

# STRUCTURAL STABILITY OF MINERALS WITH THE PYRITE, MARCASITE, ARSENOPYRITE AND LÖLLINGITE STRUCTURES

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## ABSTRACT

The structural stabilities of the disulphides, diarsenides and sulpharsenides of iron, cobalt and nickel are explained on the basis of ligand field theory. The structural stabilities can be correlated with the number of non-bonding  $d$  electrons of the metal atom in the structure, and can be explained by the tendency of the compounds to form structures in which maximum electron spin-pairing takes place.

The pyrite structure, which is favoured by metals with six or more non-bonding  $d$  electrons, and which includes pyrite, cattierite, vaesite, cobaltite and gersdorffite, is characterized by metal-sulphur octahedra joined at corners, with no apparent interaction between the  $d$  electrons of neighbouring metal atoms. The other structures are all characterized by shared octahedral edges along one direction, so that the metal atoms are brought into relatively close proximity. In the marcasite structure, which includes marcasite and rammelsbergite, both with six non-bonding  $d$  electrons, the metal atoms repel each other because of completely filled  $t_{2g}$  levels. In the arsenopyrite structure, which includes arsenopyrite and safflorite, both of which have five  $d$  electrons that do not participate in metal-sulphur bonding, pairs of metals are drawn together to permit spin-pairing of the odd electrons. In löllingite, in which the iron atom is assumed to have four non-bonding  $d$  electrons, the  $d$  orbitals in the  $c$  crystallographic direction are emptied, permitting close iron-iron approaches in this direction, as well as complete spin-pairing of the electrons in the two remaining  $t_{2g}$  orbitals.

## INTRODUCTION

The disulphides, diarsenides and sulpharsenides of iron, cobalt and nickel crystallize in structures characterized by "dumb-bells" of closely-bound anion pairs (S-S or As-S), tetrahedral coordination of three cations and one anion around each anion, and octahedral coordination of six anions around each cation. However, there are significant differences between the various structures involved, and it is the purpose of this paper to investigate the relationship between composition and structure of these minerals, and to attempt to arrive at an explanation for this relationship.

## CRYSTAL STRUCTURES

The structures in which these minerals crystallize can be divided into four groups: pyrite, marcasite, arsenopyrite and löllingite, or minor variations thereof (the pararammelsbergite polymorph of  $\text{NiAs}_2$  may be

an exception; its structure has not yet been reported). The significant feature of these structures, for the purpose of this paper, is the manner in which the octahedra (comprising one metal atom surrounded by six anions) are combined, and consequently the opportunities for metal-metal interaction.

In the pyrite structure (Bragg 1913), the octahedra share only corners (Figure 1a), which results in the metals being too far apart from each other for a significant degree of interaction. In pyrite, itself, the nearest Fe-Fe distance is 3.82 Å. This is considerably in excess of the critical separation required for direct Fe-Fe interaction in a sulphide lattice, which is given by Goodenough (1963, p. 284) as 2.9 to 3.1 Å. The inter-metallic distances in the other pyrite-type minerals are somewhat greater than that in pyrite (Table 3).

In the structures of marcasite, arsenopyrite and löllingite, the octahedra share edges lying in the 001 plane; as a consequence of this, the inter-metallic distances across the shared edge are reduced, which provides a greater possibility for direct metal-metal interaction in a direction parallel to the *c* crystallographic axis. Despite the similarity between these three structures, there are relatively minor differences that nevertheless appear to be of some significance: compared to marcasite (Buerger 1931), löllingite has an appreciably compressed *c* axis (Buerger 1937), and in arsenopyrite\* (Buerger 1936), the metal atoms are displaced along the *c* axis in such a way that short metal-metal distances alternate with longer ones; i.e., the metals come together in pairs. These structural features are shown in Figure 1.

#### ELECTRON CONFIGURATIONS

The iron, cobalt and nickel atoms have the electron distributions shown in Table 1. As can be seen, these atoms are distinguished by the number of electrons contained in the 3*d* sub-shell.

In FeS<sub>2</sub>, consideration of either ionic or covalent bonding models leads to the conclusion that the six *d* electrons of iron do not participate in metal-sulphur bonding (Pearson 1965). The same arguments lead to the non-participation of the *d* electrons of cobalt and nickel in CoS<sub>2</sub> or NiS<sub>2</sub>. However, replacement of a sulphur atom by arsenic, as in FeAsS, results in a deficit of one electron per formula unit (arsenic, a group V element, has one less bonding electron than sulphur, a group

\*Strictly speaking, the arsenopyrite structure is also characterized by ordering of the arsenic and sulphur, and the disordered form is more correctly referred to as the CoSb<sub>2</sub> type (Zhdanov & Kuz'min 1962). However, for the sake of simplicity, the term "arsenopyrite structure" will be used throughout this paper to indicate both ordered and disordered forms.

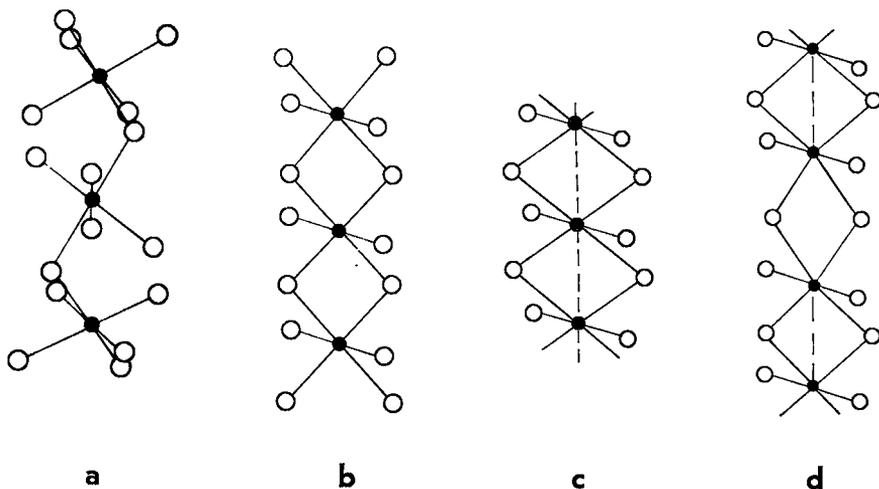


FIG. 1. Combination of octahedra in (a) pyrite, (b) marcasite, (c) löllingite, and (d) arsenopyrite. Metal atoms are solid circles; anions, open.

TABLE 1. THE ELECTRON DISTRIBUTION IN THE SUB-SHELLS OF THE IRON, COBALT AND NICKEL ATOMS

	1s	2s	2p	3s	3p	3d	4s	Total = At. No.
Fe	2	2	6	2	6	6	2	26
Co	2	2	6	2	6	7	2	27
Ni	2	2	6	2	6	8	2	28

VI element). If electron-pair bonds between the cations and anions are to be maintained, then this deficit must be made up by an electron from the metal atom, thereby reducing the complement of  $d$  electrons by one. Replacement of both sulphur atoms by arsenic, as in the case of  $\text{FeAs}_2$ , requires two electrons from the metal. The number of unbonded  $d$  electrons for iron, cobalt and nickel when combined with the various anions, is shown in Table 2.

Ligand field theory has shed considerable light on the effect of the ligand environment on the behaviour of the  $d$  electrons of transition elements (e.g. Orgel 1960; Graddon 1961). One of the concepts deriving from this theory is that in an octahedral environment, the  $d$ -electron sub-shell of the transition-metal atom is split into two levels, the one of lower energy ( $t_{2g}$ ) containing three orbitals, and the one of higher energy, ( $e_g$ ) two. If the energy difference between these two levels is small, this splitting will have no appreciable effect on the electron distribution, and the electrons can be put into the five available orbitals one at a time,

TABLE 2. THE NUMBER OF NON-BONDING *d*-ELECTRONS IN THE VARIOUS COMPOUNDS

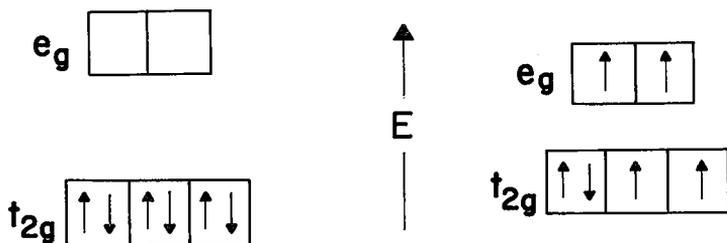
	S <sub>2</sub>	AsS	As <sub>2</sub>
Fe	6	5	4
Co	7	6	5
Ni	8	7	6

with the electron spins parallel (as required by Hund's rule), and with no spin pairing until each orbital contains one electron. This is called the high-spin state. If the energy difference between the two levels is sufficiently large, the electrons in the lower ( $t_{2g}$ ) level will be spin-paired before any electrons are introduced into the higher level ( $e_g$ ); this is called a low-spin state. The two possibilities for iron in an octahedral ligand environment are shown in Figure 2.

The two possible configurations for the same atom, shown in Figure 2, have important magnetic consequences. The high-spin state will have a paramagnetic susceptibility corresponding to four unpaired electron spins, whereas the low-spin state will have zero paramagnetic susceptibility.

Applying this to pyrite, we find that pyrite has a magnetic moment close to zero (Serres 1953; Benoit 1955) which indicates that the iron is in the low-spin state (Figure 2a). This, in turn, implies a relatively large energy separation between the  $e_g$  and  $t_{2g}$  levels and, therefore, a strong ligand field.

The magnetic susceptibility of marcasite (Serres 1953) also indicates almost complete spin-pairing. However, in marcasite, the octahedral edges are shared, (Figure 1b), providing the possibility for interaction between adjacent iron atoms along the  $c$  axis, particularly since the iron



### a) Strong Ligand Field

### b) Weak Ligand Field

FIG. 2. Diagrammatic representation of the distribution of six *d* electrons in (a) low-spin and (b) high-spin states. The small arrows represent directions of electron spin. E signifies the direction of increasing energy.

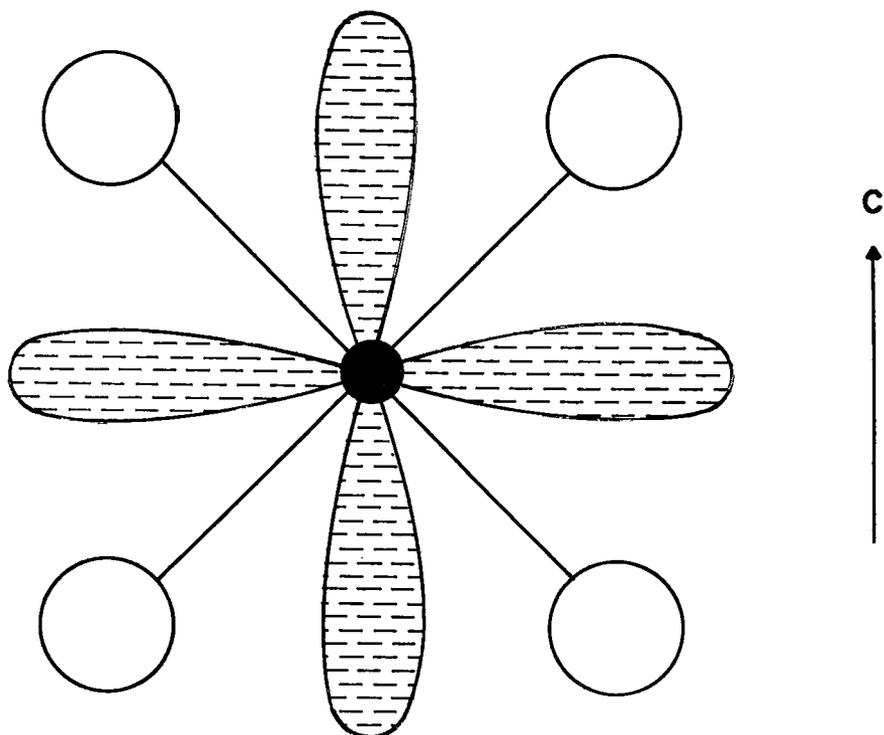


FIG. 3. A highly diagrammatic section of an iron-sulphur octahedron parallel to the *c* axis showing the disposition of the one set of *d* orbitals (shaded).

atoms across the shared edge are precisely in the direction of one of the *d* orbitals (Figure 3). The distance between these iron atoms is equivalent to the length of the unit cell, 3.38 Å, which is significantly greater than the critical distance for Fe-Fe interaction. Furthermore, the angle subtending the shared octahedral edge is 82°, which is appreciably less than the ideal octahedral angle of 90°. This implies mutual repulsion of the iron atoms, rather than attraction (Figure 4). This can be attributed to the mutual repulsion of the filled *d* electron clouds representing the *d* orbital directed along the *c* axis.

In FeAs<sub>2</sub>, there are four unbonded *d* electrons. These electrons cannot achieve complete spin-pairing if they are placed into the three *t<sub>2g</sub>* orbitals. Full spin-pairing, however, can be attained if the total number of available orbitals is reduced from three to two. This can be done if it is assumed that the one orbital is emptied of its electrons, and the four electrons are restricted to the remaining two (Goodenough 1960; Pearson 1965). The most likely orbital to be emptied is the one parallel to the *c* axis, since it

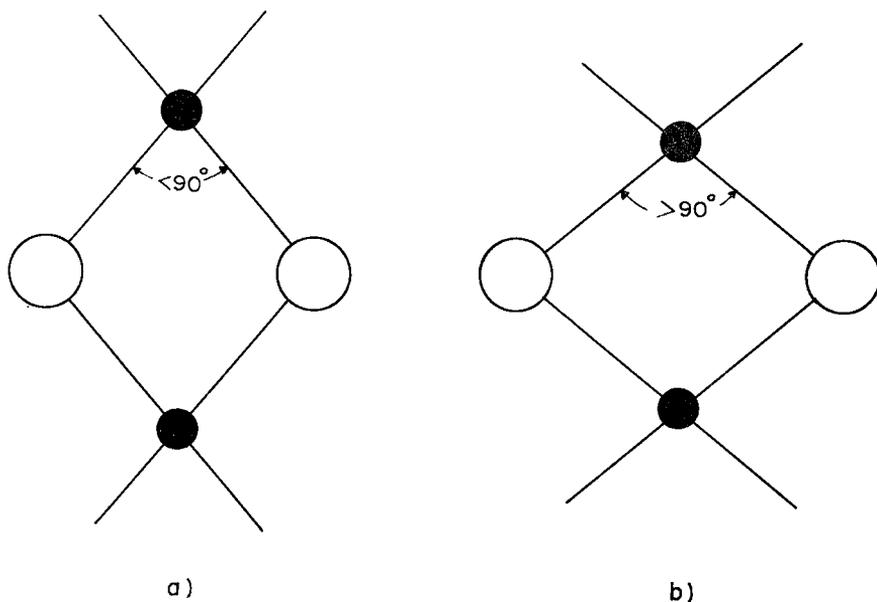


FIG. 4. The effect of (a) repulsion, and (b) attraction of metal atoms across the shared octahedral edge.

is the unique orbital. Under these conditions, the electron clouds of the  $d$  orbitals of adjoining iron atoms would no longer repel each other, as in the case of marcasite, and the iron atoms could therefore approach each other relatively closely. This results in a contraction along the  $c$  axis, for which Pearson (1965) has proposed the term "compressed marcasite", but which will here be called the löllingite structure (Buerger 1932). This compression leads to a short Fe-Fe distance (2.85 Å) in löllingite, and an octahedral angle subtending the shared edge of  $106^\circ$  instead of the ideal  $90^\circ$ . This interpretation of the complete spin-pairing of the four  $d$  electrons is supported by magnetic measurements, which indicate a very low magnetic moment for the iron in löllingite (Wintenberger, 1962).

In FeAsS, the iron atom has five unbonded  $d$  electrons (Table 2), which cannot be fully paired in the three  $t_{2g}$  orbitals. It has been pointed out (Goodenough 1960; Hulliger & Mooser 1965; and Pearson 1965) that spin-pairing can be achieved if the unpaired electron in one of the  $t_{2g}$  orbitals of the one atom is paired with the unpaired electron of the adjacent metal atom across the octahedral edge (Figure 5). To facilitate this pairing (or as a consequence of it), the metal atoms involved move toward each other. This results in the pairing of iron atoms along the  $c$  axis, leading to alternating short (2.89 Å) and long (3.53 Å) distances

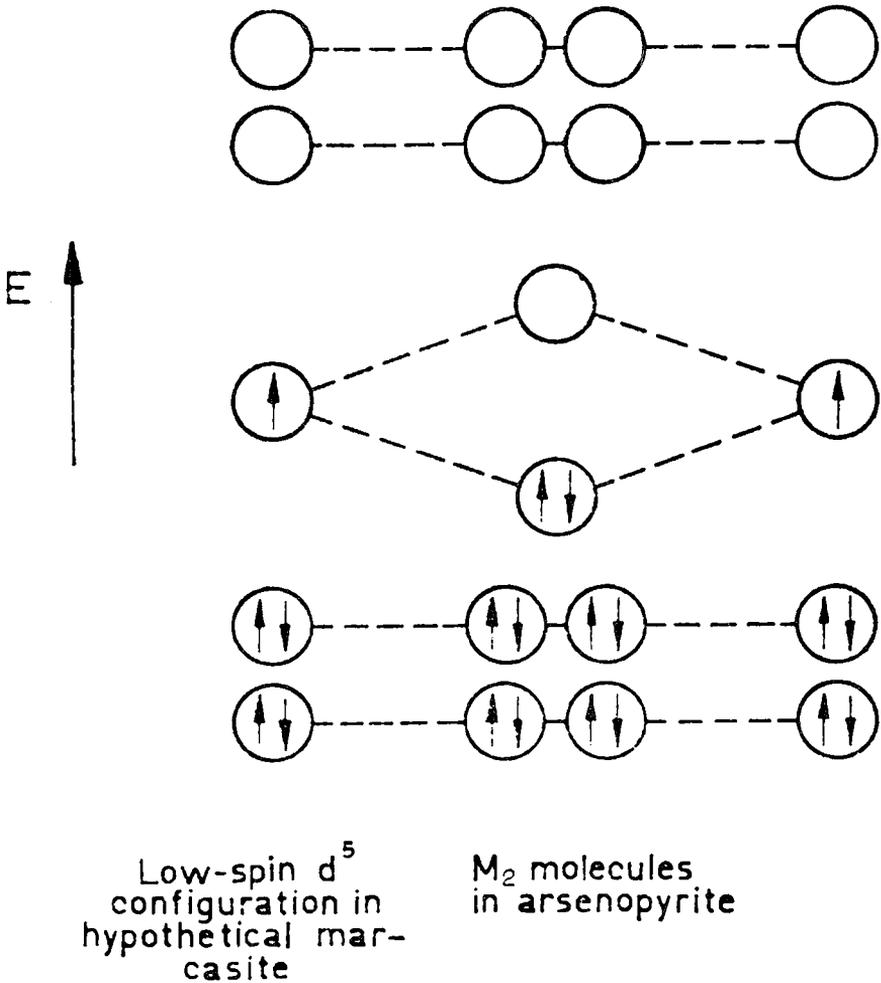


FIG. 5. Schematic representation of the occupation of the cation  $d$  levels in arsenopyrite (from Hulliger & Mooser 1965). The columns at the extreme left and right portions of the diagram represent the electron distributions of  $d^5$  cations (e.g. Fe in FeAsS) in the hypothetical case of no interaction between the electrons of adjacent cations. The central portion of the diagram represents the actual case in arsenopyrite, where the odd electrons of the two adjacent  $d^5$  cations are spin-paired, resulting in a decrease in energy.

between the iron atoms in the arsenopyrite structure. The magnetic evidence (Wintenberger 1962), which indicates zero magnetic moment, supports this concept.

The cobalt and nickel compounds can be considered within a similar theoretical framework. CoAsS and NiAs<sub>2</sub> are isoelectronic with FeS<sub>2</sub>

(i.e. six non-bonding electrons—see Table 2) and should therefore crystallize in the pyrite or marcasite structure. CoAsS has a modified pyrite structure as the mineral cobaltite (Giese & Kerr, 1965), and NiAs<sub>2</sub>, as rammelsbergite, has the marcasite structure (Kaiman, 1946). Both minerals have very low magnetic susceptibilities, as expected (Wintenberger 1962; Bennett & Heyding 1966).

CoAs<sub>2</sub> is isoelectronic with FeAsS (5 non-bonding *d* electrons) and should therefore crystallize in the arsenopyrite structure with spin-pairing of the odd electrons. Recent studies have shown that CoAs<sub>2</sub> has the arsenopyrite structure (Darmon & Wintenberger 1966), and magnetic measurements (Bennett & Heyding 1966) confirm the spin-pairing.

Up to this point all the compounds discussed have metals with six or less non-bonding electrons. This leaves the 7- and 8-electron compounds: CoS<sub>2</sub> and NiAsS with 7, and NiS<sub>2</sub> with 8 (Table 2), all of which crystallize in the pyrite or a closely related structure (Kerr 1945; Bayliss & Stephenson 1967; Peacock & Henry 1948.) In the low-spin state, the *t*<sub>2g</sub> orbitals are completely filled with paired electrons, which would appear to render the arsenopyrite and löllingite structures impossible. The electrons in excess of six (one in the case of CoS<sub>2</sub> and NiAsS, and two in the case of NiS<sub>2</sub>) must of necessity go into the two *e*<sub>g</sub> orbitals with their spins unpaired. Magnetic evidence (Benoit 1955; Hulliger 1959) tends to support this, although Miédan-Gros *et al* (1963) reported zero magnetic moment for NiAsS; the discrepancy between this value and Hulliger's needs to be resolved.

The reason for these 7- and 8-electron compounds favouring the pyrite structure over that of marcasite may be attributed to the repulsive effect of the electrons in the so-called anti-bonding *e*<sub>g</sub> orbitals on the metal-sulphur bonds. As pointed out by Elliott (1960), the occupation of these orbitals leads to a progressive expansion of the unit cell from FeS<sub>2</sub> through CoS<sub>2</sub> to NiS<sub>2</sub>, and a resulting increase in the metal-sulphur distances. This effect appears to be responsible for the instability of the marcasite structure relative to the pyrite structure.

### CONCLUSIONS

The structural stabilities of the disulphides, diarsenides and sulphar-senides of iron, cobalt and nickel can be explained by the tendency of these compounds to crystallize in structures that permit the maximum spin-pairing of the non-bonding electrons of the 3*d* sub-shell of the metals. In the pyrite and marcasite structures this can be done by complete occupancy of the *t*<sub>2g</sub> level; in the arsenopyrite structure, by pairing of the odd electrons on adjacent metal atoms; and, in the löllingite structure, by emptying one of the *t*<sub>2g</sub> orbitals.

The metal-to-metal distances and the angles subtending the shared octahedral edges for all the minerals discussed are compiled in Table 3. In the pyrite structure there is no sharing of octahedral edges, and all the minerals with this structure have long metal-metal separations, virtually eliminating the possibility of interaction. In minerals with the marcasite structure there is sharing of octahedral edges, but the subtending angles are less than  $90^\circ$ , which indicates metal-metal repulsion across the edges; the metal-metal distances, though less than in pyrite, nevertheless also

TABLE 3. COMPILATION OF METAL-METAL DISTANCES AND OF ANGLES SUBTENDING THE SHARED OCTAHEDRAL EDGES IN THE MINERALS DISCUSSED

Structural Type and Compound	Metal-Metal Distance (Å)	Angle Subtending the Shared Octahedral Edge	References to Cell Parameters
<i>Pyrite</i>			
FeS <sub>2</sub>	3.82	—	Elliot (1960)
CoS <sub>2</sub>	3.90	—	"
NiS <sub>2</sub>	4.01	—	"
CoAsS	3.99	—	Giese, Kerr (1965)
NiAsS	4.02	—	Bayliss & Stephenson (1967)
<i>Marcasite</i>			
FeS <sub>2</sub>	3.38	82°	Buerger (1937)
NiAs <sub>2</sub>	3.53	83°	Kaiman (1947)
<i>Löllingite</i>			
FeAs <sub>2</sub>	2.85	106°	Buerger (1932)
<i>Arsenopyrite</i>			
FeAsS	2.89	99°	Buerger (1936)
	3.53	82°	
CoAs <sub>2</sub>	2.78	106°	Darmon &
	3.47	88°	Wintenberger (1966)

appear to be too great for interaction. In löllingite, the large subtending angle and short intermetallic distance signifies interaction between adjoining metal atoms. In arsenopyrite, short distances and large angles alternate with long distances and small angles, which results from the coupling of metal atoms into pairs.

Brief mention should be made of mineral hauerite, MnS<sub>2</sub>, which has the pyrite structure. It does not fit into the scheme developed here because the manganese atom in hauerite is in a high-spin state (five electrons with parallel spins), whereas iron, cobalt, and nickel are all in the low-spin state in the compounds discussed. This can be attributed to the relatively high pairing energy and low orbital-separation energy of the Mn<sup>+2</sup> ion relative to those of the other transition metal ions (Graddon 1961, p. 29). As a result of this, there is no pronounced tendency for manganese sulphide to crystallize in those modifications that appear to be stabilized by a high degree of electron spin-pairing.

A question that has gone unanswered is why the marcasite structure is stable in spite of the fact that the apparent repulsion of metal atoms across the shared octahedral edge would be expected to oppose edge sharing, and thereby reduce the stability of the structure. Pearson (1965) has suggested the possibility of a complex bonding scheme in which second-nearest-neighbour sulphur atoms contribute to the bonding. A preliminary examination of the structures of sulphides and arsenides characterized by anion "dumb-bells" indicates a tendency for the "dumb-bells" to line up with adjoining ones to form rectangles or squares. This has been noted in skutterudite ( $\text{CoAs}_8$ ), patronite ( $\text{VS}_4$ ), marcasite, löllingite and arsenopyrite. In the latter three structures, the anion pairs lie in the  $a$ - $b$  plane and are aligned so as to form a ladder-like arrangement parallel to the  $c$  axis, which is achieved by sharing octahedral edges. It is tempting to postulate that there is an over-all tendency for all the minerals discussed in this paper to have structures in which the "dumb-bells" are joined in this fashion. Where this tendency is promoted by the electronic configuration of the cations (löllingite and arsenopyrite), the "dumb-bells" are drawn more closely together and the structure is compressed along the  $c$  axis. Where this tendency is opposed by the electronic configuration of the cations, the structure is expanded along the  $c$  axis (marcasite) or, in extreme cases, the "dumb-bell" pairing breaks down completely (pyrite structure).  $\text{FeS}_2$  appears to represent the marginal case in which there is a very small energy difference between the pyrite and marcasite structures, both being stable at room temperature.

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