). Extension to a three-dimensional cubic lattice gives

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

(20-3)

or, for a lattice with \( \alpha = \beta = \gamma = 90^\circ \) but with \( a \neq b \neq c \)

\[
\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}.
\]

(20-4)

Equation (20-3) gives the interplanar distance for planes of specified Miller indices, but it is sometimes convenient to class as belonging to a given type all planes which are parallel to each other, regardless of actual Miller index. Thus (100) and (200) planes may be called (100)-type planes, (111) and (222) planes may...
be called (111)-type planes, and so on. The distinction is illustrated further as follows. The largest interplanar distances for a simple cubic crystal are, in order, \( d_{100}, d_{110}, \) and \( d_{111}, \) and their ratios are given by Eq. (20-3) as

\[
\text{simple cubic: } d_{100} : d_{110} : d_{111} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}.
\]

The largest interplanar distances for a bcc lattice are, again in order, \( d_{110}, d_{200}, \) and \( d_{222} \) (see Fig. 20-24):

\[
\text{bcc: } d_{110} : d_{200} : d_{222} = \frac{1}{\sqrt{2}} : \frac{1}{2} : \frac{1}{2\sqrt{3}}.
\]

These latter two planes may be referred to as (100)- and (111)-type planes, however, and the ratios reported as

\[
\text{bcc (type planes): } d_{100} : d_{110} : d_{111} = \frac{1}{2} : \frac{1}{\sqrt{2}} : \frac{1}{2\sqrt{3}} = 1 : \frac{2}{\sqrt{2}} : \frac{1}{\sqrt{3}}.
\]

Similarly,

\[
\text{fcc (type planes): } d_{100} : d_{110} : d_{111} = 1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}}
\]

(the demonstration is left to the reader). As will be seen in the next section, x-ray diffraction studies may in some cases yield an interplanar spacing where the type but not the actual Miller index of the planes is known.

A final point of geometry is the following. In the case of simple structures it will often be true that a set of planes contains all of the atoms or ions of the crystal. Thus if a metal crystallizes in the bcc structure, the (200) planes as a set pass through or contain all of the atoms of the crystal. The same is true for the sets of (110) and (222) planes. The crystal can thus be viewed as consisting of layers of (200) planes having a surface concentration \( \sigma_{200} \) atoms cm\(^{-2}\) and separated by \( d_{200} \) cm. The quotient \( \sigma_{200}/d_{200} \) must therefore equal the volume concentration of atoms in the crystal, \( C \) atoms cm\(^{-3}\). The crystal can alternatively be regarded as consisting of layers of (110) planes separated by \( d_{110} \), so that \( \sigma_{110}/d_{110} = C \). Thus for any set of planes which contains all the atoms of the crystal, it follows that

\[
\frac{\sigma_{111}}{d_{111}} = C.
\]

Equation (20-5) is often quite useful. It tells us that the highest surface density of atoms will occur on that set of planes of largest interplanar spacing. These are the (110) planes in the bcc structure and the (111) planes in the fcc case, for example. Such planes tend to have the lowest surface free energy and therefore tend to be prominent faces in actual crystals. They also tend to slip or to cleave the most easily, as is noted in Section 20-3A.

### 20-5 Diffraction by Crystals

X rays were first observed in experiments around 1890 with cathode ray tubes (see Section 22-1); by 1895 J. J. Thomson was describing the effect of this penetrating radiation on the electrical properties of gases. Later, in 1898, G. G. Stokes and G. J. Stoney suggested that x rays were electromagnetic in nature and the classic first experiment establishing x-ray diffraction was done in Munich in 1912 at the suggestion of M. von Laue.
X rays are produced by atoms which have lost a $K$ or $L$ electron as a result of a collision with some high-energy particle. Referring to Eq. (16-19), if a $K$, or $n = 1$, electron is lost from, say, a copper atom ($Z = 29$) and an $L$, or $n = 2$, electron falls into the vacancy, the energy of the emitted radiation is $0.5(29)^2 \left(\frac{1}{1^2} - \frac{1}{2^2}\right) = 315 \text{ a.u. or } 8584 \text{ eV}$ of energy. The wavenumber of radiation of this energy per quantum is

$$
(8584)(8.066) = 6.92 \times 10^4 \text{ kK} = 6.92 \times 10^7 \text{ cm}^{-1},
$$
corresponding to 1.44 Å. X-ray wavelengths are thus comparable to atomic radii.

Modern equipment still consists essentially of a Crookes tube, in which a beam of perhaps 20-kV electrons impinges on a target, usually copper, iron, or tungsten. The emitted x-ray radiation is generally filtered (see Section 22-4 on the critical absorption of x rays) and then collimated by means of slits so as to produce a narrow, monochromatic beam.

Before discussing three-dimensional diffraction effects it should be explained why it is that x rays act as though they are reflected specularly from each plane of a crystal. The interaction of an x-ray quantum with an atom may be regarded as an absorption followed by resonance emission (Section 19-3), that is, by emission at the same wavelength. This process is a virtual one; it constitutes a hypothetical mechanism yielding the same result as does the wave mechanical treatment of scattering. The effect is that each atom becomes a secondary, isotropic emitter of the x radiation, as illustrated in Fig. 20-25 for a single line of atoms.

A more detailed analysis is as follows. We suppose there to be incident radiation at angle $\theta$ to the line of atoms ABC. The radiation first hits atom A, which then emits isotropically, and by the time the wavefront reaches atom B the secondary radiation from atom A has a wavefront given by circle 1A. When the radiation reaches atom C the wavefronts of secondary radiation for atoms A and B are now given by circles 2A and 2B. Still later the reemitted radiation has reached circles 3A, 3B, and 3C. Where similarly numbered circles cross, the emitted radiation is in phase, as for example, at point a, the crossing between circles 2A and 2B, and

**FIG. 20-25.** Scattering of x rays from a single line of atoms.
point \( b \), the crossing between circles \( 3A \) and \( 3B \). As the circles move outward with time, the line along which the radiation is in phase is that given by the line \( ab \). Alternatively, points \( b \) and \( c \) represent concurrent in-phase conditions and define the wavefront of the secondary radiation. Either reasoning leads to the conclusion that the direction of the secondary radiation is at the same angle \( \theta \) to \( ABC \) as is the incident radiation, independent of the spacing between atoms, provided it is uniform.

This analysis is geometric and qualitative but serves to explain the rigorous result that the secondary radiation is mutually interfering except in the direction of specular reflection. We may now proceed to the three-dimensional situation.

A. **The Bragg Equation**

The first diffraction experiment was made with the use of “white” \( \chi \) radiation, that is, radiation having a range of wavelengths, and a single crystal (of copper sulfate). Later, around 1912, W. Bragg and his son developed an approach which was, at that time, much easier to apply and to interpret. This consisted in using monochromatic \( \chi \) radiation and varying the orientation of the crystal.

The situation is illustrated in Fig. 20-26. We take each ray of incident radiation to be specularly “reflected” by a given layer of atoms, shown end-on in the figure. Reflections then occur from the successive layers, and we now ask what condition must be met for the reflected radiation to be in phase. Considering just the first two layers, the difference in path length for the respective rays is the distance \( abc \). From the construction, this distance is \( 2ab \) or \( 2d \sin \theta \). Thus \( 2d \sin \theta \) must be an integral number of wavelengths if the reflected radiation is to be in phase. The Bragg condition is thus

\[
n\lambda = 2d \sin \theta,
\]

where \( n \) is an integer. If \( n = 1 \), the reflection is called first order, if \( n = 2 \), second order, and so on. Note, however, that a second-order reflection for a given spacing \( d \) is at the same angle as a first-order reflection from planes of spacing \( d/2 \). Thus second-order reflections from (100) planes of a simple cubic crystal should be indistinguishable from first-order reflections from a hypothetical set of (200) planes. It is more convenient to treat the order of a reflection in this alternative way and

![FIG. 20-26. The Bragg scattering condition.](image-url)
to write Eq. (20-6) as simply
\[ \lambda = 2d_{hkl} \sin \theta. \]  
(20-7)

For cubic crystals combination with Eq. (20-3) gives
\[ \sin^2 \theta = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2). \]  
(20-8)

**B. Bragg Diffraction Patterns**

Figure 20-27 shows schematic plots of reflected intensity \( I \) versus \( \theta \) for KCl and NaCl. A single crystal is oriented so that (100)-, (110)-, or (111)-type planes (or crystal faces) are perpendicular to the x-ray beam and the crystal is then rotated so that the angle of incidence \( \theta \) is varied. As the angles for successive Bragg conditions are met, an increase in intensity of scattered radiation is observed by means of a detector whose angular position is also rotated so that it always "sees" radiation at the specular angle. The schematic arrangement is shown in Fig. 20-28.

In the case of NaCl the first-order peaks are found in a particular experiment to occur at 5°18', 7°31', and 4°36' for reflections from (100)-, (110)-, and (111)-type planes, respectively. The interplanar distances are then in the ratio of the reciprocals of the \( \sin \theta \) values, or \( d_{100} : d_{110} : d_{111} = 1/0.0924 : 1/0.1307 : 1/0.0801 = 1.0707 : 1.154 = 1:1/\sqrt{2} : 2/\sqrt{3} \). This is just the ratio predicted in the preceding section for a fcc structure. The early experimentalists knew from the symmetry of

![Intensity versus θ for Bragg scattering from (100)-, (110)-, and (111)-type planes of (a) NaCl and (b) KCl.](image)
NaCl crystals that they were in the cubic system and from the ratio test could determine which type. By reversing the density calculation of the preceding section, \( a \) could be calculated, and from this the wavelength of the x rays used.

Most other alkali halide crystals show an analogous set of intensity patterns but, as illustrated in Fig. 20-27(b), that for KCl gives \( \sin \theta \) values of 0.0811, 0.1145, and 0.1405 for reflections from (100)-, (110)-, and (111)-type planes, respectively, using the same x rays. This yields a set of ratios \( d_{100} : d_{110} : d_{111} = 1 : 0.707 : 0.577 = 1 : 1/\sqrt{2} : 1/\sqrt{3} \), or that corresponding to a simple cubic structure. Referring to Fig. 20-15, the explanation lies in the nature of the (111)-type planes. In the case of NaCl the \( \text{Na}^+ \) ions are contained by one set of (111) actual planes and the \( \text{Cl}^- \) ions, by a second set lying midway between. The reflections from the (111) actual planes are partially but not completely canceled by the out-of-phase reflections from the planes containing the other kind of ion. Thus in Fig. 20-27 the first peak for (111)-type planes for NaCl is weaker than usual. In the case of KCl the two ions are isoelectronic and scatter x rays about equally; the effect is that \( \text{K}^+ \) and \( \text{Cl}^- \) ions appear to be identical in the diffraction experiment. Reflections from the \( \text{Cl}^- \) (111)-type planes therefore cancel those from the \( \text{K}^+ \) (111)-type planes. The result is that the largest interplanar distance showing a net diffraction intensity is that for (222) actual planes. Alternatively expressed, x rays do not distinguish \( \text{K}^+ \) from \( \text{Cl}^- \) and KCl appears as a simple cubic lattice of side \( a/2 \), where \( a \) is the side of the actual fcc unit cell.

The example is introduced to illustrate the point that the intensity of Bragg reflections from a given \((hkl)\) set of planes depends on the densities and nature of atoms on these and on intervening planes as well. A more formal approach is given in Section 20-ST-2.

**C. Powder Patterns**

The Bragg method is not only historic but is also of current usefulness. The application is mainly to a crystalline powder. The individual particles are assumed to be in random orientation, so that the monochromatic x rays will always find some particle with the correct orientation for reflection from each \((hkl)\) set of planes. The experiment consists in irradiating a thin tube filled with the powdered sample, using a collimated beam of monochromatic x rays. Those crystals whose
particular \((hkl)\) planes are at the Bragg angle \(\theta\) to the beam then give a reflection at an angle \(\theta\) to the crystal planes, or \(2\theta\) to the incident beam. As illustrated in Fig. 20-29, one may use a circular strip of photographic film to intercept the diffracted radiation, which then shows as curved lines on the film. Alternatively, a traveling radiation counter may be used. The \(\sin \theta\) value for each line is calculated from the apparatus geometry.

The next task is to assign \((hkl)\) values to the lines. This can be done if the crystal is known to be in the cubic, tetragonal, or orthorhombic class but is otherwise rather difficult. Often the "powder pattern" is used much as are infrared absorption spectra, namely as a kind of fingerprinting of the particular substance. A mixture of materials may then be analyzed semiquantitatively by calculating in what proportion pure substance powder patterns are present.

The procedure for assigning actual \((hkl)\) values to individual lines can be illu-

### Table 20-2. Indices of Cubic Crystals

<table>
<thead>
<tr>
<th>Indices ((hkl))</th>
<th>(h^2 + k^2 + l^2)</th>
<th>Allowed reflection</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Simple cubic</td>
<td>bcc</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>×</td>
</tr>
<tr>
<td>110</td>
<td>2</td>
<td>×</td>
</tr>
<tr>
<td>111</td>
<td>3</td>
<td>×</td>
</tr>
<tr>
<td>200</td>
<td>4</td>
<td>×</td>
</tr>
<tr>
<td>210</td>
<td>5</td>
<td>×</td>
</tr>
<tr>
<td>211</td>
<td>6</td>
<td>×</td>
</tr>
<tr>
<td>220</td>
<td>8</td>
<td>×</td>
</tr>
<tr>
<td>300, 221</td>
<td>9</td>
<td>×</td>
</tr>
<tr>
<td>310</td>
<td>10</td>
<td>×</td>
</tr>
<tr>
<td>311</td>
<td>11</td>
<td>×</td>
</tr>
<tr>
<td>222</td>
<td>12</td>
<td>×</td>
</tr>
<tr>
<td>320</td>
<td>13</td>
<td>×</td>
</tr>
<tr>
<td>321</td>
<td>14</td>
<td>×</td>
</tr>
<tr>
<td>400</td>
<td>16</td>
<td>×</td>
</tr>
</tbody>
</table>

*a The sum of the squares of three integers cannot have the values \((7 + 8n)^4\), where \(m\) and \(n\) are arbitrary integers.

<table>
<thead>
<tr>
<th>Observed $\sin^2 \theta$</th>
<th>Result of dividing by 0.073</th>
<th>Integers having these ratios $(hkl)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0729</td>
<td>1</td>
<td>3 (111)</td>
</tr>
<tr>
<td>0.0977</td>
<td>1.33</td>
<td>4 (200)</td>
</tr>
<tr>
<td>0.194</td>
<td>2.65</td>
<td>8 (220)</td>
</tr>
<tr>
<td>0.267</td>
<td>3.65</td>
<td>11 (311)</td>
</tr>
<tr>
<td>0.291</td>
<td>4.01</td>
<td>12 (222)</td>
</tr>
<tr>
<td>0.389</td>
<td>5.33</td>
<td>16 (400)</td>
</tr>
</tbody>
</table>

The presentation in Section 20-5 emphasized the Bragg method and powder patterns as a straightforward yet actively useful approach to x-ray diffraction. It is not, however, the method used for crystal structure determination where any degree of complexity exists. The difficulty with the Bragg method is that of indexing fairly easily if the crystal is in the cubic system. From Eq. (20-8) the $\sin^2 \theta$ values are proportional to $h^2 + k^2 + l^2$. The first step is to tabulate the film data in order of increasing $\sin^2 \theta$. Since $h^2 + k^2 + l^2$ must be an integer, we then look for the smallest set of integers that are in the ratios of the $\sin^2 \theta$ values. Only certain integral values for $h^2 + k^2 + l^2$ are possible for each type of cubic crystal. In the case of a simple cubic crystal, the sum cannot have the values 7, 15, or 23, for example, since there are no three integers the sum of the squares of which equals one of these numbers. The sum can only have the values 2, 4, 6, 8,... for a bcc crystal and only the values 3, 4, 8, 11, 12,... for a fcc one, as summarized in Table 20-2. We can then determine which set the observed series of $\sin^2 \theta$ values matches.

An example should be helpful at this point. We suppose that a particular sample of finely divided lead shows the following $\sin^2 \theta$ values with x rays of 1.54 Å: 0.0729, 0.0972, 0.194, 0.267, 0.292, and 0.389. The procedure is shown in Table 20-3. We first divide each number by 0.0729 and observe that the result is not a set of integers. Examination indicates that multiplying each number by three will yield integers, as shown in the third column. These integers are just those allowed by Table 20-2 for a fcc structure, and we then index each entry accordingly. In an actual experiment each $\sin^2 \theta$ value would now be divided by the assigned $h^2 + k^2 + l^2$ value to obtain a series of values of $\lambda^2/4a^2$, which would be averaged. In the present example we take this average to be $0.0729/3 = 0.0243$, and from the known $\lambda$ of 1.54 Å calculate $a$ to be 4.94 Å. We could proceed to check the result by calculating the density of lead.

COMMENTARY AND NOTES

20-CN-1 Modern Crystal Structure Determination

The presentation in Section 20-5 emphasized the Bragg method and powder patterns as a straightforward yet actively useful approach to x-ray diffraction. It is not, however, the method used for crystal structure determination where any degree of complexity exists. The difficulty with the Bragg method is that of indexing...
the diffraction lines (such as shown in Fig. 20-29). If the crystal unit cell contains many atoms and especially if it is not cubic, it can be virtually impossible to find a unique set of assignments. Alternative methods are available which avoid the loss of information in the powder method which occurs through not knowing the orientation of the crystals that give a particular reflection. These methods are described briefly below.

Once a set of reflections has been indexed and their intensities measured, the next problem is that of deducing the crystal structure. The lattice type or symmetry can often be determined from an examination of a crystal under a polarizing microscope. The symmetry of the crystal habit helps to establish the Bravais lattice involved; the behavior under polarizing light may suffice to limit the space group to at least a few possibilities. The presence or absence of certain reflections is usually sufficient to complete the assignment.

A. Rotation-Oscillation Methods

One gains enormously in ability to index diffractions by using monochromatic x radiation and a single crystal which can be mounted so that one of its crystal axes is perpendicular to the x-ray beam. In the rotating crystal method, as the crystal turns various planes come into the Bragg angle with respect to the incident beam. The diffraction consists of spots generated in a series of horizontal layers on the film, as illustrated in Fig. 20-30. Those reflections at the same level as the crystal arise from planes parallel to the rotation axis, and those reflections above and below arise from planes whose inclination to the axis can be calculated. Thus each spot can immediately be assigned one index. The remaining indexing can still be very difficult if the crystal has many atoms in the unit cell, and a yet better procedure is available.

The next step is to displace the film synchronously with what is usually an oscillation rather than a continuous rotation of the crystal. In this way the orientation of the crystal is known for each diffraction spot. The Weissenberg method, as it is called, thus allows each spot to be fully indexed. The method produces series of diffraction spots which lie on curved lines, however, and in the precession

![FIG. 20-30. Rotating crystal method.](image-url)
method, the motions of the crystal and the film are so regulated that the spots lie on straight lines.

B. Electron Density Projections

A crystal appears to x rays as a collection of scattering centers, each of intensity approximately proportional to the number of electrons possessed by a particular atom in the unit cell. The information provided by x-ray diffraction is therefore that of the distribution of electron density \( \rho(x, y, z) \) in the crystal. Since this distribution is a periodic one, it is very convenient to represent it as a set of cosine and sine terms—that is, as a Fourier series.

The formal expansion of \( \rho(x, y, z) \) is

\[
\rho(x, y, z) = \frac{1}{V} \sum_{h} \sum_{k} \sum_{l} F_{hkl} \exp\left[-2\pi i \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right) \right],
\]

where \( V \) is the volume of the unit cell and \( F_{hkl} \) is called the structure factor (see Section 20-ST-3). This form recognizes that the electron density is periodic with repeat distances of \( a, b, \) and \( c \). If one could evaluate each term from the diffraction data, the resulting \( \rho(x, y, z) \) would be the crystal structure. The problem is that the intensity measurements yield \( |F_{hkl}|^2 \) but not the sign of \( F_{hkl} \) itself.

A number of rather sophisticated procedures have been developed to help get around the problem. It is possible, for example, to determine the distribution of interatomic distances from the indexed intensity data alone. With this information and some educated guesses the crystallographer may be able to arrive at a trial structure. Even if approximate, such a structure will allow a calculation of the sign of each \( F_{hkl} \), and now the experimental intensity data can be used to calculate an actual \( \rho(x, y, z) \). The result usually appears as electron density contour maps calculated for one or another projection. Such a result for anthracene is shown in Fig. 20-31.

Another “trick” is to incorporate very heavy atoms (such as iodine) in the molecule. The intense scattering by such atoms dominates the diffraction pattern and it may be possible to determine the positions of the heavy atoms and thus the sign of their \( F \) factor. Sometimes a natural grouping, such as a benzene ring, can be recognized in the diffraction pattern and subtracted from it.

C. Use of Radiation Other than X Rays

The fundamental equations of this chapter are not restricted to any particular kind of radiation. The main restriction is that inherent in the Bragg equation, namely that since \( \sin \theta \) cannot exceed unity, \( \lambda \) must be less than \( d_{hkl}/2 \). Thus the wavelength of the radiation used must be less than half of the interplanar spacings to be determined. This means that radiation of no more than about 1 Å can be used.

In view of the de Broglie relationship (16-7), particles have a wave nature and should also exhibit diffraction effects. Thus 40,000-eV electrons would have \((4 \times 10^{4})(1.602 \times 10^{-12}) = 6.408 \times 10^{-8}\) erg kinetic energy, corresponding to a
momentum of $1.075 \times 10^{-17}$ g cm sec$^{-1}$. The wavelength is then $6.625 \times 10^{-27}/1.075 \times 10^{-17} = 0.0616$ Å. Electrons of this energy do indeed show diffraction effects and may be used for structure determinations. Electrons, being charged, interact more strongly with matter and are more rapidly absorbed than x radiation. As a consequence, very thin samples must be used. Standard electron microscopes may, for example, be put in a diffraction mode of operation so as to show the diffraction pattern for very thinly sliced samples. Because electrons can be focused by means of magnetic lenses, it is also possible to obtain a direct picture. Figure 20-32 shows a modern high-resolution electron microscope photograph of a thin flake of Nb$_{22}$O$_{54}$. In this photograph, the view is down the $b$ axis of the crystal; the white areas are channels containing octahedra of NbO$_6$ and the dark circles correspond to tetrahedrally coordinated clusters of Nb atoms.

Returning to diffraction studies, we find that it is possible to obtain molecular structures from the diffraction of a monoenergetic beam of electrons by a molecular gas. The situation here is similar to that of the powder method since each individual molecule is in random orientation, and the analysis is similar except that one now deals with distances between atoms in a molecule rather than with interplanar

distances. One finds for the intensity of the scattered beam at angle $\theta$

$$I(\theta) = \sum_i \sum_j F_i F_j \frac{\sin x_{ij}}{x_{ij}},$$

(20-10)

where $F$ is the atomic scattering factor, and $x_{ij}$ is given by

$$x_{ij} = \frac{4\pi r_{ij}}{\lambda} \sin \frac{\theta}{2}.$$

(20-11)

The distances $r_{ij}$ are those between atoms $i$ and $j$ in the molecule. Equation (20-10) is known as the Wierl equation. It is possible to transform the $I(\theta)$ results into a radial distribution function (much as in the case of Fig. 8-1) and from this one can usually infer the molecular bond lengths and angles.

Alternatively, neutron scattering may be employed. The same calculation as the preceding applies but now with $m$ equal to the neutron mass, about 2000 times larger than that of the electron. Neutrons of momentum $1.08 \times 10^{-17}$ g cm sec$^{-1}$, and hence wavelength 0.0616 Å, have 1/2000 the energy or about $3 \times 10^{-11}$ erg molecule$^{-1}$, corresponding to a “temperature” of about 1000 K. Neutrons of thermal or room-temperature energy have wavelengths, then, of around 1 Å and such neutrons may be provided by nuclear reactors (see Section 22-CN-2). A velocity selector (such as illustrated in Section 2-CN-2) may then be used to provide a monoenergetic beam. The technique is a relatively difficult one, and the chief advantage in using it is that, unlike the case with x rays, the scattering of neutrons is large for light atoms. Neutron diffraction has, for example, been used to locate protons in ice and in metal hydrides, a very difficult task with x rays.

FIG. 20-32. High-resolution electron micrograph of the Nb$_2$O$_5$4 lattice (see text). Arrows mark locations of crystal defects. (From S. Iijima, Department of Physics, Arizona State University.)
Chapter 20: The Solid State

20-CN-2 Some Structures of Biological Importance

It is, of course, beyond the scope of this text to delve into the determination of complex crystal structures, but it seems worthwhile to illustrate the extent to which modern crystallography has been developed. A number of high-molecular-weight biological materials can be obtained in crystalline form, and some extremely difficult structure analyses have been made on such crystals.

One of the great triumphs of x-ray crystallography is the determination of the structure of vitamin B\textsubscript{12} by Dorothy Hodgkin and her co-workers. The formula of this very complex molecule is shown in Fig. 20-33; it consists of two principal parts, a nucleotide and a coordination complex of Co(III). The cobalt ion is chelated to four nitrogen atoms in a square planar ring and to cyanide ion and another nitrogen atom along the axis perpendicular to the ring. The entire structure, except for the cyanide, is called cobalamin. The analysis of the many thousands of individual diffraction spots to finally obtain the three-dimensional structure of vitamin B\textsubscript{12} required the joint effort of a large international team of investigators.

A second crystallographic triumph was the determination of the structure of hemoglobin, illustrated in Fig. 20-34. This is, of course, a large protein molecule, a principal function of which is to coordinate an iron atom (shown in the figure). The iron reversibly takes up a molecule of oxygen, thus giving hemoglobin its oxygen-carrying property. More recently, a great deal of crystallographic work has been done on the structure of nucleic acids, RNA (ribonucleic acid) and DNA (deoxyribonucleic acid). We are now dealing with molecular weights up to several million, and while x-ray diffraction has confirmed the double helical structure, complete structural analyses have not so far been possible (see Section 21-6).

FIG. 20-33. Structure of vitamin \textsubscript{B}12. The cyanide attached to the Co atom is introduced during the isolation and crystallization procedure.
20-CN-3 The Band Model for Solids. Semiconductors

We have so far considered a crystal to be made up of discrete atoms in a repeating structure. The wave mechanical picture, while basically not much different, does introduce an aspect of great importance with respect to the energy levels of electrons in a crystal. The point is that while completely isolated atoms would have energy levels as described in Chapter 16, when these are brought into proximity in a crystal, electron exchange begins to be possible. Suppose, for example, we had a crystal consisting of hydrogen atoms, or, more realistically, of hydrogen-like atoms, such as lithium. Considering first just one pair of atoms, then, as given by Eqs. (18-13) and (18-14), the single equal energy states of each atom combine to give a bonding and antibonding pair. In terms of the present discussion the point is that the mixing of wave functions between two atoms generates a pair of new states, one above and one below the original isolated atom state. In a crystal some number $N$ of atoms mix their electrons wave mechanically,
and the result is $N$ states distributed in a band roughly centered at the original isolated atom state. The degree of this mixing increases as the atoms approach, and the situation is shown schematically in Fig. 20-35. In the case of a crystal of lithium the band due to the 1s states does not span enough range of energy to overlap with that from the 2s ones. The 1s band will have $N$ states and just $2N$ electrons, that is, two 1s electrons from each atom, to exactly fill it.

The 2s band is only half-filled, however, since only $N$ outer electrons are present. There are thus many close-lying excited states accessible to these electrons, with the consequence that they have a Boltzmann-type distribution of kinetic energies and can move easily from one point to another. Hence the electrical conductivity of lithium.

A metal such as beryllium would exactly fill its 2s band, but it turns out that the 2p overlaps with it, so that again the outer electrons are able to move freely. The wave mechanical picture of metallic conduction is thus one of bands only partially filled with electrons. The mobility of the electrons is adversely affected by the thermal vibrations of the lattice, which disrupt its regularity. As a consequence, metallic conductivity tends to decrease with increasing temperature.

The profile of a band, that is, the plot of $N(E)$, the number of energy states, versus energy $E$, might look as in Fig. 20-36. Metals correspond to the situation shown in Fig. 20-36(a,b), that is, to an incompletely filled band or to overlapping bands. If, however, the highest energy band is completely filled and well separated from the next one, then electrons cannot move since there are no easily accessible excited states; the substance is then an insulator. An example is diamond, which has a completely filled band well separated from the next higher one, as in Fig. 20-36(c). Finally, it may happen that while a band is filled, the next higher one is so close that little additional energy is needed to promote electrons to it, as illustrated in Fig. 20-36(d). Such a substance will show an electrical conductivity which strongly increases with temperature, as the electron population of the
upper band increases and leaves vacancies in the lower one. Such materials are called intrinsic semiconductors. Germanium has an energy gap of 0.72 eV, and gray tin one of only 0.1 eV; both behave in this manner.

It is also possible to produce electron mobility by incorporating suitable impurities in the lattice of an insulator or intrinsic semiconductor. The impurity should be able to substitute for one of the regular lattice atoms so as not to distort the lattice appreciably. Suppose, for example, a boron atom is substituted for carbon in the diamond lattice or for silicon or germanium in their crystals. The boron atoms act as C⁺, Si⁺, or Ge⁺ ions, being one electron short, and the effect is to produce holes or vacancies in the highest energy band. The energy match is not exact, and while the boron atoms act as acceptors of electrons, some promotion energy is needed. Similarly, if P atoms are introduced, these act like C⁻, Si⁻, or Ge⁻ atoms, and with a little additional energy the extra electron can be promoted into the next higher unfilled band of the crystal. The effect of either impurity is to greatly increase the semiconductor property of the crystal. Such crystals also tend to exhibit photoconductivity since light energy can also promote electrons to allow conduction.

It might be mentioned that the bands in an insulator (which do not overlap) are not uniform through the crystal but are bounded geometrically by zones called Brillouin zones the shapes of which are determined by the crystal symmetry. The situation can be viewed as a confinement of electrons due to their reflection by crystal planes. In conductors, the Brillouin zones overlap, so that free motion through the crystal is possible.

**20-CN-4 Crystal Defects**

Actual crystals do not consist of the perfect lattice array implicit in the discussion so far. First, many apparently crystalline materials are actually microcrystal-
line, that is, they consist of small crystalline domains or grains welded together at their boundaries. This is often true of metals and especially of alloys, which may really be eutectic mixtures. The presence of such domains affects the mechanical and electrical properties of the crystal. The x-ray diffraction pattern becomes essentially that for a powder, and if the domains are very small, the diffraction lines will also be diffuse.

This is a macroscopic, adventitious imperfection. There are two other types which are always present in an otherwise perfect crystal. First, atoms or ions may be missing from various individual lattice sites, as illustrated in Fig. 20-37(a) for the case of an ionic crystal. The crystal as a whole remains electrically neutral so that positive and negative ion vacancies must occur in pairs. (An excess of even $10^{-10}$ mole of one over the other would give a crystal an electrostatic charge of perhaps one million volts!) This type of imperfection is known as a Schottky defect. The second situation is that in which an extra atom or ion has found an abnormal or interstitial position, as in Fig. 20-37(b); the particular situation shown is that in which a positive ion has left its lattice site, leaving a vacancy. Such defects are called Frenkel defects.

These two types of imperfection are known as point defects. Individual atom or ion displacements are involved and there is a definite energy requirement to be met. The population of point defects in a crystal is therefore governed by the Boltzmann principle, and any crystal is expected to have some equilibrium concentration of them. The fraction of such lattice vacancies will be about $10^{-5}$ at 1000 K, corresponding to a typical energy of 20 kcal mole$^{-1}$. More detailed treatments estimate the entropy as well as the energy requirement.

A second major type of imperfection is that known as a dislocation. This is an organized concentration of point defects and is also termed a lattice defect. The presence of such defects does not represent a thermodynamic equilibrium but rather is a consequence of the history of formation of the crystal and of its subsequent mechanical experience.

One important type of lattice defect is that known as an edge dislocation, illustrated in Fig. 20-38. Here an extra lattice half-plane is present; the crystal below the slip plane $AB$ is in tension and above it the crystal is in compression. The dislocation line is the slip plane at $C$ (perpendicular to the plane of the figure). The dislocation emerges at the surface as a step or, conversely, pressure applied at the surface above $AB$ has caused a slip of one lattice unit; the surface layers are in register, but the compression has localized around the dislocation line $C$. 

**FIG. 20-37.** Point defects: (a) Schottky defects; (b) Frenkel defects.
Continued motion of $C$ to the left would result eventually in its emergence and the whole upper half of the solid would then have flowed one lattice unit. The process is much like moving a rug by pushing a crease down it.

This dislocation may be characterized by tracing a counterclockwise circuit around $C$, counting the same number of lattice points in the plus and minus directions along each axis or row. Such a circuit closes if the crystal is perfect but if a dislocation is present, it does not, as illustrated in the figure. This circuit is known as a Burgers circuit; its failure to close distinguishes a dislocation from a point defect. The ends of the circuit define a vector, the Burgers vector $b$, and the magnitude and angle of the Burgers vector are used to define the magnitude and type of dislocation.

The second major type of dislocation is the screw dislocation, illustrated in Fig. 20-39; each cube represents an atom or lattice site. The geometry of this may
be imagined by supposing that a block of rubber has been sliced part way through and one section bent up relative to the other. A screw dislocation can be produced by slip on any plane containing the dislocation line $AB$ [Fig. 20-39(b)], and the effect is that the crystal plane involved takes the form of a spiral ramp. A photomicrograph of a carborundum crystal is shown in Fig. 20-40, illustrating emergent screw dislocations on the surface of the crystal. The presence of dislocations is often made evident by an examination of the crystal surface; it may help to subject it to a mild etching.

FIG. 20-40. Screw dislocation in a carborundum crystal. [From A. R. Verma, Phil. Mag. 42, 1005 (1951).]
The density of dislocations is usually stated in terms of the number of dislocation lines intersecting unit area in the crystal; it ranges from about $10^8$ cm$^{-2}$ for "good" crystals to perhaps $10^{12}$ cm$^{-2}$ in cold-worked metals. Thus, dislocations are separated by $10^2$–$10^4$ Å; every crystal grain larger than about 100 Å will normally have dislocations; one surface atom in 1000 is apt to be near a dislocation. Note the several dislocations evident in Fig. 20-32.

Dislocations greatly reduce the mechanical strength of a crystal; a normal specimen of metal has an experimental elastic limit about 1000 times smaller than the value for the perfect crystal. Also, the presence of emergent dislocations on crystal surfaces is very important to crystal growth. A saturated melt or solution can form new crystals only with difficulty, because of the Kelvin effect (Section 8-9) whereby the surface energy of a small crystal adds to its molar free energy and hence changes its melting temperature or solubility. It is much easier for the atoms or ions to deposit on an existing crystal surface, and especially so if they can locate at a step. Crystals often grow by successive new layers starting and then sweeping across the surface. A screw dislocation is also very effective as a site for crystal growth since crystal units depositing at an emergent screw step merely rotate it. Surface screw dislocations have been observed to be turning slowly as a crystal grows, in direct confirmation of this mechanism.

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**SPECIAL TOPICS**

**20-ST-1 Symmetry Notation for Crystals**

The crystallographer deals with the same symmetry operations as were defined in Chapter 17 in connection with molecular symmetry. The nomenclature is somewhat different, however. A rotation axis is designated by the number giving its order, or relative to the Schoenflies symbols (Section 17-2), $1 = C_1$, $2 = C_2$, and so on. A rotation followed by an inversion through a center of symmetry is written $T$, $2$, and so on. The symbol $m$ denotes a plane of symmetry or mirror plane; thus $2/m$ means the symmetry elements $C_2$ and $\sigma_h$. A succession of $m$'s means mutually perpendicular planes of symmetry; $mmm$ denotes three mutually perpendicular planes.

The lattice symmetries of the seven primitive lattices are given in the last column of Table 20-1. Not all the symmetry elements are generally listed, only those sufficient to define the lattice. Thus, for a primitive cubic lattice all other symmetry elements are implied by the designation $m\overline{3}m$, which means a mirror plane, a threefold axis lying in the mirror plane, and a second mirror plane perpendicular to the first.

The 32 point groups may be generated by considering the various symmetry operations consistent with each type of lattice. For example, the monoclinic lattice has the symmetry elements $2/m$ and the possible point groups are $2$, $m$ (or $\overline{2}$), and $2/m$. The orthorhombic lattice has the symmetry $2/mm$ or $mmm$, and comprises the point groups $2m$ ($mmm2$ or $\overline{2}m$), $22$ (same as $222$), and $2/mm$. The lattice of the triclinic system has the full symmetry $\overline{1}$ but need have only the symmetry $1$. Each lattice type thus has a certain maximum possible point group symmetry, with various lesser sets of symmetry features also being consistent with it.
From the point of view of a real crystal, the basis (see Section 20-1) may be consistent with the full lattice symmetry—a simple example being the case where an atom occupies each lattice point—or may be consistent with only some of the possible symmetry features. In this second case the crystal will belong to one of the less symmetric point groups for the lattice.

A complication is that it is not sufficient to consider only point group symmetry elements. Some new symmetry operations enter which involve translation. The first is called a **screw axis**, designated by the integers \( p q \), where \( p \) is the order of the axis (1, 2, 3, 4, or 6) and \( q/p \) is the fraction of a unit cell length whereby the point is translated following the rotation. Points 1, 2, and 3 in Fig. 20-41(a) show the operation \( 3_2 \). Points 2 and 3 are obtained by two successive 120° rotations and advancements of two-thirds of the unit distance. Points 1', 1", 2', and 3' follow on carrying out unit translations.

The second principal space symmetry element is that called a **glide plane**, which combines reflection in a mirror plane and translation parallel to the plane. A glide plane is designated by \( a, b, \) or \( c \) if the translation is \( a/2, b/2, \) or \( c/2 \). An \( a \) glide operation is shown in (010) in Fig. 20-41(b). A particular combination of lattice symmetry and point group symmetry, including translational operations, is called a **space group**, and the addition of the latter operations combines the 32 point groups and the 14 Bravais lattices to yield 230 space groups.

The nomenclature for space groups cannot be pursued very far here, but we can describe one scheme briefly. The first symbol is \( P, C, F, \) or \( I \), designating the Bravais lattice type (see Table 20-1). This is followed by the point group symbol modified by the introduction of translational symmetry elements if needed. Thus \( P2_1/c \) is related to the point group \( 2/m \), and the space group is therefore in the monoclinic system. The designation indicates a primitive monoclinic lattice with a twofold screw axis and a glide plane perpendicular to it.

**FIG. 20-41.** *Illustration of (a) the screw axis operation \( 3_2 \) and (b) a glide plane operation.*
We discussed in Section 20-5B how intervening (111)-type planes of Cl\(^{-}\) ions reduce, by interference, the intensity of scattering from the planes of Na\(^{+}\) ions in NaCl, and essentially cancel the intensity for K\(^{+}\) ion planes in KCl. The analysis can be put on a more general and a more quantitative basis as follows.

We consider first a simple rectangular lattice with incident radiation such that reflections from (21) planes are in phase, as shown in Fig. 20-42(a), that is, the phase difference is \(2\pi\). Recalling Eq. (16-25), the wave may be described by the mathematical form

\[ \psi = Ae^{2\pi i q/\lambda}, \]

where, to avoid confusion, we use \(q\) to denote distance; \(A\) is the amplitude of the wave. For the set of rays shown as solid lines in Fig. 20-42, \(q = \lambda\), hence the statement that the phase difference is just \(2\pi\). Alternatively, if the point of reflection of the rays moves from (1) to (2), the phase of the reflected radiation changes by \(2\pi\).

We can prorate this change; the distance from (1) to (2) is \(a/h\), where \(h\) is the Miller index of the plane. A reflection from some intermediate plane, such as the dashed one shown, would be shifted in phase by the fraction \(x/(a/h)\) times \(2\pi\) or \(P_x = ((hx/a)2\pi\), where \(P_x\) is the \(x\) component of the phase shift. The dashed plane also lies a distance \(y\) from the origin and, similarly, \(P_y = (ky/b)2\pi\). The total phase shift is then \(P_x + P_y = 2\pi[(hx/a) + (ky/b)]\). On extension to three dimensions, the result is

\[ P_{\text{tot}} = 2\pi\left(\frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c}\right). \]

\[ (20-12) \]

**FIG. 20-42.** (a) Phase relation for scattering by a set of planes lying between (21) planes. (b) Scattering by an atom at position \((x/a, y/b)\).
This turns out to be general for any lattice of unit lengths \(a\), \(b\), and \(c\) and any plane displaced from the point of origin of the lattice by lengths \((x/a)\), \((y/b)\), and \((z/c)\).

The actual scattering is done by individual atoms of the lattice, and a unit cell having two kinds of atoms might appear as shown in Fig. 20-42(b). A plane of index \((hkl)\) or, in the two-dimensional case, \((hk)\) can then be passed through each atom, and the scattering amplitude per unit cell due to that atom is given by its atomic scattering factor \(f\). The phase shift associated with reflections from the plane is given by Eq. (20-12), and the net amplitude for all reflections from the unit cell is obtained by summing each contribution to \(\psi\) in Eq. (16-25),

\[
F_{hkl} = \sum_j f_j \ e^{2\pi i [(hx/a)+(ky/b)+(lz/c)]},
\]

The quantity \(F_{hkl}\) is called the structure factor of a crystal. The intensity of the diffracted radiation [due to that incident on \((hkl)\) planes with the proper Bragg angle] is given by \(|F_{hkl}|^2\). Thus if an x-ray diffraction pattern can be indexed as to \(hkl\) values for each reflection, the measured intensity gives \(|F_{hkl}|^2\).

We illustrate the use of Eq. (20-13) to calculate \(F_{hkl}\) as follows. Consider first the case of \(\alpha\)-Fe, which crystallizes in the bcc system. The repeating unit (which must be used) consists of iron atoms at positions \((0,0,0)\) and \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\), in units of the lattice unit distance \(a\). Substitution into Eq. (20-13) gives

\[
F_{hkl} = f_{Fe} \left\{ e^{2\pi i [(1)(0) + (0)(0) + (0)(0)]} + e^{2\pi i [(\frac{1}{2})(0) + (0)(\frac{1}{2}) + (0)(\frac{1}{2})]} + e^{2\pi i [(0)(\frac{1}{2}) + (\frac{1}{2})(0) + (\frac{1}{2})(0)]} \right\}
\]

We can now calculate \(F\) for particular planes, remembering that \(e^{i\theta} = \cos \theta + i \sin \theta\). For example, the amplitude of scattering from \((100)\) planes will be

\[
F_{100} = (f_{Fe} \cos(2\pi[(1)(0) + (0)(0) + (0)(0)]) + i \sin(2\pi[(1)(0) + (0)(0) + (0)(0)])
+ \cos(2\pi[(\frac{1}{2})(0) + (0)(\frac{1}{2}) + (0)(\frac{1}{2})])
+ i \sin(2\pi[(0)(\frac{1}{2}) + (\frac{1}{2})(0) + (\frac{1}{2})(0)])
= f_{Fe}[1 + (i)(0) + (-1) + (i)(0)] = 0.
\]

Thus the intensity of reflections from \((100)\) planes should be zero. This particular result could have been arrived at by qualitative reasoning, since in a bcc structure \((100)\) planes would contain only half of the atoms, the rest lying on a second set of planes half way in between. Reflections from this second set would be exactly out of phase with those from the first set, so intensity cancellation should be complete.

We next consider \((200)\) planes and obtain

\[
F_{200} = f_{Fe}[1 + (i)(0) + (1) + (i)(0)] = 2f_{Fe}.
\]

The amplitude is just that for the two atoms of iron in the unit cell. The amplitude for any other Miller index plane can be obtained by inserting the desired \((hkl)\) values in Eq. (20-14).

As a second example, we can use NaCl. The \(Na^+\) ions are at the positions \((0,0,0)\), \((\frac{1}{2}, 0, \frac{1}{2})\), \((\frac{1}{2}, \frac{1}{2}, 0)\), and \((0, \frac{1}{2}, \frac{1}{2})\) in the repeating unit and those of \(Cl^-\).
are at \((\frac{1}{2}, 0, 0), (0, \frac{1}{2}, 0), (0, 0, \frac{1}{2})\), and \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\). Equation (20-13) becomes

\[
F_{\text{Na}^+} = f_{\text{Na}^+} \left\{ e^{2\pi i [(h)(0)+(k)(0)+(l)(0)]} + e^{2\pi i [(h)(\frac{1}{2})+(k)(0)+(l)(0)]} + e^{2\pi i [(h)(0)+(k)(\frac{1}{2})+(l)(0)]} + e^{2\pi i [(h)(0)+(k)(0)+(l)(\frac{1}{2})]} \right\} \\
+ f_{\text{Cl}^-} \left\{ e^{2\pi i [(h)(\frac{1}{2})+(k)(0)+(l)(0)]} + e^{2\pi i [(h)(0)+(k)(\frac{1}{2})+(l)(0)]} + e^{2\pi i [(h)(0)+(k)(0)+(l)(\frac{1}{2})]} \right\} \\
+ e^{2\pi i [(h)(0)+(k)(0)+(l)(0)]} + e^{2\pi i [(h)(\frac{1}{2})+(k)(\frac{1}{2})+(l)(\frac{1}{2})]} \\
+ e^{2\pi i [(h)(\frac{1}{2})+(k)(\frac{1}{2})+(l)(\frac{1}{2})]} + e^{2\pi i [(h)(\frac{1}{2})+(k)(\frac{1}{2})+(l)(\frac{1}{2})]}. \tag{20-15}
\]

The amplitude for (111) planes becomes

\[
F_{111} = f_{\text{Na}^+}[1 + (i)(0) + (1) + (i)(0) + 1 + (i)(0)] \\
+ f_{\text{Cl}^-}[-1 + (i)(0) + (-1) + (i)(0) + (-1) + (i)(0) + (-1) + (i)(0)] \\
= 4f_{\text{Na}^+} - 4f_{\text{Cl}^-}.
\]

There will be a net intensity, but one proportional to \((f_{\text{Na}^+} - f_{\text{Cl}^-})^2\), and thus reduced in value. This is illustrated in Fig. 20-27, which shows the Bragg intensity pattern for reflections from (111)-type planes of NaCl. In the case of KCl, \(f_K\) is about equal to \(f_{\text{Cl}^-}\), hence the nearly zero intensity of first-order reflections from (111)-type planes in this case.

Returning to the NaCl case, note that \(F_{111}\) could be either positive or negative, depending on the relative values of \(f_{\text{Na}^+}\) and \(f_{\text{Cl}^-}\), but also on which set of ions is taken to be sodium. Standard tables of \(f\) values for atoms and ions allow the first point to be determined, but the sign of \(F_{111}\) is needed to establish which ions are which in the unit cell. A basic problem in crystal diffraction measurements is that intensities give only \(|F_{hkl}|^2\) values and not the signs of the structure factors. As discussed in the Commentary and Notes section, it is the latter that are needed to obtain the actual assignment of atoms in the unit cell.

It should be mentioned that the intensity of a diffraction line or spot depends not only on the \(F_{hkl}\) value for each plane but also on some essentially trivial geometric factors which have to do with the general angular dependence of diffraction. First, the intensity of scattering of electromagnetic radiation is intrinsically angle-dependent [note Eq. (10-49)]. As a consequence, the intensity will, for this reason alone, vary as \(1 + \cos^2 2\theta\). Second, if we imagine a crystal being rotated through the Bragg angle for a given reflection, the time spent in the region of this angle is a function of \(\theta\). For powders we can speak alternatively of the fraction of randomly distributed crystals which are properly oriented for a given reflection. The factor allowing for this effect is of the form \(1/((\sin^2 \theta \cos \theta))\). The general scattering intensity will fall off with increasing \(\theta\) as a result of these factors, and the Bragg reflections thus appear as peaks on a descending curve of intensity. It is after correction for these geometric effects that one obtains actual \(F_{hkl}^2\) values.

### 20-ST-3 Lattice Energies

#### A. Rare Gas Crystals

The total cohesive energy of a crystal may in principle be calculated if one has detailed knowledge of the forces of attraction and of repulsion between molecules.
In practice, the calculation has been limited almost entirely to lattices whose points are occupied by atoms or ions.

A rare gas crystal represents about the simplest possible case. The structure is fcc and the usual assumption is that the Lennard–Jones potential function

$$\epsilon(r) = -\alpha r^{-6} + \beta r^{-12} \quad [\text{Eq. (1-71)}]$$

is applicable. The first term on the right gives the attractive potential due to dispersion (Section 8-ST-1), and the second amounts to a mathematically convenient way of providing a rapidly increasing potential at small distances. In the case of a cubic lattice, the distance \(d\) from an origin to some other point is just

$$d = (x^2 + y^2 + z^2)^{1/2} \quad \text{or} \quad d = a(m_1^2 + m_2^2 + m_3^2)^{1/2}, \quad (20-16)$$

where \(a\) is the side of the unit cell and the \(m\)'s are integers. The potential energy \(\epsilon\) of an atom in the interior is obtained by summing the interaction potential over all lattice sites,

$$2\epsilon = -\alpha a^{-6} \sum_{(m_1, m_2, m_3)_{\text{even}}} \frac{1}{(m_1^2 + m_2^2 + m_3^2)^3} + \beta a^{-12} \sum_{(m_1, m_2, m_3)_{\text{even}}} \frac{1}{(m_1^2 + m_2^2 + m_3^2)^6}$$

or

$$2\epsilon = -\alpha a^{-6} A_a + \beta a^{-12} B_a. \quad (20-17)$$

The sums are restricted to even values of \((m_1 + m_2 + m_3)\) since a fcc structure corresponds to a simple cubic one in which every other site is vacant; this means, however, that \(a\) is taken to be one-half the side of the full fcc unit cell. The sums are set equal to \(2\epsilon\) to compensate for the double counting of atoms, that is, each interaction is a mutual one, only half of which should be assigned to the particular atom in question. It is apparent that \(\epsilon\) is just the energy of vaporization of an atom, that is, the energy to remove one atom entirely from the lattice, the structure then closing up to eliminate the vacancy created.

The sums \(A_a\) and \(B_a\) in Eq. (20-17) are geometric ones whose values are independent of \(a\), and the coefficients \(\alpha\) and \(\beta\) may be estimated from the nonideality of the behavior of the corresponding gas (Section 1-ST). It has been possible to make in this way fairly good calculations of energies of vaporization.

### B. Ionic Crystals

The application of the foregoing procedure to ionic crystals has been of much more interest and importance. One now usually neglects the dispersion term, considering that the Coulombic attraction between unlike ions dominates the attractive part of the potential, which may be written as

$$\epsilon(r) = \frac{z_1 z_2 e^2}{r} + \frac{b e^2}{r^n}, \quad (20-18)$$

where \(z_1\) and \(z_2\) are the charges on the ions in question and the repulsion term is
where \( A \) and \( B \) are essentially these geometric sums, \( A \) being known as the Madelung constant and \( B \) also containing the constant \( b \). Unlike the case with a rare gas crystal, it is difficult to evaluate \( b \) directly, and we therefore treat \( \alpha \) as a parameter which is at the equilibrium value when \( \frac{de}{da} = 0 \). On carrying out the differentiation, an expression for \( B \) in terms of \( A \) is found, whereby the former may be eliminated from Eq. (20-20) to give

\[
\epsilon = \frac{Ae^2}{a} + \frac{Be^2}{a^n},
\]

(20-20)

where \( A \) and \( B \) are essentially these geometric sums, \( A \) being known as the Madelung constant and \( B \) also containing the constant \( b \). Unlike the case with a rare gas crystal, it is difficult to evaluate \( b \) directly, and we therefore treat \( a \) as a parameter which is at the equilibrium value when \( \frac{de}{da} = 0 \). On carrying out the differentiation, an expression for \( B \) in terms of \( A \) is found, whereby the former may be eliminated from Eq. (20-20) to give

\[
\epsilon_0 = -\frac{Ae^2}{a_0} \left(1 - \frac{1}{n}\right),
\]

(20-21)

where \( \epsilon_0 \) and \( a_0 \) are now the equilibrium energy and distance (again \( a_0 \) is half the side of the unit cell). The lattice energy \( E_0 \) is defined as the energy released in the formation of one mole of the crystal from the gaseous ions, \( E_0 = -N_0 \epsilon_0 \).

This approach may be extended to any ionic crystal, \( A \) now being the geometric sum appropriate for the lattice type,

\[
E_0 = \frac{N_0 Ae^2 Z^2}{a_0} \left(1 - \frac{1}{n}\right),
\]

(20-22)

where \( Z \) is defined as the highest common factor of the ionic charges (one for \( \text{NaCl, Na}_2\text{O, Al}_2\text{O}_3,... \) and two for \( \text{MgO, TiO}_2,... \)). Table 20-4 gives the Madelung constants of several common minerals. The repulsion exponent \( n \) may be estimated from the compressibility of the crystal; values range from 6 to 10 for various substances. A slightly better treatment appears to result if the repulsion term is

**TABLE 20-4. Madelung Constants**

<table>
<thead>
<tr>
<th>Structure</th>
<th>Madelung constant</th>
<th>Structure</th>
<th>Madelung constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>1.7476</td>
<td>TiO₂ (rutile)</td>
<td>4.816</td>
</tr>
<tr>
<td>CsCl</td>
<td>1.7627</td>
<td>TiO₂ (anatase)</td>
<td>4.800</td>
</tr>
<tr>
<td>ZnS (zincblende)</td>
<td>1.6381</td>
<td>CdI₂</td>
<td>4.71</td>
</tr>
<tr>
<td>ZnS (wurzite)</td>
<td>1.641</td>
<td>SiO₂ (β quartz)</td>
<td>4.4394</td>
</tr>
<tr>
<td>CaF₃ (fluorite)</td>
<td>5.0388</td>
<td>Al₂O₃ (corundum)</td>
<td>25.0312</td>
</tr>
</tbody>
</table>
written as the exponential \( be^{-r/p} \), in which case the procedure yields

\[
E_0 = \frac{N_0 A e^2 Z^2}{a_0} \left(1 - \frac{r}{\rho}\right).
\]  

(20-23)

Of course, \( a_0 \) is obtainable from x-ray diffraction studies, so the lattice energies of simple crystals may be calculated absolutely. Strictly speaking, the result is for 0 K; the differential \( dG/da \) rather than \( d\epsilon/da \) is needed otherwise to give the equilibrium condition, \( G \) being the lattice free energy.

### C. The Born–Haber Cycle

Lattice energies can be related to other thermodynamic quantities by means of a cycle known as the Born–Haber cycle. The formation of a solid salt \( MX \) from the elements may be formulated in two alternative ways:

\[
\begin{align*}
MX(c) & \rightleftharpoons E_0 \quad M^+(g) + X^-(g) \\
M(c) + \frac{1}{2}X_2(g) & \rightleftharpoons S + W \quad M(g) + X(g)
\end{align*}
\]  

(20-24)

where \( I \) is the ionization potential of the gaseous metal atom, \( A \) the electron affinity of the gaseous halogen atom, \( D \) the dissociation energy of \( X_2(g) \), \( S \) the sublimation energy of the metal, and \( \Delta H_t \) the heat of formation of \( MX(c) \) from the elements. The change in energy must be independent of path, so \( \Delta H_t \) is equal to the algebraic sum of the other quantities:

\[
\Delta H_t = S + \frac{1}{2}D + I - A - E_0.
\]  

(20-25)

### Table 20-5. Thermochemical Data and Electron Affinities at 0 K \(^{\text{a,b}}\)

<table>
<thead>
<tr>
<th>Salt</th>
<th>( -\Delta H_t ) (298 K)</th>
<th>( S ) (298 K)</th>
<th>( \frac{1}{2}D ) (298 K)</th>
<th>( H_t (^{\text{c}}) )</th>
<th>( H_t (^{\text{d}}) )</th>
<th>I</th>
<th>( E_0 ) (Theory) (^{\text{a,b}})</th>
<th>( A ) (^{\text{a,b}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaF</td>
<td>136.3</td>
<td>25.9</td>
<td>18.9</td>
<td>3.0</td>
<td>1.9</td>
<td>118.4</td>
<td>218.7</td>
<td>79.7</td>
</tr>
<tr>
<td>KF</td>
<td>134.5</td>
<td>21.5</td>
<td>18.9</td>
<td>3.0</td>
<td>2.3</td>
<td>100.0</td>
<td>194.4</td>
<td>79.8</td>
</tr>
<tr>
<td>LiCl</td>
<td>96.0</td>
<td>38.4</td>
<td>28.9</td>
<td>3.0</td>
<td>1.8</td>
<td>124.4</td>
<td>202.0</td>
<td>84.5</td>
</tr>
<tr>
<td>NaCl</td>
<td>98.2</td>
<td>25.9</td>
<td>28.9</td>
<td>3.0</td>
<td>2.5</td>
<td>118.4</td>
<td>185.9</td>
<td>85.1</td>
</tr>
<tr>
<td>KCl</td>
<td>104.2</td>
<td>21.5</td>
<td>28.9</td>
<td>3.0</td>
<td>2.8</td>
<td>100.0</td>
<td>169.4</td>
<td>85.1</td>
</tr>
<tr>
<td>RbCl</td>
<td>103.4</td>
<td>19.5</td>
<td>28.9</td>
<td>3.0</td>
<td>3.0</td>
<td>96.3</td>
<td>164.0</td>
<td>84.2</td>
</tr>
<tr>
<td>CsCl</td>
<td>106.9</td>
<td>18.7</td>
<td>28.9</td>
<td>3.0</td>
<td>3.3</td>
<td>89.7</td>
<td>155.9</td>
<td>88.7</td>
</tr>
<tr>
<td>NaBr</td>
<td>86.0</td>
<td>25.9</td>
<td>26.8</td>
<td>3.0</td>
<td>2.8</td>
<td>118.4</td>
<td>176.7</td>
<td>80.2</td>
</tr>
<tr>
<td>KBr</td>
<td>93.7</td>
<td>21.5</td>
<td>26.8</td>
<td>3.0</td>
<td>3.0</td>
<td>100.0</td>
<td>162.4</td>
<td>79.6</td>
</tr>
<tr>
<td>NaI</td>
<td>68.8</td>
<td>25.9</td>
<td>25.5</td>
<td>3.0</td>
<td>3.1</td>
<td>118.4</td>
<td>165.4</td>
<td>73.3</td>
</tr>
<tr>
<td>KI</td>
<td>78.3</td>
<td>21.5</td>
<td>25.5</td>
<td>3.0</td>
<td>3.2</td>
<td>100.0</td>
<td>153.0</td>
<td>72.5</td>
</tr>
</tbody>
</table>

* Data given in kilocalories per mole.
* Enthalpy to take \( M(g) \) and \( X(g) \) from 298 K to 0 K.
* Enthalpy to take \( MX(c) \) from 298 K to 0 K.
Equation (20-25) may be used in various ways. Since the electron affinity $A$ is the least accurately known, one use of the equation is to obtain an indirect value for it. The various quantities are given in Table 20-5 for several alkali metal halides. Note that all of the quantities make an appreciable contribution to $E_0$.

## 20-ST-4 Ionic Radii

It was pointed out in Section 20-4 that nearest-neighbor atoms or ions in a crystal are regarded as being in contact; the more correct statement is that they have approached to the point of being at the potential minimum or balance between attraction and repulsion. In effect, we define the crystal size of atoms or ions on this basis. Thus in NaCl the side of the unit cell is, by definition, equal to $2r_{Na^+} + 2r_{Cl^-}$; the body diagonal in CsCl is, again by definition, equal to $2r_{Cs^+} + 2r_{Cl^-}$.

Crystal lattice dimensions thus in general give a sum of radii for a pair of oppositely charged ions and some additional information is needed if individual ionic radii are to be obtained. Since molar refraction is a measure of atomic or ionic volume (Section 3-3), one method has been to use this as a basis for dividing the internuclear distance. The currently accepted procedure, however, is one due to Pauling whereby isoelectronic ions (such as K$^+$ and Cl$^-$, or Na$^+$ and F$^-$) are taken to have radii inversely proportional to their effective nuclear charge (Section 16-3). Thus for NaF, $r_{Na^+} + r_{F^-} = 2.31$ Å and the screening constant $\sigma$ is taken from spectroscopy to be 4.5, so that the respective $Z_{eff}$ values are $11 - 4.5 = 6.5$ and $9 - 4.5 = 4.5$. We write $(C/6.5) + (C/4.5) = 2.31$, whence the constant $C = 6.14$ for ions of the neon configuration. The radius of Na$^+$ is then $6.14/6.5 = 0.95$ Å and that of F$^-$ is $6.14/4.5 = 1.36$ Å. One may proceed to estimate radii for a hypothetical ion, such as O$^-$; $Z_{eff}$ is now $8 - 4.5 = 3.5$, so $r_{O^-} = 6.14/3.5 = 1.75$ Å.

By applying these assumptions to crystallographic data for sums of radii, Pauling has calculated a number of crystal radii for ions of various charges, a selection of which is given in Table 20-6. It is to be remembered that these rules are semi-empirical, so that particular sums of radii may come close to but will not in general give the measured crystallographic sum exactly.

<table>
<thead>
<tr>
<th>TABLE 20-6. Crystal Radii$^{a,b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^+$</td>
</tr>
<tr>
<td>0.60</td>
</tr>
<tr>
<td>Na$^+$</td>
</tr>
<tr>
<td>0.95</td>
</tr>
<tr>
<td>K$^+$</td>
</tr>
<tr>
<td>1.33</td>
</tr>
<tr>
<td>Cu$^+$</td>
</tr>
<tr>
<td>0.96</td>
</tr>
</tbody>
</table>

$^a$ Data given in angstroms.

Points to notice are that in an isoelectronic series of ions the radius decreases steadily with increasing net positive charge, attributed to the increasing mutual attraction of the electrons. Conversely, ions increase in size with increasing net negative charge. The comparison between $M^{5+}$ and $M^{3-}$ for the Group V ions dramatically illustrates this charge effect. Note, too, that the radius of $O^{2-}$ is 1.40 Å as compared to 1.75 Å for $O^-$. Knowledge of the individual ionic radii helps to understand why certain MX crystals have the NaCl structure, others the ZnS one, and still others that of CsCl. Considering first the NaCl structure, the face of the unit cell appears as shown in Fig. 20-43(a), where $r_2$ is the radius of the smaller of the two ions, ordinarily that of the cation. The oppositely charged ions are in contact, but not the like charged ones. However, as $r_2$ is decreased relative to $r_1$ a point is reached, shown in Fig. 20-43(b), such that the larger, like charged ions have just come in contact. This condition is known as one of double repulsion, meaning that further approach will be resisted not only by Coulombic repulsion but also by the general strong repulsion of the electronic clouds [as given by the $1/r^n$ term in Eq. (20-18)]. One would expect the lattice energy of the crystal to decrease dramatically from this point on. The radius ratio $r_2/r_1$ for this critical condition can be calculated from the geometry of the situation. The right angle triangle shown in the figure yields the relationship $(r_1)^2 + (2r_1)^2 = (2r_1 + 2r_2)^2$, whence $r_2/r_1 = 0.41$.

The condition for double repulsion in the CsCl structure may similarly be calculated to be $r_2/r_1 = 0.73$, and that for the ZnS structure to be 0.22. The energetics of the situation is illustrated in Figure 20-44. In the absence of double repulsion the CsCl structure should have the largest lattice energy since each ion has eight nearest neighbors. However, when the radius ratio drops to 0.73, double repulsion sets in, and the CsCl structure becomes unstable relative to the NaCl one, with six nearest neighbors. This in turn yields to the ZnS structure with four nearest neighbors when $r_2/r_1$ drops below 0.22.

These radius ratio effects, as they are called, can be invoked in explanation of a number of the shifts in structure that occur in the various series of MX, MX$_2$, ... ionic lattices.

**FIG. 20-43.** (a) Face of the unit cell of the NaCl structure. (b) Condition of double repulsion—negative ion-negative ion contact just occurs.
FIG. 20-44. Qualitative variation of lattice energy with radius ratio for CsCl, NaCl, and ZnS structures.

GENERAL REFERENCES


CITED REFERENCES


EXERCISES

20-1 Explain what the Miller indices are for the planes of set III in Fig. 20-10.

Ans. (130).

20-2 Explain how many ions of each kind are present in the unit cell of (a) BN, (b) ZnS, and (c) ZnO.

Ans. (a) two of each, (b) four of each, (c) two of each.
20-3 Explain how many ions of each kind are present in the unit cell of (a) \( \text{CaF}_2 \), (b) \( \text{TiO}_2 \), and (c) diamond.

\textit{Ans.} (a) four Ca, eight F; (b) two Ti, four O; (c) eight.

20-4 The element Po has a simple cubic structure of side \( a = 3.34 \text{ Å} \). Calculate the density of Po.

\textit{Ans.} \( 9.4 \text{ g cm}^{-3} \).

20-5 The density of solid Xe is \( 2.7 \text{ g cm}^{-3} \) at \(-140°C\), the unit cell being ccp. Assuming no change in the radius of Xe, calculate the density of a bcc crystalline form.

\textit{Ans.} \( 2.48 \text{ g cm}^{-3} \).

20-6 Show that \( d_{100} : d_{110} : d_{111} = 1 : 1/\sqrt{2} : 2/\sqrt{3} \), referring to type planes of a fcc structure.

20-7 Calculate the surface density of ions of either kind in (110)-type planes of NaCl; \( a = 5.627 \text{ Å} \).

\textit{Ans.} \( 8.93 \times 10^{14} \text{ ions cm}^{-2} \).

20-8 If a fcc crystal of an element gives a diffraction peak at \( \theta = 6°30' \) for (240) planes (actual), at what angle will a peak occur for diffraction from (264) planes?

\textit{Ans.} \( 10°55' \).

20-9 Calculate the density of Pb from the data of Section 20-5C.

\textit{Ans.} \( 11.4 \text{ g cm}^{-3} \).

20-10 Extend the listing of \( h^2 + k^2 + l^2 \) values of Table 20-2 up to 35, giving for each the possible \((hkl)\) value(s).

20-11 Show that the close packing of spheres leaves 26\% void space.

20-12 Show that the diamond structure given in Fig. 20-19 does indeed lead to a \( \text{C—C—C} \) angle of \( 109°28' \).

20-13 The density of CaO is \( 3.35 \text{ g cm}^{-3} \). The oxide crystallizes in one of the cubic systems, with \( a = 4.80 \text{ Å} \). How many molecules of CaO are in the unit cell and which type of cubic system is it?

\textit{Ans.} four; NaCl type.

20-14 The element Mo crystallizes in one of the cubic systems. A diffraction experiment using \( 1.089 \text{ Å} \) x rays and a powdered sample showed reflections at \( 9°58', 14°14', 17°31', 20°18', 22°50', 25°13', 27°19' \) (and further ones at higher angles). Show which cubic system is involved and calculate the value of \( a \) (the side of the unit cell) and the density of Mo.

\textit{Ans.} bcc, \( 3.14 \text{ Å} \), \( 10.3 \text{ g cm}^{-3} \).

20-15 The element Ta crystallizes in the bcc system. If \( d_{289}(\text{actual planes}) \) is \( 0.900 \text{ Å} \) and \( 0.400-\text{Å x rays} \) are used, calculate (a) the density of Ta, and (b) the angle of incidence at which there should be the first-order Bragg reflection from (230)-type planes (careful!).

\textit{Ans.} (a) \( 17.6 \text{ g cm}^{-3} \), (b) \( 26°23' \).
20-1 The repeating unit for KIO₃ is a cube with edge \( a = 4.46 \) Å. The atoms occupy the following points: K in \((0, 0, 0)\); I in \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\); O in \((0, \frac{1}{2}, \frac{1}{2}), (\frac{1}{2}, 0, \frac{1}{2}), \text{and} (\frac{1}{2}, \frac{1}{2}, 0)\). The values give the coordinates of the center of the atom in fractions of \( a \). How many oxygen atoms are the closest neighbors of each I? Of each K? What spatial figure is formed by those oxygen atoms that surround an I atom? Find the shortest distance between I and O; between K and O.

20-2 BeS is found to be cubic from microscopic examination. A powder pattern obtained with Cu x rays (1.539 Å) gives lines at the following values of \( \sin^2 \theta \): 0.0746; 0.0992; 0.2011; 0.2767; 0.3019; 0.4030; 0.4786; 0.5027; 0.6038; 0.6789. Show which type of cubic lattice is present (index the \( \sin^2 \theta \) values; that is, assign values of \( hkl \) to each). Calculate the side of the unit cell and the number of atoms per unit cell (the density is 2.36).

20-3 The mineral spinel contains 37.9\% Al, 17.1\% Mg, and 45\% oxygen. The density is \( 3.57 \) g cm\(^{-3}\). The smallest unit (unit cell) in the crystal is a cube of edge 8.09 Å. How many atoms of each kind are in the unit cell?

20-4 Cuprous chloride (CuCl) forms an NaCl-type lattice. Its density is 4.135 g cm\(^{-3}\) and the strongest reflection of x rays was obtained from the set of (111)-type planes at an angle of 6°30'. Calculate the wavelength of the x rays.

20-5 The distance between \( \frac{1}{2}31 \) planes in tantalum is 1.335 Å. Tantalum forms a face-centered lattice. Calculate the density of tantalum.

20-6 Calculate the size of the sphere which can be accommodated in the octahedral hole of the fcc structure; cube edge = \( a \), atom radius = \( r \).

20-7 Calculate the structure factors for the (111) and (213) planes of NaCl in terms of the atomic structure or scattering coefficients. See Section 20-ST-2.

20-8 Show that the presence of one twofold axis at a lattice point of the two-dimensional oblique lattice implies all the other axes shown in Fig. 20-2(b).

20-9 List the symmetry elements of a square lattice. Indicate these in the manner of Fig. 20-2(b). (See also Section 20-ST-1.)

20-10 Explain to what point group the mosaics of Fig. 20-1 belong.

20-11 What is the highest order diffraction line of (100) that can be observed from a CsCl crystal with x radiation of 1.54 Å? (Remember that \( \sin \theta \) cannot exceed unity.)

20-12 The \( \sin^2 \theta \) values observed on a sample of MgO powder with 0.710 Å x rays are as follows: 0.02134, 0.02857, 0.05734, 0.07846, 0.08613, 0.11437, 0.13671, 0.14358, 0.17219, 0.22939, 0.25836. Show to which type of MX cubic lattice the data correspond and the side of the unit cell. The density of MgO is 3.58 g cm\(^{-3}\). [Data from Wyckoff (1931).]

20-13 Using Eq. (20-4), calculate \( d_{\text{shl}}/a \) as a function of \( c/a \) for a tetragonal lattice. Cover the range \( c/a = 2 \) to \( c/a = 0.2 \), and \( h^2 + k^2 + l^2 \) values up to 10. Plot the results as \( \log (d_{\text{shl}}/a) \) versus \( c/a \), using semilogarithmic graph paper. Graphs of this kind are useful in fitting powder diffraction data. As an example, the data of Problem 20-12 can be converted to a series of numbers proportional to the corresponding \( d \)’s. If these numbers are marked on a strip of the same semilogarithmic scale, the strip can be slid up and down along the \( c/a = 1 \) line until a match is obtained; the \( (hkl) \) values can then be assigned directly.
Spheres of 1.5 Å diameter are in a close-packed arrangement. Calculate the side of the unit cell if the arrangement is ccp and the values of a and c if it is hcp.

SPECIAL TOPICS PROBLEMS

Problems marked with an asterisk require fairly lengthy calculations.

20-1 Calculate \( F_{hkI} \) for the first four diffraction lines (of nonzero intensity) for diamond.

20-2 Calculate \( F_{hkI} \) for \( h^2 + k^2 + l^2 = 1, 2, 3, 4, 5 \) for a fcc metal whose atomic scattering factor is 11.

20-3 Explain the alternative symmetry notation for the point groups (a) \( C_{2v} \), (b) \( 2 \overline{mm} \), (c) \( 2/m, 2/m, 2/m \), (d) \( C_{4v} \).

20-4 Calculate the lattice energy for NaCl assuming \( n = 8 \).

20-5 Calculate the lattice energy for CaF\(_2\) assuming \( n = 8 \). The parameter \( a_0 \) is taken to be the Ca-F distance.

20-6 Calculate the lattice energy of AgCl from the following data. Heat of vaporization to give AgCl(g) is 54; heat of reaction \( \text{Ag}(g) + \text{Cl}(g) = \text{AgCl}(g) \) is \(-72\); electron affinity of Cl is 84; ionization energy of Ag(g) is 174 (all values in kilocalories).

20-7 Calculate the proton affinity for ammonia, that is, \( E \) for the process \( \text{NH}_3(g) + \text{H}^+(g) = \text{NH}_4^+(g) \), from the following data. Heat of vaporization of \( \text{NH}_4\text{Cl(s)} \) to \( \text{NH}_4^+(g) \) and \( \text{Cl}^-(g) \) is 153; proton affinity of \( \text{Cl}^-(g) \) is 327; heat of formation of \( \text{NH}_4\text{Cl(s)} \) from \( \text{HCl}(g) \) and \( \text{NH}_3(g) \) is \(-42\) (values in kilocalories).

20-8 Show that the value of the radius ratio \( r_2/r_1 \) for onset of double repulsion in CsCl is 0.73.

20-9 Estimate from the data of Table 20-6 the screening constant that is used in proportioning ionic radii between ions isoelectronic with argon.

20-10 ScN crystallizes in the NaCl structure. Calculate the side of the unit cell and the expected density.

20-11* Evaluate the sums \( A_a \) and \( B_a \) of Eq. (20-17) using a sufficient number of terms to be reasonably assured of convergence. Using estimated values of \( a \) and \( b \) (note Section 1-ST-1), calculate the heat of vaporization of argon.

20-12* Calculate the relative intensities for the NaCl reflections \( h^2 + k^2 + l^2 = 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 \). Include angular dependence factors of Section 20-ST-2; assume x rays of 1.54 Å and that the atomic scattering factors are 4 and 8 for Na\(^+\) and Cl\(^-\), respectively.