Interstices: chúng ta sẽ dịch là "hốc trống"

Interstices in Crystals

It has been shown that the particles are closely packed in the crystals even then there is some empty space left in between the spheres. This is known as **interstices** (or interstitial site of holes or empty space or voids).

Theo yêu cầu của khách hàng, trong một năm qua, chúng tôi đã dịch qua 16 môn học, 34 cuốn sách, 43 bài báo, 5 sổ tay (chưa tính các tài liệu từ năm 2010 trở về trước) Xem ở đây

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3.6   Other Inorganic Compounds

As we have seen in the descriptions of simple crystal structures in Sections 3.2-3.5, the concept of the packing of spheres into arrangements that are close-packed is of great practical use. It is also useful for circumstances where there are departures from the most close-packed ideal arrangement shown by c.c.p. crystal structures or h.c.p. crystal structures where $c/a = -N/8/3$, so that a 'close-packed' arrangement of one type of atom or ion (not necessarily in contact) occurs, with the interstices filled or partly filled with smaller atoms (or ions). Simple examples of such structures have already been considered in Section 3.5. In this section we consider other examples where the chemistry is less simple, or where the packing departs significantly from the ideal close-packed arrangement.

3.6.1 Perovskite (Pm3m)

This primitive cubic crystal structure is a very common structure of crystals of compounds of the type MM'X3. It is named after the mineral perovskite, CaTiO3, which has this crystal structure above 900 °C; at room temperature, CaTiO3 has an orthorhombic crystal structure belonging to the space group Pnma (see Section 2.15). In this crystal structure, the calcium (M) and oxygen (X) ions taken together form a c.c.p. arrangement with the titanium (M) ions in the octahedral voids (Figure 3.22). The coordination number of Ca is 12, that of
Ca O OO Ti
Figure 3.22 The crystal structure of

3.6 Các hợp chất vô cơ khác

Như chúng ta đã thấy trong phần mô tả về các cấu trúc tinh thể đơn giản ở Mục 3.2-3.5, khái niệm xếp các hình cầu vào một kết cấu được gọi là xếp chặt, là một khác niệm có ý nghĩa thực tiễn cao. Nó cũng áp dụng được trong các trường hợp có sự lệch so với cấu trúc xếp chặt lý tưởng nhất chẳng hạn như cấu trúc tinh thể c.c.p hoặc cấu trúc h.c.p trong đó $c/a = -N/8/3$, vì thế cấu trúc "xếp chặt" của một loại nguyên tử hoặc ion xuất hiện (không nhất thiết phải tiếp xúc), với các hốc trống được lấp đầy hoặc lấp đầy một phần bằng các nguyên tử nhỏ (hoặc các ion). Các ví dụ đơn giản về những cấu trúc như thế đã được xét trong Phần 3.5. Trong phần này, chúng ta xét các ví dụ khác trong đó bản chất hóa học phức tạp hơn, hoặc trong đó sự xếp chặt lệch rất nhiều so với cấu trúc xếp chặt lý tưởng.

3.6.1 perovskite (Pm3m)

perovskite, Pm3m

Ti is 6 and that of O is 2. The atomic coordinates in the primitive unit cell are Ti (2,2,1), Ca (0, 0, 0) and O (,2,0), (,2,2), (2, 0,2). The description of the perovskite crystal structure in terms of the packing of titanium octahedra will be deferred to Section 4.4.

There are many slightly distorted forms of the perovskite structure that are important in solid-state devices. At room temperature, barium titanate, BaTiO3 (P4mm), has a crystal structure that is a tetragonally distorted form of the Pm3m high-temperature structure. At lower temperatures, further distortions convert this into an orthorhombic crystal structure (Amm2) and a rhombohedral crystal structure (R3m) [10]. Pb(Zr1-xTix)O3, in which the Zr and Ti ions both occupy the M position, has two different rhombohedral (R3m and R3c) crystal structures [11] and a tetragonal (P4mm) form at room temperature, dependent on the value of x. The high-temperature superconducting oxide YBa2Cu3O7-s, where 8 is a small fraction << 1 indicating an oxygen deficiency, has a variety of crystal structures all based on a three-layered distorted perovskite structure [12]. Thus, for example, the super¬conducting phase for values of x of the order of 0.1 or less has an orthorhombic Pmmm crystal structure. The sheets of Cu and O atoms parallel to (001) in this structure are critical to the superconducting behaviour of this oxide.

3.6.2 a-Al2O3 (R3c), FeTiO3 (R3) and LiNbO3 (R3c)

Sapphire (a-Al2O3 or corundum) possesses a large unit cell with the oxygen ions in an h.c.p. arrangement. Aluminium ions occupy the octahedral interstices. Since the formula is Al2O3, only two-thirds of these are filled, as shown in Figure 3.23. The structure can be easily described by locating the 'missing' aluminium ions. If all the atomic positions are projected on to (0001) of the hexagonal cell and Roman letters denote the oxygen ion positions and Greek letters the positions of missing aluminium ions, the stacking sequence is Ag Bg2 Ag3 Bg A g2 Bg3 A g1 ., where the positions g1, g2, g3 are indicated by their suffixes in Figure 3.23.

The hexagonal unit cell is then six oxygen layers high, and contains six formula units of Al2O3. At room temperature, the lattice parameters of the hexagonal cell are a = 4.759 A,

Figure 3.23 The structure of sapphire (a-Al2O3 or corundum). The large circles represent oxygen ions in two adjacent sheets. Between the sheets shown, aluminium ions lie in the octahedral interstices g2 and g3, while the positions gj are empty. In the next layer of aluminium ions, positions gj and g3 would be filled and g2 empty

c = 12.993 A and so c/a = 2.731.

If c/a were to equal $2^2 = 2.828$, the oxygen ions would be in an ideal h.c.p. arrangement (the factor of $-J3$ greater than $-\sqrt{8/3}$ arises from the 30°

rotation of the x- and y-axes of the rhombohedral unit cell relative to the x- and y-axes defining the ideal h.c.p. arrangement). The lattice translations in (0001) of the triply prim¬itive hexagonal cell are marked in Figure 3.23. The rhombohedral primitive cell contains two formula units of Al2O3 and has a = 5.128 A and a = 55.27°. If the oxygen ions were in the ideal h.c.p. arrangement, the value of a would be 53.78°.

FeTiO3 (ilmenite, R3) has the same structure as a-Al2O3 except that the Fe and Ti atoms are distributed in alternating octahedral sheets. In LiNbO3 (R3c), the Li and Nb atoms are distributed in the same octahedral sheet so that one species occupies the g2 position while the other occupies the g3 position. The crystal structure of LiNbO3 can also be described as a distorted form of the ideal perovskite structure.

3.6.3 Spinel (Fd3m), Inverse Spinel and Related Structures

The spinel structure, shown by MgAl2O4 and by other mixed oxides of di- and trivalent metals, has a unit cell containing 32 oxygen ions in almost perfect cubic close packing. Since there would be four oxygen ions per unit cell if only the oxygen ions were present, it is apparent that the edge of the unit cell for spinel is twice that which would be expected for the oxygen ions alone in cubic close packing. Eight of the 64 tetrahedral interstices in the unit cell Figure 3.24 One-eighth of the unit cell of spinel, MgAl2O4

are filled by the divalent Mg ions and 16 of the 32 octahedral interstices are filled with the trivalent Al ions. The Mg ions considered as a group of ions form a structure of the diamond type (Figure 3.24). One-eighth of the face-centred cubic unit cell is shown in this figure.

Some oxides of composition MM'2O4 show a structure called 'inverse' spinel to distin-guish it from the 'normal' spinel which we have just described. MgFe2O4 is an example of an inverse spinel. In this oxide, the oxygen ions are arranged in cubic closest packing and the same two types of interstice are involved. However, the cations are arranged differently. Ideally, of the 16 iron ions per unit cell, eight occupy the eight tetrahedral interstices. The 16 octahedral interstices are occupied by the remaining eight iron ions and by the eight magnesium ions. The Mg and Fe can occur at random amongst the occupied octahedrally coordinated sites. To emphasize the difference from a normal spinel, the formula of this inverse spinel is sometimes written Fe(MgFe)O4, or generally M(MM')O4. In fact, the structure of MgFe2O4 deviates somewhat from this ideal; the number of iron atoms in tetrahedral sites is not exactly equal to the number in octahedral sites.

Chrysoberyl, BeO.Al2O3 (Pnma), is isomorphous with the olivine (Mg1-xFex)2SiO4 group of minerals. In this case the oxygen ions are arranged in a slightly distorted h.c.p. struc-ture [13]. As for the spinels, the metal ions in chrysoberyl are distributed

amongst the tetrahedral and the octahedral sites; in the case of chrysoberyl, half of the octahedral sites are occupied by Al ions and one-eighth of the tetrahedral sites by Be.

3.6.4 Garnet (laid)

The concept of the occupation of the interstices in a structure by different types of ion is useful in describing the garnet structures. While these are perhaps best known as gem- stones, garnets are very important in many solid-state physics devices. Various garnets can be ferrimagnetic (e.g. YIG, see below) and can form excellent laser hosts (e.g. YAG).

Figure 3.25 Coordination about the oxygen ions (solid black circles) in a garnet structure showing the {C3} tetrahedral site (striped circle), the [A2] octahedral site (solid white circle) and the (D3) dodecahedral site (spotted circle)

The garnets occur naturally as the silicates of various di- and trivalent metals. The archetypal garnet mineral has a formula $3MO.M'_2O_3.3SiO_2$ or $M_3M'_2Si_3O_{12}$, where M is a divalent metal ion and M' a trivalent ion. The technologically important examples of yttrium iron garnet, $Y_3Fe_5O_{12}$ (YIG), and yttrium aluminium garnet, $Y_3Al_5O_{12}$ (YAG), do not contain silicon. The substitution is possible because in a typical natural garnet such as grossular, $3CaO.Al_2O_3.3SiO_2$, it is possible to substitute 'YAl' for 'CaSi'. Replacing all the Ca and Si in this way produces $3YAlO_3.Al_2O_3$; that

is, $Y_3Al_5O_{12}$. Because these substitutions are pos¬sible, a general formula {C3}[A2](D3)O12 is often used for garnets, where O denotes the oxygen ion or atom and C, A and D denote cations.

The space group is Ia3d and so the crystal structure clearly has a b.c.c. lattice. There are eight formula units per unit cell. There are 96 so-called h sites, which are occupied by oxygen. {C3} denotes an ion in a tetrahedral site; that is, a site surrounded by four oxygen ions. In grossular, $3CaO.Al_2O_3.3SiO_2$, these sites would be occupied by silicon. There are 24 of these sites per unit cell. [A2] represents an octahedral site, which is surrounded by six oxygen ions; there are 16 of these per unit cell. These would be occupied by alumin¬ium in grossular. (D3) denotes the so-called dodecahedral site, which is surrounded by eight oxygen ions; this would be occupied by Ca in grossular. This site is variously described as a triangular dodecahedron, hence the name, or as a distorted cube. It is illus¬trated in Figure 3.25. A triangular dodecahedron is a polyhedron with 12 faces, each of which is a triangle.

The substitution of an enormous number of cations for one another is possible within the garnet structure. For example, trivalent rare earth ions can be introduced. If strict chemical rules of valence applied then {C} sites would be occupied by four valentcations, such as silicon, [A] by trivalent ions, such as Al, rare earth, Y or Fe^{3+} ions and so on, and (D) by divalent ions, such as Ca, Mg, Fe^{2+}

or others. The ability to substitute two cations to balance

Figure 3.26 The structure of calcite (CaCO3). The primitive rhombohedral unit cell is shown in bold. This contains two formula units of CaCO3. The other cell outlined is the smallest 'cleavage rhombohedron' and contains four units of CaCO3. (After Figure 140 in [14], p. 292.)

the charges of two other cations gives rises to a whole host of possibilities for substitution. Hence, a single simple valence rule cannot be followed. Furthermore, since the substitution of large ions such as the rare earths is possible, the oxygen ions are pushed apart to accom¬modate the cations, while retaining the cubic I lattice.

3.6.5 Calcite, CaCO3 (R3c)

Many complicated structures are most easily described as distorted forms of the simpler ones. For instance, the structure of calcite (one form of CaCO3) can be derived from that of sodium chloride by identifying the sodium ions with calcium ones and the carbonate radi¬cal CO3 with Cl. If the sodium chloride structure is imagined to be compressed along a [111] body diagonal until the angle between the axes, originally 90°, becomes 101.89°, we produce the doubly primitive cell of calcite containing four formula units. Cleavage occurs parallel to {100} of this cell. The CO3 group is triangular, with the C in the centre of the triangle and the plane of the triangle normal to the direction [111] of this

rhombohedral cell. This cell is not a true unit cell - it is a subcell of a true multiply primitive rhombohe¬dral unit cell in which the repeat direction along [111] needs to be doubled.

The primitive unit cell of calcite contains just two formula units of CaCO3. It is shown in Figure 3.26, where it is compared with the cleavage rhombohedral pseudo unit cell.

Calcium ions are at (0, 0, 0) and (,1,2). The centre of the CO3 radical is at ±(u, u, u). Note that u is close to 1 in all examples of this structure; in calcite it is 0.259.

The primitive cell of calcite has a = 6.375 A and a = 46.07°; the cleavage pseudo unit cell has a = 6.424 A and a = 101.89°, while the true multiply primitive cleavage unit cell has a = 12.828 A and a = 101.89°. The hexagonal unit cell describing the calcite crystal structure has a = 4.989 A and c = 17.062 A.

3.7   Interatomic Distances

Interatomic distances can be derived from the measured lattice parameters of simple struc¬tures with the same accuracy as the parameters of the unit cell. For instance, in copper the separation of the centres of adjacent atoms is simply 1/^2 times the cell edge. Values of the interatomic distances for most metals and for some other elements deduced in this way are given in Section A7.1 of Appendix 7. They are often useful in considering 'atomic radii', if the crystal structure is viewed as being made up of spheres in contact. A

difference is found between the values of the atomic radii deduced from different crystal structures of the same element when the element shows allotropic forms. The mineralogist Victor M. Goldschmidt showed that contractions of about 3 and 12% occur when a given element alters its structure from one of coordination 12 (e.g. c.c.p.) to one of coordination 8 and 4, respectively.

In crystals of compounds, interatomic distances can again be deduced from measured lattice parameters. They are useful in considering structures of compounds in terms of hard spheres in contact. However, there is a problem in dividing up the distance between two unlike atoms or ions so as to give each its own characteristic radius. This problem can only be solved by making a theoretical estimate of the size of at least one ion. Consequently, all values of ionic radii are part experimental, part theoretical in origin. Some values of ionic radii are also given in Section A7.1 of Appendix 7.

In crystals of compounds, the state of ionization of an atom may be quite different from that in the crystal of the element, and its size will differ accordingly. The value of the ionic radius of a metal is usually less than that of the atomic radius, defined as half the distance of closest approach of atoms in the element. This is because metals form positive ions in which the electrons are drawn inwards by the excess positive charge on the nucleus. Conversely, the ionic radius of an electronegative element

is usually much greater than the atomic radius.

3.8   Solid Solutions

Many pure metals dissolve large quantities of other elements to form solid solutions. If the solute element is also metallic then the solute atom merely substitutes for the solvent atom in the crystal structure, as shown schematically in Figure 3.27 a. Such a solution is called a substitutional solid solution. Another type is the interstitial solid solution, in which the solute element resides between the atoms of the solvent (Figure 3.27b). Other elements besides the metals, and also inorganic compounds, form solid solutions, but, since the great majority of the elements are metallic and many of them have similar chemical properties, the formation of solid solutions is most important for the metals.

Solid solutions, rather than chemical compounds, are more likely to form the more simi¬lar are the chemical properties of the components. Gold dissolves silver in all proportions and NaCl dissolves KCl. Interstitial solid solutions are often formed when elements that are expected to form small atoms or ions (e.g. H, C, B, O, N) dissolve in a crystal. The two types of solution may in all cases be distinguished by density measurements and measurements of the volume of the unit cell of the solid solution. The density p of the crystal is given by:

where M is the molecular weight (in

Mg), V is the volume of the unit cell (in m3) and v is the number of formula units per unit cell. In the pure material, v is an integer. In a substitutional solid solution, v is the same integer, but M alters to the average molecular weight M given by the chemical composition of the solution. In an interstitial solution, v is again the same for the solute but the density is increased. In a binary interstitial solution (two components), the value of p is:

where nsi/ns is the ratio of the mole fraction of solute interstitial to that of solvent and Msi is the molecular weight of the solute interstitial. An example of the determination of the type of solid solution is given in Problem 3.9.

The various component atoms of a solid solution are usually randomly distributed among the sites available for them, but in some, below a certain temperature the distribution ceases to be random and what is called ordering occurs. Ordering is most easily described for a metallic solid solution. Part of the (111) plane of a disordered alloy of copper, shown as circles, contain¬ing 25 at% of gold, shown as shaded spheres, is shown in Figure 3.28a. Above a temperature of about 390 °C, the copper and gold atoms occur in any of the positions at the lattice points of a c.c.p. lattice. There is no preferred position for gold or copper. Therefore, while on average a (111) plane will have 25 at% gold and 75 at% copper, small regions of the plane chosen at random may have more, or less, than 25 at% gold. The part of the plane of the disordered form of Cu3Au chosen at

random in Figure 3.28a happens to be deficient in Au and richer in Cu.

In equilibrium below 375 °C, a (111) plane would appear as in Figure 3.28b - the gold atoms are all surrounded by copper atoms and there is a regular arrangement of both the gold and the copper atoms. Such a structure is called an ordered solid solution. It is apparent from Figure 3.28c that in the fully ordered state for Cu3Au a conventional unit cell can be chosen with the gold atoms at cube corners (0, 0, 0) and the copper atoms at the midpoints of all of the faces. This cell is the primitive unit cell of a simple cubic superlattice. In this particular case, the superlattice is known as the L12 superlattice. The space group symmetry of the crystal structure changes from Fm3m in the high-temperature disordered phase to Pm3m in the low-temperature ordered phase. In this example, the conventional unit cells of the high-temperature disordered phase and low-temperature ordered phase are identical in volume, but the primitive unit cell of the ordered phase has a volume four times that of the primitive unit cell of the disordered phase.

Order-disorder changes occur in many solid solutions. The fully ordered state is always of lower symmetry than the disordered one, and usually possesses a lattice with larger cell dimensions, which is called a superlattice.

The essential grouping in the ordered state of this alloy, Cu3Au, is one with all the gold atoms surrounded by copper atoms, as shown in Figure 3.28c. When ordering starts in a large crystal it may be 'out of step' in the various parts of the crystal. If this occurs, the ordering may be perfect within various regions of the crystal (as in Figures 3.28b and c). These regions are called domains. Where the domains are in contact, the requirement that gold atoms are surrounded by copper atoms is not met, as is shown in Figure 3.28d. The dotted line in Figure 3.28d indicates the trace in (111) of what are called antiphase domain boundaries. In three dimensions, the boundaries are walls separating neighbouring domains. Since the neighbouring atoms are not fully ordered at the domain boundaries, the bounda¬ries represent a source of extra energy in an ordered crystal. Heating a crystal for a long time near to the ordering temperature can lead to their complete removal.

The order we have just described is called long-range order because within any domain one type of lattice site is preferred for a particular atom. Many solid solutions, while not showing long-range order, do not show a truly random distribution of the atoms; unlike atoms occur more frequently as near neighbours than they would by pure chance. Such a state of affairs is called short-range order. This is very common and is shown by some ordered solutions when they are heated above their ordering temperatures.

The structures of some ordered solid solutions are illustrated in Figure 3.29. Examples of materials showing these structures are given in Table 3.5. The B2 (or L20) order- disorder change is characterized by a b.c.c. structure in the disordered state which changes to the caesium chloride structure on ordering. This occurs in CuZn. The per¬fectly ordered structure has the composition AB (Figure 3.29a). The superlattice is then simple cubic.

The D03 superlattice type with perfectly ordered composition AB3 also has a b.c.c. structure in the disordered state. This superlattice type occurs in Fe3Al. The ordered state is shown in Figure 3.29b. It is most easily described by saying that the superlattice is composed of four equal interpenetrating face-centred cubic lattices with the origins at (0, 0, 0) for lattice 1, (1,0,0 for lattice 3, (4, 4,1) for lattice 4 and (, 4,4) for lattice 2. The ordered state con¬sists of B atoms occupying the sites of lattices 2, 3 and 4 with A atoms at type 1 lattice sites.

The L12 superlattice has already been described (Figure 3.28c). The fully ordered condi¬tion requires the composition AB3, as in Cu3Au. A related superlattice type, also of ideal composition AB3, is called D019 and is typified by Mg3Cd. The disordered state is the close- packed hexagonal structure. The ordered structure (Figure 3.29c) can be described as four interpenetrating h.c.p. structures
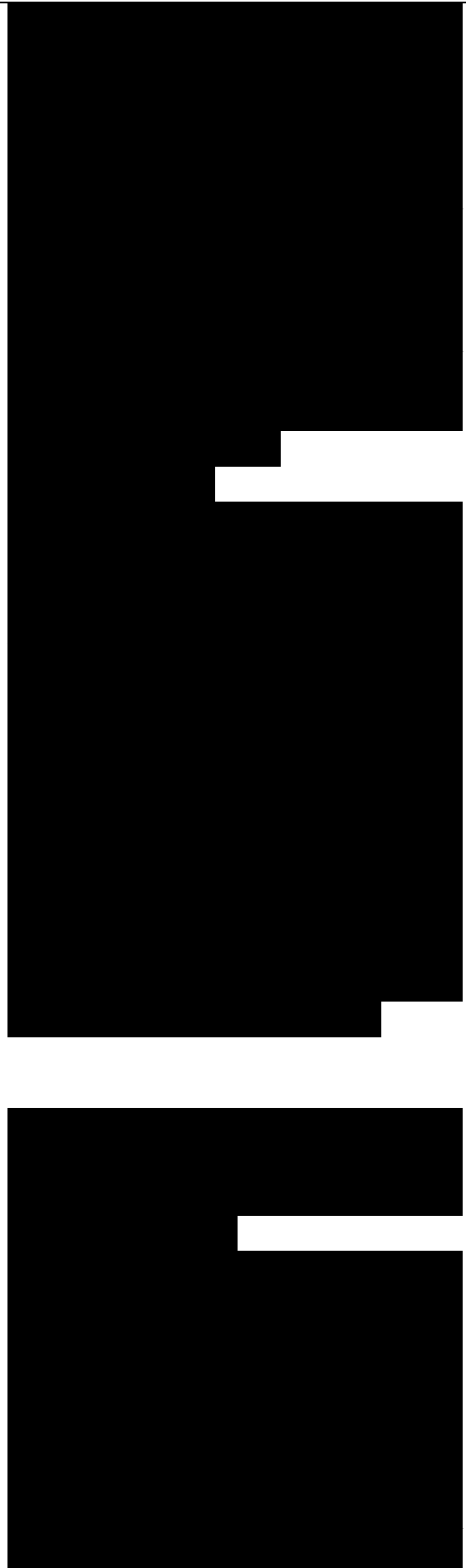
in parallel orientation, with the c-axis the same length as in the ordered alloy but the lattice parameter aos twice that of the corresponding disordered alloy. The origins of the sublattices in the ordered state are at (0, 0, 0) for sublattice 1, (,1,0) for sublattice 2, (, 0,0 for sublattice 3 and (0,1,0 for sublattice 4. B atoms occupy the sites of sublattices 2, 3 and 4 and A atoms are found at the points of sublattice 1.

3.9 Polymers

Many of the unique physical properties associated with polymers result from their ability to crystallize. In general, polymers are synthesized by the repeated addition to the growing chain of one or more small chemical units called monomers. Polymers can typically have molecular weights between several hundred and several million. The predominant bond between atoms in a polymer molecule is the covalent bond, with a dissociation energy of the order of 2 eV. The same type of strong bond is found in diamond. Many polymers have

Figure 3.29 Structures of ordered solid solutions: (a) 82, (b) D03, (c) D019 Table 3.5 Some examples of superlattice types

a The designation 82 etc. arises because in the literature the designation of structure type used in the early volumes of Strukturbericht is often followed. The term L20 is still occasionally used when referring to ternary alloys with the 82 crystal structure. (See the Suggestions for Further Reading at the end of the

chapter.)	▮▮▮▮▮