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

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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 *C*222 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) 361–395.

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 Jong[4], 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 arseno-pyrite group as given by de Jong[4].

	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 axes[5], 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 dissertation[1]), 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 Suletjelma, Norway, for which the following analysis is quoted:

	weight per cent	ratio
Fe	33.93 }	1.4
Co	6.81 }	
As	38.40	1
S	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 $hk0$ 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
Fe	32.48	.581 }	1
Co	1.16	.0197 }	
As	48.72	.650	1.08
S	18.80	.587	.98
	101.16		

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.
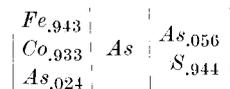
The theory of reducing abnormal analyses has been discussed by the writer in another place[1]), with special consideration to members of the marcasite group. Assuming that the extra-ideal atoms enter the structure of arsenopyrite in proxy solution, as they do in the case of marcasite and löllingite, the general formula for the Franklin arsenopyrite may be written:

$$\begin{vmatrix} Fe_u \\ Co_v \\ As_w \end{vmatrix} As_1 \begin{vmatrix} As_x \\ S_y \end{vmatrix}$$
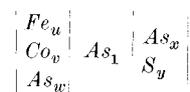
The atomic ratios require following conditions:

$$\begin{cases} u + v + w = 1 \\ x + y \quad\;\; = 1 \\ \dfrac{w + 1 + x}{y} = \dfrac{.650}{.587} \\ \dfrac{u}{v} = \dfrac{.581}{.0197} \\ \dfrac{u + v}{1 + w + x} = \dfrac{.581 + .195}{.650} \end{cases}$$

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:

$$\begin{vmatrix} Fe_{.943} \\ Co_{.933} \\ As_{.024} \end{vmatrix} As \begin{vmatrix} As_{.056} \\ S_{.944} \end{vmatrix}$$

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 is[2]):

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

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.

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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 symmetry[1] C_{2l}. 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 ζ values of the layer lines, determined by comparison with Bernal's charts[2], 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 15° 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 Bernal[2] 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) 117—160.

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 lattice[1]), 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 films[2]), 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 translations[3]) 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_{2l}. 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
$a =$	6.42 Å	.675	.6758
$b =$	9.51	1.	1.
$c =$	5.65	.594	.5945
$V =$	345.		

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

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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 $Cmmm - V_h^{19}$, $Cmm = C_{2v}^{11}$, and $C222 = V^6$ are possible.

The Gudmundstorp Gudmundite.

Material. — Gudmundite, $FeSbS$, known only from Gudmunstorp, Norway, has recently been described by Johansson[1]. 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_{2i}. In the case of this particular crystal the c axis rotation film, although displaying a position symmetry C_{2i}, had an intensity distribution C_2 (Fig. 1). In view of the fact that this could not be duplicated with other crystals it was at first thought that this anomalous low symmetry
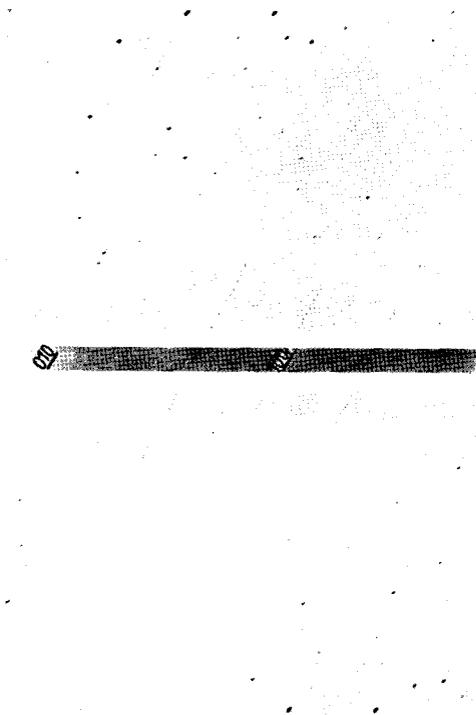

Fig. 1. Zero layer Weissenberg photograph obtained from tiny gudmundite crystal for rotation about the c axis (b axis for new orientation discussed beyond). This photograph is characterized by a position symmetry C_{2i}, but has the inferior intensity distribution symmetry C_2. It is shown in part II 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, 1. Gudmundit, ein neues Mineral innerhalb der Markasitgruppe: Z. Kristallogr. (A) 68 (1928) 87—91.

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 θ. 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 θ 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 θ 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 $+45°$, $-45°$, 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:

$$A \sim \sqrt{\sin^2 h\theta_1 + \cos^2 h\theta_1} + \sqrt{\sin^2 h\theta_2 + \cos^2 h\theta_2} \ldots \ldots$$

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	$h\theta_1 = 90° + A$ $h\theta_2 = 90° - A$	$h\theta_1 = \chi$ $h\theta_2 = \chi + 180°$
sine terms vanish when h is odd	$h\theta_1 = \quad + A$ $h\theta_2 = \quad - A$	$h\theta_1 = \chi$ $h\theta_2 = \chi + 180°$

(1)

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

zero eliminates the sine term no matter what the value of h is, so that crystals showing this sort of absent class in, say, $h00$ spectra must be effectively centrosymmetrical in bc projection for these spectra, for this alternative, i. e., they must show some sort of projected symmetry. This is an important criterion for the elimination of certain structures.

It follows from the above discussion that in the arsenopyrite type, the appearance of $0k0$ only in orders divisible by 4, and the appearance of $00l$ only in odd orders indicates the following parameter distributions for all atoms:

$$\left\{\begin{matrix} \Theta_{b1} = 45° + \varDelta \\ \Theta_{b2} = 45° - \varDelta \end{matrix}\right\} \quad \text{or} \quad \left\{\begin{matrix} \Theta_{b1} = \chi_b \\ \Theta_{b2} = \chi_b + 90° \end{matrix}\right\} \tag{2}$$

$$\left\{\begin{matrix} \Theta_{c1} = 90° + \varDelta \\ \Theta_{c2} = 90° - \varDelta \end{matrix}\right\} \quad \text{or} \quad \left\{\begin{matrix} \Theta_{c1} = \chi_c \\ \Theta_{c2} = \chi_c + 180° \end{matrix}\right\} \tag{3}$$

The arsenopyrite structural type contains 8 formula weights per unit cell, so that, in arsenopyrite, for example, 8 atoms of each of the three Fe, As, and S must be accounted for. The cell is C-centered so that, allowing for the translation duplication in an end centered cell, there must remain 4 kinds of atoms each to account for. Because of the occurrence of the missing spectra, above discussed, these 4 kinds can be treated as not more than 2 pairs with symmetrically disposed parameters. If, furthermore, the crystal contains a symmetry element such as a true or projected symmetry center in the bc plane, then the number of independent parameters is reduced to one per element per degree of freedom.

In order to test the possibility of the presence of a projected center of symmetry in the bc plane, parameters were searched for which would satisfy the spectra using a centro-symmetrical structure factor, intensities being calculated with the aid of the relation:

$$I \sim \frac{1 + \cos^2 2\theta}{2 \sin 2\theta} \cdot A^2$$

where $A = F_{Fe} \cos h\Theta_{Fe} + F_{As} \cos h\Theta_{As} + F_S \cos h\Theta_S$.

Starting with the preliminary location of the heavier atoms and a trial elimination of impossible regions, a set of values of Θ for Fe, As, and S in arsenopyrite have been arrived at which give a thoroughly satisfactory intensity check for the $0kl$ spectra of these crystals. These values are as follows:

	Arsenopyrite	
	Θ_b	Θ_c
Fe	$\sim 0°$	$\sim 0°$
As	$54°$	$46°$
S	$60°$	$48°$

A further discussion and justification of these values will be given on
subsequent pages. The fact that such a thoroughly satisfactory set of
values can be found, based upon the use of a structure factor lacking sine
terms, may be regarded as proof of the presence of a symmetry center
or a projected symmetry center on the bc plane in the structure.

The correct space group must give a satisfactory explanation of the
positions of the atoms in terms of these parameters. It should be observed
that the iron atoms have parameters permitting them to occupy special
positions without degrees of freedom, if necessary, but that the other
atoms have parameters of such obviously general values that they can
only occupy such special positions as have appropriate degrees of freedom
in the b and c directions.

This approach, it should be stated, was not the one first employed.
It is placed here in this order because it provides a clear proof of the
incorrectness of the orthodox symmetry of the arsenopyrite group and
an equally clear argument for the correctness of the structure finally
derived.

Possible Orthorhombic Structures.

Since the arsenopyrite group is regarded as orthorhombic, with no
evidence to the contrary, with the exception, here reported, of the distri-
bution of intensities on the Weissenberg film of a small gudmundite
crystal, the possible orthorhombic arsenopyrite structures are appro-
priately discussed first. The combined Weissenberg data for the group
indicate that such structures can have no glide planes and can have no
screw axes parallel with c; therefore only space groups $Cmmm$, Cmm and
$C222$ need be explored. The most probable space group would be $Cmmm$,
of course, for no crystallographic data or figures[1]) hint at less than holohe-
dral orthorhombic symmetry.

The arguments advanced in the subsequent pages of this section
have for their object the elimination of the orthorhombic space groups.
There are a number of ways of doing this. In order to save space, the
following plan is employed: A permissible space group must provide for
quartering sheets, i. e., sheets with a parameters either $\pm \frac{1}{8}$, or 0 and $\frac{1}{4}$.
In each of these sheets it must further provide for equipoints of ranks
totalling 8, i. e., 4 per C-centered pair of quartering sheets, and having
two positions per sheet with both degrees of freedom, corresponding with
the necessary variable b and c parameters of the As (or Sb) and S atoms.

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1) Goldschmidt, Victor, Atlas der Kristallformen, vol. I (1913), tables 117
bis 124, figures 1—132.

This is equivalent to requiring that if As (or Sb) and S atoms occupy special positions, they must be symmetry planes.

It should be emphasized that a more formal elimination of the orthorhombic space groups can be given. The present argument has the advantage of minimum discussion.

Space group $Cmmm$. — This space group contains 2-, 4-, 8-, and 16-fold equipoints. Since only 8 atoms of each element must be accommodated, the atoms cannot be in the general position. If quartering sheets are selected at $\pm \frac{1}{8}$, then no special positions are available having both b and c parameters variable. If quartering sheets are selected at 0 and $\frac{1}{4}$, then it is possible to place the variable position atoms on $4o$ for the 0 sheet, which provides for both degrees of freedom, but there are no special positions of this character for the quartering sheet. The space group $Cmmm$ $= V_h^{19}$ is therefore eliminated because it cannot provide equipoints giving rise to the observed intensities.

Space group Cmm. — This space group contains no projected center of symmetry on the bc plane, and hence may be eliminated on the ground that the correct structure contains such a projected center. More particularly, this space group contains equipoints of ranks 2, 4, and 8. Unless the atoms requiring two degrees of freedom are in the general positions, then the arguments advanced for the elimination of $Cmmm$ hold here also. If these atoms are in the 8-fold, general positions, and some fortuitous projected quasi-center of symmetry is assumed, then it is still impossible to account for the absent classes of $0k0$ because the symmetry elements of the space group definitely link the 8 atoms in a different way than required for the disappearance of these classes. This space group is therefore eliminated on the grounds that it cannot account for observed intensities.

Space group $C222$. — This space group contains 2-, 4-, and 8-fold equipoints. Unless the atoms requiring the two degrees of freedom are placed in the general position, it is impossible to find equipoints permitting the required variation in parameters and at the same time giving quartering sheets. If these atoms are placed in the 8-fold general positions, they must have $\Theta_a \approx \pm \frac{1}{8}$. The iron atoms then automatically occupy the special positions $4g$ and $4h$ from their required parameters and from the 100 quartering requirement. The structure so derived from the application of the correct parameters does not give the missing classes of the $0k0$ spectra, however, because the symmetry operations of the space group make the 8 atoms dependent in a different way than indicated in (2) and (3) above. This space group is therefore eliminated on the grounds that it cannot account for all the intensities.

Possible Structures of Lower Symmetry.

Mimetic twinning. — The foregoing discussion definitely points to the necessity of a symmetry lower than orthorhombic for the arsenopyrite group. If this is the case, then it is necessary to account for the orthorhombic diffraction effects clearly displayed by the Weissenberg photographs. Twinning of some sort would furnish an appropriate explanation. Such evidence was searched for by examining in reflected polarized light, oriented single crystals of arsenopyrite polished on a special device

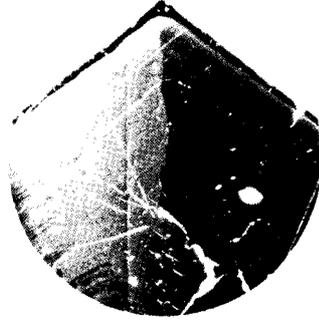developed for this purpose. The twinning has actually been observed and is shown in Figure 2. This type of twinning has apparently already been observed by Scherer[1]) as a result of etching the brachydome. Scherer explained his etching results as follows:

> The condition that there appears on the base, four compartments which behave equally, indicates twin formation. This presupposes the assumption of asymmetrical individuals and therefore has little claim on truth. It is clear to me that probably the etch lines result from the varying degrees of solubility of the component parts of the crystal...

Fig. 2. Polished surface of a Spindelmühle arsenopyrite crystal in reflected, polarized light, crossed nicols, × 50. The surface of the section is nearly parallel to (001), the a axis is up and down, the b axis left and right. The upper angle is the trace of what has been supposed to be the junction of ($\bar{1}\bar{1}0$) with ($\bar{1}10$). The dark and light halves are the two individuals of a twin, the suture between them being the trace of the composition surface. All notation is referred to the old arsenopyrite orientation.

The extinction effects of the individuals in reflected polarized light leave no doubt that the composite nature of the crystals is due to twinning and not to growth zones.

Superstructures based upon the marcasite plan. — With the inferior character of the symmetry of the group established, the space groups of lower symmetry giving the same diffraction effects next come up for consideration. These are the space groups $C2/m$, Cm, $C2$, $C\bar{1}$ and $C1$. These may be explored for structures satisfying the intensity conditions on the same basis that the orthorhombic space groups were explored. Thus, Cm and $C1$ can be eliminated on the ground that they do not contain projected centers of symmetry in the bc plane, and $C2/m$ can be eliminated on the ground that it cannot account for the absent orders of $0k0$, thus leaving only space groups $C2$ and $C\bar{1}$ for consideration.

At this point it is important to leave the formal approach, and to regard arsenopyrite as a superstructure based upon the marcasite plan.

1) Scherer, Friedrich, Studien am Arsenkiese, Z. Kristallogr. (A) 21 (1893) 354—387.

If this is done it accounts perfectly for the absent classes of spectra. This is dealt with more fully in an accompanying paper[1]).

Superstructures have two aspects: compositional and geometrical. Chemically, the marcasite type crystals may be regarded as of formula type $A B B$ while the arsenopyrite type crystals may be regarded as of formula type $A B' B''$; i. e., in the arsenopyrite type the B atoms are differentiated into two classes, B' and B''. This differentiation calls for an appropriate alternation of the two classes of B atoms[2]) as a consequence of which a superstructure may result. This geometrical aspect is known from the cell dimensions of the simple and superstructure crystals.

It is possible to derive all the general superstructures compatible with a given set of compositional and geometrical conditions[3]). This has been carried out in the case of the arsenopyrite type superstructure in an accompanying paper[3]). There it is shown that there are 5 possible distinct arsenopyrite structures based upon the marcasite type packing and consistent with type and dimensions of the arsenopyrite space lattice. These are designated:

$$ab'ba'$$ monoclinic, $C2_1/d$
$$ad'bc'$$ monoclinic, $C2$ (enantiomorphous)
$$cd'dc'$$ monoclinic, $C2_1/d$
$$ae'be'$$ monoclinic, Cm
$$ce'de'$$ monoclinic, Cm.

Plan of superstructure investigation. — The problem now resolves itself into an elimination of incorrect superstructures and a determination of the parameters of the correct structure. The two Cm structures are eliminated, as already noted, because they cannot account for projected centers of symmetry on the bc plane and, quite apart from this symmetry objection, cannot give rise to the observed absent orders of $0k0$. There remain three possible superstructure types, one in $C2$ and two in $C2_1/d$. It may be said at the outset that the two holohedral structures are the most probable ones in view of the symmetry distribution displayed by one of the gudmundite crystals (page 90—91).

Each of these structures is capable of giving rise to the correct, or at least approximately correct, pinacoid spectral series (the significance

1) Buerger, M. J., A systematic method of investigating superstructure applied to the arsenopyrite crystal structural type. Z. Kristallogr. (A) 94 (1936) 425—438.

2) Buerger, M. J., The temperature-structure-composition behavior of certain crystals, Proc. Nat. Acad. Sci. U.S.A. 20 (1934) 444—453.

3) Buerger, M. J., A systematic method of investigating superstructures, applied to the arsenopyrite crystal structural type. Z. Kristallogr. (A) 94 (1936) 425—438.

of "approximate" here refers to the exact location of the iron atoms which will be discussed under the appropriate structures). The structures differ, however, in their 110 and $1\bar{1}0$ intensity series and also in the physical significance of the slight variation of the Θ_a parameters from the approximate values of $0°$ and $90°$, a variation which is necessary for the spoiling of the $4h.0.0$ intensity series from the ideal *regular decline* to the actually observed *gradual decline*. The trial spoiling of this regular series cannot be made directly by calculating the intensities of the $h00$ series because this series has only one quarter of its quota of reflections and is rather intensitive to slight parameter changes; the trial variation of the Θ_a parameters is best made by studying the changes brought about in the $hh0$ and $h\bar{h}0$ series whose reflections are present in all orders.

Structure $ad'bc'$ (monoclinic sphenoidal). — It will be shown in the next section that there are certain extinctions present in the diffraction effects of the crystals of the arsenopyrite group which are not recognized until the holohedral possibilities, $ab'ba'$ and $cd'dc'$, are given consideration. These extinctions receive no explanation from the less symmetrical $C2$ structure now under consideration and it may therefore be eliminated from further consideration.

Monoclinic holohedral structures. — These structures require a number of general comments:

1) In the first place, they both belong to space group C_{2h}^5, which may be set up in a number of ways. It is customarily set up, referred to the primitive lattice with axial glides, as $P2_1/c$ or $P2_1/a$, or referred to the primitive lattice with diagonal glide as $P2_1/n$. It may also be set up referred to the doubly primitive, B-centered lattice which requires the diamond glide, d, with quarter cell glide components; this is $B2_1/d$. In the case of the arsenopyrite group of crystals, the latter general type of set-up is preferable because it brings out the nearly orthogonal, pseudo-orthorhombic character of the crystals and retains axes which are comparable with the axes of the related marcasite group of crystals. The screw axis which, by universal convention, is placed normal to the side pinacoid, B, in the monoclinic system, is actually found normal to C with the axial orientation customarily used for the arsenopyrite and marcasite groups of minerals. In view of the fact that the correct structure of arsenopyrite will be shown to belong to this monoclinic space group, it will be necessary to make an interchange of at least the customary arsenopyrite b and c axes to conform with the convention of orienting monoclinic crystals. It is further desirable to have the new orientation such that it will leave arsenopyrite with the same orientation as rutile (whose c axis is fixed by symmetry) and manganite (whose customary orientation need not be changed with the discovery that it is monoclinic and not orthorhombic). The reason for wishing comparable orientations is that manganite has the arsenopyrite structure[1]) and that

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1) Buerger, M. J., The symmetry and crystal structure of manganite, $Mn(OH)O$. Z. Kristallogr. (A) in press.

arsenopyrite may be thought of as derived from a rutile structure by several gene-
ralizations[1]). The following interchange of axes in arsenopyrite is therefore desirable:

old arsenopyrite axes		new monoclinic arsenopyrite axes
a	$\rightarrow$	c
b	$\rightarrow$	a
c	$\rightarrow$	b

In all subsequent discussion of arsenopyrite, the new monoclinic orientation will
be used.

2) The appearance of orthorhombic diffraction symmetry in the arsenopyrite
group indicates that, if one of the two monoclinic holohedral structures is correct,
the twins are so arranged that the following orientation relations hold in the twinned
composite:

	first individual	twinned individual
primitive lattice	a	c
	c	a
B-centered lattice	$[101]$	$[10\bar{1}]$
	$[10\bar{1}]$	$[101]$

The X-ray diffraction of the twinned composite therefore gives rise to a composite
pattern in which the following reflections record at the same position on the film:

	first individual	twinned individual
primitive lattice	$h0l$	$l0h$
B-centered lattice	$h0l$	$\bar{h}0l$

The composite nature of the pattern from twinned samples must be taken account
of in considering both the space group extinctions and the calculations of intensities
for comparison with observed intensities.

3) The glide plane and screw axis of the space group introduce customary
extinctions but these are complicated and obscured by the choice of B-centered
lattice and by the presence of twinning. The extinction rules are indicated in the
following scheme:

Primitive lattice, $P2_1/c$

	first individual	twinned individual in-dexed on reference frame of first individual
extinction rule for indi-vidual:	$h0l$ absent when l is odd	$h0l$ absent when h is odd
extinction rule for twinned composite indexed on reference frame of first individual:	$h0l$ absent when both h and l are odd.	

1) Buerger, M. J., The crystal structure of marcasite. Amer. Mineralogist 16
(1931) 392—393.

B-Centered lattice, $B2_1/d$

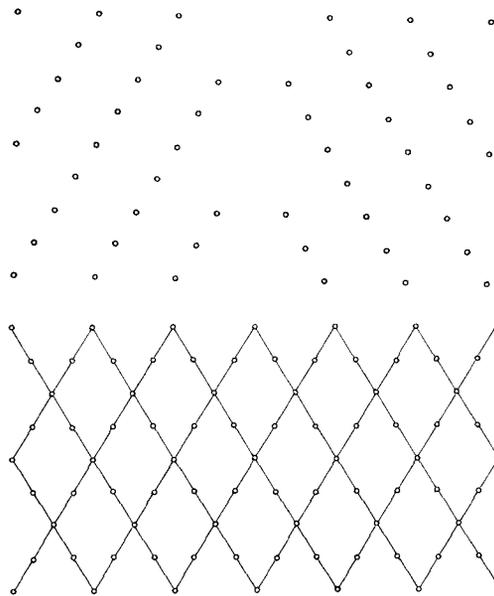|	first individual	twinned individual indexed on reference frame of first individual
extinction rule for individual:	$h0l$ absent when $h + l = 4 - 2n$	$h0l$ absent when $- h + l = 4 - 2n$ or $h + l = 4 - 2n$
extinction rule for twinned composite indexed on reference frame of first individual:	$h0l$ absent when $\pm(h \pm l) = 4 - 2n$	

where n = any integer.

Fig. 3. Zero levels of arsenopyrite reciprocal lattices normal to the b axis (new orientation). The upper left shows the reciprocal lattice of one individual, the upper right shows the reciprocal lattice of the other individual of an arsenopyrite twin. The lower diagram shows the diffraction effect reciprocal lattice of the twinned composite. This only shows apparent extinctions which are common extinctions to both individuals of the twin. Such extinctions are located at the centers of the meshes formed by drawing in the even-numbered, primitive reciprocal lattice grid lines.

The screw axis also introduces the extinction of $0k0$ in odd orders, referred to either the primitive of B-centered lattice.

If the twinned aspect of the crystal sample is recognized, the extinction effects due to the glide plane may be easily discerned either directly on the Weissenberg film or on reconstructed reciprocal lattice[1]) by referring to primitive lattice coordinates, a transformation easily made by inspection on the Weissenberg film itself. In the reconstructed reciprocal lattice, all even numbered net lines parallel with the two primitive coordinate axes are drawn in (Fig. 3). The centers of the resulting

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

meshes are the locus of indices *odd*, 0, *odd*. These reflection positions should be unoccupied.

This set of extinction rules is found to be obeyed perfectly by gudmundite, by manganite, and also by arsenopyrite subject to the deviations
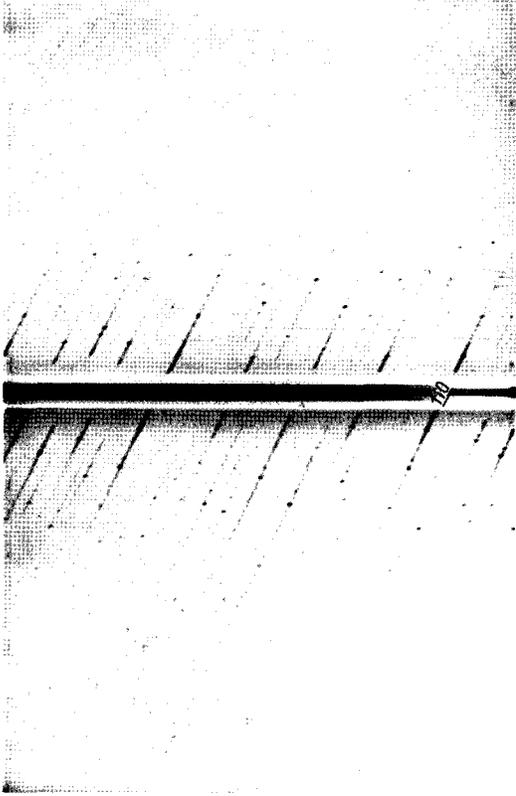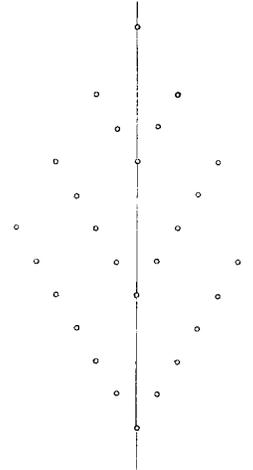

<div align="center">Fig. 4 A.   Fig. 4 B.</div>

Fig. 4. Zero layer Weissenberg photograph for c axis (new b axis) rotation of a fragment of a gudmundite crystal. The crystal is twinned, but is sufficiently absorbing so that substantially only one half of the crystal reflects above, and the other half reflects below the center line in the middle region of the photograph. In this region the half photographs consequently show the symmetry C_2 and the extinctions characteristic of $B2_1/d$. The diagram shows the relation of reciprocal lattices in the two halves of the twin.

noted beyond for this particular species. In the case of gudmundite, it was mechanically possible to break away half of a fourling because of its elongation in the c axis direction. The resulting crystal was thick enough so that in a certain rotation range ((401) to ($\overline{4}$01) reflecting) only reflec- .

tions from one individual of the resulting twin recorded on the b axis equator film, the reflections of the other being screened by absorption (Fig. 4). Within this range, the twinning is not observed and the extinctions are exactly those required for the untwinned $B2_1/d$. Since the absent odd orders of 010 of gudmundite are in accord with the screw 2_1, this space group gives a unique explanation of the remarkable absent classes of spectra in the arsenopyrite group of crystals.

A violation of the space group extinctions by the ordinary arsenopyrite should now be noted. In the case of arsenopyrite, the absent spot positions are actually occupied in many cases by very weak ones, which show up best with the cleaner cobalt radiation. The violation is especially noticeable in the case of the pinacoid reflections: 010, 030, 050 (which eliminated a screw axis from consideration in part I), also 200 and 600. These anomalous reflections are confined to the species arsenopyrite and completely fail in the cases of gudmundite and manganite. These reflections may be attributed to a lowered symmetry caused by regular distribution of foreign atoms in arsenopyrite: Arsenopyrite has a variable content of its three elements. By proxy solution, for example, excess arsenic may proxy for iron, as in the case of the Franklin mineral, or *vice versa*, as in the case of the Suletjelma danaite. If the proxying atom distributes itself only within the alternate sheets (an expectable kind of packing for distortion economy, for example) then the screw axes and glide planes are lost, the crystal becomes triclinic, space group $B\bar{1}$, and the anomalous reflections arise. In view of the fact that a perfect check between calculated and observed intensities for one of the monoclinic holohedral structures can be obtained even in the case of arsenopyrite, this explanation may be received as the correct one.

The pinacoidal intensities are best calculated with the aid of parameters referred to the B-centered lattice. The intensity calculations for the permissible pinacoid reflections take the form:

$$I \sim \frac{1 + \cos^2 2\theta}{2 \sin 2\theta} \ (\Sigma F \cos n\Theta_{a,c})^2$$

where $\Theta_{a,c} =$ the angular parameter referred to the B-centered lattice.

$n =$ the order of the reflection referred to the B-centered lattice.

The c parameters are best fixed by a study of the B-centered $101 + 10\bar{1}$ reflection orders. The calculations for these reflections are best treated as

referred to the primitive lattice where they become the orders of $100 + 010$. The structure factor referred to the primitive lattice is:

$$4 \cos (h\varphi_a + l\varphi_c + [k + l]\pi/2) \cos (k\varphi_a - [k + l]\pi/2) .$$

For the intensities of the orders of $100 + 010$, the calculations take the form:

$$I \sim \frac{1 + \cos^2 2\theta}{2 \sin 2\theta} \{(\Sigma F \cos h\varphi_a)^2 + (\Sigma F \cos l\varphi_c)^2\}$$

where $\varphi_{a,c} =$ the angular parameters along the a and c directions of the primitive lattice.

The following simple relations permit easy transformation from the B-centered to primitive lattices and reverse:

P from B	B from P
$\varphi_a = \Theta_a - \Theta_c$	$\Theta_a = \frac{1}{2}(\varphi_a + \varphi_c)$
$\varphi_c = \Theta_a + \Theta_c$	$\Theta_c = \frac{1}{2}(-\varphi_a + \varphi_c)$
$x_a = X_a - Y_c$	$X_a = \frac{1}{2}(x_a + y_c)$
$y_a = X_a + Y_c$	$Y_c = \frac{1}{2}(-x_a + y_c)$
$h_p = \frac{1}{2}(h_c - l_c)$	$h_c = h_p + l_p$
$l_p = \frac{1}{2}(h_c + l_c)$	$l_c = -h_p + l_p$

In the following two monoclinic holohedral possibilities, the main structural difference is that in the first case, $ab'ba'$, the iron atoms occupy symmetry centers, while in the second case, $cd'dc'$, the iron atoms are in the general position. The rest of the atoms are in the general position in both structures.

Structure $ab'ba'$ (monoclinic holohedral). — The first monoclinic holohedral structural possibility is shown diagrammatically in Fig. 5. Since the iron atoms occupy positions without degrees of freedom,

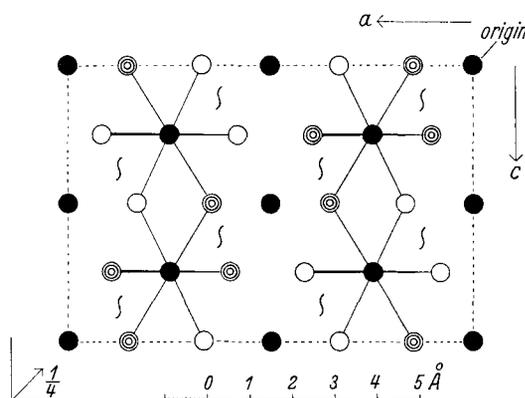Fig. 5. The possible superstructure $ab'ba'$, projected on (010) (new orientation), showing distribution of symmetry elements (centers occupied by iron atoms). Iron atoms are shown black, arsenic atoms ringed, sulfur atoms as single circles. For clearness the bonding of the iron atoms to their immediate coördination environments is indicated only for the environments entirely within the B-centered cell.

the only method of spoiling the ideal nature of the 0. 0. 4l intensity series is through variation of the Θ_c parameters of the As and S atoms. The parameter scheme is then as follows:

Arsenopyrite

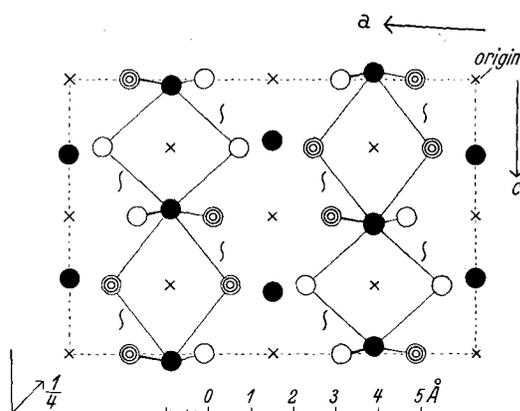|	Θ_a	Θ_b	Θ_c		φ_a	φ_b	φ_c
Fe	$0°$	$0°$	$0°$		$0°$	$0°$	$0°$
As	$53°$	$46°$	$0° + \delta_1$		$53° - \delta_1$	$46°$	$53° + \delta_1$
S	$60°$	$48°$	$180° + \delta_2$		$-120° - \delta_2$	$48°$	$240° + \delta_2$

Fig. 6. The possible superstructure $cd'dc'$, projected on (010) (new orientation) showing distribution of symmetry elements. Iron atoms are shown black, arsenic atoms ringed, sulfur atoms as single circles. For clearness, the bonding of the iron atoms to their immediate coördination environments is indicated only for the environments entirely within the B-centered cell. The deviation of the iron atoms from the (001) planes by the parameter δ is obvious. This is the correct structure, with cell and parameters to scale for arsenopyrite.

It is impossible to duplicate the observed intensity series with these variations. Furthermore, such variations are extremely unlikely from a physical point of view because they imply different spacings between similar atom pairs in different parts of the structure.

Structure $cd'dc'$ (monoclinic holohedral). — This structural possibility, which is shown diagrammatically in Fig. 6, is believed to be the correct one because it not only provides an excellent agreement between calculated and observed intensities, but because it is physically and chemically reasonable. All atoms are in the general position. The only physically important variation in the c parameters is a slight shift in the positions of the iron atoms due to their being packed between large and small atoms along the c axis, thus:

the parameter scheme is:
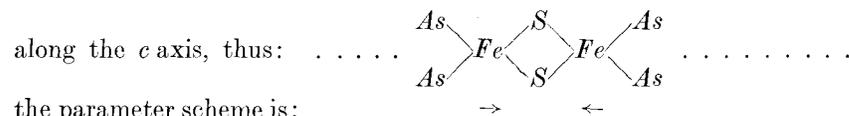
Arsenopyrite.

	Θ_a	Θ_b	Θ_c	φ_a	φ_b	φ_c
Fe	0°	0°	90° + δ	— 90° — δ	0°	90° + δ
As	53°	46°	0°	53°	46°	53°
S	60°	48°	180°	--120°	48°	240°

Table II shows the excellent comparison between observed and calculated intensities for the final arsenopyrite structure when δ -= 9°. Data for the species gudmundite will appear shortly.

Table II. Comparison of calculated and observed reflection intensities for arsenopyrite.

orders of 100		orders of 101 + 10$\bar{1}$		orders of 001		orders of 010	
calculated	observed	calculated	observed	calculated	observed	calculated	observed
8 -= 402	8	2 = 7040	2			2 = 1240	2
	⩔						∨
12 = 240	12	1 = 423	(not	gradual	gradual	8 -= 462	8
	∨		recorded)				⩔
4 = 164	4	7 -- 260		decline	decline	4 -= 296	
	⩔		⩔				4,6
20 -= 76	20	5 -= 232				6 -= 236	
	∨		4, 5, 6, 7				⩔
16 = 0.4	16	6 -= 222				14 -= 45	14
			∨				∨
		4 -= 204				12 -= 11	
							12,10
		14 -= 133				10 -= 7	
			14, 10				
		10 = 122					
		9 -= 35					
			∨				
		8 -= 34	3, 9, 8				
		3 -= 28	∨				
		12 = 2.8					
		11 -- 1.4	11, 12, 13				
		13 = 0.9					

Discussion of the Arsenopyrite Structure.

Table III summarizes the crystal structure of arsenopyrite in conventional monoclinic orientation and referred to the B centered lattice.

Tabe IV gives the interatomic distances between nearest neighbors in the structure.

Table III. Arsenopyrite crystal structure data.

Orientation transformation: customary orientation   new orientation

$$a \rightarrow c$$
$$b \rightarrow a$$
$$c \rightarrow b$$

Ideal Arsenopyrite
(presumably of ideal $FeAsS$ composition)

Crystal system and class: monoclinic holohedral
Unit cell, B-centered:

$$a = 9.51 \text{ Å}$$
$$b = 5.65$$
$$c = 6.42$$
$$\beta = 90°$$

formula weights
of $FeAsS = 8$

Space group: $B2_1/d$
Equipoints: all atoms in general position

Parameters:

	Θ_a	Θ_b	Θ_c	x_a	y_b	z_c
Fe	0°	0°	99°	0	0	.275
As	53°	46°	0°	.147	.128	0
S	60°	48°	180°	.167	.132	.500

Common Arsenopyrite

$$\left(\text{presumably of ordered proxy solution composition: } \frac{Fe \quad As \mid S}{A \mid B \mid C} \right)$$

Crystal system and class: triclinic holohedral
Unit cell, B-centered:

$$a = 9.51 \text{ Å}$$
$$b = 5.65$$
$$c = 6.42$$
$$a = \beta = \gamma = 90°$$

formula weights
of $\frac{Fe \mid As \mid S}{A \mid B \mid C} = 8$

Space group: $B\bar{1}$
Equipoints: all atoms in general position

Parameters:

	Θ_a	Θ_b	Θ_c	x_a	y_b	z_c
Fe_1	0°	0°	99°	0	0	.275
Fe_2	90°	180°	−9°	.250	.500	−.025
As_1	53°	46°	0°	.147	.128	0
As_2	37°	226°	90°	.103	.628	.250
S_1	60°	48°	180°	.167	.132	.500
S_2	30°	228°	−90°	.083	.632	−.250

Table IV. Interatomic distances between nearest neighbors in arsenopyrite.

atom	coördinates	neighbor	coördinates			distance
Fe	xyz	As	$-x-\frac{1}{4},$	$y-\frac{1}{2},$	$-z+\frac{1}{4}$	2.36 Å
		As	$x,$	$y,$	z	2.37
		As	$-x,$	$-y,$	$-z$	
		S	$x-\frac{1}{4},$	$-y+\frac{1}{2},$	$z-\frac{1}{4}$	2.19
		S	$x,$	$y,$	z	2.28
		S	$-x,$	$-y,$	$-z+1$	
		Fe	$-x,$	$-y,$	$-z+1$	2.89
		Fe	$-x,$	$-y,$	$-z$	3.53
As	xyz	Fe	$-x+\frac{1}{4},$	$y+\frac{1}{2},$	$-z+\frac{1}{4}$	2.36
		Fe	$x,$	$y,$	z	2.37
		Fe	$-x,$	$-y,$	$-z$	
		S	$-x+\frac{1}{2},$	$-y,$	$-z+\frac{1}{2}$	2.30
		S	$x,$	$y,$	z	3.22
		S	$x,$	$y,$	$z-1$	
		S	$x-\frac{1}{4},$	$-y+\frac{1}{2},$	$z-\frac{1}{4}$	3.03
		As	$-x,$	$-y,$	$-z$	3.15
		2As	$x+\frac{1}{4},$	$-y+\frac{1}{2},$	$z+\frac{1}{4}$	3.18
		2As	$-x+\frac{1}{4},$	$y-\frac{1}{2},$	$-z+\frac{1}{4}$	3.28
S	xyz	Fe	$x+\frac{1}{4},$	$-y+\frac{1}{2},$	$z-\frac{1}{4}$	2.19
		Fe	$x,$	$y,$	z	2.28
		Fe	$-x,$	$-y,$	$-z+1$	
		As	$-x+\frac{1}{2},$	$-y,$	$-z+\frac{1}{2}$	2.30
		As	$x,$	$y,$	z	3.22
		As	$x,$	$y,$	$z+1$	
		As	$-x+\frac{1}{4},$	$y-\frac{1}{2},$	$-z+\frac{1}{4}$	3.32
		S	$-x,$	$-y,$	$-z+1$	3.51
		2S	$x+\frac{1}{4},$	$-y+\frac{1}{2},$	$z+\frac{1}{4}$	3.16
		2S	$-x+\frac{1}{4},$	$y+\frac{1}{2},$	$-z+\frac{1}{4}$	3.35

A photograph of a scale model[1]) of the arsenopyrite structure is shown in Fig. 7. For comparison with the related marcasite and löllingite structures, this model, which contains one arsenopyrite cell and a few environing atoms, has been terminated at the customary marcasite origins and has been photographed in customary marcasite orientation. The correct arsenopyrite origin is at $[0\frac{1}{2}\frac{1}{2}]$, referred to customary marca-

1) Buerger, M. J., and Butler, Robert D., A technique for the construction of models illustrating the arrangement and packing of atoms in crystals. Amer. Mineralogist 21 (1936) 150—172.
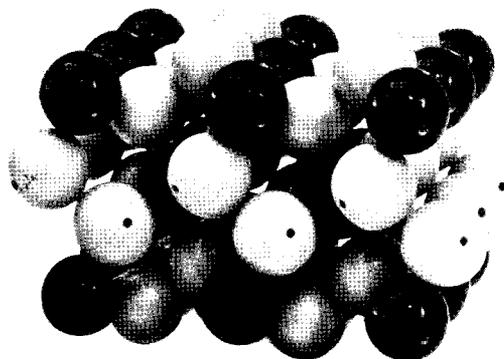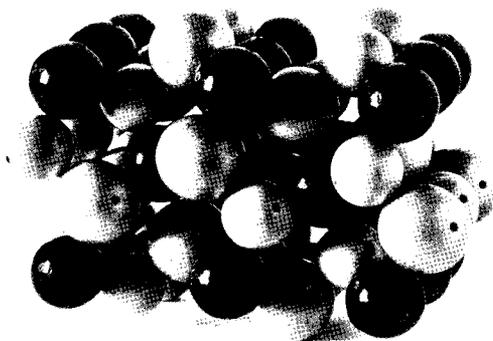
Fig. 7 A.

Fig. 7 B.

Fig. 7. Scale models showing the basic marcasite structure and the arsenopyrite
        superstructure based upon it, both in old marcasite orientation.

A. Four unit cells of marcasite, with some additional environing sulfurs to com-
   plete pairs.

B. Unit cell of arsenopyrite, with some additional environing arsenics and sulfurs to
   complete pairs. The black balls represent iron, large white balls arsenic, and
   small white balls sulfur. The model is very closely to scale except that the sul-
   fur atom is 1.00 Å instead of the correct size of 1.10 Å.

site cell, origin and orientation. Further aspects of the structure may be seen in Fig. 8, which gives three elevations of the model and shows the arsenopyrite orientation and origin.
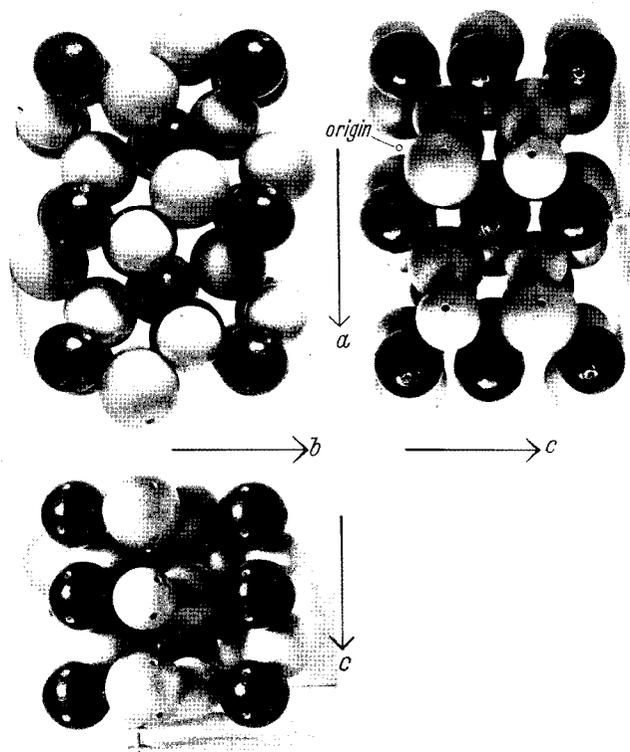

Fig. 8. Views normal to the three pinacoids of the *B*-centered unit cell of arseno-pyrite, showing the new monoclinic axes and the new origin. This model has been very slightly generalized by moving the irons atoms slightly out of the correct positions in the *a b* plane.

Each iron atom has six neighbors at the corners of a somewhat distorted octohedron. One face of the octohedron is a triangle of three arsenic atoms while the opposite face is a triangle of three sulfur atoms. This arrangement is a duplicate of that found about the cobalt atom in the cubic cobaltite structure.

The sulfur atom is surrounded by three iron atoms and one arsenic atom at the corners of a somewhat distorted tetrahedron. In a corresponding manner, the arsenic atom is surrounded by three iron atoms and one

The distances between iron and non-metal on the shared edge of the octohedral coördination of the iron atom are in excess of the above distances by .04—.05 Å. This is identical with the situation found in both löllingite and marcasite:

	$Fe + As$		$Fe + S$	
	arsenopyrite	löllingite	arsenopyrite	marcasite
observed distance to corner of unshared edge	2.32	2.33	2.23	2.21
observed distance to corner of shared edge	2.37	2.37	2.27	2.24
$\varDelta$	$+.05$	$+.04$	$+.04$	$+.03$

This increase in interatomic spacing may be ascribed to a shell repulsion across the shared edge.

It is very illuminating to inquire into the meaning of the small iron radius which seems to be characteristic of the arsenopyrite and löllingite crystals. If Pauling and Huggins'[1] radius of 1.23 Å is accepted as a criterion for Fe^{2+}, then it is certain that iron in this state is excluded from arsenopyrite and löllingite. On the other hand, although there is no precedent for the existence of Fe^{3+}, its radius may be derived by extrapolation from Pauling and Huggins' table:

Valence	Fe	Co	Ni
II	1.23	1.32	1.39
III	1.13	1.22	1.31
IV		1.12	1.21

This is almost exactly that observed in arsenopyrite, namely 1.125 Å. The ability of arsenopyrite to take excess As^{III} into proxy solution in place of Fe (see pages 86—87) would be difficult to understand if As^{III} proxied for Fe^{II}, but appears quite natural if As^{III} proxies for Fe^{III}.

The small radius of Fe in löllingite is similarly to be correlated with iron in the ferric state. It may be concluded that the formulae of arsenopyrite and löllingite may be written $Fe^{III}AsS$ and $Fe^{III}As_2$. It is also quite possible that the small radius of Fe in marcasite may likewise indicate a formula $Fe^{III}S_2$, as contrasted with pyrite, where the larger radius of Fe indicates the formula $Fe^{II}S_2$. In view of the importance of this possible correlation, another parameter study of marcasite is being undertaken to give better information regarding interatomic distances.

1) Pauling, Linus, and Huggins, M. L., Covalent radii of atoms and interatomic distances in crystals containing electron pair bonds. Z. Kristallogr. (A) **87** (1934) 228.

Summarized Characteristics of Arsenopyrite-like Crystals.

The marcasite type of packing is now known to constitute the basic structure of several crystals, including the marcasite group proper (FeS_2), the löllingite group (FeP_2, $FeAs_2$ and $FeSb_2$), and the mineral of doubtful formula, hydrophylite ($CaCl_2$?). The rough structure of manganite $Mn(OH)O$ is also marcasite-like. Further investigation is certain to extend this list. An appropriate variation in formula of the marcasite type by proxy solution results in a superstructure of the arsenopyrite type. It is certain that future investigation will reveal further arsenopyrite-like crystals (in a paper now in press, it is shown that the ionic crystal, manganite, $Mn(OH)O$ has this structure[1])). In view of the many inherent difficulties involved in the recognition of the correct crystal structure of arsenopyrite-like crystals, it appears desirable to summarize the general features and diffraction effects of this structural type. All axes in the following summary are referred to the new arsenopyrite orientation:

1. The arsenopyrite structure, of formula type $AB'B''$, is a super-structure based upon the simpler marcasite type, of formula type AB_2. The systematic alternation of the B' and B'' atoms is the physical and geometrical cause of the existence of the superstructure.

2. The alternation of B' and B'' atoms, and their attendant structural alterations, take place according to the symmetry of the space group C_{2h}^5, which is set up as $B2_1/d$ to preserve orthogonal axes comparable with marcasite-like axes. This cell contains 8 formula weights of $AB'B''$. (A simpler cell containing only 4 formulae may be had by setting up the space group as $P2_1/c$, but this is a geometrically more difficult cell without any obvious advantages.)

3. The crystals are monoclinic holohedral, but tend to grow together in twins and fourlings with the pseudo-orthorhombic pinacoids (100) and (001) as twinning planes. The twinned composite has orthorhombic symmetry and therefore gives orthorhombic diffraction effects, etc. which are the cause of misleading symmetry data.

4. The pseudo-orthorhombic cell has the b axis of the corresponding marcasite type cell (arsenopyrite orientation), but has a and c axes double the corresponding marcasite axes.

5. The pseudo-orthorhombic cell is B-centered.

6. The B-centering and screw axis give rise to customary and easily recognized X-ray extinctions.

1) Buerger, M. J., The symmetry and crystal structure of manganite, $Mn(OH)O$. Z. Kristallogr., in press.

7. The glide plane gives rise to customary X-ray extinctions but these are ordinarily obscured beyond formal recognition by twinning. The glide plane extinctions for single crystals and apparent extinctions for twinned composites referred to either primitive or B-centered lattice are as follows:

	referred to primitive lattice, space group $P2_1/c$	referred to B-centered lattice, space group $B2_1/d$
extinctions for single crystal	$h0l$ absent when l is odd	$h0l$ absent when $h + l = 4-2n$
apparent extinctions for twinned composite.	$h0l$ absent when both h and l are odd	$h0l$ absent when $h \pm l = 4-2n$

where n is any integer

8. The reflections from (001) constitute a *gradually declining* intensity series due to the arrangement of atoms in almost plane (001) sheets. The series fails to display a perfectly *regular intensity decline* only because the A atoms deviate by a parameter, δ, from positions in otherwise perfectly plane (001) sheets. The deviation is caused by the different radii of B' and B'' atoms, between pairs of which the A atoms are packed.

9. The structure may deviate from the ideal chemical formula $AB'B''$ by proxy solution. The substitution of ideal formula atoms by the extra-ideal ones apparently may take place preferentially in alternate (001) sheets. This destroys the rigorous existence of the glide plane and screw axis of the space group C_{2h}^5. As a result, weak X-ray reflections appear in positions where the ideal structure requires extinctions. This is a further generalization on the original marcasite plan and has the still lower symmetry of the space group $B\bar{1}$, wich is triclinic holohedral.

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