

8 THE STRUCTURES OF SOME SIMPLE COMPOUNDS

INTRODUCTION

8.01. In this chapter we shall discuss the structures of a number of simple compounds of composition A_mX_n , and also of some complex oxides and sulphides of composition $A_mB_nX_c$. We shall find among these compounds representatives of ionic, covalent and molecular structures.

AX STRUCTURES

Halides

8.02. The structures of a number of AX halides are shown in table 8.01 and are discussed in the following paragraphs.

Table 8.01. The structures of some AX halides

Caesium chloride structure (c.n. 8:8)			Sodium chloride structure (c.n. 6:6)				Zincblende or wurtzite structure (c.n. 4:4)			
—	—	—	LiF	LiCl	LiBr	LiI	—	—	—	—
—	—	—	NaF	NaCl	NaBr	NaI	—	—	—	—
—	—	—	KF	KCl	KBr	KI	—	—	—	—
RbCl*	RbBr*	RbI*	RbF	RbCl	RbBr	RbI	—	—	—	—
CsCl	CsBr	CsI	CsF	CsCl*	—	—	CuF	CuCl	CuBr	CuI
—	—	—	—	—	—	—	—	—	—	—
—	—	—	AgF	AgCl	AgBr	—	—	—	—	—
NH ₄ Cl	NH ₄ Br	NH ₄ I*	—	NH ₄ Cl*	NH ₄ Br*	NH ₄ I	NH ₄ F	—	—	—

* These structures are not found at normal temperatures and pressures.

Alkali halides

8.03. We have already considered in detail the structures of the alkali halides, all of which crystallize with either the sodium chloride or the caesium chloride arrangement (§§ 3.04 and 3.05). All of these compounds are essentially ionic, and the degree of ionic character depends on the difference in electronegativity of the atoms concerned; it is thus a maximum in caesium fluoride and a minimum in lithium iodide. As we have seen, the radius ratio r^+/r^- is the primary factor in determining whether a given halide possesses the sodium chloride or the caesium

8.03

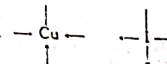
AX structures

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chloride structure. It is not, however, the only factor, for some halides (e.g. KF, RbCl and RbBr) do not have the structure to be expected on purely geometrical grounds and others exhibit at high temperatures and pressures structures different from those found under normal conditions: at high pressures RbCl, RbBr and RbI have the caesium chloride structure and at high temperatures CsCl has that of sodium chloride.

Silver and cuprous halides

8.04. The ionic radii of Cu^+ and Ag^+ (0.96 and 1.26 Å, respectively) are intermediate between those of Na^+ and K^+ , and on the basis of purely geometrical considerations all the halides of these metals would be expected to resemble the alkali halides in their structures. In fact, however, AgI and the four cuprous halides have the zincblende structure (§ 3.06), and only CuCl and AgBr have the expected sodium chloride arrangement; and of these AgCl and AgBr are insoluble in water and unstable to light. In AgI the interatomic distance is actually less than in AgBr, and in this salt, and in all the cuprous halides, the binding is primarily covalent. In cuprous iodide, for example, the four bonds from each copper and iodine atom can be represented thus:



In this way the copper atom (with electronic configuration 2, 8, 18, $4s^1$) effectively acquires seven electrons to give the krypton configuration 2, 8, 18, $4s^2$, $4p^6$, and its four bonds may be regarded as sp^3 hybrids (of one $4s$ and three $4p$ orbitals) with the normal tetrahedral configuration. In terms of the concept of formal charges the atoms must be represented as Cu^{2+} and I^{3-} .

8.05. The structure of silver iodide is of interest also in another respect. This compound is trimorphous. The γ -form, stable at room temperature, has the zincblende structure described above, but at 137°C it changes to a β -form with the closely related wurtzite structure (§ 3.07). In these two arrangements the sites occupied by the iodine atoms are disposed as in cubic and hexagonal close packing, respectively, so that the structures may be regarded as a close-packed array of iodine atoms with the silver atoms in the tetrahedral interstices. In α -AgI, stable above 146°C, a less tightly packed cubic body-centred arrangement of iodine atoms obtains, but now the silver atoms have no fixed

positions and are able to wander freely in a fluid state throughout the structure. At this temperature the electrical conductivity rises abruptly and the framework of silver atoms may be regarded as 'melting' into itself; the final breakdown of the iodine framework takes place only when the true melting point of 555 °C is reached. In its α -form silver iodide is another example of a defect structure.

Ammonium halides

8.06. In the majority of its salts the ammonium ion NH_4^+ behaves as a spherical ion of radius about 1.48 Å. This radius is very close to that of the rubidium ion, and the corresponding ammonium and rubidium salts are therefore often isostructural. Thus NH_4Cl , NH_4Br and NH_4I all have the sodium chloride structure at a sufficiently high temperature, although at lower temperatures they also exhibit the caesium chloride arrangement. Ammonium fluoride, however, crystallizes with the wurtzite structure with an $(\text{NH}_4)\text{-F}$ distance of 2.66 Å, a distance appreciably less than that to be expected on the basis of the radii of the ions ($1.48 + 1.36 = 2.84$ Å). The reason for this abnormal behaviour of ammonium fluoride is important and will be discussed later (§12.04).

The occurrence of the NH_4^+ ion in the highly symmetrical sodium chloride and caesium chloride structures is seemingly inconsistent with its tetrahedral configuration and can be explained only on the assumption that the ion effectively acquires spherical symmetry by free rotation under the influence of the energy of thermal agitation. We shall encounter many other examples of structures in which ions or molecules are in free rotation, either at all temperatures or above a certain transition temperature; all are examples of yet a further type of defect structure.

Hydrides and hydroxides

8.07. The majority of the structures of compounds containing hydrogen are so distinctive in their properties that they are best discussed as a class apart (see chapter 12). These remarks, however, do not apply to the salt-like hydrides or to the hydroxides of the more electropositive metals, many of which form typically ionic structures resembling the corresponding halides in their properties.

The hydrides AH of all the alkali metals are known; they all form stable, colourless crystals of relatively high melting point and all have the sodium chloride structure in which the hydrogen occurs as the negative ion H^- of radius 1.54 Å. This radius is intermediate between

the radii of the ions F^- and Cl^- , so that the structural resemblance between hydrides and halides is readily understandable.

In the limited number of AOH hydroxides which have as yet been studied the OH^- ion behaves as a spherical entity of radius 1.53 Å (again intermediate in size between the F^- and Cl^- ions), and some of the crystal structures are analogous to those of the corresponding halides. Thus KOH (at high temperatures) has the sodium chloride structure.

Oxides and sulphides

8.08. The oxides and sulphides of composition AO and AS show a far wider range of structural types than the AX halides. Some of these compounds are primarily ionic but in others the bonding is predominantly covalent; there are, moreover, some important differences between oxides and sulphides to which we refer later (§8.60). The structures we shall consider are summarized in table 8.02, but there are also others which we shall not discuss.

Table 8.02. The structures of some AX oxides and sulphides

Sodium chloride structure (c.n. 6:6)		Zincblende structure (c.n. 4:4)		Wurtzite structure (c.n. 4:4)	PdO and related structures (c.n. 4:4)	NiAs structure (c.n. 6:6)
—	—	BeO	BeS	—	—	—
MgO	MgS	—	—	—	—	—
CaO	CaS	—	—	—	—	—
SrO	SrS	—	—	—	—	—
BaO	BaS	—	—	—	—	—
VO	—	—	—	—	—	—
MnO	MnS	—	—	MnS	—	VS
FeO	—	—	—	—	—	FeS
CoO	—	—	—	—	—	CoS
NiO	—	—	—	—	—	NiS
—	—	—	—	—	PdO	PdS
—	—	—	—	—	PtO	PtS
—	—	—	—	—	CuO	—
—	—	—	ZnS	ZnO	—	—
—	—	—	CdS	CdS	—	—
—	—	—	HgS	—	—	—
—	PbS	—	—	—	—	—

Oxides

8.09. The oxides of all the alkaline earth metals except beryllium, and also of some of the transition metals, have the typically ionic sodium chloride structure, an arrangement consistent with the radius ratio of

the ions concerned and with the large differences between their electro-negativities. Beryllium oxide, BeO, has the zincblende structure. This, too, is consistent with the picture of ionic bonding, on account of the very small radius of the Be^{2+} ion, but it is, nevertheless, probable that in this structure the bonds have an appreciable degree of covalent character. If, however, they are treated as purely ionic, BeO is one of the few examples of an ionic AX compound in which the radius ratio is sufficiently small to give the 4:4 co-ordinated zincblende structure.

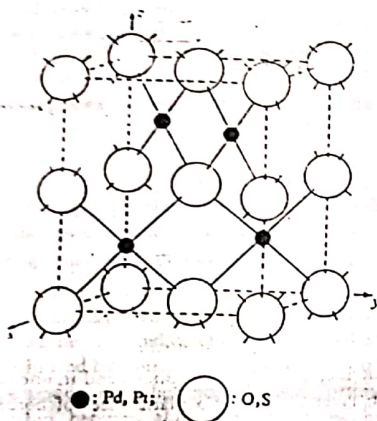
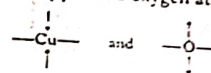


Fig. 8.01. Clinographic projection of the unit cell of the tetragonal structure of PdO, PtO, PdS and PtS.

8.10. The influence of covalent bonding in the oxides is shown more clearly in the structures of ZnO, PdO, PtO and CuO. Zinc oxide has the wurtzite structure, although the sodium chloride arrangement would be expected if the bonding was ionic on account of the relatively large radius of the ion Zn^{2+} . The structure of PdO and PtO is shown in fig. 8.01 and will be seen to be quite different from any we have as yet encountered in ionic crystals. Each oxygen atom is tetrahedrally co-ordinated by metal atoms, but the metal atoms themselves are surrounded by four oxygen atoms disposed in a plane almost at the corners of a square. The structure of CuO is a slightly distorted variant of the

same arrangement. This distribution of bonds is an elegant example of the stereochemistry of the metals concerned, all of which (in the divalent state) can form four planar dsp^2 hybrid bonds. Thus CuO, for example, the four bonds from each copper and oxygen atom can be represented as



In this way the copper atom acquires a share in six extra electrons to achieve the configuration 2, 8, 18, $4s^2 4p^5$, and it is hybridization of one $3d$, one $4s$ and two $4p$ orbitals which forms the dsp^2 bond. In PdO the corresponding bond structure gives rise to the configuration 2, 8, 18, 18, $5s^2 5p^4$. One d , one s and two p orbitals are again available for dsp^2 hybridization, but it is possible that the single unpaired electron in the $4p$ orbital in copper accounts for the structural difference between CuO and PdO, and for the fact that there are no isomorphous compounds of copper and palladium.

The distinction between these planar bonds in divalent copper and the tetrahedral sp^3 bonds in univalent copper will be noted.

Sulphides

8.11. The sulphides of the alkaline earth metals are isostructural with the corresponding oxides (see table 8.02) and, except BeS, are all essentially ionic structures. The sulphides MnS and PbS also have the sodium chloride arrangement. The sulphides of V, Fe, Co and Ni, however, are different in structure from the oxides, showing that the tendency towards covalent bonding is more pronounced in sulphides than in oxides, as is to be expected from the relative electronegativities of oxygen and sulphur. The sulphides of Pd and Pt have structures closely resembling those of the corresponding oxides, and again reveal the characteristic planar distribution of the four dsp^2 bonds in these elements.

The nickel arsenide structure

8.12. The sulphides of V, Fe, Co and Ni have a structure not represented among the oxides. This arrangement, found also in NiAs after which it is named, is illustrated in fig. 8.02. Each A atom is co-ordinated by six X neighbours at the corners of a distorted octahedron but the six A neighbours of an X atom are disposed at the corners of a trigonal prism. The co-ordination, however, is not as simple as this description would imply, for each A atom has also two other atoms of the same kind

(those vertically above and below it) only slightly more remote than its X neighbours. The bonding is obscure and may vary from one compound to another, but it is probable that the $A-X$ bonds are primarily covalent and that metallic bonds operate in addition between the A atoms in a vertical direction. This is consistent with the pronounced anisotropy of the structure: the thermal expansion of nickel arsenide itself is eight times greater perpendicular to the principal axis than along this direction.

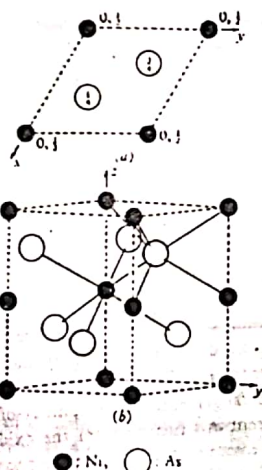


Fig. 8.02. (a) Plan of the unit cell of the hexagonal structure of nickel arsenide, $NiAs$, projected on a plane perpendicular to the z axis. (b) Clinographic projection of the same structure. The two As atoms represented by heavy circles are those within the unit cell; the others lie outside the cell but have been added to show the co-ordination about the Ni atom at $0, 0, 1$.

The nickel arsenide structure occurs not only in the sulphides but also in many other compounds containing a transition metal and one of the elements Sn, Pb, As, Sb, Bi, Se and Te . Many of these systems are essentially intermetallic in their properties and will be discussed further in the chapter devoted to alloys. Here, however, it is interesting to note that as the system becomes more metallic so the bonding in the vertical direction becomes stronger. Thus in FeS the $Fe-S$ and $Fe-Fe$ distances

differ by 0.44 \AA , whereas in $CoSb$, owing to compression of the structure in the z direction, this difference has shrunk to 0.02 \AA .

Nitrides

8.13. A large number of elements form nitrides of composition AX . Those of the group 3 metals Al, Ga and In have the wurtzite structure and are normal covalent compounds since the number of electrons available is just that required to form four tetrahedral bonds about each atom. Formally the structures could alternatively be regarded as ionic, containing the ions A^{3+} and N^{3-} , and on this picture, too, the co-ordination would be fourfold on account of the small radius ratio r^+/r^- . Such a viewpoint is, however, hardly tenable, for the difference in electronegativity (1.5 in the case of AlN) is insufficient to give more than a limited degree of ionic character to the bond.

8.14. The nitrides (and phosphides) of many of the transition metals form crystals with the sodium chloride structure. This description, however, must not be interpreted as implying that they are ionic in character, for in fact they display many of the properties of intermetallic systems. For this reason a discussion of these nitrides is deferred to chapter 13.

Boron nitride

8.15. Boron nitride, BN , is polymorphous and in one form has a layer structure. Each layer consists of a plane sheet of boron and nitrogen atoms, each co-ordinated by three of the other kind at the corners of an equilateral triangle. The planar distribution of the three bonds about the boron atom arises, as we have seen (§4.08), from sp^2 hybridization, and that about the nitrogen atom, which is to be contrasted with the pyramidal distribution of bonds in ammonia, must arise from the same cause. Nitrogen in its ground state has the configuration $1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^1$, but if the two $2f$ electrons are uncoupled and one is promoted to, say, the p_x orbital we obtain the configuration $1s^2, 2s^1, 2p_x^1, 2p_y^2, 2p_z^2$ with the unpaired $2s, 2p_x$ and $2p_y$ orbitals available for sp^2 hybridization. The bonding in boron nitride is thus similar to that in graphite, but with this difference: in graphite the carbon atoms, after sp^2 hybridization, have a p_z orbital containing one electron standing perpendicular to the plane of the rings, and overlap between these produces a delocalized π bond to which the electrical conductivity may be ascribed; in boron nitride

the corresponding p_z orbitals are vacant in the boron atom and are occupied by two electrons in that of nitrogen. Overlap to form π bonds is therefore no longer possible.

Carbides and silicides

8.16. Many carbides and silicides of composition AX are formed by transition metals. These carbides and silicides are characterized by very high melting points, extreme hardness, optical opacity and relatively high electrical conductivity. Many of them have the sodium chloride structure but they are not ionic compounds; rather do they resemble the corresponding nitrides and phosphides in simulating alloy systems in many of their properties. For this reason they will be discussed later.

Other carbides, notably those of the more electropositive metals, are quite different in their properties, being colourless, transparent insulators resembling inorganic salts rather than metal systems. These carbides are ionic; some typical structures will be described in the sections of this chapter devoted to AX_2 and A_mX_n compounds.

Silicon carbide

8.17. Silicon carbide (carborundum, SiC) is of especial interest on account of its rich polymorphism, no fewer than six structures being known. As is to be expected, each carbon and silicon atom is tetrahedrally co-ordinated by four atoms of the other kind, and two of the forms of carborundum have the zincblende and wurtzite structures. The close relationship between these two structures has already been discussed (§4.13), and is emphasized by the many AX compounds (including ZnS itself) in which both are found. It is illustrated in fig. 8.03, where the cubic zincblende structure has been drawn with one of the cube diagonals vertical and parallel to the principal axis of the wurtzite structure. When viewed in this way it will be seen that both structures can be visualized as formed by the superposition of a series of puckered sheets of atoms, but that in zincblende successive sheets are identical (albeit translated) whereas in wurtzite they differ and are related by a rotation through 180° about the principal axis. In the two structures the sequence of sheets can therefore be symbolized as

$\dots AAAA\dots$ and $\dots ABAB\dots$,

respectively. The remaining four forms of carborundum are formed by

the superposition of these same two puckered sheets but in more complex sequences, as for example,

$\dots AABBAABB\dots$ or $\dots AABBBBAABBB\dots$

where the span of the repeat unit is indicated by bold symbols. In one form the structure repeats only after 33 layers, and the c dimension of the hexagonal unit cell is 82.9 \AA . The relationship between these complex structures of carborundum and the simpler zincblende and wurtzite arrangements may be compared with that between the structure of praseodymium and those of the simple close-packed metals (§7.23).

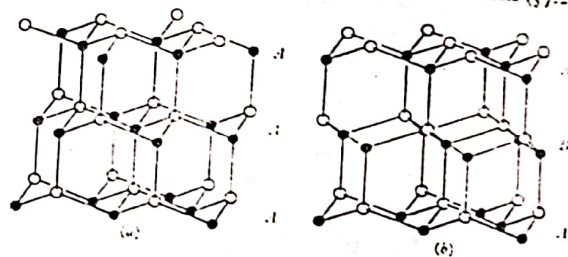


Fig. 8.03. Clinographic projections of the structures of (a) zincblende and (b) wurtzite showing the sequence of layers in the two structures.

AX_2 STRUCTURES

8.18. The different structures adopted by AX_2 compounds are far more numerous and show a far greater diversity of type than those found in AX compounds. Here we shall discuss only a limited number of structures of common occurrence, but it must be borne in mind that there are in addition many other compounds in which the structural arrangement is different.

Halides

8.19. The structures of the AX_2 halides which we shall discuss are shown in table 8.03.

Ionic halides

8.20. A considerable number of AX_2 halides are essentially ionic, and have structures determined by the relative sizes of the ions concerned.

The rutile structure

8.22: A co-ordination of 6:3 occurs in several AX_2 structures, of which the commonest is the tetragonal rutile structure (fig. 8.05), named after one of the mineral forms of TiO_2 . In this structure each A atom is

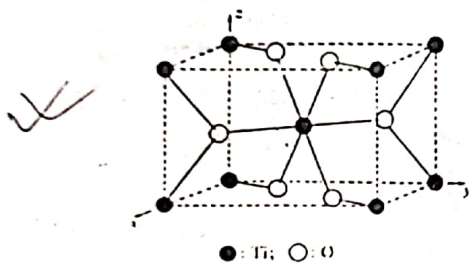


Fig. 8.05. Clinographic projection of the unit cell of the tetragonal structure of rutile, TiO_2 .

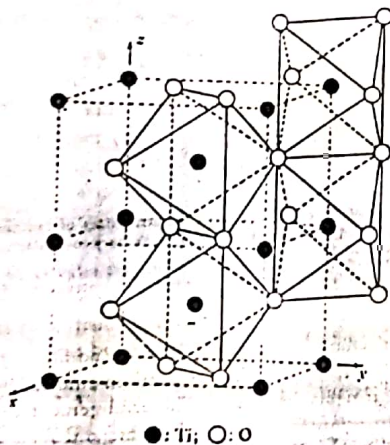


Fig. 8.06. Clinographic projection of the tetragonal structure of rutile, TiO_2 , showing the co-ordinating octahedra of anions round the cations and the way in which these octahedra are linked in bands by sharing horizontal edges.

surrounded by six X neighbours at the corners of a slightly distorted regular octahedron, while the three A atoms co-ordinating each X atom lie in a plane at the corners of a nearly equilateral triangle. If several

unit cells of this structure are considered it will be seen that each of the co-ordinating octahedra of X atoms shares its two horizontal edges with adjacent octahedra. The octahedra are thus linked in bands, which run vertically through the structure and pass through the centre and corners of the unit cell, as shown in fig. 8.06.

The β -cristobalite structure

8.23. A co-ordination of 4:2 is found among AX_2 halides only in BeF_2 , which has the (idealized) β -cristobalite structure, named after one of the forms of SiO_2 . The cubic unit cell of this structure is shown in:

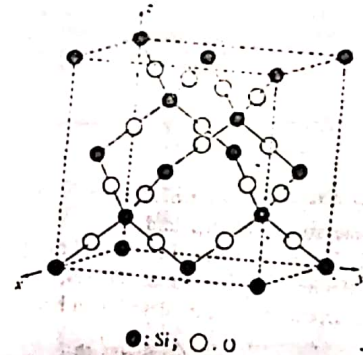


Fig. 8.07. Clinographic projection of the unit cell of the (idealized) cubic β -cristobalite structure.

fig. 8.07, and it will be seen that the structure can be most simply described as an arrangement of A atoms occupying the positions of the carbon atoms in diamond (or of the zinc and sulphur atoms in zinc-blende), with an X atom midway between each pair of A atoms. Every A atom is therefore surrounded by four X neighbours at the corners of a regular tetrahedron, while every X atom is co-ordinated by only two neighbours arranged diametrically opposite to one another.

8.24. The three structures just described are found in a number of AX_2 halides in which the bonding is primarily ionic, and it will be seen from table 8.04 that the great majority of the compounds quoted have the structure to be expected on the basis of the radius ratio of the

ions concerned. Broadly speaking, we may say that these symmetrical structures occur in those halides in which the *A* and *X* atoms differ widely in electronegativity: thus they are common in fluorides, rare in chlorides and bromides (where they are formed only by the strongly electropositive alkaline earth metals), and unknown in iodides.

Table 8.04. The radius ratios of some AX₂ halides

Fluorite structure $r^+/r^- > 0.7$	Rutile structure $0.7-0.3$	β -Cristobalite structure < 0.3
BaF ₂ 0.99	MnF ₂ 0.59	BeF ₂ 0.23
PbF ₂ 0.88	FeF ₂ 0.59	
SrF ₂ 0.83	PdF ₂ 0.59	
HgF ₂ 0.81	CaCl ₂ 0.55	
BaCl ₂ 0.75	ZnF ₂ 0.54	
CaF ₂ 0.73	CoF ₂ 0.53	
CdF ₂ 0.71	NiF ₂ 0.51	
SrCl ₂ 0.63	CaBr ₂ 0.51	
	MgF ₂ 0.48	

When the difference in electronegativity is too small to give rise to a typically ionic structure other and more complex structural arrangements result. There are many of these, and many of them are found in only a limited number of compounds. Others, however, are of sufficiently common occurrence to warrant description here.

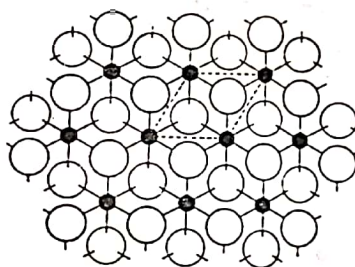
Molecular halides

The cadmium chloride and cadmium iodide structures

8.25. Many AX₂ halides, particularly those of the transition metals, show one or other of the closely related cadmium chloride and cadmium iodide structures. Both of these structures are formed by the superposition of a series of composite layers, each of which consists of a sheet of cadmium atoms sandwiched between two sheets of atoms of the halogen. The arrangement of one such layer is shown in fig. 8.08, and it will be seen that a characteristic feature of the structure is the asymmetry of the co-ordination: the cadmium atoms are symmetrically surrounded by six halogen atoms at the corners of an octahedron, whereas the three cadmium neighbours of each halogen atom all lie to one side of it. In cadmium iodide the structure as a whole is built up by the superposition of such layers in identical orientation, and the structure can therefore be described in terms of the very simple hexagonal unit cell

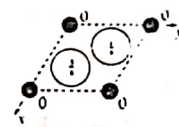
shown in fig. 8.09. It will be noted that if the cadmium atoms are ignored the distribution of the iodine atoms alone is that found in hexagonal close packing.

The cadmium chloride structure differs from that of cadmium iodide only in the geometrical disposition of successive layers; these layers are now so arranged that the halogen atoms are in cubic close packing. This close relationship between the two structures is emphasized by the behaviour of CdBr₂ and NiBr₂. These compounds both have the



● : Cd; ○ : Cl or I

Fig. 8.08



● : Cd; ○ : I

Fig. 8.09

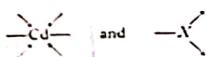
Fig. 8.08. Plan of a single layer of the structures of cadmium chloride, CdCl₂, and cadmium iodide, CdI₂, projected on a plane perpendicular to the *z* axis. The unit cell of cadmium iodide is indicated.

Fig. 8.09. Plan of the unit cell of the hexagonal structure of cadmium iodide, CdI₂, projected on a plane perpendicular to the *z* axis.

cadmium chloride structure, but in addition they possess defect structures derived from that of cadmium chloride by stacking successive layers in irregular sequence. The arrangement of the bromine atoms alone is therefore sometimes as in cubic and sometimes as in hexagonal close-packing; in this respect the structure resembles that of cobalt (87.21).

8.26. It is clear that the bonding in the cadmium chloride and cadmium iodide structures cannot be purely ionic, for adjacent atoms in neighbouring layers are of the same kind and the forces between them can be only of the van der Waals type. Indeed, this is also evident from

the large interlayer spacing in these structures; in cadmium chloride, for example, the Cd-Cl distance within the layers is 2.74 Å whereas the Cl-Cl distance between adjacent layers is 3.68 Å. Moreover, in their physical properties the structures reveal the weakness of this interlayer bonding, for they generally display excellent cleavage parallel to the layers and a marked anisotropy in thermal expansion. The structures can, therefore, be regarded as molecular arrangements in which each sheet constitutes a single molecule of infinite extent in two dimensions, as in the structures of arsenic and graphite, and in which the bonding in the sheets is due to covalent links. Thus in the case of halides of cadmium the bond system round the two atoms can be written



In this way the cadmium atom (with the configuration 2, 8, 18, 18, 5s²) effectively acquires ten electrons to give the configuration 2, 8, 18, 18, 5s²5p⁶5d⁴, and there are available one 5s, three 5p and two 5d orbitals to form sp³d² hybrid bonds with the characteristic octahedral distribution actually observed (see table 4.01). It should be noted, however, that the bonds are not of the same kind in all of the halides. In ferrous iodide, for example, the iron atom (2, 8, 14, 4s²) acquires the configuration 2, 8, 18, 4s², 4p⁶, and the bond formation is due to two 3d, one 4s and three 4p orbitals. These d²sp³ hybrid bonds, however, are also octahedrally disposed.

Although we have just treated the cadmium chloride and cadmium iodide structures as covalent it nevertheless seems probable that the A-X bonds within the sheets still retain an appreciable degree of ionic character and that their true state is better described as a resonance between covalent and ionic bonding in which the influence of the former predominates. The reason for this view is that the difference in electronegativity of the A and X atoms appears still to have an influence in determining which of these closely related structures is formed, that of cadmium chloride being the more ionic of the two. Thus it will be seen from table 8.03 that the cadmium chloride structure is found in many chlorides but that the cadmium iodide arrangement is favoured by the corresponding bromides and iodides. In fact in some cases (e.g. the halides of Mg, Ca, Mn, Cd, etc.) it is possible to trace a progressive transition from a typically ionic structure through those of cadmium chloride and cadmium iodide as we pass from the fluoride to the iodide

and as the difference in electronegativity progressively diminishes. The view that the bonding is at least partially ionic in some of the halides is also supported by magnetic evidence.

The mercuric iodide structure

8.27. Another structure of the layer type is found in HgI₂. Here each mercury atom is co-ordinated by only four halogen neighbours, arranged at the corners of a regular tetrahedron, and each of these halogen atoms

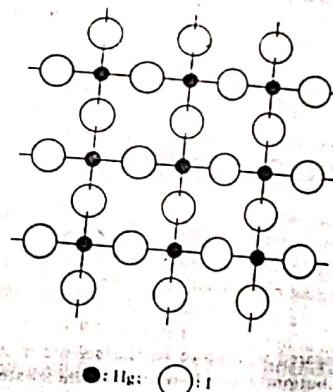


Fig. 8.10. Plan of a single layer of the structure of mercuric iodide, HgI₂.

is bound to only two mercury neighbours to give a sheet of the form shown in fig. 8.10. The structure as a whole is made up by the superposition of such sheets. The bond structure round the two atoms may be represented as



Each mercury atom (with the configuration 2, 8, 18, 32, 18, 6s²) in this way acquires six electrons to give the configuration 2, 8, 8, 32, 18, 6s²6p⁶, and one 6s and three 6p orbitals are available to form the tetrahedral sp³ hybrid bonds actually observed.*

* Structures of the CdCl₂, CdI₂, and HgI₂ types are often described as 'layer lattices'. The phrase is unfortunate, for the word 'lattice' has a specific meaning in crystallography which is not here applicable. 'Layer structures' is a better term.

The palladium chloride and related structures

8.28. Yet another essentially molecular arrangement is found in the structures of PdCl_2 , CuCl_2 and CuBr_2 . Although these structures differ in detail, in all of them the metal atom is co-ordinated by four halogen atoms at the corners of a square, and these squares are joined by opposite edges to form indefinitely extended planar chains. These chains are disposed in the structure with their axes parallel (as shown for PdCl_2 in fig. 8.11) and constitute infinite one-dimensional molecules which

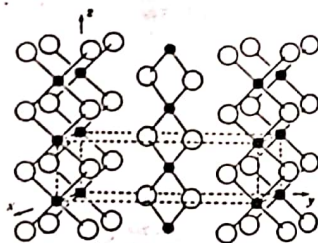
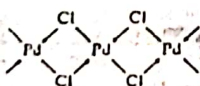


Fig. 8.11. Cinographic projection of the orthorhombic structure of palladium chloride, PdCl_2 . The unit cell is indicated by broken lines.

○: Pd; ○: Cl

may be compared with those in the selenium structure (§ 7.06). The planar distribution of bonds round the metal atoms is the same as in the structures of the oxides of the same elements (§ 8.10), and represents the characteristic spatial disposition of dsp^2 hybrid bonds. Thus in PdCl_2 , say, the bond structure within the chain may be represented



The mercuric chloride structure

8.29. The structure of HgCl_2 is of interest in that it consists of discrete Cl-Hg-Cl molecules, in contrast to the infinite two-dimensional molecules found in HgI_2 (§ 8.27). These linear molecules are arranged in the crystal in a manner similar to that of the I_2 molecules in iodine (§ 7.03), and are bound to one another only by van der Waals bonds. In this compound the mercury atom acquires the configuration 2, 8, 18, 32,

18, $6s^2 6p^2$, so that one $6s$ and one $6p$ orbital are available to form the two linearly directed sp hybrid bonds. It is thus possible to formulate bond configurations which account satisfactorily for each of the very different structures of HgCl_2 and HgI_2 , but it is less easy to understand just exactly why they should be so different, consisting in the former case of discrete molecules and in the latter of molecular sheets. In fact isolated HgI_2 molecules do, indeed, exist in the vapour, and it is interesting to note that there is an appreciable difference in Hg-I distance as between crystal and vapour, corresponding to the difference in bond character. This distance is 2.78 Å for the sp^3 bonds in the crystal and 2.61 Å for the stronger sp bonds in the molecules in the vapour. The structure of HgBr_2 is intermediate in character between those of CdI_2 and HgCl_2 ; it is a layer structure in which each mercury atom is co-ordinated by a distorted octahedron of bromine neighbours, the distortion being such as to bring two of these neighbours much closer than the other four.

Hydrides and hydroxides

8.30. Ionic hydrides of composition AH_2 are formed only by the alkaline earth metals; they contain the H^- ion, are salt-like in character and may be compared with AH hydrides of the alkali metals. The remaining AH_2 hydrides are quite different in their properties, in respect of which they most closely resemble metal systems. They are therefore more conveniently discussed later (§§ 13.57-13.59).

We have already seen that in a limited number of AOH hydroxides the OH group behaves as a negative ion of radius 1.35 Å, intermediate between the radii of the F^- and Cl^- ions, and that the structures of these hydroxides are analogous to those of the corresponding halides. The same is true of certain of the $A(\text{OH})_2$ hydroxides. None of these hydroxides has any of the symmetrical structures characteristic of truly ionic bonding, but those of Mg , Ca , Mn , Fe , Co , Ni and Cd have the cadmium iodide structure. Some other hydroxides, however, have structures quite different from those of the halides. These structures, and the reason for their abnormal properties, are discussed in §§ 12.10-12.12.

Oxides and sulphides

8.31. The oxides and sulphides of composition AO_2 and AS_2 resemble the AO and AS compounds in showing a wide variety of structural types. Some of those which we shall consider are summarized in table 8.2. It will be seen from this table that oxides and the corresponding

sulphides are not in general isostructural. We revert to this point later (§ 8.60).

Table 8.05. The structures of some AX_2 oxides and sulphides

Fluorite structure (c.n. 8:4)	Rutile structure (c.n. 6:3)	Silica structures (c.n. 4:2)	Cadmium iodide structure	Molybdenum sulphide structure	Chain structure
ZrO ₂	GeO ₂	SiO ₂	TiS ₂	MoS ₂	SiS ₂
HfO ₂	SnO ₂	GeO ₂	ZrS ₂	WS ₂	
PbO ₂	PbO ₂		SnS ₂		
CaO ₂	TiO ₂		Ta ₂ S ₅		
PrO ₂	VO ₂		PbS ₂		
ThO ₂	NbO ₂				
PaO ₂	TaO ₂				
UO ₂	CrO ₂				
NpO ₂	MoO ₂				
PuO ₂	WO ₂				
AmO ₂	MnO ₂				
	IrO ₂				

Oxides

8.32. On account of the strongly electronegative character of oxygen many oxides AO_2 are primarily ionic, and have symmetrical structures of the fluorite, rutile and β -cristobalite types, already described (§§ 8.21-8.23), composed of A^{4+} and O^{2-} ions. The particular structure which obtains is determined by geometrical considerations, as will be seen from the radius ratios quoted for some of these oxides in table 8.06. Layer structures of the cadmium chloride and cadmium iodide types, which are common in AX_2 compounds containing less electronegative anions, are not found among oxides.

Table 8.06. The radius ratios of some AX_2 oxides

Fluorite structure $r^+/r^- > 0.7$	Rutile structure 0.7-0.3	Silica structures < 0.3
CeO ₂ 0.72	PbO ₂ 0.60	GeO ₂ 0.38
ThO ₂ 0.68	SnO ₂ 0.51	SiO ₂ 0.29
PrO ₂ 0.66	TiO ₂ 0.49	
PaO ₂ 0.65	WO ₂ 0.47	
UO ₂ 0.64	OsO ₂ 0.46	
NpO ₂ 0.63	IrO ₂ 0.46	
PuO ₂ 0.63	RuO ₂ 0.45	
AmO ₂ 0.61	VO ₂ 0.43	
ZrO ₂ 0.57	CrO ₂ 0.40	
HfO ₂ 0.56	MnO ₂ 0.39	
	GeO ₂ 0.38	

The silica structures

8.33. The structure of silica, SiO_2 , of particular interest and importance because of its relationship to the silicate minerals to be discussed later. Silica is polymorphous and occurs naturally as three forms stable in the temperature ranges indicated:

Quartz (below 870 °C)	Tridymite (870-1470 °C)	Cristobalite (above 1470 °C)
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In addition, there are α and β modifications of each of these forms, differing only slightly in structure. The idealized structure of β -cristobalite has already been described (§8.23 and fig. 8.07); the actual structure differs from this in that the oxygen atoms are somewhat displaced from the straight lines joining pairs of silicon atoms so that the two bonds to each oxygen atom are no longer collinear. The structure of tridymite is also 4:2 co-ordinated and can be regarded as related to that of wurtzite in exactly the same way as the structure of cristobalite is related to that of zincblende: if the zinc and sulphur atoms in wurtzite are replaced by silicon atoms, and if oxygen atoms are introduced midway between each pair of these atoms, the (idealized) structure of tridymite results. In quartz 4:2 co-ordination is again found, but now the co-ordinating tetrahedra about the silicon atoms are yet differently arranged to give a denser structure which is discussed in detail in §9.15. (The nature of the Si-O bond in silica calls for brief discussion. The difference in electronegativity between silicon and oxygen is 1.7, and this value corresponds to a bond which is about 40 per cent ionic. It is therefore not possible to regard silica in its various forms as a purely ionic compound, and the Si-O bond must be treated as possessing a considerable degree of covalent character. This view is supported by the fact that the oxygen atoms in all the structures are displaced from the line joining silicon atoms, an arrangement clearly energetically impossible in a truly ionic structure and showing a tendency towards the characteristic spatial disposition of covalent bonds.)

Peroxide and superoxide structures

8.34. The structures of certain AO_2 compounds not shown in table 8.05 also merit brief consideration. The peroxides CaO_2 , etc., of the alkaline earth metals, although ionic, are quite different from the oxides so far discussed in that in them the anions are the diatomic units O_2^{2-} :

similarly, in the superoxides KO_2 , RbO_2 and CsO_2 diatomic ions O_2^- are found. All these oxides are therefore more closely related to AX than to AX_2 compounds. The structure of SrO_2 is shown in fig. 8.12 and it will be seen that it may be regarded as the sodium chloride arrangement with Sr^{2+} and linear O_2^{2-} ions in place of Na^+ and Cl^- . The O_2^{2-} ions are all arranged with their axes parallel to one edge of the unit cell, the symmetry of which is accordingly lowered from cubic to tetragonal. The other peroxides and superoxides have similar structures.

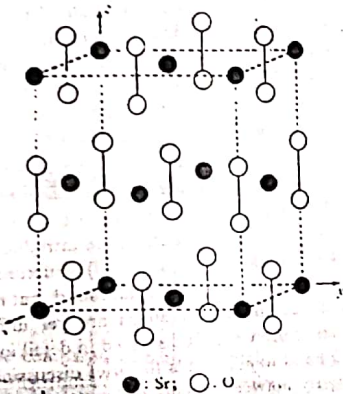


Fig. 8.12. Clinographic projection of the tetragonal structure of strontium peroxide, SrO_2 . The cell shown is not the smallest possible tetragonal cell but has been chosen to emphasize the relationship to the sodium chloride structure.

Carbon dioxide

8.35. The structure of carbon dioxide, CO_2 , is purely molecular. Discrete, linear $\text{O}=\text{C}=\text{O}$ molecules are arranged with the carbon atoms at the corners and face centres of a cubic unit cell and with the axes of the molecules parallel to the cube diagonals (fig. 8.13). This is an elegant example of a typically molecular structure, for it will be seen that the centres of the molecules are disposed as in cubic close packing, and that the arrangement of the molecules themselves is as compact as is consistent with their aspherical shape. The interatomic distance between the oxygen atoms of adjacent molecules is about 3.2 \AA , corresponding to the weak van der Waals forces which hold them together, and the C-O distance within each molecule is 1.16 \AA . This latter distance is

significantly less than would be expected on the basis of the simple structure $\text{O}=\text{C}=\text{O}$ and probably arises from resonance between this structure and the forms



Although these two forms are polar they will, of course, contribute equally to the resonance hybrid so that the resultant moment will be

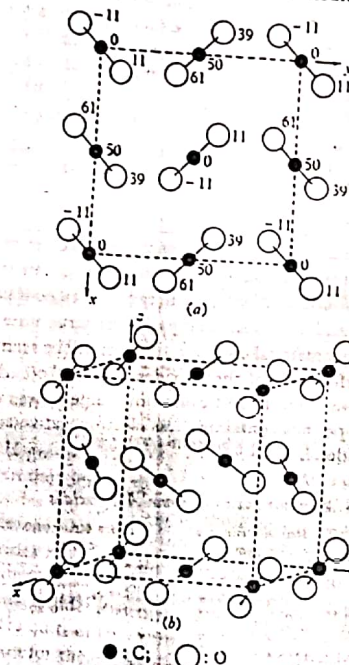


Fig. 8.13. (a) Plan of the unit cell of the cubic structure of carbon dioxide, CO_2 , projected on a plane perpendicular to the z axis. The heights of the atoms are expressed in units of $c/100$. (b) Clinographic projection of the same structure.

zero, as is in fact observed. We have here yet another example of a structure in which a precision determination of bond length throws light on the nature of the interatomic binding.

Sulphides

8.36. Sulphur is less electronegative than oxygen, and in consequence no sulphide of composition AS_2 crystallizes with any of the typically ionic structures commonly found among the oxides AO_2 . A number of sulphides have the cadmium iodide layer structure, but many others, particularly those of the transition metals, have structures unrepresented among the compounds so far considered. A few of these are of sufficiently common occurrence to warrant discussion.

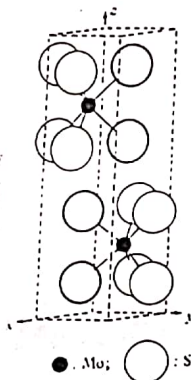
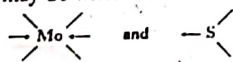


Fig. 8.14. Clinographic projection of the unit cell of the hexagonal structure of molybdenum sulphide, MoS_2 . The four S atoms represented by heavy circles are those within the unit cell; the others lie outside the cell but have been added to show the co-ordination about the Mo atoms.

The molybdenum sulphide structure

8.37. The structure of molybdenum sulphide, MoS_2 (fig. 8.14), resembles the structures of cadmium chloride and cadmium iodide in that it is a layer arrangement in which each layer consists of a sheet of A atoms sandwiched between two sheets of X atoms. The co-ordination about the A atoms, however, is no longer octahedral, the six X neighbours being arranged at the corners of a trigonal prism (cf. the co-ordination of Ni about As in nickel arsenide, § 8.12). The layers are superposed in such a way that alternate layers are identical, and are held together only by weak van der Waals bonds. The structure is thus another example of a molecular arrangement in which each layer constitutes an infinite two-dimensional molecule. The bond distribution about the two atoms may be written as



In this way the molybdenum atom of configuration $2, 8, 18, 13, 4d^5$ effectively acquires eight electrons to give the configuration $2, 8, 18, 18, 5s^2 5p^2$. The orbitals involved in bond formation are four $4d$, one $5s$ and one $5p$, and hybridization of these gives d^3p bonds with the characteristic trigonal prismatic disposition actually observed (see table 4.01).

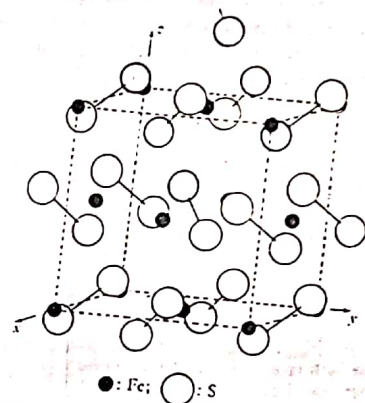
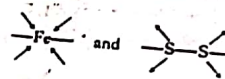


Fig. 8.15. Clinographic projection of the unit cell of the cubic structure of pyrites, FeS_2 ; some S atoms outside the unit cell are shown. Six of the S atoms are represented by heavy circles to emphasize the octahedral co-ordination about the Fe atom at the centre of the top face.

The pyrites and marcasite structures

8.38. In the pyrites and marcasite structures of FeS_2 discrete S_2 groups are found. Geometrically the pyrites structure (fig. 8.15) is closely related to that of sodium chloride, from which it may be regarded as being derived by replacing Na by Fe and Cl by S_2 groups. This description, however, conceals the nature of the co-ordination, for the $S-S$ distance within the S_2 group is such that each iron atom is surrounded by six sulphur atoms at the corners of a nearly regular octahedron, while each sulphur atom is bound to one other sulphur atom and to three iron atoms. The bond distribution about the atoms can thus be written



The octahedral bonds about the iron atom are d^2sp^3 hybrids formed by two $3d$, one $4s$ and three $4p$ orbitals (see table 4.01), and the bonding throughout the structure is wholly covalent. The crystal may thus be regarded as constituting a single giant molecule, just as a crystal of diamond is a single molecule of carbon. It is interesting to note that the $[FeS_6]$ octahedra in the structure share faces, and that the shared edges bounding these faces are actually longer than the unshared edges. This is additional evidence for the covalent character of the bonding; in ionic crystals co-ordinating polyhedra of anions rarely share faces, and when they do so the shared edges are usually shortened owing to the mutual repulsion of the cations.

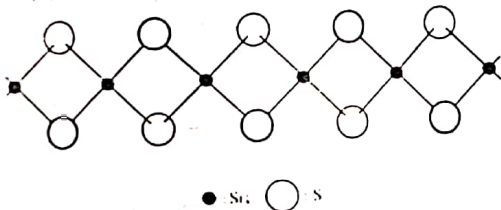


Fig. 8.16. The structure of the chain molecule of SiS_2 . Each Si atom is tetrahedrally co-ordinated by S, and the tetrahedra are linked into an infinite chain by sharing opposite edges.

Silicon disulphide

8.39. The structure of SiS_2 is of interest by virtue of its comparison with that of SiO_2 . As in SiO_2 , the silicon atoms are tetrahedrally co-ordinated, but, owing to the less ionic character of the bonding, the tetrahedra in SiS_2 are able to approach more closely and so share opposite edges to form infinite molecular chains of the form shown in fig. 8.16. In all the forms of silica the co-ordinating tetrahedra share only corners. The chains in the SiS_2 structure are packed together in much the same manner as the chains in selenium (§7.06), so that each is symmetrically surrounded by six others.

Carbides

8.40. The great majority of carbides of composition AC_3 resemble intermetallic systems in many of their properties, and will be discussed later (§§ 13.37-13.39). Some, however, principally the compounds of the more electropositive metals, are strikingly different in their properties

and form typically ionic crystal structures. Thus the carbides CaC_2 , SrC_2 , BaC_2 , LaC_2 , CeC_2 , PrC_2 and NdC_2 all have tetragonal structures analogous to that of SrO_2 (fig. 8.12) with the O_2^{2-} ions replaced by C_2^{4-} and with $c/a > 1$. The structure of ThC_2 (fig. 8.17) is closely related, and again may be compared with that of sodium chloride; but now the axes of the C-C ion lie perpendicular to the principal axis, instead of parallel to it, and give a tetragonal cell with $c/a < 1$.

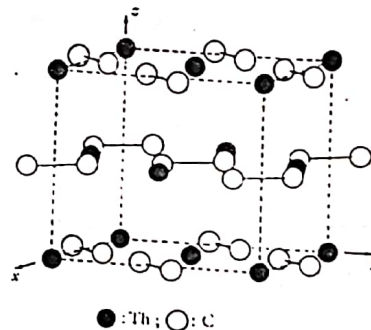


Fig. 8.17. Clinographic projection of the tetragonal structure of thorium carbide, ThC_2 . The cell shown is not the smallest possible tetragonal cell but has been chosen to emphasize the relationship to the sodium chloride structure.

A₂X STRUCTURES

8.41. Many structural types are represented among A_2X compounds. We shall describe only two, which are of common occurrence among metallic oxides and sulphides. There are, of course, also numerous molecular structures of this composition. Among these the structure of ice is of particular importance and is discussed separately in § 12.05.

The anti-fluorite structure

8.42. Many of the oxides, sulphides, selenides and tellurides of the alkali metals (e.g. Li_2O , Li_2S , etc.) have the so-called anti-fluorite structure, i.e. a fluorite structure in which the positions of the anions and cations are interchanged. Most of these can be regarded as essentially ionic compounds. The co-ordination is 4:8.

The cuprite structure

8.43. The mineral cuprite, Cu_2O , and the corresponding silver oxide, Ag_2O , have the very simple cubic structure shown in fig. 8.18, with 2:4 co-ordination. The oxygen atoms are located at the corners and centre of the unit cell, and the copper atoms occupy the centres of four of the eight cubelets into which the cell may be divided. The arrangement of the copper atoms alone is thus as in cubic close packing. Each oxygen atom is co-ordinated by four copper neighbours at the corners of a regular tetrahedron, but each copper atom has only two oxygen neighbours

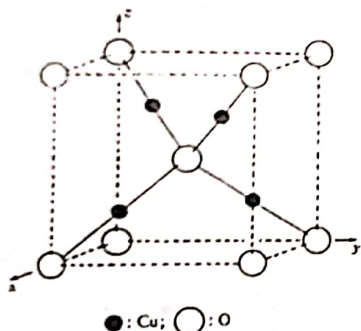
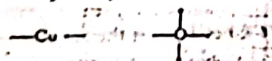


Fig. 8.18. Clinographic projection of the unit cell of the cubic structure of cuprite, Cu_2O .

symmetrically disposed about it on a straight line. This structure is unique among inorganic compounds in that it consists of two identical interpenetrating frameworks which are not directly bonded together: starting from any one atom it is possible to reach half, but only half, of the remainder by travelling along Cu-O bonds.

The bond structure in Cu_2O may be formulated thus



This arrangement gives the copper atom the electronic configuration 2, 8, 18, $4s^1 4p^3$, so that the orbitals involved in the bonds are one $4s$ and one $4p$; hybridization of these gives sp bonds with the characteristic

linear configuration actually observed (see table 4.61). This is the fourth simple copper compound whose structure we have considered, the others being CuI (§8.04), CuO (§8.10) and CuCl_2 (§8.25), and it is interesting to compare the stereochemistry of univalent and divalent copper in these structures. In both CuO and CuCl_2 the Cu^{II} atom forms four coplanar dsp^2 bonds, in CuI the Cu^I atom again forms four bonds but now they are sp^3 bonds tetrahedrally disposed, while finally in Cu_2O the Cu^I atom forms two sp bonds arranged in line.

A_2X_3 STRUCTURES

8.44. Among compounds of this type few typically ionic crystals are found, and the structures are generally of far greater diversity and complexity than those of the relatively simple compounds so far considered. With increasing valency of the cation the tendency towards covalent bonding becomes more and more pronounced, and layer or molecular structures are increasingly common. Thus among A_2X_3 compounds only the fluorides and a few oxides have symmetrical structures, while many of the other halides, hydroxides, oxides and sulphides have layer structures differing from each other in detail but all displaying the general features already described as characteristic of such structures. Probably no A_2X_3 compounds with $z > 3$ have ionic structures, and in the majority of them purely molecular arrangements are found.

The aluminium fluoride structure

8.45. One symmetrical structure of common occurrence among A_2X_3 compounds is that of aluminium fluoride, AlF_3 , shown (in a somewhat idealized form) in fig. 8.19. Aluminium ions are situated at the corners of the cubic unit cell, with fluorine ions at the mid-points of the cell edges. The co-ordination is thus 6:2, and each Al^{3+} ion is surrounded by a regular octahedron of F^- ions. These octahedra are linked together by sharing only corners. This structure (or a slightly deformed variant of it) is found in the fluorides AlF_3 , SeF_3 , FeF_3 , CoF_3 , RhF_3 and PdF_3 and in the oxides CrO_3 , WO_3 and ReO_3 .

The corundum and haematite structures

8.46. The oxides Al_2O_3 and Fe_2O_3 are both polymorphous, and exist in several forms. The α form of these oxides (corundum and haematite), and also the oxides Cr_2O_3 , Ti_2O_3 , V_2O_3 , $\alpha\text{-Ga}_2\text{O}_3$ and Rh_2O_3 , have a

structure which may be described as a hexagonal close-packed array of oxygen atoms with metal atoms in two-thirds of the octahedrally co-ordinated interstices. Each metal atom is thus co-ordinated by six oxygen atoms, each of which in its turn has four metal atom neighbours. The co-ordination is 6:4. The γ form of Al_2O_3 and Fe_2O_3 has a quite different structure which is described below (§ 8.57).

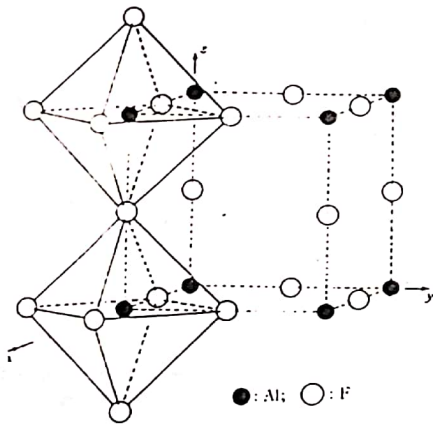


Fig. 8.19. Clinographic projection of the unit cell of the (idealized) cubic structure of aluminium fluoride, AlF_3 . Two co-ordinating $[AlF_6]$ octahedra are indicated to show their linkage by sharing corners.

$A_m B_n X_z$ STRUCTURES

8.47. The composition $A_m B_n X_z$ clearly embraces a vast number of compounds, including, among others, the salts of the inorganic acids. At this point, however, it is convenient to confine our discussion for the most part to those compounds in which A and B both represent electro-positive elements while X is a non-metal, usually oxygen, sulphur or a halogen. We shall therefore be concerned here with the complex oxides, sulphides and halides of two metals, all of which can be regarded as primarily ionic compounds with structures containing atoms A , B and X in the ionized state. Naturally the oxides are by far the most important and it is they which have been most extensively studied. Many of these

oxides prove to be of particular crystallographic significance on account of a number of interesting structural features which they display, while in recent years some have also assumed great practical importance by virtue of their ferroelectric properties. A discussion at some length is therefore warranted.

ABX_3 structures

8.48. Two structures are of common occurrence among ABX_3 compounds and are usually named after the minerals perovskite, $CaTiO_3$, and ilmenite, $FeTiO_3$.

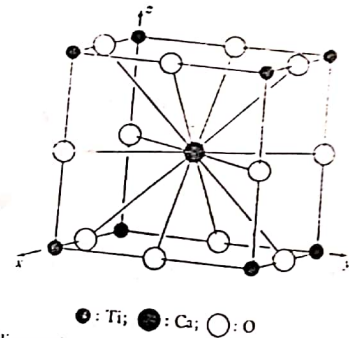


Fig. 8.20. Clinographic projection of the unit cell of the (idealized) cubic structure of perovskite, $CaTiO_3$.

The perovskite structure

8.49. The perovskite structure in its idealized form is cubic and has the atomic arrangement shown in fig. 8.20, with one formula unit of $CaTiO_3$ in the unit cell. (Titanium atoms occupy the corners of the cell, a calcium atom is at its centre and the oxygen atoms lie at the mid-points of its edges. Each Ca is thus 12- and each Ti 6-co-ordinated by oxygen neighbours while each oxygen is linked to four Ca and two Ti atoms.) As is to be expected (it is the larger metal atom (or ion), calcium in this case, which occupies the position of higher co-ordination.) It will be noted that geometrically (the structure can be regarded as a close-packed array of $(O + Ca)$ atoms, with Ti atoms occupying some of the octahedrally co-ordinated interstices.) Its close relationship to the structure

of AlF_3 (see fig. 8.10) will also be observed: if the Ca atoms are omitted those of Ti and O occupy the positions of Al and F, respectively, in the latter structure.

It is clear that in such a symmetrical structure a simple relationship must exist between the radii of the component ions. Ideally this relationship is

$$r_A + r_X = \sqrt{2}(r_B + r_X),$$

where A is the larger cation, but it is found that in practice the structure appears whenever the condition

$$r_A + r_X = t\sqrt{2}(r_B + r_X)$$

holds. Here t is a 'factor of tolerance' which may lie within the approximate limits 0.7-1.0. If t lies outside these limits other structures obtain.

8.50. The perovskite structure is found in some fifty or more complex oxides and fluorides, some of which are listed in table 8.07. Several points of importance emerge from a consideration of this list.

In the first place we note that in all the compounds the A ions are large (e.g. K, Ca, Sr, Ba) and comparable in size with the oxygen or fluorine ion, as is to be expected since the A and X ions together form a close-packed array. Similarly, the B ions are small, since they must have a radius appropriate to 6-co-ordination by oxygen or fluorine. These conditions are, of course, merely another expression of the fact that the radii satisfy the relation given above with a tolerance factor within the range quoted. Quite generally, we may say that for oxides and fluorides the radii of the A and B ions must lie within the ranges 1.0-1.4 Å and 0.45-0.75 Å, respectively.

Table 8.07. Some compounds with the perovskite structure

Not all of these compounds have the ideal structure of fig. 8.20 (see text)

$NaNbO_3$	$CaTiO_3$	$CaSnO_3$	$BaPrO_3$	$YAlO_3$	$KMgF_3$
$KNbO_3$	$SrTiO_3$	$SrSnO_3$	$SrHfO_3$	$LaAlO_3$	$PbMgF_3$
$NaWO_3$	$BaTiO_3$	$BaSnO_3$	$BaHfO_3$	$LaCrO_3$	$KNiF_3$
	$CdTiO_3$	$CaCeO_3$	$BaThO_3$	$LaMnO_3$	$KZnF_3$
	$PbTiO_3$	$SrCeO_3$		$LaFeO_3$	
	$CaZrO_3$	$BaCeO_3$			
	$SrZrO_3$	$CdCeO_3$			
	$BaZrO_3$	$PbCeO_3$			
	$PbZrO_3$				

A second point of interest is that among oxides the perovskite structure is not exclusively restricted to those compounds in which the A and B ions are divalent and quadrivalent, respectively, as is shown by the

fact that $KNbO_3$ and $LaAlO_3$ have this structure. It thus appears that the valencies of the individual cations in the structure are of only secondary importance, and that any pair of ions can occur provided that they have radii appropriate to the co-ordination and an aggregate valency of 6 to confer electrical neutrality on the structure as a whole; among the oxides listed in table 8.07 are compounds with pairs of cations of valencies 1 and 5, 2 and 4, and 3 and 3. This point is made even more clearly by the fact that the perovskite structure is also found in a number of oxides (not shown in table 8.07) in which the A and/or B sites are not all occupied by atoms of the same kind. Thus $(K_1La_2)TiO_3$ has the perovskite structure with the A ions replaced by equal numbers of ions of K and La, while in $Sr(Ga_1Nb_1)O_3$ the B ions are replaced by equal numbers of Ga and Nb. In $(Ba_1K_2)(Ti_1Nb_1)O_3$ the same structure is again found, with $(Ba+K)$ in place of A and $(Ti+Nb)$ in place of B . It is, of course, clear that such arrangements must constitute defect structures, for a single unit cell will typify the structure as a whole only if we consider the A and/or B sites to be statistically occupied by equal numbers of the substituent ions.

A still more extreme example shows that the perovskite structure can even occur with some of the A sites unoccupied. Sodium tungsten bronze has the ideal composition $NaWO_3$, with the perovskite structure, but this compound shows very variable composition and colour, and is better represented by the formula Na_xWO_3 with $1 > x > 0$. In the sodium-poor varieties the structure remains essentially unaltered but some of the sites normally occupied by sodium are vacant. To preserve neutrality one tungsten ion is converted from W^{5+} to W^{6+} for every site so unoccupied, and this change in ionization gives rise to the characteristic alteration in colour and explains its association with the sodium content. In the extreme case, when no sodium is present, we have WO_3 , the structure of which is closely related to that of AlF_3 . We have already shown how this structure, in its turn, is related to that of perovskite. A third point to be noted from table 8.07 is that among the compounds with the perovskite structure are many 'titanates', 'niobates', 'stannates', etc., which would normally be regarded as inorganic salts. Structurally, however, there is no justification for this view. We shall later find that in the true salts of inorganic acids finite complex anions have a discrete existence in the crystal structure: in calcium carbonate, for example, the anions CO_3^{2-} are clearly recognizable and the structure as a whole is built up of these anions and of Ca^{2+} cations arranged in a manner very

similar to that of the ions in sodium chloride. In calcium 'titanate' on the other hand, each titanium ion is co-ordinated symmetrically by six oxygen neighbours and no TiO_3^{2-} complex ion can be discerned. Thus, in spite of the resemblance between the empirical formulae CaCO_3 and CaTiO_3 , the compounds are in structure entirely distinct, and while the former is a salt the latter should more properly be regarded as a complex oxide.

The final point which we would make about the perovskite structure is that the 'ideal' highly symmetrical cubic structure so far described is found in only a limited number of the compounds given in table 8.07. At high temperatures, or when the tolerance factor is very close to unity, this simple structure does indeed often occur, but in many compounds the actual structure is a pseudosymmetric variant of the ideal arrangement, derived from it by small displacements of the atoms. In some cases these displacements result in a slight distortion of the unit cell, the symmetry of which is accordingly reduced, and in others the deformation is such that adjacent cells are no longer precisely identical so that the true unit cell comprises more than one of the smaller ideal units. The number of these pseudosymmetric structures is too great to describe in detail here, but it is important to stress that in many cases the degree of departure from the ideal arrangement is only very slight. Thus BaTiO_3 has a tetragonal unit cell with axial ratio $c/a = 1.01$ derived from the cubic cell by an extension parallel to one of the cube edges of only 1 per cent. Even so, these departures from the ideal structure are of profound importance, for it is to them that the ferroelectric properties of many of these oxides must be ascribed. Ferroelectricity is not compatible with the high symmetry of the ideal structure, and it is only in those members of the perovskite family which have structures of lower symmetry that the property can occur.

The ilmenite structure

8.51. When the A ion in an ABX_3 compound is too small to form the perovskite structure, say when its radius is less than about 1.0 \AA , the alternative ilmenite arrangement sometimes occurs. This structure is closely related to that of corundum and haematite (§8.46) and may be described as an hexagonal close-packed array of X ions (usually oxygen ions) with A and B ions each occupying one-third of the octahedrally co-ordinated interstices. Thus both A and B ions are now 6-co-ordinated by anion neighbours.

8.52. A few oxides with the ilmenite structure are listed in table 8.08. It will be seen from this list that, with the exception of CdTiO_3 , all are oxides in which the A ion is considerably smaller than the corresponding ion in the perovskite structure. The dimorphism of CdTiO_3 , which at high temperatures has the perovskite structure, is readily explained by the fact that the radius of the Cd^{2+} ion (0.97 \AA) is very close to the critical value for transition between the perovskite and ilmenite arrangements. Again it will be noted that the list includes a number of 'titanates' which should more properly be described as complex oxides.

Table 8.08. Some compounds with the ilmenite structure

MgTiO_3	FeTiO_3	CdTiO_3^*	$\alpha\text{-Al}_2\text{O}_3$	$\alpha\text{-Fe}_2\text{O}_3$
MnTiO_3	CoTiO_3	LiNbO_3	Ti_2O_3	Rh_2O_3
	NiTiO_3		V_2O_3	Ga_2O_3

* Low temperature form.

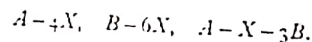
All the oxides listed in table 8.08 are isomorphous, and solid solution between them is common. Thus MgTiO_3 and FeTiO_3 form solid solutions of composition $\text{Mg}_x\text{Fe}_{(1-x)}\text{TiO}_3$ in which the Mg and Fe ions occupy the A sites at random, and FeTiO_3 and $\alpha\text{-Fe}_2\text{O}_3$ at high temperatures form a complete range of solid solution between the two extreme compositions. In this latter case, as the proportion of $\alpha\text{-Fe}_2\text{O}_3$ increases the Fe^{3+} and Ti^{4+} ions in FeTiO_3 are progressively replaced by Fe^{3+} ions until ultimately these occupy both A and B positions.

AB_2X_4 structures

8.53. The only AB_2X_4 structure which we shall discuss is that of spinel, MgAl_2O_4 .

The spinel structure

8.54. The spinel structure is found among a very large number of oxides AB_2X_4 and also in a limited number of sulphides, selenides, fluorides and cyanides of the same composition, some of which are recorded in table 8.09. The cubic unit cell of this structure is shown in fig. 8.21 and contains 32 X ions. Each A ion is tetrahedrally co-ordinated by four and each B ion is octahedrally co-ordinated by six X neighbours, and each X ion is bound to one A and to three B ions. The co-ordination may therefore be summarized thus:



It will be realized from fig. 8.21 that if the X ions alone are considered the positions of these ions could be described in terms of a cubic sub-cell of volume only one-eighth that of the true cell, with the X ions at its corners and face centres. In other words, the structure is one in which the A ions are arranged as in cubic close packing, with the A and B ions in the tetrahedrally and octahedrally co-ordinated interstices, respectively.

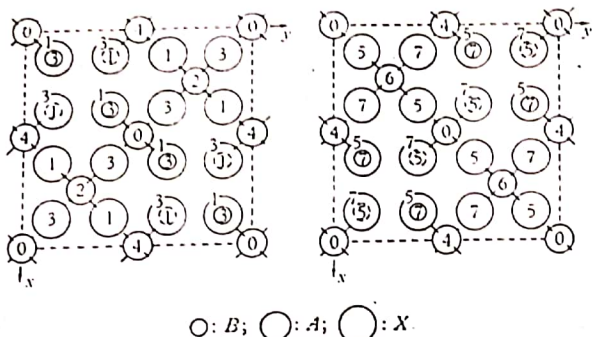


Fig. 8.21. Plan of the unit cell of the cubic structure of spinel, AB_2X_4 , projected on a plane perpendicular to the z axis. The heights of the atoms are indicated in units of $\frac{1}{4}c$. For clarity the lower and upper halves of the cell are shown separately, and only the co-ordination about the A ions is indicated.

In the majority of the oxides with the spinel structure A is a divalent and B a trivalent ion, but this condition is not essential, and it is found (as in the perovskite structure) that the total cation charge is the most significant factor and that other cation combinations which yield a neutral structure are admissible.

8.55. The structure so far described is the 'normal' spinel structure and is the arrangement found in many AB_2O_4 oxides. Some oxides of this composition, however, have an alternative 'inversed' structure, which may be best described in terms of a specific example, such as $MgFe_2O_4$. In this oxide the pattern of sites in the structure and the distribution of the oxygen ions is exactly as in the normal spinels. The arrangement of the cations, however, is different: the 4-co-ordinated

Table 8.09. Some compounds with the spinel structure

BeLi ₂ F ₄	MgCr ₂ O ₄ *	MgFe ₂ O ₄ †	FeNi ₂ O ₄	MgGa ₂ O ₄
MoNa ₂ F ₄	MnCr ₂ O ₄ *	TiFe ₂ O ₄ †	GeNi ₂ O ₄	ZnGa ₂ O ₄
WN ₂ O ₄	FeCr ₂ O ₄ *	MnFe ₂ O ₄	FeNi ₂ S ₄	CaGa ₂ O ₄
ZnK ₂ (CN) ₄	CoCr ₂ O ₄ *	FeFe ₂ O ₄ †	NiNi ₂ S ₄	MgIn ₂ O ₄
CdK ₂ (CN) ₄	NiCr ₂ O ₄ *	Fe ₂ O ₄	MgRh ₂ O ₄ *	CaIn ₂ O ₄
HgK ₂ (CN) ₄	CuCr ₂ O ₄ *	CoFe ₂ O ₄ †	ZnRh ₂ O ₄ *	MnIn ₂ O ₄
TiMg ₂ O ₄ †	ZnCr ₂ O ₄ *	NiFe ₂ O ₄ †	TiZn ₂ O ₄ †	FeIn ₂ O ₄
VMg ₂ O ₄ †	CdCr ₂ O ₄ *	CuFe ₂ O ₄ †	SnZn ₂ O ₄ †	CaIn ₂ O ₄
MgV ₂ O ₄ *	MnCr ₂ S ₄	ZnFe ₂ O ₄ *	MgAl ₂ O ₄ *	NiIn ₂ O ₄
FeV ₂ O ₄ *	FeCr ₂ S ₄	CdFe ₂ O ₄ *	SrAl ₂ O ₄	CaIn ₂ O ₄
ZnV ₂ O ₄ *	CoCr ₂ S ₄	AlFe ₂ O ₄	CrAl ₂ O ₄	CaIn ₂ O ₄
	CdCr ₂ S ₄	PbFe ₂ O ₄	MoAl ₂ O ₄	HgIn ₂ O ₄
	HgCr ₂ S ₄ *	MgCo ₂ O ₄	MnAl ₂ O ₄ *	
	ZnCr ₂ Se ₄ *	TiCo ₂ O ₄	FeAl ₂ O ₄ *	
	CdCr ₂ Se ₄ *	CoCo ₂ O ₄	CoAl ₂ O ₄ *	
	TiMn ₂ O ₄	CuCo ₂ O ₄	NiAl ₂ O ₄	
	MnMn ₂ O ₄ *	ZnCo ₂ O ₄ *	CuAl ₂ O ₄	
	ZnMn ₂ O ₄ *	SnCo ₂ O ₄ †	ZnAl ₂ O ₄ *	
		CoCo ₂ S ₄	Al ₂ O ₃	
		CuCo ₂ S ₄	ZnAl ₂ S ₄	

* Normal structure. † Inversed structure.

sites are occupied, not by the Mg^{2+} ions, but by one-half of the Fe^{2+} ions, while the rest of these ions, together with all the Mg^{2+} ions, are distributed at random over the sites of 6-co-ordination. If we wish to emphasize this distinction we may write the formula of the inversed structure as $Fe(MgFe)O_4$. The structure type of the compounds listed in table 8.09 is indicated, where known.

8.56. The factors which determine the appearance of one or other of the two spinel structures are by no means clear. It might be expected that the 4-co-ordinated sites would always be occupied by the smaller cations, so that spinels with $r_A < r_B$ would have the normal and those with $r_A > r_B$ the inversed structure. This, however, is far from being the case, and if anything the reverse is more nearly true. Thus there appears to be a tendency for tri- and quadrivalent ions to prefer 6-co-ordinated sites (except for the ions Fe^{3+} , In^{3+} and Ga^{3+} , which prefer 4-co-ordination) and for the ions Zn^{2+} and Cd^{2+} to show a special preference for 4-co-ordination. We can therefore arrange ions in a series

- Zn²⁺, Cd²⁺
- Fe³⁺, In³⁺, Ga³⁺
- Other divalent ions
- Other trivalent ions
- Quadrivalent ions

such that of the two metal ions in any given spinel the one standing higher in the series will tend to occupy the 4-co-ordinated sites. Thus we should expect the majority of $A^{2+}B_1^{3+}O_4$ spinels (all except those containing Fe^{3+} , In^{3+} or Ga^{3+} ions without Zn^{2+} or Cd^{2+} ions) to have the normal structure and all $A^{2+}B_2^{3+}O_4$ spinels to have the inversed arrangement, as indeed appears to be the case where the structure type is known. As specific examples of the application of this principle we may contrast the structures of the following pairs of compounds

Normal structure	Inversed structure
MgV_2O_4	VMg_2O_4
$MgCr_2O_4$	$MgFe_2O_4$
$ZnFe_2O_4$	$CuFe_2O_4$
$NiCr_2O_4$	$NiIn_2O_4$

8.57. The inclusion of magnetite, Fe_3O_4 , in table 8.09 is of interest. This oxide has the inversed spinel structure, and its relationship to the other spinels is made clear by writing the formula as $Fe^{2+}(Fe^{2+}Fe^{3+})O_4$. It is probable that the semi-conducting properties of magnetite can be attributed to an interchange of electrons between the Fe^{2+} and Fe^{3+} ions in the B sites, and that semi-conductivity in other spinels is associated, as here, with the presence of ions of different valencies in crystallographically equivalent positions.

Of even greater interest is the relationship of the spinels to Al_2O_3 and Fe_2O_3 , for it has long been known that many spinels can take up indefinite quantities of these oxides in solid solution. As normally prepared, Fe_2O_3 exists in the α form with the structure already described (§8.46), but, by the careful oxidation of Fe_3O_4 , a γ form, with an entirely different structure, is obtained. The cubic unit cell of this new structure is of about the same size as that of the spinel structure of Fe_3O_4 , and the arrangement first proposed was one in which the iron ions occupied the same sites as in the spinel with the necessary four additional oxygen ions per unit cell accommodated in interstices in the structure. It was, however, difficult to understand how such large ions as those of oxygen could be introduced into a structure already so closely packed, and it is now recognized that the actual structure must be regarded, not as a spinel structure with an excess of oxygen, but rather as a spinel structure with a cation deficiency. The structure of $\gamma\text{-}Fe_2O_3$ (and of $\gamma\text{-}Al_2O_3$) is one in which 32 oxygen ions per unit cell are arranged exactly as in spinel, with the corresponding number of iron or aluminium ions,

namely $21\frac{1}{2}$, distributed at random over the 24 sites normally occupied by the cations. On the average there are therefore $2\frac{1}{2}$ vacant cation sites per unit cell.

In the light of this structure the conversion of Fe_3O_4 into $\gamma\text{-}Fe_2O_3$ by oxidation is readily understood. The unit cell of Fe_3O_4 contains 8 Fe^{2+} , 16 Fe^{3+} and 32 O^{2-} ions. As oxidation proceeds the oxygen ions are undisturbed but the Fe^{2+} ions are replaced by two-thirds their number of Fe^{3+} ions. Finally, when all eight Fe^{2+} ions have been thus replaced, an extra $5\frac{1}{2}$ Fe^{3+} ions have been introduced and $2\frac{1}{2}$ sites are left vacant. In a similar way we can understand the ready solid solution of Al_2O_3 in the spinels. Starting, say, with $MgAl_2O_4$, the aluminium content may be gradually increased by the substitution of Al^{3+} for Mg^{2+} . In other solid solutions which we shall discuss later electrical neutrality is preserved in such a substitution by another simultaneous substitution elsewhere in the structure, but here it is achieved simply by the appearance of vacant sites in positions which would normally be occupied by cations. When the substitution has been completed just $2\frac{1}{2}$ such sites appear per unit cell and the $\gamma\text{-}Al_2O_3$ structure results.

SOME CHEMICAL CONSIDERATIONS

8.58. In the present chapter we have described the structures of a considerable number of relatively simple compounds, mostly the halides, oxides and sulphides of the metallic elements. It has been convenient to present these structures collectively in this way because many of the principles of structural architecture are illustrated as well by simple structures as by those which are more complex. Some of these principles are discussed more fully in the next chapter, but at this point it is desirable that we should summarize certain of the more important conclusions of the present chapter by a brief review in which the chemical rather than the geometrical significance of the structures is considered.

8.59. In considering the halides, oxides and sulphides of the metallic elements it is important to bear in mind from the start that almost always the non-metallic atoms or ions are far larger than those of the metals. For this reason the greater part of the volume of the structure is occupied by non-metallic atoms, and in many cases, as we have seen, the structure may be described as a close-packed framework of these atoms

with those of the metallic element disposed in its interstices. Often this framework is in itself so stable that it is a matter of relatively little moment which particular metal atoms are present and which particular interstices they occupy. Accordingly, solid solution and variable composition are common. Examples of this among complex oxides have already been given, but one further example of an even simpler compound may be quoted.

The oxide FeO has already been described as a simple ionic compound with the sodium chloride structure, in which, of course, the oxygen ions are arranged as in cubic close packing. It is found, however, that the composition rarely corresponds to the ideal formula, and that much more commonly a considerable excess of oxygen is present, corresponding, say, to an approximate composition $\text{FeO}_{1.10}$. As in the relationship of $\gamma\text{-Fe}_2\text{O}_3$ to Fe_3O_4 , it is impossible to countenance the presence of excess oxygen in a structure already close packed, and a more accurate description is in terms of a deficiency of iron, say $\text{Fe}_{0.9}\text{O}$. The pattern of oxygen sites is as in the ideal structure, but as Fe^{2+} ions are replaced by Fe^{3+} vacant cation sites appear in the structure. Since these sites are randomly arranged their exact number, and accordingly the exact composition, are matters of no significance. The relevance of this to the chemical laws of fixed composition and simple proportions is apparent, and is discussed more fully in the next chapter (§9.35).

8.60. One further question which may be briefly discussed at this point is the relationship of oxides to sulphides. Although oxygen and sulphur are closely related chemically there are, nevertheless, important differences which are reflected in the corresponding structures. In the first place, oxygen is more electronegative than sulphur, and simple ionic structures are therefore far more common in oxides than in sulphides. Thus simple symmetrical ionic structures often occur in oxides of composition AO and AO_2 but in sulphides are found only in the AS_2 compounds of the most electropositive metals; symmetrical AS_4 structures are unknown (see tables 8.02 and 8.05). On the other hand, the sulphides show a range of more complex structures not represented among oxides, and often the sulphide structure is surprisingly complex when that of the corresponding oxide is simple, as, for example, in the pairs of compounds FeO and FeS, MoO_2 and MoS_2 , SiO_2 and SiS_2 , and others. Furthermore, many common sulphides have no counterpart among oxides, and vice versa. Thus FeS_2 is of widespread occurrence as

the minerals pyrites and marcasite but FeO_2 does not exist; PbO_2 is a common oxide whereas PbS_2 is unknown.

At the other extreme, many sulphides show a marked resemblance to intermetallic systems, displaying variation in composition to a much more marked degree than the oxides and having the lustre and electrical conductivity characteristic of such systems. The selenides and tellurides show the same distinctive properties to an even more pronounced degree.