A COMMON ORIENTATION AND A CLASSIFICATION FOR CRYSTALS BASED UPON A MARCASITE-LIKE PACKING

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Introduction

A marcasite-like arrangement of atoms is common to a rather large number of crystals. It is now desirable to organize the many data in this field for crystallographic purposes:

(a) by adopting a common orientation for these crystals based upon their structural *similarity*, and
(b) by providing a classification of these crystals based upon their structural *differences.*

These matters are treated in the present paper. It is also desirable to outline the fields within which the several structures may exist and the relations between these structures and the structures of neighboring fields. This crystallo-chemical discussion is reserved for a paper to appear shortly.

Orientation

It is now known that the arsenopyrite minerals definitely have marcasite-like crystal structures.[1] The ideal arsenopyrite structure is monoclinic, the false orthorhombic character of the group being caused by mimetic twinning on the pinacoids. The position of the 2-fold axis is parallel with the customary *c* axis. Since the 2-fold axis in monoclinic crystals is fixed by convention as the *b* axis, an axial interchange is required in the arsenopyrite group. A similar interchange is required in the axes of the truly orthorhombic marcasite and löllingite groups, in order to maintain the obvious relation between these groups and the arsenopyrite group. One of two alternative axial interchanges is necessary:

Old arsenopyrite orientation		New orientation required by the monoclinic character of ideal arsenopyrite	
		Alternative (1)	Alternative (2)
a	——→	*a*	*c*
b	——→	*c*	*a*
c	——→	*b*	*b*

The marcasite-like packing is a generalization of the rutile packing.[2]

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[1] Buerger, M. J., The symmetry and crystal structure of the minerals of the arsenopyrite group: *Zeit. Krist.*, (A) 95, pp. 83–113, **1936.**

[2] Buerger, M. J., The crystal structure of marcasite: *Am. Mineral.*, vol. **16,** pp. 392–393, **1931.**

It is therefore desirable, if possible, to make the new orientation of the marcasite-like minerals such that their structural orientations correspond with the rutile structural orientation. In the rutile structure, the metal coordination is octohedral. One of the important aspects of the packing is the linking of these octohedra into strings parallel with the 4-fold axis, by the sharing of edges. According to convention, the 4-fold axis is the c axis of tetragonal crystals, and this aspect of the structural orientation is therefore fixed. In the marcasite structure the direction of the strings of octohedra has been discovered to be parallel with the a axis of the arbitrarily chosen orthorhombic setting. To bring the marcasite-like minerals into conformity with the rutile setting, therefore, one of the following two alternative axial interchanges is necessary in the marcasite-like minerals:

Old marcasite orientation		New orientation required for correspondence with rutile structure	
		Alternative (I)	Alternative (II)
a	→	c	c
b	→	b	a
c	→	a	b

It will be observed that the old marcasite setting may be brought into harmony with both the symmetry requirement of arsenopyrite and the symmetry requirement of rutile because interchange alternatives (2) and (II) are identical. The axial interchanges for all crystals based upon a rutile-like or marcasite-like packing may now be summarized as follows:

	Old		New
for Rutile Group Hydrophylite Manganite	No interchange from customary orientation necessary.		
for Marcasite Löllingite Group Arsenopyrite Group	a b c	→ → →	c a b

In the following discussion the *new* orientations are employed.

THE SEVERAL GROUPS OF MARCASITE-LIKE CRYSTALS

General.—All of the crystals discussed in this paper may be thought of as descending from the rutile structural type by either one, two, or three generalizations or specializations. These relations are summarized in Table 1. This table provides only some of the aspects which should be taken into consideration in the classification of these crystals; at least the AB_2 crystals are of several types.

Rutile group.—The rutile group requires little discussion in this place. The reader is referred, however, to the discussion bearing on the relation of this group to the marcasite group, which will appear in a subsequent contribution. The crystals belonging to the rutile group are listed in Strukturbericht.[3]

Marcasite group proper.—The marcasite group is usually made to cover not only marcasite but also the löllingite type and the arsenopyrite type crystals as well. Arsenopyrite is now known to have a different symmetry from marcasite as well as certain multiple axes. There is also a very real difference between marcasite and the löllingite crystals which should be recognized by placing them in different categories.

The difference between marcasite and the löllingite group is fundamentally due to the lack of chemical parallelism and consequent difference in bonding. This shows up in the shape of the octahedral coordination environment of the iron (or other corresponding metal atom), which, in turn, is reflected in the axial ratio, particularly the length of the *c* axis. In describing this difference, it is convenient to consider the octahedron as having an equator and poles, the shared edges of the octahedra consisting of one of the two opposite pairs of edges of the equator. In marcasite, contrary to a statement by Pauling and Huggins,[4] the shared edge is shortened, as indicated by the following figures[5] (and compared with $CaCl_2$, discussed beyond):

Edge	Edge length			
	marcasite, FeS_2		hydrophylite, $CaCl_2$	
equator edge, unshared	3.37Å		4.20Å	
		$\Delta=.24$		$\Delta=.31$
meridian edge, unshared (equator to pole)	av. 3.13		3.89	
		$\Delta=.17$		$\Delta=.34$
equator edge, shared	2.96		3.55	

The presence of a shortened shared edge is commonly regarded as a criterion for ionic crystals.[4] It is possible that marcasite is of partially ionic, and only partially of non-polar character, which would help to account for its abnormally large sulfur atoms, abnormally small iron atoms[6] and excessively great electrical resistance, all compared with

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[3] Ewald, P. P., and Hermann, C., *Strukturbericht* 1913–1928, pp. 155–158, **1931.**

[4] Pauling, Linus, and Huggins, M. L., Covalent radii of atoms and interatomic distances in crystals containing electron-pair bonds: *Zeit. Krist.*, (A) 87, p. 216, **1934.**

[5] Buerger, M. J., The crystal structure of marcasite: *Am. Mineral.*, vol. **16**, p. 391, **1931**.

[6] See, however, reference 1.

pyrite. In part, the shortened shared edge may be due to the repulsion between the negatively charged surfaces of the unbonded atoms which approach one another across the shared edge.

As a result of the lengthening of the unshared equatorial edge, the marcasite group proper is characterized by a *c* axis (new orientation) somewhat longer than the normal side of the coordination octahedron of the metal atom. The löllingite type is sharply distinguished from the marcasite type on this basis, as discussed in the next section. (See also Table 2.)

Hydrophylite has a marcasite-like packing although this is apparently unrecognized by van Bever and Nieuwenkamp,[7] who determined the structure. Originally described as $CaCl_2$, the mineral hydrophylite is now regarded as having the composition[8] $KCaCl_3$. Artificial material apparently of ideal composition, $CaCl_2$, may be prepared.[7] Nevertheless the formula may still be regarded as somewhat doubtful, and it is barely possible that this mineral may really have a manganite-like character.

The deviation of the hydrophylite structure from the rutile prototype is exceedingly slight and the crystals are therefore highly pseudo-tetragonal. The slight departure from the rutile structure is due to the slight deviation of the Cl atoms toward pairing. This appears to be due to the large Cl radius, i.e., the Ca:Cl radius ratio is small compared with the Fe:S radius ratio in marcasite. This is discussed further in a subsequent contribution.

The löllingite group.—The löllingite group is sharply distinguished from the marcasite group by being composed of coordination octahedra whose *unshared equatorial edges are greatly shortened.* The shared edge is correspondingly lengthened:[9]

Edge	Edge length		
	FeP_2	$FeAs_2$	$FeSb_2$
equator edge unshared	2.72Å	2.85Å	3.19Å
meridian edge unshared (equator to pole)	av. 3.20	av. 3.33	av. 3.67
equator edge shared	3.69	3.78	4.15

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[7] van Bever, A. K., and Nieuwenkamp, W., Die Kristallstruktur von Calciumchlorid, $CaCl_2$: *Zeit. Krist.*, (A) 90, pp. 374–376, **1935.**

[8] Dana-Ford, *A Textbook of Mineralogy,* 4th revised edition, p. 464, **1932.**

[9] Buerger, M. J., The crystal structure of löllingite, $FeAs_2$: *Zeit. Krist.*, (A) 82, pp. 185, **1932.**

The shortening of the unshared edge undoubtedly represents a bond between the B atoms across this edge (Fig. 1). It results in an excessively short *c* axis which distinguishes the morphology of the löllingite group from that of the marcasite group, a distinction which is clearly brought out by Table 2.

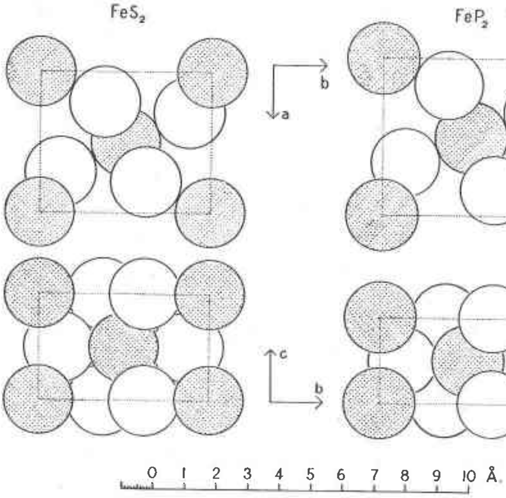

FIG. 1. The fundamental cause of the widely differing axial ratios of the marcasite group and the löllingite group. The illustration shows the plan and elevation of the unit cell of a representative of each group, the representatives being composed of isoperiodic atoms, i.e., the FeP_2 differs from the FeS_2 only by having its *B* atom one atomic number lower, and its valence therefore one greater. The additional valence causes the *P* atoms of the same iron coordination to bond themselves to one another in the *c* direction. This reduces the *c* dimension and increases *a* and *b*. The axial ratios of the two types of crystals are therefore distinct.

Key: shaded, iron atoms; unshaded, sulfur atoms (left diagram) or phosphorus atoms (right diagram). All atoms are drawn to scale from calculations from original crystal structure data.

Bäckströmite.—The existence of an hypothetical mineral, bäckströmite, $Mn(OH)_2$, has been deduced from orthorhombic pseudomorphs[10] now composed of pyrochroite. If bäckströmite truly represents a possible crystal, then the crystal structure is probably of the general marcasite type. The crystal structure is probably that of manganite with identity periods degenerate and symmetry raised due to the presence of identical *B* atoms. The hydrogen bonds probably exist along zigzag

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[10] See discussion by Koechlin, R., in Doelter, C. and Leitmeier, H., *Handbuch der Mineralchemie*, III_2, pp. 845–846, **1926**.

oxygen chains running in the direction of the *a* axis, connecting oxygens of different, as well as the same, cation coordinations.

The arsenopyrite group, gudmundite type.—Within the appropriate field, compounds corresponding with the ideal formula $AB'B''$ are monoclinic holohedral with doubled marcasite *a* and *c* axes.[11] This is here designated as the gudmundite type, for gudmundite displays the *x*-ray diffraction extinctions characteristic of this symmetry. Arsenopyrite itself is so prone to deviate from the ideal analysis that it usually falls into the next (triclinic) subdivision. Probably crystals of ideal monoclinic arsenopyrite exist, but investigation has not yet proceeded far enough to show this. The ideal monoclinic nature of gudmundite is apparently due to its relatively ideal composition, which, in turn, is probably due to the relatively great radius difference between $\mathrm{Sb^{III}}$, on one hand, and $\mathrm{Fe^{III}}$ and S on the other, which inhibits the proxying of one of these atoms by the other.

Manganite also probably belongs to the gudmundite type.[12] The $\mathrm{B'-B''}$ pairing is caused in this crystal by an (OH)–O bond.

The arsenopyrite group, common arsenopyrite type.—The presence of ferric iron in arsenopyrite permits the arsenic and iron of the ideal formula to be replaced by one another freely.[13] Cobalt may also function as iron, and finally, arsenic may proxy for a certain amount of sulfur, which tends to make arsenopyrite approach the structure of löllingite. Apparently these replacements, especially the last, occur preferentially in alternate sheets, for the screw axes and glide planes which relate neighboring sheets to one another vanish, as shown by the substitutions of weak reflections for the extinct reflections required by the screw axes and glide planes. The common arsenopyrite is therefore triclinic. This is doubtless true also of the related species glaucodot, $\left|\begin{matrix}\mathrm{Co}\\\mathrm{Fe}\end{matrix}\right|\mathrm{AsS}$ and wolfachite, $\mathrm{Ni}\left|\begin{matrix}\mathrm{As}\\\mathrm{Sb}\end{matrix}\right|\mathrm{S}$. It is impossible to ascertain whether manganite rigorously belongs here or with the ideal gudmundite type, for its O and (OH) scatter *x*-rays identically, and a partial replacement of one by the other, which would render the structure triclinic, could not be detected.

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[11] Buerger, M. J., The symmetry and crystal structure of the minerals of the arsenopyrite group: *Zeit. Krist.*, (A) 95, pp. 83–113, **1936.**

[12] Buerger, M. J., The symmetry and crystal structure of manganite, Mn(OH)O: *Zeit. Krist.*, (A), in press.

[13] Buerger, M. J., The symmetry and crystal structure of the minerals of the arsenopyrite group: *Zeit. Krist.*, (A) 95, pp. 110–111, **1936.**

COORDINATED CRYSTALLOGRAPHIC DATA

In accordance with the discussion concerning common orientation and subdivision into groups, the crystallographic constants of the crystals based upon a marcasite-like packing are summarized in Table 2. Only constants based upon data obtained by x-ray methods have been used in this compilation. The accuracy of the values given is probably not very high, the limits of error lying between ±1% and ±.1%. Due to the common occurrence of solid solution, either of extraneous impurity atoms or of excess of one of the atoms already present in the ideal formula, it is not justifiable to quote values of greater apparent accuracy than those given in Table 2, unless the quotation applies to crystals of a definite locality or origin (i.e., composition).

TABLE 1

DERIVATION OF MARCASITE-LIKE CRYSTALS BY SUCCESSIVE SPECIALIZATIONS OF RUTILE PROTOTYPE

Formula type	Atomic specialization	Resulting crystallographic consequences	Crystal system	Crystals	
AB_2	(PROTOTYPE)		tetragonal	RUTILE GROUP	
AB_2	approach of B atoms in pairs	specialization of a_1 and a_2 axes to become a and b axes	orthorhombic	MARCASITE GROUP LÖLLINGITE GROUP BÄCKSTRÖMITE?	
$AB'B''$	specialization of 2 B atoms to become B' and B'' species	loss of symmetry and development of superstructure having a and c axes doubled	monoclinic	gudmundite type	ARSENOPYRITE GROUP
$\begin{array}{ccc} A & B' & B'' \\ X & Y & Z \end{array}$	preferential substitution of ideal formulary atoms by extra-formulary atoms in alternate (001) sheets	loss of screw axes and glide planes	triclinic	common arsenopyrite type	

The table brings out some interesting points: The distinction between the constants of the marcasite group and the löllingite group is striking, especially with regard to the ratio *c*:*b*, as illustrated in Fig. 1

TABLE 2

AXES AND AXIAL RATIOS (NEW ORIENTATION) OF CRYSTALS BASED UPON A MARCASITE-LIKE PACKING

Group		Member		Axes					
				absolute			ratio		
				a	*b*	*c*	*a*	*b*	*c*
RUTILE PROTOTYPE		rutile	TiO_2	4.58Å	4.58Å	2.95Å	1.000	1	.644
MARCASITE GROUP		hydrophylite	$CaCl_2$	6.24	6.43	4.20	.970	1	.653
		marcasite	FeS_2	4.44	5.39	3.37	.824	1	.625
LÖLLINGITE GROUP		iron diphosphide	FeP_2	4.97	5.67	2.72	.876	1	.480
		löllingite	$FeAs_2$	5.25	5.92	2.85	.887	1	$.481_5$
		iron diantimonide	$FeSb_2$	5.82	6.52	3.19	.893	1	.489
		safflorite	$CoAs_2$	—	—	—	—	—	—
		rammelsbergite	$NiAs_2$	—	—	—	—	—	—
ARSENOPYRITE GROUP	gudmundite type	gudmundite	FeSbS	10.04	5.93	6.68	1.694	1	1.126
		manganite	Mn(OH)O	8.86	5.24	5.70	1.690	1	1.088
	common arsenopyrite type	arsenopyrite	FeAsS	9.51	5.65	6.42	1.683	1	1.136
		glaucodot	$\left\vert\begin{matrix}\mathrm{Co}\\\mathrm{Fe}\end{matrix}\right\vert\mathrm{AsS}$	9.62	5.73	6.67	1.678	1	1.164
		wolfachite	$\mathrm{Ni}\left\vert\begin{matrix}\mathrm{As}\\\mathrm{Sb}\end{matrix}\right\vert\mathrm{S}$	—	—	—	—	—	—

and for the reason discussed under *the löllingite group*. The löllingite group is an extraordinarily compact group showing slight and gradual variation of axial ratio with changing atomic radii. The marcasite group shows a much greater internal variation but it consists, as yet, of only two crystals composed of atoms of widely differing dimensions and bonding characteristics. When and if the group is expanded by the discovery of other members, it may be expected to show gradations.

The close agreement in axial ratio between manganite and the arsenopyrite minerals should also be observed. This, of course, is in good accord with the discovery that these have similar structures.

Finally, it should be pointed out again that the splitting of the arsenopyrite group into the gudmundite type and the common arsenopyrite type is a purely formal procedure based upon the fact that the chemically ideal type of this structure is monoclinic while the chemically impure type is triclinic. The relation is presumably a completely gradational one dependent upon impurity content. Alternatively, the relation between these two types may be looked upon as one in which the general case is triclinic, which degenerates to a special monoclinic case when the impurity content approaches zero.