

On the Relationships between the Structure Types Pyrite, Marcasite, and Arsenopyrite

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The pyrite, marcasite, and arsenopyrite structure types are subjected to a comparative study. The difference between the pyrite and marcasite type is substantial and concerns mainly the arrangement of the characteristic pairs of non-metal atoms, whereas that between the marcasite and arsenopyrite types is relatively small. A hypothetical mechanism for the transformation from pyrite to marcasite type structure is suggested on the basis of a postulated reorientation of half of the non-metal pairs in the pyrite lattice. This *pair reorientation model* explains the axial proportions of one of the classes of marcasites (class A; specified by the average axial ratios $c/a=0.547$, $c/b=0.482$) as being essentially a consequence of the packing of the non-metal pairs. Circumstantial evidence is presented for the impossibility of obtaining completely regular coordination polyhedra in the structure types pyrite, marcasite, and arsenopyrite, while retaining the implied composition, coordination numbers, and pairing of the non-metal atoms.

In dealing with crystalline solids, the intrinsic relationships between various structure types are often used to correlate structural dependent properties of groups of compounds, with the ultimate purpose of gaining improved insight on the chemical bonding.

Pyrite and marcasite are closely related structure types, since both show:

- (1) the composition TX_2^* (in the nominal case),
- (2) octahedral coordination of $6X$ -atoms around each T -atom,
- (3) tetrahedral coordination of $1X$ - and $3T$ -atoms around each X -atom, and thus,
- (4) characteristic $X-X$ pairs.

These four features ** are also common to two additional structure types of related compounds, *viz.* arsenopyrite ($FeAsS$; binary prototype $CoSb_2$) and the

* Throughout this paper the symbols T and X are used to denote the metal and non-metal atoms, respectively.

** The points 1 to 4 are not independent requirements, since any three of them imply the fourth, provided the terms octahedral and tetrahedral coordination are substituted by the corresponding coordination numbers of 6 and 4, respectively.

recently reported¹ α -NiAs₂ (the proper prototype being AuSn₂²). Other closely related structure types are obtained on relinquishing one or more of the above characteristics.

The basic pyrite and marcasite type structures are also found in connection with compounds which deviate from the implied stoichiometry, *i.e.* those defect forms in which vacancies are statistically distributed in the metal sub-lattice. It is superfluous to distinguish between the ideal and defect forms as separate structure types, whereas an ordered distribution of vacancies in the metal sub-lattice of the pyrite type structure produces such distinctive types as Rh₃Se₈³ and IrSe₃⁴ which, however, will not be considered here.

If the requirement of octahedral coordination around *T* (point 2) is removed, the structure type PdS₂⁵ is obtained, for example, whereas abandonment of tetrahedral coordination around *X* or the *X*–*X* pair configuration (points 3 and 4), for example, leads to the structure types Cd(OH)₂ (or distorted forms of it, *e.g.*, NbTe₂,⁶ β -MoTe₂,⁷ WTe₂,⁷ and ReSe₂⁸) and IrSe₂.⁹ Such structure types will not be considered further in this paper, however.

In none of the compounds with the pyrite, marcasite, and arsenopyrite types of structure are regular coordination octahedra or tetrahedra observed, and their deviations from regularity increase, broadly speaking, in the above sequence. The fact that the coordination polyhedra of the relevant compounds are irregular is not conditional on their actual unit cell dimensions and positional parameters. The symmetries of the structure types are on the contrary incompatible with completely regular coordination polyhedra while retaining the requirements 1–4 (*vide supra*).

It is, however, reasonable to modify the requirement of complete regularity for the tetrahedron surrounding *X* so as to allow the *X*–*X* bond distance to become different from the three *T*–*X* bond distances, while retaining the ideal value of (\sim) 109.47° for the six tetrahedral angles. Even this restriction on the regularity of the tetrahedron is insufficient to obtain a completely regular octahedron in the three structure types.

A general proof could probably be furnished of the impossibility of realizing a crystal structure with completely regular octahedra and the last-mentioned type of (regular) tetrahedra while also retaining the requirements 1–4. This assumption seems chemically plausible since the total influence of the surroundings on a completely regular coordination polyhedron must be subject to the same symmetry requirements (with respect to its centre) as applies to the polyhedron itself. In the contrary case, the polyhedron becomes deformed and the structure will accordingly represent a compromise between the opposing tendencies.

Regarding the structure types in question, a regular octahedron around *T* would, for example, require that a given *T*–*X* bond direction is a fourfold axis, whereas the requirements 1–4 imply that this bond direction must at the same time be one of the axes in the tetrahedron (*i.e.* a threefold axis when the coordination is completely regular). These symmetry requirements are mutually incompatible, and the observed reductions in their symmetries are accordingly consistent with the above deductions. Hence, for the structure types of present interest the causes of the deviations from regularity of the coordination polyhedra must be related primarily to the fact that they show the above

features 1–4. A discussion of the cause of the irregularity which is limited only to the one kind of polyhedron, without taking into account the other, appears therefore to be inadequate.

RELATIONSHIPS BETWEEN THE STRUCTURE TYPES

A comparison of the crystallographic data for the binary compounds having the pyrite, marcasite, and arsenopyrite type structures (*cf.* Refs. 10–16) shows very clearly the expediency of dividing the marcasite family into two classes according to the axial proportions * of the unit cell:

class A; specified by $c/a = 0.547$, $c/b = 0.482$

class B; specified by $c/a = 0.744$, $c/b = 0.619$

(The figures represent average values for all known members of each class.)

Class A consists of binary and ternary compounds whose T atoms have an outer configuration of localized non-bonding electrons, d^j , where $0 \leq j \leq 4$, whereas class B is found only for binary compounds with configurations corresponding to $6 \leq j \leq 9(10)$. For ternary phases with formal d^j configurations within the range $4 < j < 6$, the observed proportions of the unit cells justify the distinction of a third transitional class, which is accordingly designated as A/B. The structural data for the binary compounds with the arsenopyrite type structure (formal d^5 configuration, *cf.* the succeeding paper¹⁵) show also the most important characteristics of class A/B.

In order to understand the origin of the classes A, A/B, and B it is firstly convenient to render an account of structural similarities and differences between pyrite, marcasite, and arsenopyrite. In addition to the above mentioned alike coordinations around the T - and X -atoms in pyrite and marcasite, the two structure types show virtually identical atomic arrangements in the plane (001) in pyrite and the diagonal plane ($\bar{1}01$) in marcasite. The dimensions of these planes are furthermore found to be approximately equal in those cases where both structure types are formed by one and the same compound (*cf.* Ref. 15). The unit cell of pyrite is shown in Fig. 1 and that of marcasite (shaded) has been added in such a way that the planes in question coincide. (The positions of the atoms are not indicated on the diagram for reasons of clarity. While inspecting Fig. 1, the reader is strongly recommended to examine models of the structure types in order to facilitate the understanding of the following text.)

While the atomic arrangement is virtually identical in the planes mentioned above, it differs in those which correspond to (002) in pyrite, since the $X-X$ pairs here point in different directions in space in the two structure types. In pyrite, these $X-X$ pairs (with centres of gravity in $0, 0, \frac{1}{2}$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) are parallel to (0 $\bar{1}$ 1) and oriented alternately parallel to each of the two body-diagonals which lie in this diagonal plane. When the two structures are joined as in Fig. 1, the corresponding pairs in marcasite lie, on the contrary, approximately

* A more cumbersome scheme (based on the angle between [101] and [10 $\bar{1}$]), suggested by Johnston *et al.*,¹⁶ leads to an equivalent classification of the compounds with the marcasite type structure.

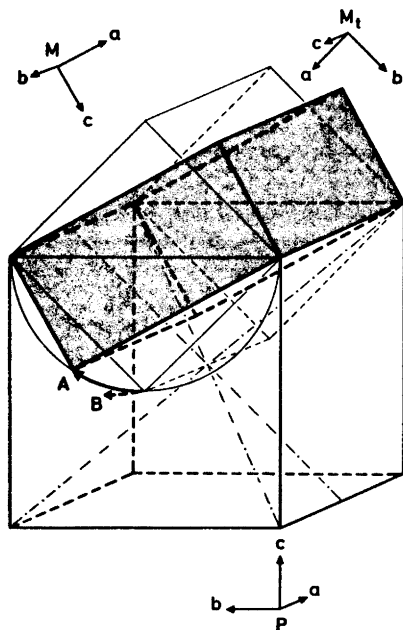


Fig. 1. A hypothetical transformation route from the unit cell of pyrite (P) to that of marcasite (M). A postulated, intermediate tetragonal cell (M_t) is indicated by the thin lines. The points A and B show the relationship between M_t and the classes A and B of the marcasite family.

parallel to (011) of pyrite, *viz.* the diagonal plane which is perpendicular to the above (0 $\bar{1}$ 1).

If such a transformation of the pyrite cell was performed, so that the $X-X$ pairs in (002) changed their direction without displacing their centres of gravity, thus producing a structure in which all pairs become parallel to (011) and alternately parallel to each of the two body-diagonals contained in this plane; then a tetragonal unit cell would be obtained. This tetragonal cell is indicated in Fig. 1 by thin lines and denoted M_t . According to the coordinate systems which are used in the diagram, the equations for transformation of the axes are: $\mathbf{a}_{M_t} = \frac{1}{2}(\mathbf{b}_P - \mathbf{c}_P)$; $\mathbf{b}_{M_t} = \frac{1}{2}(-\mathbf{b}_P - \mathbf{c}_P)$; $\mathbf{c}_{M_t} = -\mathbf{a}_P$, where the index P refers to the pyrite cell.

The further transformation from the tetragonal cell to the orthorhombic marcasite cell may be imagined to take place by changes in length and direction of the axes while retaining the right angles (*e.g.* as indicated in Fig. 1), adjustments of the locations of the T -atoms as well as of the $X-X$ pairs being required during this process.

The above geometrical description of the pyrite-marcasite transformation does not take into account the breaking and establishment of bonds which necessarily must accompany a real structural transformation. The largest difference between the atomic arrangements in the two structure types concerns the fact that the coordination octahedra share corners only in pyrite, whereas in marcasite they have both corners and edges* in common.

* Pauling¹⁷ has incorrectly attributed shared octahedral faces to the marcasite type structure. This mistake has apparently been transmitted to other books on inorganic chemistry (see *e.g.* Phillips and Williams¹⁸).

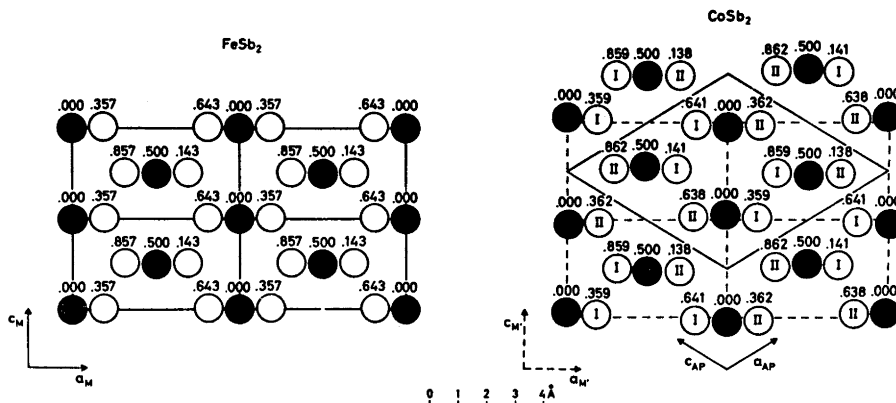


Fig. 2. The relationship between the structure types marcasite (M) and arsenopyrite (AP) illustrated by projections along [010] of the structures FeSb_2 and CoSb_2 . The lengths of the projection axes are respectively 6.5376(5) and 6.3879(4) Å. (Data taken from Refs. 19–21.) The true unit cells are represented by full lines whereas the pseudo-marcasite variant (M') of the arsenopyrite cell is indicated by broken lines.

The structure types marcasite and arsenopyrite are more closely related, as indicated for the binary examples FeSb_2 and CoSb_2 in Fig. 2. The relationship between the axes of the two structure types are nominally governed by the equations: $\mathbf{a}_{\text{AP}} = \mathbf{a}_{\text{M}} + \mathbf{c}_{\text{M}}$; $\mathbf{b}_{\text{AP}} = \mathbf{b}_{\text{M}}$; $\mathbf{c}_{\text{AP}} = -\mathbf{a}_{\text{M}} + \mathbf{c}_{\text{M}}$, where the indices M and AP refer to marcasite and arsenopyrite, respectively. For many purposes it is convenient to consider a pseudo-marcasite variant (M') of the arsenopyrite cell (see Fig. 2) defined by: $\mathbf{a}_{M'} = \frac{1}{2}(\mathbf{a}_{\text{AP}} - \mathbf{c}_{\text{AP}})$; $\mathbf{b}_{M'} = \mathbf{b}_{\text{AP}}$; $\mathbf{c}_{M'} = \frac{1}{2}(\mathbf{a}_{\text{AP}} + \mathbf{c}_{\text{AP}})$ in relation to the true unit cell of arsenopyrite. The monoclinic angle between $\mathbf{a}_{M'}$ and $\mathbf{c}_{M'}$ is approximately 90° (among the binary compounds with the arsenopyrite type structure this angle is found²¹ to range between 90.35° in CoSb_2 and 91.11° in IrP_2).

The marcasite type structure is completely described by the dimensions of the three axes and three (or two) positional parameters,^{19,22} whereas that of arsenopyrite requires knowledge of three axes, one angle, and the specification of nine positional parameters.²¹ The most important adjustment to the structure by a transition from marcasite to arsenopyrite (*cf.* Fig. 2) concerns the movement of the *T*-atoms along \mathbf{c}_{M} ($\mathbf{c}_{M'}$). These displacements of the *T*-atoms (*i.e.* relative to the marcasite type structure) produce alternately shorter and longer *T*–*T* distances in the direction just mentioned and consequently give the arsenopyrite type structure the distinct feature of having *T*–*T* pairs. Associated with this pair-formation the two *X*–*T*–*X* angles with “bisecting”-line along $\mathbf{c}_{M'}$ (equal in the marcasite type structure described according to space group $Pn\bar{m}$) become distinctly different. (One of them becomes considerably larger than 90° (as in the class A marcasites¹⁹), whereas the other becomes less than 90° (as in the class B marcasites²²).

An imagined transition from pyrite to marcasite must be characterized as being fairly radical, whereas the alterations associated with a transformation from marcasite to arsenopyrite are relatively small and are, for example, realized gradually in ternary phases by successive substitution.

A HYPOTHETICAL MODEL FOR TRANSFORMING
BETWEEN THE PYRITE AND MARCASITE TYPE STRUCTURES

Interatomic bond distances vary for a given combination of atoms *inter alia* with the coordination numbers (see, *e.g.*, Ref. 17) and the configuration of localized unpaired electrons.²³ When two or more modifications of a compound are known, and the above parameters are unchanged within these modifications, then the bonding interatomic distances will be retained approximately constant. These conditions are clearly satisfied for those compounds which take both the pyrite and marcasite type structures (*cf.* Ref. 15).

The symmetry of the pyrite type structure implies that each and all interatomic distances (and angles) are fixed when the lattice constant a_p and the positional parameter x are known.

The relations:

$$(X - X)_p = a_p \sqrt{3} (1 - 2x) = D \quad (1)$$

and

$$(T - X)_p = a_p \sqrt{3x^2 - 2x + \frac{1}{2}} \quad (2)$$

apply to the bonding interatomic distances.

The assumption that the bond distances are approximately equal in the pyrite and marcasite modifications of a given compound can be utilized for a more quantitative description of the imagined transition between the structure types.

The unit cell dimensions increase approximately linearly with increasing size of the X -atoms (*e.g.* expressed by the bond distance within the $X-X$ pairs) for the homologous series of pyrites as well as of marcasites. Since the size of the X -atoms evidently has a commanding influence on the unit cell dimensions it is reasonable to assume that the difference in the means of packing of the $X-X$ pairs (see the preceding section) will determine distances between neighbouring $X-X$ pairs in relevant directions in the two structure types.

The straight line through the points $\frac{1}{2}, 0, 0$ and $\frac{1}{2}, 1, 1$ in the pyrite cell (Fig. 1) joins the centres of three neighbouring $X-X$ pairs. A hypothetical transformation from pyrite to marcasite implies for example that the $X-X$ pair with centre in $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ must be turned around from its original orientation along the body-diagonal $[111]$ to $[\bar{1}\bar{1}\bar{1}]$. (The other $X-X$ pairs in (002) of the pyrite cell must analogously be turned around to become parallel to (011) . Since the $X-X$ pair is non-spherical, this reorientation will introduce a shortening of the distance between the neighbouring $X-X$ pairs.

The relative magnitude of this shortening will depend upon the actual geometrical shape of the $X-X$ pair.

It is assumed here that the pair has the shape of a short sausage, *viz.* a cylinder with both diameter and length D (the interatomic $X-X$ pair distance) which is terminated by two additional hemispheres, so that the total length of the body becomes $2D$. This approximation is considered to be adequate because of the present incomplete knowledge of the shape which should be attributed to such an $X-X$ pair. Wahl²⁴ has recently presented a calculation of (total) electron density curves for some di-atomic molecules which

shows that their shape will depend strongly upon the electron density at which the surface is being defined. If for example the O_2 -molecule is ascribed a length which is twice the $O-O$ distance, the contour curves of Wahl would give a body with approximately the above sausage shape.

The situation will be even more complicated in the actual structures since each $X-X$ pair is bonded to six T -atoms. These circumstances will be equal in the pyrite and marcasite type structures, however, and the shape of the pair may accordingly be apprehended as approximately unchanged during the reorientation process. Along the line connecting $\frac{1}{2}, 0, 0$ and $\frac{1}{2}, 1, 1$ (Fig. 1) the $X-X$ pair with centre in $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ (still by way of example) will in the pyrite type structure have an extension of $\sim 2D$. After the reorientation it will occupy a space of $\sim D$ along the same line. The shortening along the connecting line is accordingly $\sim D$.*

The connecting line originally has the length $a_p \sqrt{2}$, and it will constitute twice the c -axis of the marcasite cell after the shortening and the displacement indicated by arrows in Fig. 1, *i.e.*:

$$2c_M \approx a_p \sqrt{2} - D \quad (3)$$

It was pointed out previously that the diagonal plane ($\bar{1}01$) of the marcasite type structure is approximately square, and that it carries the same atomic arrangement as (001) in the pyrite type structure.

The $T-X-X-T$ chains, which are located along the edges of these planes, may be assumed to undergo minor alterations during the hypothetical transformation from pyrite to marcasite type structure. This may be formulated by the equations:

$$b_M \approx a_p \quad (4)$$

$$\sqrt{a_M^2 + c_M^2} \approx a_p \quad (5)$$

Substitution of eqns. 1 and 4 into 3 gives:

$$\begin{aligned} 2c_M &\approx b_M \sqrt{2} - b_M \sqrt{3}(1-2x) \\ c_M/b_M &\approx \frac{1}{2}\sqrt{2} - \frac{1}{2}\sqrt{3}(1-2x) \end{aligned} \quad (6)$$

From eqns. 4 and 5 follows:

$$c_M/a_M = \frac{c_M/b_M}{[1 - (c_M/b_M)^2]^{\frac{1}{2}}} \quad (7)$$

* The shortening should be found, more precisely, as the difference between the extensions of the projections of the body onto the connecting line before and after the reorientation, but these projections would be very strongly dependent on the shape of the pair unit. The length-axis of the body is turned $\sim 70.5^\circ$ ($2 \arcsin 1/3 \sqrt{3}$) by the reorientation and with the chosen sausage-shape the projections are, respectively, $1.82D$ and D . It is, however, no improvement to apply such a detailed consideration before more information concerning the actual shape of the body becomes available.

The so-called ideal value $x = 3/8$ for the positional parameter of the pyrite type structure leads to:

$$c/a \approx 0.56 \text{ and } c/b \approx 0.49$$

where the index M has been omitted, since any misconception is unlikely. On comparison of these values with the observed axial proportions for the marcasites it is seen that remarkably good agreement is found for class A (*vide supra*).

Even this simplified model (from now on named the *pair reorientation model*) indicates that it is class A which may be considered to be the "normal" class of the marcasites, since the axial ratios within this class may be explained as a result of the type of packing of the $X-X$ pairs. It is accordingly superfluous to introduce the assumption of additional compressing forces (*cf.*, *e.g.*, Pearson¹⁴) in order to account for the axial proportions of this class.

The fact that there exist marcasites with larger axial ratios (*i.e.* the occurrence of the classes A/B and B) makes it natural to invoke a working hypothesis which, on the contrary, implies that expanding forces prevail in these classes.

Only the geometrical consequences which follow from the different packing types of the $X-X$ pairs in the pyrite and marcasite type structures are accounted for in the above pair reorientation model. However, associated with the reorientation, some $T-X$ bonds must be broken and reestablished. It is sufficient to assume that one $T-X$ bond per $X-X$ pair is shifted from one of the X -atoms within the pair to the other, and *vice versa*.

Although the pair reorientation model is hypothetical, it is an experimental fact that transformations from pyrite to marcasite type structures, and *vice versa*, can be introduced by varying the external conditions (*e.g.* temperature and pressure). There exists furthermore a stable transitional form in the compound $\alpha\text{-NiAs}_2$.¹

In the latter structure (deformed) TX_6 -octahedra share corners and *one* edge with neighbouring octahedra, whereas the octahedra in the pyrite type structure share only corners, and in the marcasite type structure corners and *two* edges. The fact that the structure of $\alpha\text{-NiAs}_2$ takes an intermediate position between the structure types pyrite and marcasite (all three structure types are in fact known for NiAs_2 ^{1,25,26}) becomes evident by considering its atomic arrangement in planes perpendicular to the c -axis. If the atomic arrangements in (001) and (002) of the pyrite type structure are denoted as A and B , respectively, the stacking sequence along its [001] is $AB/AB/ \dots$ and accordingly approximately $AA/AA/ \dots$ for the marcasite type structure in the corresponding direction. Using the same notation, the stacking sequence is approximately $ABBA/ABBA/ \dots$ along the c -axis of the $\alpha\text{-NiAs}_2$ structure. $\alpha\text{-NiAs}_2$ can be imagined to be transformed into the pyrite or marcasite modification by reorientation of the $X-X$ pairs in two of the previously mentioned planes (*viz.* Nos. 3 and 4 or Nos. 2 and 3 in the above stacking sequence) together with adjustments within the layers.

THE INADEQUACY OF CERTAIN MODELS IN CONNECTION
WITH THE MARCASITES

In the literature, there occur, broadly speaking, four models which have been used in endeavours to explain the peculiarities within the marcasite family, *i.e.* Buerger's,¹⁰ Rosenqvist's,²⁷ Hulliger and Mooser's,^{12,13} and Pearson's.¹⁴ Other authors (see, *e.g.*, Refs. 11, 26, 28, 29) base their considerations wholly or partly on these models, in that they either study only a limited selection of compounds, or discuss a particular type of data.

Buerger¹⁰ maintains that there occur additional $X-X$ bonds along [001] in class A of the marcasites and in weak form perhaps also in class B. In this way he explains the relatively short c -axes in class A, and the larger than expected radii for the X -atoms in tetrahedral coordination.

The suggested occurrence of additional $X-X$ bonds in class A is, in the first place, contradicted by the fact that the $X-X$ distances along [001] are considerably longer than the corresponding single bond distances observed within the $X-X$ pairs; and in the second place that the assumption of additional $X-X$ bonds leads to unreasonable valences for the T - and/or the X -atoms (*cf.*, *e.g.*, Huggins³⁰).

Rosenqvist²⁷ assumes that the distinction between the classes A and B depends on the number of unpaired electrons localized on the T -atoms, and that magnetic coupling between neighbouring T -atoms tends to shorten the c -axes within the former class. This model must clearly be rejected in the light of more recent data which indicate that cooperative magnetism within the marcasite family is limited to the case of CrSb_2 ,^{31,32} and furthermore that the majority of compounds in class A are in fact diamagnetic (see Ref. 15).

Pearson¹⁴ has undoubtedly set up the most complicated model for explanation of peculiarities within the marcasite family; his model being composed of several independent hypotheses. He assumes for example, in common with Buerger, that additional $X-X$ bonds along [001] occur within class A. Although Pearson argues for this point of view by considering van der Waals distances and by the application of Paulings¹⁷ bond-order formula, his model suffers in this respect from the same weakness as Buerger's. It must in this connection be emphasized that neither considerations based on van der Waals distances, nor the use of the bond-order formula, are justified in macromolecules of the type which occur in the marcasite type structure.

Due to the observed semiconducting properties of marcasites of the class A, Pearson is led to postulate that the X -atoms have complete valence shells, despite the additional $X-X$ bonds, and he accordingly ascribes to these compounds a complicated mixed bonding scheme.

A further hypothesis by Pearson is the assumption of $T-T$ interaction along [001] in class A. He does not state explicitly that this interaction is to be interpreted as bonding, which is maintained by Donohue *et al.*²⁶ to be present in this class. Pearson indicates that $T-T$ interactions may explain what he describes as structural compression in class A.

A universal $T-T$ bonding in class A is, for example, contradicted by the facts that $\text{Mo}_{2/3}\text{As}_2$ (with d^0 configuration on Mo) belongs to this class, and that CrSb_2 is found to have two unpaired electrons per Cr-atom. Pearson's model also suffers from the weakness that it implies an unspecified combination of hypotheses. Useful predictions are accordingly impossible. A probable reason for Pearson's choice of such a complicated bonding scheme lies in the fact that he attempted to explain data which have later been proved to be erroneous, *e.g.* that FeSb_2 was thought to have two localized unpaired electrons (*cf.* Refs. 31,32).

Hulliger and Mooser^{12,13} apply the Jahn-Teller theorem to explain the distinction between the class A marcasites on the one hand, and the class B marcasites and pyrites on the other. This aspect of their model is inconsistent with the available experimental data (see an earlier paper by the present authors²²) and must accordingly be rejected, although some of the consequences of the model appear to be essentially correct (*cf.* Ref. 15).

A common feature of these four models is that in class A the attention is focused on effects which could compress the unit cell along the *c*-axis, by the introduction of notations of the kind "shortened *c*-axes" (Buerger; Rosenqvist) or "compressed unit cells" (Pearson; Hulliger and Mooser). These notations have probably prevented a search for effects which could explain why class B is expanded, *i.e.* effects which, on the contrary, are lacking in class A.

REFERENCES

1. Stassen, W. N. and Heyding, R. D. *Can. J. Chem.* **46** (1968) 2159.
2. Schubert, K., Breiner, H. and Gohle, R. *Z. Metallk.* **50** (1959) 152.
3. Hohnke, D. and Parthé, E. *Z. Krist.* **127** (1968) 164.
4. Parthé, E. *Third International Conference on Solid Compounds of Transition Elements, Oslo 1969*, p. 151.
5. Grønvold, F. and Røst, E. *Acta Cryst.* **10** (1957) 329.
6. Brown, B. E. *Acta Cryst.* **20** (1966) 264.
7. Brown, B. E. *Acta Cryst.* **20** (1966) 268.
8. Alcock, N. W. and Kjekshus, A. *Acta Chem. Scand.* **19** (1965) 79.
9. Barricelli, L. B. *Acta Cryst.* **11** (1958) 75.
10. Buerger, M. J. *Z. Krist.* **97** (1937) 504.
11. Haraldsen, H. *Avhandl. Norske Videnskaps-Akad. Oslo I. Mat. Naturv. Kl.* **1947** No. 4.
12. Hulliger, F. and Mooser, E. *Progr. Solid State Chem.* **2** (1965) 330.
13. Hulliger, F. and Mooser, E. *J. Phys. Chem. Solids* **26** (1965) 429.
14. Pearson, W. B. *Z. Krist.* **121** (1965) 449.
15. Brostigen, G. and Kjekshus, A. *Acta Chem. Scand.* **24** (1970) 2993.
16. Johnston, W. D., Miller, R. C. and Damon, D. H. *J. Less-Common Metals* **8** (1965) 272.
17. Pauling, L. *The Nature of the Chemical Bond*, Cornell University Press, Ithaca 1960.
18. Phillips, C. S. G. and Williams, R. J. P. *Inorganic Chemistry*, Oxford University Press, London 1965, Vol. I.
19. Holseth, H. and Kjekshus, A. *Acta Chem. Scand.* **23** (1969) 3043.
20. Zhdanov, G. S. and Kuz'min, R. N. *Soviet Phys. Cryst.* **6** (1962) 704.
21. Kjekshus, A. *Acta Chem. Scand.* *In press*.
22. Brostigen, G. and Kjekshus, A. *Acta Chem. Scand.* **24** (1970) 1925.
23. Pearson, W. B. *Z. Krist.* **126** (1968) 362.
24. Wahl, A. C. *Science* **151** (1966) 961.
25. Holseth, H. and Kjekshus, A. *Acta Chem. Scand.* **22** (1968) 3284.
26. Donohue, P. C., Bither, T. A. and Young, H. S. *Inorg. Chem.* **7** (1968) 998.
27. Rosenqvist, T. *N.T.H.-Trykk*, Trondheim 1953.
28. Llewellyn, J. P. and Smith, T. *Proc. Phys. Soc.* **70** (1957) 1113.
29. Bennet, S. L. and Heyding, R. D. *Can. J. Chem.* **44** (1966) 3017.
30. Huggins, M. L. *Z. Krist.* **96** (1937) 384.
31. Holseth, H. and Kjekshus, A. *J. Less-Common Metals* **16** (1968) 472.
32. Holseth, H., Kjekshus, A. and Andresen, A. F. *Acta Chem. Scand.* *In press*.

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