

An example quoted is the transformation of  $\text{Fe}_3\text{O}_4$  to  $\alpha\text{-FeOOH}$ . It has been deduced that this occurs in nature because pseudomorphs of  $\alpha\text{-FeOOH}$  after  $\text{Fe}_3\text{O}_4$  have been found. Many examples of pseudomorphous replacement are known, some of them being relevant to ore minerals. For example maghemite is described<sup>4</sup> as being formed under certain conditions of oxidation from magnetite or from limonite gels (containing goethite) by a process analogous to its synthesis in the laboratory through moderate heating of lepidocrocite. Maghemite is also formed by decomposition of pyrite ( $\text{FeS}_2$ ) by heating it in slightly alkaline aqueous systems under oxidising conditions. It has been suggested that this is due to replacement of sulphur in the pyrite lattice by oxygen, a different type of topotactic transformation. This is dealt with in Sec. 5.3.2.

#### 1.2.4. *Sulphides*

The sulphides of the alkali and alkali earth metals are ionic in character and have structures which resemble those of oxides. Sulphides of other metals have bonds with substantial covalent character and many of them have physical properties which resemble those of alloys rather than salts. They are semiconductors, have a metallic lustre and high reflectivity and, particularly in the case of the transition metal sulphides, many do not have compositions corresponding to the normal valencies of the metals. Examples are  $\text{NiAs}$  and  $\text{Co}_3\text{S}_4$ . Covellite,  $\text{CuS}$ , rather than being  $\text{Cu}^{\text{II}}$  sulphide has a structure in which part of the sulphur has paired to form  $\text{S}_2^{2-}$  ions and the solid is a diamagnetic metallic conductor, copper being present as  $\text{Cu}^+$ .

Description of sulphides in terms of purely ionic models, the ions being considered as charged spheres of a particular radius, can help to predict types of structure and cation substitution likely to occur, as in the case of oxides. However, it provides no information about the electronic structures of the solids or their properties which depend on the behaviour of electrons in them. Although the valence bond approach still provides useful information a major advance in understanding transition metal sulphides took place when crystal field theory was applied to them in the 1960's. Subsequently the molecular orbital and the band theories have been applied. The latter is applicable to multiatomic assemblies in principle but it is difficult to use it quantitatively with crystals having more than a few atoms per unit cell. These aspects of the chemistry of mineral sulphides are of peripheral importance in hydrometallurgy at present, although the position may change as greater theoretical insight is gained. A specialist text is available.<sup>5</sup>

The phase diagrams of many binary metal sulphides are exceedingly complex. In the copper-sulphur system the following exist: (Sec. 5.3.3):  $\text{Cu}_{1.993-2.000}\text{S}$ , chalcocite;  $\text{Cu}_{1.934-1.965}\text{S}$ , djurleite;  $\text{Cu}_{1.79-1.765}\text{S}$ , digenite;  $\text{Cu}_{1.75}\text{S}$ , anilite;  $\text{Cu}_{1+x}\text{S}$  where  $x$  is 0.05–0.10, blaubleidender covellite;  $\text{Cu}_{1.000}\text{S}$ , covellite. In addition three more minerals have been discovered recently: spionkopite,  $\text{Cu}_{1.4}\text{S}$ ; yarrowite,  $\text{Cu}_{1.125}\text{S}$  and geerite,  $\text{Cu}_{1.60}\text{S}$ . All of these solids change to other forms or to phases of other compositions at particular elevated temperatures. The low temperature orthorhombic form of chalcocite,  $a\text{-Cu}_2\text{S}$  has a unit cell containing 96 formula units with  $a = 11.881 \text{ \AA}$ ,  $b = 27.323 \text{ \AA}$  and  $c = 13.491 \text{ \AA}$ . The sulphur atoms are in hexagonal close packing but the exact distribution of the copper atoms in the holes is not known. In some sulphides the metal atoms are in an ordered array, in others they are distributed statistically.

Because the metal-sulphur bonds in many sulphides have significant covalent character, involving electron sharing, a particular metal will be able to form only a limited number of bonds and they will form in specific directions in space relative to one another. The most common arrangements are four bonds directed tetrahedrally and six bonds directed octahedrally. The metal atoms are present in tetrahedral or octahedral holes in the sulphur framework respectively.

More than one metal may be present in a sulphide phase. A number of copper-iron sulphides occur as minerals; the most common is chalcopyrite,  $\text{CuFeS}_2$ , the others being bornite,  $\text{Cu}_5\text{FeS}_4$  and cubanite,  $\text{CuFe}_2\text{S}_3$ . Chalcopyrite has a relatively simple lattice structure based on the zinc blende,  $\text{ZnS}$  and ultimately the diamond lattice. Carbon forms four tetrahedrally arranged covalent bonds; in the diamond crystal each atom is linked to four equidistant neighbours and the linking extends throughout the whole crystal. If alternate carbon atoms are replaced by Zn and S the zinc blende structure results, each zinc atom being surrounded tetrahedrally by four sulphur atoms and each sulphur by four zinc atoms. If the zinc is now replaced by alternate copper and iron atoms the chalcopyrite structure is produced. If this replacement is done using a single unit cell of  $\text{ZnS}$  the crystal of chalcopyrite is not produced by repeating it in three dimensions. The unit produced from one unit cell of  $\text{ZnS}$  must be repeated in one direction to form the unit cell of chalcopyrite. Thus the structure of chalcopyrite is based on a superstructure of  $\text{ZnS}$ , zinc blende. Quaternary compounds with the tetrahedral structure also occur; for example the structure of stannite,  $\text{Cu}_2\text{FeSnS}_4$ , is produced by replacing half of the iron atoms in two unit cells of chalcopyrite by tin.

Metals requiring 6-coordination cannot occur in zinc blende or other tetrahedral structures but are commonly found to assume the nickel arsenide (NiAs) structure. In this, each atom has six nearest neighbours of the other kind but whereas an arsenic atom is surrounded by six nickel atoms at the apices of a trigonal prism the nearest neighbours of a nickel atom are six arsenic atoms arranged octahedrally around it. In addition each nickel atom has two other nickel atoms sufficiently close to be bonded to it. In NiAs there are six arsenic atoms with Ni–As interatomic distances 2.43 Å and two nickel atoms with Ni–Ni distance 2.52 Å. The nickel arsenide structure has the property of being able to take up in solid solution a considerable excess of the transition metal, resembling typical alloys in this respect.

Pyrrhotite, iron (II) sulphide, has the NiAs structure but does not have the stoichiometric composition FeS, being iron deficient in an intact sulphur lattice. These sulphides are considered in Sec. 5.3.2. The structures of pyrite and marcasite (both FeS<sub>2</sub>) are different. They contain discrete S<sub>2</sub><sup>2-</sup> groups in which the sulphur atoms are joined by a covalent bond, the S–S distance being 2.10 Å. The pyrite structure is based on the sodium chloride lattice (face centred cubic) the Fe atoms and the centres of the S<sub>2</sub> groups taking the places of Na and Cl.

The nickel arsenide structure is adopted by many solids of composition MX in which M is a transition metal, particularly a Group VIII metal and X is an element in the late B subgroups, Sn, As, Sb, Bi, S, Se, Te. The pyrite structure is characteristic of solids of composition MX<sub>2</sub> of the same elements. In substances such as arsenopyrite, FeAsS, the lattice has lower symmetry but is still based on the pyrite structure. The marcasite structure is a less symmetrical arrangement of the same structural units, Fe and S<sub>2</sub>, based on the sodium chloride lattice but having lower symmetry. Some special cases occur, however, for example MoS<sub>2</sub> has a layered structure so that like graphite it can be used as a lubricant.