

The Symmetry and Crystal Structure of the Minerals of the Arsenopyrite Group.

By M. J. Buerger, Massachusetts Institute of Technology, Cambridge (Mass.).

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Abstract.

This paper presents an extended study leading to the correct crystal structure of arsenopyrite ($FeAsS$) and the arsenopyrite group of crystals. Exceptional difficulties prevent the usual easy crystal structure approach.

Part I presents a review of the literature together with the results of three distinct new cell studies: 1. an oscillation and laue study of the Franklin arsenopyrite, 2. an equi-inclination Weissenberg study of the Spindelmühle arsenopyrite, and 3. an equi-inclination Weissenberg study of the Gudmundstorp gudmundite. The new data differ from those found in the literature. The photographs apparently indicate space groups $Cmmm$, Cmm , or $C222$ for this family of crystals.

Part II presents a study of the crystal structure of the group, leading to the crystal structure of arsenopyrite in particular. It is first shown that no orthorhombic space group which comes up for possible consideration can satisfy the intensity data.

The approach is then changed and it is shown that the arsenopyrite structure may be derived by considering arsenopyrite as a superstructure based on the marcasite type. There are only five possible superstructures having the required dimensional characteristics; all are monoclinic. A study of oriented polished arsenopyrite crystal sections in reflected polarized light then reveals the fact that the usual arsenopyrite "crystals" are twinned composites, the individuals of which have a symmetry no higher than monoclinic holohedral. The possible X-ray extinction effects of the several possible superstructures are discussed for single individuals and for twinned composites. The Weissenberg data are then re-examined and the correct space group and superstructure selected. The final arsenopyrite structure gives perfect checks between observed and calculated intensities. The crystal structure data are summarized in Table III and the general cell characteristics and diffraction effects are summarized in the last section of this paper.

An important incidental result of this study has been the discovery of the existence of Fe^{III} in the non-polar state. This has a radius of 1.12 or 1.13 Å, in agreement with extrapolations from the radii of transition metals in several directions. The iron in arsenopyrite, löllingite, and possibly marcasite is in the state Fe^{III} . This accounts for the ease with which As^{III} proxies for Fe in arsenopyrite, etc.

Part I. General Cell Characteristics.

Introduction.

The research herein recounted was initiated in the spring of 1931 by the writer as a part of a program of study of the crystal structures of the minerals of the marcasite group^{1) 2)}. The initial work on the arsenopyrite group was carried on using the oscillating crystal method. This provided data for the determination of the unit cell and apparent orthorhombic space group of the Franklin arsenopyrite. Since the space group derived by this study not only differed from that already published by de Jong, but also did not provide for the marcasite-like type of packing expected from considerations of chemical, dimensional and certain diffraction intensity similarity, it was thought best to withhold preliminary results until these were checked by further work.

The conviction that arsenopyrite must have a marcasite-like packing suggested that the space group had been incorrectly determined due possibly to the uncertainty in indexing reflections in the oscillating crystal method and possibly to the failure of this method to give more than meager symmetry information. In view of the fact that these shortcomings were general drawbacks in any crystallographic investigation it was felt worth while to develop first the possibilities of the

1) Buerger, M. J., The crystal structure of marcasite. *Amer. Mineralogist* **16** (1931) 364–395.

2) Buerger, M. J., The crystal structure of löllingite, $FeAs_2$. *Z. Kristallogr. (A)* **82** (1932) 165–187.

Weissenberg method in these directions. This has been done in a series of papers published elsewhere^{1) 2) 3)}. With this more certain theoretical backing it is possible to interpret the apparently anomalous X-ray diffraction effects with very fruitful results.

The experimental results recorded here fall under three headings: the original oscillating crystal study of the Franklin arsenopyrite, a newer Weissenberg study of the Spindelmühle arsenopyrite, and a Weissenberg study of the Gudmundstorp gudmundite. The first two studies give quite independent data derived from crystals of two different occurrences.

Literature.

Several members of the arsenopyrite group have been investigated by de Jong⁴⁾, using powder and rotating crystal methods with iron radiation (apparently mostly the powder method). The data so obtained lead de Jong to the cell constants which are listed in Table I. The space group derived for the minerals was not specifically

Table I. Cell constants for certain members of the arsenopyrite group as given by de Jong⁴⁾.

	Arsenopyrite, $FeAsS$		Glaucodot, $\begin{matrix} Fe \\ Co \end{matrix} AsS$	
	absolute	ratio	absolute	ratio
a	6.44	1.352	6.67	1.386
b	4.76	1	4.81	1
c	5.63	1.182	5.73	1.191
z	4		4	
calculated density	6.28		6.00	

given by de Jong. Since, however, the arsenopyrite-like minerals are included in a general paper on the crystal structure of the marcasite group and referred to de Jong's marcasite axes⁵⁾, presumably the space group derived for the marcasite group, namely, V_h^{11} , was supposed to cover the arsenopyrite-like minerals as well. Although

1) Buerger, M. J., The Weissenberg reciprocal lattice projection and the technique of interpreting Weissenberg photographs. *Z. Kristallogr. (A)* **88** (1934) 356–380, also **90** (1935) 563.

2) Buerger, M. J., The application of plane groups to the interpretation of Weissenberg photographs. *Z. Kristallogr. (A)* **91** (1935) 255–289.

3) Buerger, M. J., An apparatus for conveniently taking equi-inclination Weissenberg photographs. *Z. Kristallogr. (A)* **94** (1935) 87–99.

4) de Jong, W. F., Bepaling van de absolute aslengten van markasiet en daarmee isomorfe mineralen. *Physica* **6** (1926) 325–332.

5) It is believed that the attempt to refer the entire marcasite group to a single set of axes on the basis of comparable powder photographs lead de Jong to assign incorrectly a doubled a axis to marcasite and löllingite.

cell dimensions for alloclase, $\begin{vmatrix} Co & As \\ Fe & Bi \end{vmatrix} S$, are not given by de Jong, it is said that material from Banat, Jugo-Slavia, gave a [powder ?] photograph like that of glaucodot, without evidence of any admixed material.

In a later, unpublished dissertation¹⁾, unavailable to the writer, but abstracted in *Strukturbericht*²⁾, de Jong recorded a further study of what appears, from identical axial dimensions, to be the same arsenopyrite studied in the earlier investigation. This is definitely stated to be danaite from Suleitjelma, Norway, for which the following analysis is quoted:

	weight per cent	ratio
<i>Fe</i>	33.93	} 1.4
<i>Co</i>	6.84	
<i>As</i>	38.40	1
<i>S</i>	20.75	1.26

In the new study, the cell axes are determined by the layer line spacings of rotation photographs, and a *b* axis, twice as long as in the earlier investigation, is derived. The space group, based upon the indexing of 17 lines of a powder photograph, is given as V_h^1 or V_h^{13} , although V_h^5 and V_h^7 are said by the abstractor to be uneliminated by the data.

With the same assumption of holohedral orthorhombic symmetry, the space group derived by the present writer for arsenopyrite studied by the oscillation method, and for both arsenopyrite and gudmundite studied by the Weissenberg method, is different from any of these, namely V_h^{19} . The one thing all these space groups have in common is the possibility of accounting for a systematic absence of hkl reflections when $h+k$ is odd. The Weissenberg films plainly show that this extinction is only a special case of a more general systematic absence of hkl reflections when $h+k$ is odd. The space group must therefore be based upon a *C*-centered lattice, not upon a simple lattice as was done by de Jong.

The Franklin Arsenopyrite.

Material. — Through the kindness of Professor Charles Palache, the writer was able carry out the first investigation with some of the original Franklin arsenopyrite^{3) 4)}.

The analysis of this material, made for E. C. Sullivan and quoted by Palache, is as follows:

	Weight per cent	atomic per cent	ratio
<i>Fe</i>	32.48	.581	} 1
<i>Co</i>	1.16	.0197	
<i>As</i>	48.72	.650	1.08
<i>S</i>	18.80	.587	.98
	<u>101.16</u>		

1) de Jong, W. F., Dissertation, Delft, 1928.

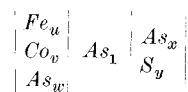
2) Ewald, P. P. and Hermann, C., *Strukturbericht*, 1913–1928, p. 283.

3) Palache, Charles, Contributions to the mineralogy of Franklin Furnace N. J.; *Am. Jour. Sci.* (4) **29** (1910) 177–178.

4) Palache, Charles, The minerals of Franklin and Sterling Hill, Sussex County, N. J. U. S. Geol. Surv. Prof. Paper **180** (1935) 33–35.

The analysis indicates a slight arsenic excess, as contrasted with that of de Jong's material, which shows a considerable arsenic deficiency.

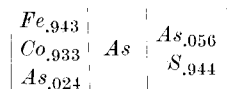
The theory of reducing abnormal analyses has been discussed by the writer in another place¹⁾, with special consideration to members of the marcasite group. Assuming that the extra-ideal atoms enter the structure of arsenopyrite in proxy solution, as they do in the case of marcasite and löllingite, the general formula for the Franklin arsenopyrite may be written:



The atomic ratios require following conditions:

$$\begin{cases} u + v + w = 1 \\ x + y = 1 \\ \frac{w + 1 + x}{y} = \frac{.650}{.587} \\ u = .581 \\ v = .0497 \\ \frac{u + v}{1 + w + x} = \frac{.581 + .195}{.650} \end{cases}$$

The solution of this system of equations determines the subscripts u , v , w , x , and y , from which the formula of the Franklin arsenopyrite may be written:



The formula weight of this is 165.35 as against 162.87 for the ideal composition $FeAsS$.

A density determination made by the writer on about 3 grams of crushed fragments of this material at 27° C lead to a corrected density of 6.223. The axial ratio is²⁾:

$$\begin{array}{ccc} a & b & c \\ .6702 & : 1 & : 1.198 \end{array}$$

Methods. — The cell dimensions, space group, and reflection intensities for the Franklin arsenopyrite were obtained from rotating and oscillating crystal procedure. The reflections, obtained from a small crystal completely bathed in the incident radiation, were recorded on $3\frac{1}{4} \times 4\frac{1}{4}$ inch flat plates at a crystal to plate distance of about 6 cm. Molybdenum radiation, screened with zirconia, was obtained from a Coolidge tube.

The rotating and oscillating crystal methods do not, unfortunately, give very satisfactory symmetry information. Such information was obtained from Laue photographs of the same small crystal.

1) Buerger, M. J., The pyrite-marcasite relation. Amer. Mineralogist **19**, (1934) 53–58.

2) Palache, loc. cit.

Symmetry. — Laue photographs taken with the incident beam parallel to each of the crystallographic axes in turn, each show the plane symmetry¹⁾ C_{2v} . This identifies the centrosymmetrical crystal class of the arsenopyrite as V_h .

Unit cell. — Complete rotation photographs of about 48 hours exposure were obtained for rotations about the three crystallographic axes. The ξ values of the layer lines, determined by comparison with Bernal's charts²⁾, lead to the following cell dimensions:

	absolute	axial ratio	axial ratio derived from surface morphological study
a	6.42 Å	.672	.6702
b	9.55	1.	1.
c	5.71	.598	$2 \times .5995$
V	350 Å ³		
a/c		1.124	$\frac{1}{2} \times 1.127$

It will be observed that the conventional arsenopyrite axial ratio has the c axis doubled. This is because the arsenopyrite cell is approximately double the marcasite cell in both a and b dimensions, and the entire marcasite group is customarily referred to the marcasite morphological axial ratio, which is the same as the true axial ratio.

The cell contents may be calculated with the aid of the relation:

$$\text{measured density} = \frac{\text{cell mass}}{\text{cell volume}} = \frac{Z \times \text{formula weight}}{\text{cell volume}}$$

Substituting the measured density, proxy solution formula weight, and cell volume determined for the Franklin arsenopyrite leads to $Z = 7.99 \approx 8$ formula weights per unit cell. If the formula weight of ideal $FeAsS$ is substituted instead of the one derived on page 87, Z turns out 8.11. The more nearly integral value of Z derived by using the formula weight derived on page 87 substantiates the chemical analysis and the assumption that the excess arsenic proxies for both deficient iron and sulfur as proxy solution.

Space group. — A series of 45° oscillation photographs were made for both b and c axis oscillations. A total range of about 90° about each axis was covered, each photograph representing a 24 hour exposure. The reflections so recorded were graphically indexed by locating the blank reciprocal lattice points on the appropriate level having the same ξ values in the oscillation range as those indicated by the Bernal²⁾ chart for the spots on the photographs. A catalog of such reflections contains only one systematically absent class, namely reflections hkl when $h + k$ is odd. This indicates that the space lattice is end centered on the (001) face, and that the space group contains no glide planes. If arsenopyrite is orthorhombic, the correct space group is, therefore, either $Cmmm$ (V_h^{19}), Cmm (C_{2v}^{11}), or $C222$ (V^6).

The Spindelmühle Arsenopyrite.

Material. — Unfortunately the original crystal of Franklin arsenopyrite used in the oscillating crystal research was lost before it could be reinvestigated by

1) Buerger, M. J., The application of plane groups to the interpretation of Weissenberg photographs. *Z. Kristallogr. (A)* **91** (1935) 257–264.

2) Bernal, J. D., On the interpretation of X-ray, single crystal, rotation photographs. *Proc. Roy. Soc. (A)* **113** (1926) 417–460.

Weissenberg methods. For this new study, crystals from the St. Peter Mine, Spindelmühle, near Hohenelbe, in the Riesengebirge of northern Bohemia, were utilized. These crystals were derived from a talcose matrix also housing some other sulfide minerals. The habit of this arsenopyrite is moderately short prismatic, with rather coarsely striated brachydome terminations.

Method. — In view of the lack of agreement between the space group derived by de Jong and the one derived by the writer by the oscillation method, a rather complete study was made of the Spindelmühle arsenopyrite by three distinct methods of interpreting equi-inclination Weissenberg photographs: (a) reconstructing the reciprocal lattice¹), assigning indices to the blank reciprocal framework points occupied by actual reciprocal lattice points, and determining the space group by analytical methods, (b) sketching in the blank reciprocal lattice lines directly on the original films²), assigning indices to the blank reciprocal lattice points occupied by actual reciprocal lattice points, and determining the space group by analytical methods, (c) determining the plane lattices, their stacking sequences and the zero-level multiple translations³) represented by the set of photographs, and thus fixing the space group by inspection. Several kinds of radiation were employed. Cobalt *K* radiation was used to obtain the set of films used for the space group study. Some supplementary duplicate runs were made with copper *K* radiation. A set of three axial zero-layer films were also made using molybdenum radiation to give higher order reflections for the parameter study.

Symmetry. — Each of the films indicated a plane symmetry C_{2v} . Taken all together these indicate that the material used had the centrosymmetrical symmetry $mmm = V_h$, apparently confirming the supposed orthorhombic symmetry of arsenopyrite (see, however, beyond, under gudmundite symmetry and structural considerations).

Space lattice type. — The reciprocal plane lattice stacking sequence normal to the *c* axis is centered diamond, 8; normal to the *a* and *b* axes it is side centered rectangular, 10. These sequences plainly indicate that the space lattice type is *C*-centered. These observations correspond with the analytical rule expressing the class of absent reciprocal lattice points, namely, hkl is absent when $h + k$ is odd.

Unit cell. — The dimensions of the unit cell, indicated by *n*-layer photographs, checked by the layer spacing of rotation photographs, and refined by measuring the ξ_w spacings of high- θ reflections on zero-layer photographs are as follows:

	absolute	axial ratio, Weissenberg method	axial ratio, optically determined
<i>a</i> =	6.42 Å	.675	.6758
<i>b</i> =	9.51	1.	1.
<i>c</i> =	5.65	.594	.5945
<i>V</i> =	345.		

These dimensions lead to approximately 8 formula weights per unit cell.

1) Buerger, M. J., The Weissenberg reciprocal lattice projection and the technique of interpreting Weissenberg photographs. *Z. Kristallogr. (A)* **88** (1934) 366–374. 2) *Id.* 374–376.

3) Buerger, M. J., The application of plane groups to the interpretation of Weissenberg photographs. *Z. Kristallogr. (A)* **91** (1935) 255–289.

Space group. — No doubled reciprocal translations are present in any of the zero-layer films. Analytically, this is equivalent to the non-existence of systematically absent blank reciprocal lattice points other than those already included in the general class hkl when $h+k$ is odd, which determines the lattice type. This apparently eliminates from consideration all space groups having characteristic glide planes and screw axes. The diffraction effect symbol is thus $mmmC$ ——. For orthorhombic symmetry (which would seem to be indicated by mmm) therefore, only space groups $Cmmm = V_h^{19}$, $Cmm = C_{2c}^4$, and $C222 = F^6$ are possible.

The Gudmundstorp Gudmundite.

Material. — Gudmundite, $FeSbS$, known only from Gudmundstorp, Norway, has recently been described by Johansson¹). The writer's material was kindly supplied by Johansson from the original stock. The chemical analysis of gudmundite yields an almost ideal $FeSbS$ formula.

Method. — The Weissenberg films for gudmundite were examined by the same three methods used in the study of the Spindelmühle arsenopyrite. Cobalt K , copper K , and molybdenum K_α radiations were utilized to obtain three different sets of Weissenberg films.

Symmetry. — With the exception of the films for one particular gudmundite crystal, the position and intensity distribution of spots on all Weissenberg photographs corresponded with the plane symmetry C_{2v} . In the case of this particular crystal the c axis rotation film, although displaying a position symmetry C_{2v} , had an intensity distribution C_2 (Fig. 4). In view of the fact that this could not be duplicated with other crystals it was at first thought that this anomalous low symmetry

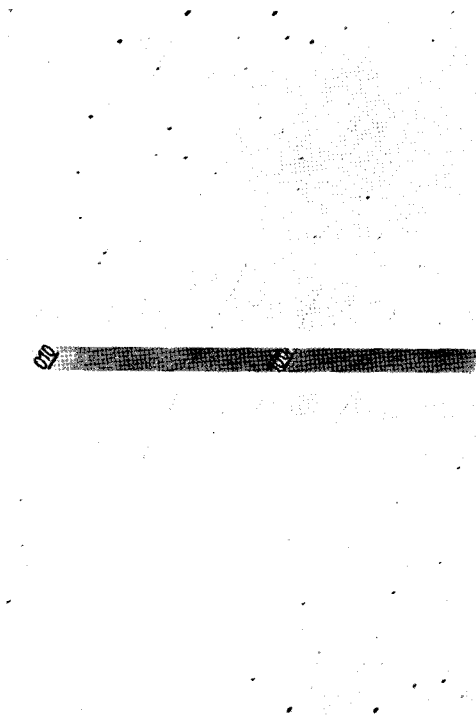


Fig. 4. Zero layer Weissenberg photograph obtained from tiny gudmundite crystal for rotation about the c axis (b axis for new orientation discussed beyond). This photograph is characterized by a position symmetry C_{2v} , but has the inferior intensity distribution symmetry C_2 . It is shown in part II that gudmundite is monoclinic; this photograph represents the rotation of a tiny, untwinned, monoclinic crystal about its 2-fold axis.

1) Johansson, K., Mineralogische Mitteilungen, 4. Gudmundit, ein neues Mineral innerhalb der Markasitgruppe: Z. Kristallogr. (A) 68 (1928) 87–94.

was due to some crystal irregularity like lineage structure affecting the focussing of the X-ray beam by the crystal. In view of the conclusions reached in the subsequent structural discussion, however, it is now apparent that this displays the true symmetry of an individual gudmundite crystal while the higher symmetry ordinarily indicated is due to twinning. (Unfortunately this tiny crystal was lost after one photograph was made with CoK radiation.) If this is the case, the true symmetry of gudmundite is 2, m , or $2/m$, i. e., it is monoclinic. Otherwise the centrosymmetrical symmetry is $mmm = V_h$.

Space lattice type. — The discussion of the space lattice type duplicates that for the Spindelmühle arsenopyrite.

Unit cell. — The dimensions of the unit cell, determined as in the case of the Spindelmühle arsenopyrite, are as follows:

	absolute	axial ratio	Johansson's optical axil ratio
a	6.68 Å	.666	.6729
b	10.04	1.	1.
c	5.93	.591	$2 \times .5934$

These values are less accurate than in the case of the Spindelmühle arsenopyrite partly because they were made with an older model camera incapable of recording the higher reflections. Johansson had too little material to permit him to make a density determination. It is therefore impossible to make a direct determination of the number of formula weights per cell, but on the basis of the isomorphism of arsenopyrite and gudmundite this can confidently be taken as 8.

Space group. — Gudmundite displays the same lack of doubled reciprocal translations as arsenopyrite does, with the following exception: The reciprocal translation along the single line $[001]$ is doubled. Either this is due to a fortuitous z parameter combination, or it indicates a two-fold screw axis parallel to the c axis. In the latter case, the space group $C222_1$ is a possibility for gudmundite, in addition to $Cmmm$, Cmm and $C222$ as given for arsenopyrite. Gudmundite, in addition, shows a fortuitous quartering of (010) .

If the symmetry of diffraction effects is taken as mmm as indicated by the majority of gudmundite crystals tested, the diffraction symbol is accordingly $mmmC$ —, or possibly $mmmC$ — 2_1 corresponding with space groups $Cmmm$, Cmm , $C222$ and possibly $C222_1$. If, on the other hand, the diffraction symmetry indicated by the anomalous small gudmundite crystal is representative of the true symmetry of the single crystal, the diffraction effect symbol is $2/mC$ — or possibly $2/mC2_1$ —. The true significance of this possibility will be discussed subsequently.

Part II. Crystal Structure.

General Considerations.

The spectra of the arsenopyrite type crystals are characterized by remarkable systematically absent (or very weak) classes not required by the operations of any space group which might apparently come up for consideration. In the first place, the $h00$ spectra are present only in orders divisible by 4 and their intensities form a gradually declining series.

It is important to distinguish between a *gradual* decline and a *regular* decline. A *regularly* declining intensity series may be defined as one due

to atoms arranged in identically populated, equally spaced, plane sheets parallel with the reflecting plane. It follows that each such reflection will be composed of contributions of all the atoms in phase, and that, therefore, each reflection will have the maximum intensity possible for its value of $\sin \theta$. The criterion for a *regularly* declining series, therefore, is that for each reflection in the series there exists no other reflection of greater intensity outside the series and having a comparable $\sin \theta$ value (a comparison easily made on a Weissenberg film). If, on the other hand, all the atoms are in sheets as above, but sheets which are almost but not quite planes, the phases are less and less in register in the higher orders, and this decreases the intensities of the higher order spectra at an abnormally rapid rate. This may be called a *gradually* declining intensity series, and the criterion for it is that there may exist spectra of greater intensity outside the series for comparable $\sin \theta$ values. This is the case with the $4n . 0 . 0$ series in the arsenopyrite group, and it plainly indicates that the structure consists of (100) sheets which are almost plane and which are spaced $a/4$ apart. The Θ_a parameter of all atoms must then be either all 0° , 90° , etc. or all $+45^\circ$, -45° , etc.

Two other systems of absent spectra, not associated with gradual declines, are characteristic of the arsenopyrite type structures. The series $0k0$ is present only in orders divisible by 4 and the series $00l$ is present only in orders divisible by 2. These absences call for a brief discussion of the possibilities of accounting for missing classes with these characteristics:

A pinacoid spectrum may be missing provided the wave scattered by each atom is destroyed by an identical atom scattering a wave of the same amplitude but opposite sign. In general, the expression for the structure amplitude of a wave scattered by a pinacoid plane contains both a sine and a cosine term and has the form:

$$A \sim \sqrt{\sin^2 h\Theta_1 + \cos^2 h\Theta_1} + \sqrt{\sin^2 h\Theta_2 + \cos^2 h\Theta_2} \dots \dots$$

With certain symmetrical distributions of $h\Theta$'s about certain values, these contributions vanish for odd values of h as indicated in the following table:

		alternative distributions		
cosine terms vanish when h is odd	$h\Theta_1 = 90^\circ + A$ $h\Theta_2 = 90^\circ - A$	$h\Theta_1 = \chi$ $h\Theta_2 = \chi + 180^\circ$		(1)
sine terms vanish when h is odd	$h\Theta_1 = \dots + A$ $h\Theta_2 = \dots - A$	$h\Theta_1 = \chi$ $h\Theta_2 = \chi + 180^\circ$		

With regard to the sine terms in the left-hand alternative, it will be noted that a symmetrical distribution on both positive and negative sides of