

## THE CRYSTAL STRUCTURE OF MARCASITE

M. J. BUERGER, *Massachusetts Institute of Technology.*

### ABSTRACT

The only attempts to investigate the crystal structure of marcasite have been made by Huggins and by de Jong. Huggins' contribution has been of the nature of guesswork. The structure proposed by him on the basis of Lewis' atomic theory ultimately proves correct, although his crystallographic substantiation of it is fortuitous and incorrect. De Jong, who attempted the only  $x$ -ray work on marcasite, arrived at dimensions for the unit cell similar to those given beyond, except that his  $a$ -axis is doubled. He gave  $V_h^{11}$  as the space group.

In this paper, the details of a complete  $x$ -ray determination of the structure of marcasite are given. No essential assumptions have been made other than that marcasite is holohedral. The rotation and oscillation method of analysis was alone used, with the crystal completely bathed in molybdenum  $K\alpha$  radiation. The determination leads to the following structure for marcasite:

Unit cell:  $a = 3.37 \text{ \AA}$

$b = 4.44 \text{ \AA}$

$c = 5.39 \text{ \AA}$

Space group:  $V_h^{12}$

Iron atoms (on symmetry centers) at:  $[[000]]$  and  $[[\frac{1}{2}\frac{1}{2}\frac{1}{2}]]$

Sulfur atoms (on reflection planes) at:  $[[0u_bv_c]]$ ,  $[[0\bar{u}_b\bar{v}_c]]$ ,

$[[\frac{1}{2}, \frac{1}{2} - u_b, \frac{1}{2} + v_c]]$ , and  $[[\frac{1}{2}, \frac{1}{2} + u_b, \frac{1}{2} - v_c]]$

where

$$\begin{cases} u_b = .203 \pm .01 \\ v_c = .375 \pm .01 \end{cases}$$

(Conventional marcasite orientation, origin at a symmetry center).

There is no complete agreement among the authors giving analytical expressions or equivalent positions of  $V_h^{12}$ . The equivalent positions are therefore rederived. It proves that Schiebold gives incorrect positions for symmetry centers and screw axes, and that Mark gives an incorrect origin of coordinates for the equivalent positions of this space group.

Marcasite possesses a 6-3 coordination structure. It is made up of units essentially equivalent to units discernable in the pyrite structure. Pyrite has a different linking of the groups which is also consistent with 6-3 coordination. The rutile structure is a special case of the marcasite structure, and the rutile and marcasite groups display a very similar crystal habit.

Marcasite appears to be composed of iron and sulfur in the atomic state. Both kinds of atoms have almost identical radii, 1.12 Å.

## TABLE OF CONTENTS

	Page
LITERATURE . . . . .	362
MATERIAL . . . . .	365
THE UNIT CELL . . . . .	366
THE SPACE GROUP . . . . .	370
Indexing . . . . .	370
Determination of Space Group . . . . .	370
Equivalent Positions of $V_h^{12}$ . . . . .	372
Possible Arrangements for Marcasite . . . . .	376
INTENSITY CONSIDERATIONS . . . . .	377
Phase Function of $V_h^{12}$ . . . . .	377
Reflection Intensities . . . . .	378
ELIMINATION OF IMPOSSIBLE MARCASITE STRUCTURES . . . . .	380
Intensity Comparisons . . . . .	380
The Marcasite Structure . . . . .	381
DETERMINATION OF PARAMETERS . . . . .	381
THE MARCASITE STRUCTURE . . . . .	387
Description . . . . .	387
Geometrical Properties . . . . .	391
RELATION TO OTHER STRUCTURES . . . . .	392
Pyrite . . . . .	392
Rutile . . . . .	392
THE CHEMICAL NATURE OF MARCASITE . . . . .	393
Radii of Sulfur and Iron Atoms . . . . .	393
State of Ionization . . . . .	394
ACKNOWLEDGEMENT . . . . .	395

## LITERATURE

Since almost the beginning of the period of crystal analysis with aid of  $x$ -rays, the structure of pyrite has been known. Indeed it was the first crystal species analyzed,<sup>1</sup> all of whose atoms were not fixed by symmetry. The structure of its polymorph, marcasite, however, has continued to remain unknown, although it has been guessed at, and an attempt has made to deduce it by  $x$ -ray means.

Believing that the Lewis theory of the structure of the atoms required the linking of sulphur and iron atoms to be the same in pyrite and marcasite, Huggins<sup>2</sup> presented a structure for marcasite

<sup>1</sup> W. Lawrence Bragg, *The Analysis of Crystals by the X-ray Spectrometer: Proc. Royal Soc. London*, (A) **89**, 1914, pp. 476-478.

<sup>2</sup> Maurice L. Huggins, *The Crystal Structures of Marcasite (FeS<sub>2</sub>), Arsenopyrite (FeAsS), and Loellingite (FeAs<sub>2</sub>): Physical Review*, (2) **19**, 1922, pp. 369-373.



based on a rearrangement of major units of the pyrite structure. Since the structure so deduced has actually proven to be correct, Huggins' figures are reproduced here. It should be pointed out that Huggins' crystallographic substantiation of this structure is totally incorrect.

Fig. 1A illustrates the arrangement about the S-S group in pyrite. By reorienting this group undisturbed, as in Fig. 1B, and linking the groups as in Fig. 2, an orthorhombic structure results. The rearrangement of groups leaves the requirements of Lewis' theory satisfied.

In attempting to justify this structure, Huggins' argument is that the axial ratio of marcasite given by Allen, Crenshaw, Johnston, and Larsen,<sup>3</sup> namely 0.7646:1:1.2176, is consistent with the ratio of lengths  $AB:AF:AA'$ , Fig. 1B. Hence, he decides, these are the directions of the  $a$ ,  $b$ , and  $c$  crystallographic axes, respectively. Since the unit cell, Figs. 1B and 2, is double the length of  $AB$  in the direction of this line, the true axial ratio of marcasite, Huggins concludes, should be: 1.5292:1:1.2176.

The fact is, however, that Huggins does not have the correct orientation. The x-ray work to be described later proves the sulfur atoms to occupy (100) planes, hence, Huggins'  $b$  is equivalent to crystallographic  $a$ . Trial calculation indicates that the axes must transform as follows:

Huggins		Crystallographic
$b$	is actually	$a$
$c$	is actually	$b$
$2a$	is actually	$c$

Using the axial ratio data adopted by Huggins, his axial ratio  $c:a:b$  should actually be  $a:b:c$  or .822:1:1.5292:1:1.2176  $1:1.2176:1.5292$ , which is fairly close to the marcasite ratio. In other words, Huggins' incorrect, apparent substantiation for the proposed structure depends on the fortuitous relation between the marcasite axes:

$$a:b:c \cong b:c:2a$$

<sup>3</sup> E. T. Allen, J. L. Crenshaw, John Johnston, and Esper S. Larsen, Die mineralischen Eisensulfide: *Zeit. Anorg. Chemie*, **76**, 1912, p. 254. This is equivalent to the more familiar article in English by the authors: *Am. J. Sc.*, (4) **33**, 1912, p. 221.

The only experimental attempt to determine the structure of marcasite has been made by de Jong.<sup>4</sup> De Jong attempted to analyze a crystal of marcasite from "Bohemia," with Fe-K radiation using only the powder method.<sup>5</sup> He also partially investigated other minerals of the marcasite group by both powder and rotating crystal methods. His results may be summarized as follows:

Axial lengths of unit cell			Formula weights per unit cell	Density		Space group
				Calculated	Literature	
<i>a</i> 6.79Å	<i>b</i> 4.45Å	<i>c</i> 5.42Å	4	4.86	4.85-4.90	V <sub>h</sub> <sup>11</sup>

De Jong did not attempt to complete the structural determination.

#### MATERIAL

All of the writer's experimental work was done on crystals derived from a single hand specimen. Although unlabeled, this was one of the familiar Joplin specimens showing a thin chert sheet on both sides of which had grown deep wine-colored sphalerite crystals, which in turn, had acted as a focus for the crystallization of marcasite. This particular specimen was chosen because its marcasite crystals, on the whole, were homogeneous, easily oriented, and provided untwinned individuals.

The marcasite crystals themselves were of diamond shaped, tabular habit, flattened parallel to {001}. The diamond shape was outlined by {110}. The basal pinacoids were not actually present, but were represented by slightly warped, highly striated surfaces of this altitude, produced by vicinal brachydome striations. None of the planes of the striations were identified with certainty, but some of the {110} planes gave fairly good signals. The average of several measurements on one crystal gave:

$$(110) \wedge (\bar{1}10) = 105^\circ 42'$$

from which it follows:  $a:b = .7577:1$

<sup>4</sup> W. F. de Jong, Bepaling van de absolute aslengten van markasiet en daarmee isomorfe mineralen: *Physica*, 6, 1926, pp. 325-332.

<sup>5</sup> *Op. cit.* p. 329 and p. 331.

A personal determination of the density on about .7 gram of carefully hand picked, crystal fragments of this material gave a value of 4.919 at 28° C.

Delicate qualitative<sup>6</sup> determinations<sup>7</sup> on a total of about .8 gram of this marcasite indicated that nickle and cobalt (elements to be expected as possible constituents replacing some iron) as well as antimony, arsenic, and bismuth (to be expected as possible replacers of some sulfur) are absent. Incidentally, lead and copper were also found to be absent. Allen, Crenshaw, Johnston, and Larsen<sup>8</sup> found the marcasite from Joplin to be of ideal FeS<sub>2</sub> proportions. Doelter and Leitmeyer<sup>9</sup> quote an analysis of Missouri marcasite by E. Arbeiter which also indicates ideal FeS<sub>2</sub>. The marcasite used in the structural determination, therefore, may be regarded as perfectly suited for the establishment of a new crystal structure type.

The absorption coefficient of marcasite is high, consequently relatively minute splinters were used in the *x*-ray determinations. Three crystals were used, mounted for rotation about the *a*, *b*, and *c* axes, respectively. Because of the poor but real cleavage along {110}, the *c* axis splinter was most nearly of uniform cross section, and was used for most of the intensity comparisons.

#### THE UNIT CELL

All *x*-ray work was done by means of the rotation and oscillation methods, following Bernal<sup>10</sup> rather closely, with the crystals completely bathed in molybdenum K $\alpha$  radiation. The axial lengths were determined by rotating the crystals about the three crystallographic axes and recording the reflection on  $3\frac{1}{4} \times 4\frac{1}{4}$  inch glass

<sup>6</sup> I was prepared to have quantitative analyses made, but our best professional analysts (including Miss Mary G. Keyes and the new laboratory for rock analyses in charge of Dr. Grout of the University of Minnesota) declined to make them, pleading inadequate equipment for sulfide analyses. Where can one obtain reliable sulfide analyses? My own experience with the routine commercial analyst is that he cannot be relied upon for scientific work.

<sup>7</sup> G. G. Marvin, analyst.

<sup>8</sup> E. T. Allen, J. L. Crenshaw, John Johnston, and Esper S. Larsen, *The Mineral Sulfides of Iron: Am. J. Sc.*, (4) 33, 1912, p. 177.

<sup>9</sup> C. Doelter and H. Leitmeyer, *Handbuch der Mineralchemie*, Bd. IV, Erste Hälfte, Dresden and Leipzig, 1926, p. 567, analysis 8.

<sup>10</sup> J. D. Bernal, *On the Interpretation of X-Ray, Single Crystal, Rotation Photographs: Proc. Royal Soc. Lond.*, (A) 113, 1926, pp. 117-160.

plates at a distance of about 6 cm. from the crystal. The following values were obtained:

$$\begin{aligned} a &= 3.37\text{\AA} \\ b &= 4.44\text{\AA} \\ c &= 5.39\text{\AA} \end{aligned}$$

In view of the fact that de Jong had already published an *a*-axis length about double that just given, special attention was given to the possibilities of an error in this determination. Of course, it is easy to overlook half-spaced, odd value, layer lines, and usually any mistake made in obtaining axial lengths is in the direction of missing these and obtaining halved axes. It is quite certain, however, that none of these appeared in any of the writer's photo-

	AXIAL RATIO <i>a:b:c</i>		Density
x-ray determination	.759:1:1.214	calculated from x-ray data	4.91
goniometric determination	.758:1: ?	actually determined	4.92
Goldschmidt's average <sup>11</sup>	.758:1:1.212		
Larsen, synthetic <sup>12</sup>	.7646:1:1.2176		
		Dana's range	4.85-4.90

graphs. These photographs include not only ordinary rotation plates placed at a distance of about 6 cm., and exposed about 17 hours, but also longer exposures of 40 hours, both at about 6 cm. with flat plates, and at about 5 cm. with cylindrical film. None of the 17 hour exposure, 15° oscillation showed any indications of missed layer lines, and, finally, every reflection was indexed without difficulty, none requiring a halved *a*-axis reciprocal lattice (*i.e.*, a doubled *a* axis in the space lattice).

The number of formula weights of FeS<sub>2</sub> associated with a unit cell may be calculated as

$$z = \frac{\text{Volume} \times \text{density}}{\text{Formula weight} \times 1.64 \times 10^{-24}}$$

$$= \frac{(3.37 \times 4.44 \times 5.39) \times 10^{-24} \times 4.92}{119.96 \times 1.64 \times 10^{-24}} = 2.03,$$

indicating two formula weights per unit cell.

<sup>11</sup> From Victor Goldschmidt, *Winkeltabellen*, Berlin, 1897, pp. 232, for which Goldschmidt says (page 413), "The elements differ strongly according to various observers. The mean of the data by Miller, Sadebeck, and Gehmacher are given."

<sup>12</sup> E. T. Allen, J. L. Crenshaw, John Johnston and Esper S. Larsen, *The Mineral Sulphides of Iron. Am. J. Sc.*, (4) 33, 1912, p. 221.

The values of this axial ratio and the density calculated from it are in good agreement with the goniometrically determined ratio and the direct density determination shown in table on page 367.

The differences between the axial ratios given and those found in the literature need not be dwelt upon. The axial ratio is unquestionably a function of the composition. The check between Goldschmidt's average and my own values is probably fortuitous.

TABLE I  
Catalog of Planes Indexed

## Pinacoids

	<i>h00</i>	<i>0k0</i>	<i>00l</i>
	—	—	—
	<b>200</b>	—	<b>002</b>
	—	—	—
	400	<b>040</b>	—
	—	—	—
	600	060	006

## Prisms and domes

<i>hko</i>	<b>110</b>	—	<b>310</b>	—	510	—	710
	—	—	—	—	—	—	—
	—	—	—	—	—	—	—
	—	240	—	440	—	—	640
	<b>150</b>	—	350	—	550	—	—
	—	260	—	460	—	—	—
	—	—	—	—	—	—	—
	<b>190</b>	—	—	—	—	—	—
<i>hol</i>	<b>101</b>	—	—	—	—	—	701, or 711
	—	<b>202</b>	—	402	—	602, or 612	—
	<b>103</b>	—	303	—	503	—	—
	—	—	—	—	—	604, or 614	—
	<b>105</b>	—	<b>305</b>	505, or 515	—	—	—
<i>okl</i>	<b>011</b>	<b>021</b>	<b>031</b>	<b>041</b>	—	061	071
	<b>012</b>	<b>022</b>	<b>032</b>	<b>042</b>	—	062	072
	<b>013</b>	<b>023</b>	<b>033</b>	<b>043</b>	053	063	084
	—	<b>024</b>	—	044	—	064	084
	<b>015</b>	025	—	045	055	—	—

TABLE I (Cont'd.)  
Catalog of Planes Indexed

Pyramids				<i>hsl</i>				
<i>1kl</i>	111	121	131	141	—	161	—	181
	112	122	132	142	152	162	172	
	113	123	133	143	—	163		
	114	—	134	—	—		164	
	115	—	135	145	—	165		
<i>2kl</i>	211	221	231	241	—	261	271	
	212	222	232	242	—	262	—	282
	213	223	233	243	253	263		
	—	224	—	244	—	264	—	284
	215	225	—	245	—	265		
<i>3kl</i>	311	321	331	341	—	361		381
	312	322	332	342	352	362		
	313	—	333	343	—	363		
	314	—	334	—	—	—	374	
	315	—	—	345	—	365		
<i>4kl</i>	411	421	431	441	—	—	471	
	412	422	—	442	—	462		
	413	—	—	443	453			
	—	424	—	444	—			
	415	—	—	445	455			
<i>5kl</i>	511	521			552			
	512	522	532	542				
	513	—	—	543				
			534					
	515, or							
	505							
<i>6kl</i>	—	—	631					
	612, or	622?						
	602							
	613							
	614, or	624						
604								
<i>7kl</i>	711, or	721, or						
	701	711						

## THE SPACE GROUP

INDEXING. Following Bernal,<sup>13</sup> the planes giving rise to reflections have been indexed by allowing the crystal to oscillate through definite 15° ranges, with an overlap of 2° between range settings. Sets of photographs were thus made for oscillations about the *a*, *b*, and *c* axes, recording being accomplished on flat plates at about 6 cm. crystal-to-plate distance. The planes so indexed are listed in heavy type in Table I. The chance of mis-indexing among these planes is very slight, for most of them appeared on all three axial sets of oscillations, and were therefore checked twice, while all but a very few appeared on at least two axial sets of oscillations.

In order to fix the sulfur parameters more closely, it was necessary to obtain reflections from planes of higher index than those recorded on the  $3\frac{1}{4} \times 4\frac{1}{4}$  plates at about a 6 cm. plate distance. For this purpose, a complete new set of oscillation and rotation photographs was made using a cylindrical camera of about a 5 cm. radius. All plates so indexed are listed in Table I in ordinary type. It is believed that the indexing is correct except for possibly some of the very high index planes where the oscillation range allowed a choice between two possibilities. In most cases, the doubt and choice have been indicated in the table.

The plane 006 alone was indexed from a complete rotation photograph by correlation of reflection sequence.

DETERMINATION OF SPACE GROUP. An analysis of the recorded reflections indicates that all classes of pyramid planes (*hkl*) are present regardless of the values of *h+k*, *h+l*, *k+l*, or *h+k+l*. Hence the space lattice can not be (001)-centered, (010)-centered, (100)-centered, face-centered, or body-centered. It must therefore be the simple orthorhombic lattice  $\Gamma_0$ . This eliminates all orthorhombic space groups except:

$$C_{2v}^1 - C_{2v}^{10}, V^1 - V^4, V_h^1 - V_h^{16},$$

by reflections actually appearing.

Of the pinacoids, prisms, and domes, the reflection of the following classes of planes only are absent:

- (a) (*hkl*) when *h+k* is odd
- (b) (*h0l*) when *h+l* is odd

<sup>13</sup> *Op. cit.*

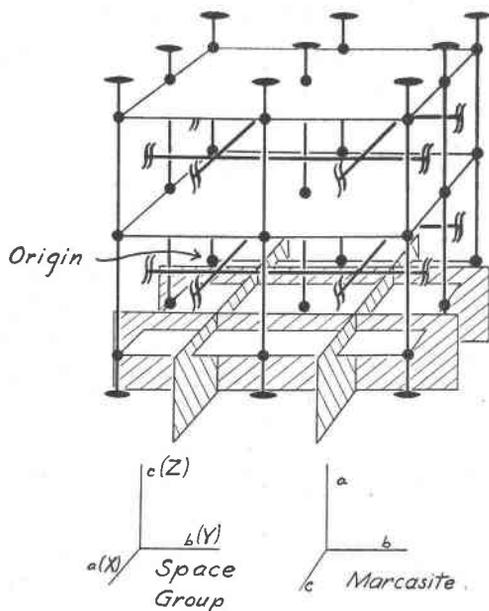


FIG. 3. Perspective view of space group  $V_h^{12}$ , with both conventional space group orientation and conventional marcasite orientation indicated. The symmetry elements are as follows: horizontal reflection planes; vertical glide planes with diagonal glides; vertical 2-fold rotation axes; horizontal 2-fold screw axes; and symmetry centers.

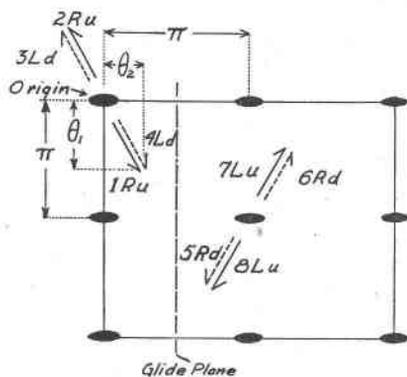


FIG. 4. Projection of some of the symmetry elements of  $V_h^{12}$  on the lower reflection plane of Fig. 3, illustrating the derivation of the coordinates of the general position by the use of the reflection planes, the  $(010)$  space group diagonal glide planes, and 2-fold axes.

- |                             |   |                              |
|-----------------------------|---|------------------------------|
| (c) $(h00)$ when $h$ is odd | } | special cases of (a) and (b) |
| (d) $(0k0)$ when $k$ is odd |   |                              |
| (e) $(00l)$ when $l$ is odd |   |                              |

Reflection of all other classes of planes are present. This eliminates all of the above space groups except:

$$C_{2v}^1, C_{2v}^7, C_{2v}^{10}, V^1, V^2, V^3, V^4, V_h^{12}, V_h^{13},$$

by reflections actually appearing.

In the rather complete list of reflecting planes available, no classes of planes (a) and (b) appeared, in spite of the fact that the dimensions and setup of the apparatus would have recorded, if present and if sufficiently intense:

at least 23 of the class  $(h k 0)$  where  $h+k$  is odd, including the special cases.

at least 17 of the class  $(h 0 l)$  where  $h+l$  is odd, including the special cases.

It may reasonably be concluded, therefore, that these planes are absent because the classes are absent, and not because of some fortuitous condition. This eliminates all space groups but  $C_{2v}^{10}$  and  $V_h^{12}$ , both of which have absent classes identical with those observed.  $C_{2v}^{10}$  is hemimorphic, so, granting marcasite is holohedral, its space group is  $V_h^{12}$ .

In order to transform from the conventional space group orientation to the conventional marcasite orientation, the  $a$  and  $c$  axes are interchanged, together with the corresponding  $h$  and  $l$  indices.

EQUIVALENT POSITIONS OF  $V_h^{12}$ . A perspective view of space group  $V_h^{12}$  is given in Fig. 3. In Fig. 4, some of the elements of the group are shown projected on the lower, horizontal reflection plane of the perspective view of the space group. By introducing an asymmetric exploring "molecule" in a general position, the multiplication of this general "molecule" by the symmetry elements of the group can be studied for the purpose of deriving the equivalent positions of the group.

For coordinates, it is convenient, for  $x$ -ray intensity work, to use phase angles, in terms of which the length of any axis of the unit cell is  $360^\circ$  or  $2\pi$ , half the length  $180^\circ$  or  $\pi$ , or, in general, any portion of the length is  $\theta_n$ . The origin of coordinates used here is a symmetry center. By placing the "molecule"  $1Ru$  in a general position,

these elements reproduce it as indicated in Table II. Other elements than the particular ones chosen as generators in the tables could be used for deriving these equivalent positions. The symbols used in the projection can be comprehended from the following illustration:  $6Rd$  signifies "the 6th 'molecule', which is Right handed, and pointing down". It is convenient to conceive of "molecules" 1, 2, 3, and 4 as being clustered about the origin  $[[000]]$  and associated with the lower horizontal reflection plane, and of "molecules" 5, 6, 7, and 8 as being clustered about  $[[\pi\pi\pi]] \approx [[\frac{1}{2}\frac{1}{2}\frac{1}{2}]]$  and associated with the next plane above. The dotted "molecules" are below the plane with which they are associated, the others are

TABLE II.  
DERIVATION OF COÖRDINATES OF GENERAL POSITION OF  $V_h^{12}$

Symmetry operation	"Molecule" operated upon	Designation of resulting "molecule"	Coordinates of resulting "molecule"	
			Space group orientation	Marcasite orientation
Vertical 2-fold rotation axis through $[[000]]$	original "molecule" 1	$1Ru$	$[[\theta_1\theta_2\theta_3]]$	$[[\theta_a\theta_b\theta_c]]$
	1	$2Ru$	$[[\bar{\theta}_1\bar{\theta}_2\bar{\theta}_3]]$	$[[\bar{\theta}_a\bar{\theta}_b\bar{\theta}_c]]$
Lower, horizontal reflection plane	2	$3Ld$	$[[\bar{\theta}_1\bar{\theta}_2\bar{\theta}_3]]$	$[[\bar{\theta}_a\bar{\theta}_b\bar{\theta}_c]]$
"	1	$4Ld$	$[[\theta_1\theta_2\theta_3]]$	$[[\bar{\theta}_a\bar{\theta}_b\bar{\theta}_c]]$
Vertical glide plane with diagonal glide	4	$5Rd$	$[[\pi + \theta_1, \pi - \theta_2, \pi - \theta_3]]$	$[[\pi - \theta_a, \pi - \theta_b, \pi + \theta_c]]$
"	3	$6Rd$	$[[\pi - \theta_1, \pi + \theta_2, \pi - \theta_3]]$	$[[\pi - \theta_a, \pi + \theta_b, \pi - \theta_c]]$
"	2	$7Lu$	$[[\pi - \theta_1, \pi + \theta_2, \pi + \theta_3]]$	$[[\pi + \theta_a, \pi + \theta_b, \pi - \theta_c]]$
"	1	$8Lu$	$[[\pi + \theta_1, \pi - \theta_2, \pi + \theta_3]]$	$[[\pi + \theta_a, \pi - \theta_b, \pi + \theta_c]]$

TABLE III. SPECIAL POSITIONS OF  $V_4^{12}$ 

Special Position	Coalescing "molecules"	Coordinates of coalesced "molecules"			Number of equivalent positions in special position	Wyckoff's designation of special position
		Space group orientation	Marcasite orientation	Wyckoff's coordinates		
"Molecules" on reflection planes	1+4	$[[\theta_1\theta_20]]$	$[[0\theta_2\theta_2]]$	$[[u\bar{v}\frac{1}{2}]]$	4	g
	2+3	$[[\theta_1\theta_20]]$	$[[0\theta_2\theta_2]]$	$[[\bar{u}u\frac{1}{2}]]$		
	5+8	$[[\pi+\theta_1, \pi-\theta_2, \pi]]$	$[[\pi, \pi-\theta_2, \pi+\theta_1]]$	$[[u+\frac{1}{2}, \frac{1}{2}-v, \frac{3}{2}]]$		
	6+7	$[[\pi-\theta_1, \pi+\theta_2, \pi]]$	$[[\pi, \pi+\theta_2, \pi-\theta_1]]$	$[[\frac{1}{2}-u, v+\frac{1}{2}, \frac{3}{2}]]$		
"Molecules" on 2-fold rotation axes through $[[000]]$	1+2	$[[00\theta_3]]$	$[[\theta_300]]$	$[[0, 0, \frac{1}{2}-u]]$	4	e
	3+4	$[[00\bar{\theta}_3]]$	$[[\bar{\theta}_300]]$	$[[00u]]$		
	5+6	$[[\pi, \pi, \pi-\theta_3]]$	$[[\pi-\theta_3, \pi, \pi]]$	$[[\frac{1}{2}, \frac{1}{2}, u+\frac{1}{2}]]$		
	6+7	$[[\pi, \pi, \pi+\theta_3]]$	$[[\pi+\theta_3, \pi, \pi]]$	$[[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}-u]]$		
"Molecules" on 2-fold rotation axes through $[[0\pi0]]$	1+2	$[[0\pi\theta_3]]$	$[[\theta_3\pi0]]$	$[[0, \frac{1}{2}, \frac{1}{2}-u]]$	4	f
	3+4	$[[0\pi\bar{\theta}_3]]$	$[[\bar{\theta}_3\pi0]]$	$[[0\frac{1}{2}u]]$		
	5+6	$[[\pi, 0, \pi-\theta_3]]$	$[[\pi-\theta_3, 0, \pi]]$	$[[\frac{1}{2}, 0, u+\frac{1}{2}]]$		
	7+8	$[[\pi, 0, \pi+\theta_3]]$	$[[\pi+\theta_3, 0, \pi]]$	$[[\frac{1}{2}0\bar{u}]]$		
"Molecules" on $[[000]]$ symmetry center	1+2+3+4	$[[000]]$	$[[000]]$	$[[00\frac{1}{2}]]$	2	a
	5+6+7+8	$[[\pi\pi\pi]]$	$[[\pi\pi\pi]]$	$[[\frac{1}{2}\frac{1}{2}\frac{1}{2}]]$		
"Molecules" on $[[00\pi]]$ symmetry center	1+2+3+4	$[[00\pi]]$	$[[\pi00]]$	$[[00\frac{3}{2}]]$	2	b
	5+6+7+8	$[[\pi\pi0]]$	$[[0\pi\pi]]$	$[[\frac{1}{2}\frac{1}{2}\frac{1}{2}]]$		
"Molecules" on $[[0\pi0]]$ symmetry center	1+2+3+4	$[[0\pi0]]$	$[[\pi0\pi]]$	$[[0\frac{1}{2}\frac{1}{2}]]$	2	c
	5+6+7+8	$[[\pi0\pi]]$	$[[\pi0\pi]]$	$[[\frac{1}{2}0\frac{1}{2}]]$		
"Molecules" on $[[\pi00]]$ symmetry center	1+2+3+4	$[[\pi00]]$	$[[00\pi]]$	$[[\frac{1}{2}0\frac{1}{2}]]$	2	d
	5+6+7+8	$[[0\pi\pi]]$	$[[\pi\pi0]]$	$[[0\frac{1}{2}\frac{1}{2}]]$		

above the plane. By putting the exploring "molecule"  $IRu$ , on the several symmetry elements of the space group instead of in a general, symmetryless position, it coalesces with one or more of its above seven derivatives, giving rise to the special positions listed in Table III.

A discussion of the space group and its equivalent positions has been given in some detail, for the following reasons:

1. In the most complete table of equivalent positions, that of Wyckoff,<sup>14</sup> there is no explicit means of knowing, so far as I can discover, what point has been used as the origin of coordinates. This may be obtained by a study of Wyckoff's figures, but only after the space group itself has been thoroughly visualized from some other source. When this has been done, the coordinates can be easily written down by inspection.

2. Mark, who published a list of equivalent positions,<sup>15</sup> lists positions identical with Wyckoff's, giving as the origin a symmetry center. This is incorrect. Both Wyckoff's and Mark's origins are evidently on 2-fold rotation axes halfway between symmetry centers. Hopeless confusion results if Mark's stated origin is relied upon for the deductions given beyond.

3. Schiebold<sup>16</sup> gives his origin of  $V_h^{12}$  as "on a twofold axis  $\parallel$  [001] in intersection with a reflection plane  $\parallel$  (001)," *i.e.*, on a symmetry center. He gives correct analytical positions of the reflection planes, glide planes, and 2-fold axes, but then fails to give any symmetry center at the origin or in equivalent positions. In fact, Schiebold's symmetry centers and screw axes are incorrectly located. Needless to say, this representation of the group is very misleading.

The best description of the space group and its equivalent positions is to be found in Niggli's work.<sup>17</sup>

<sup>14</sup> Ralph W. G. Wyckoff, *The Analytical Expression of the Results of the Theory of Space Groups: Carnegie Institution of Washington, Publication No. 318*, second edition, 1930.

<sup>15</sup> Hermann Mark, *Handbuch der angewandten physikalischen Chemie*; Bd. 14, Die Verwendung der Röntgenstrahlen in Chemie u. Technik: Leipzig, 1926, pp. 460-461.

<sup>16</sup> Ernst Schiebold, Über eine neue Herleitung und Nomenklatur der 230 kristallographischen Raumgruppen: *Abhandlungen der mathematisch-physischen Klasse der Sächsischen Akademie der Wissenschaften*, Vol. 40, No. 5, 1929, p. 88.

<sup>17</sup> Paul Niggli, *Geometrische Kristallographie des Discontinuums*, Leipzig, 1919, pp. 198-199.

POSSIBLE ARRANGEMENTS FOR MARCASITE. Since there are two formula weights of  $\text{FeS}_2$  per unit cell, two iron atoms and four sulfur atoms must be associated with each cell. Space group  $V_h^{12}$  has only 2-fold, 4-fold, and 8-fold positions available, therefore the iron and sulfur must be distributed as follows:

Irons in one of the four 2-fold positions,  $a, b, c,$  or  $d$

Sulfurs either:  $\left\{ \begin{array}{l} \text{by twos in the remaining 2-fold positions,} \\ \quad a, b, c, \text{ or } d, \\ \\ \text{or by fours, in one of the three 4-fold positions,} \\ \quad e, f, \text{ or } g. \end{array} \right.$

The total possible marcasite arrangements are therefore those shown in Table IV. Not all of these structures are different however. By changing the origin of coordinates of each of the sets of coordinate positions by  $\pi$  in the three axial directions, it becomes evident that a number of these combinations are identical, leaving only the following independent:

Symmetry determined	One parameter	Two parameter
1 $abc$	13 $ae$	21 $ag$
2 $abd$	14 $af$	22 $bg$
3 $acd$	15 $be$	23 $cg$
	16 $bf$	24 $dg$

Finally, by allowing the variables  $\theta_a, \theta_b,$  and  $\theta_c$  to assume all values between 0 and  $2\pi$ , it can be shown that all possible marcasite structural possibilities can be represented by:

Symmetry determined	One parameter	Two parameter
1 $abc$	13 $ae$	21 $ag$
2 $abd$	14 $af$	
3 $acd$		

This makes a total of no more than six possible structures.

TABLE IV. MAXIMUM NUMBER OF POSSIBLE MARCASITE STRUCTURES INDICATED BY SPACE GROUP

Combination number	Iron positions	Sulfur positions	
1	<i>a</i>	<i>bc</i>	} 12 symmetry-fixed structures. Sulfurs on symmetry centers
2	<i>a</i>	<i>bd</i>	
3	<i>a</i>	<i>cd</i>	
4	<i>b</i>	<i>ac</i>	
5	<i>b</i>	<i>ad</i>	
6	<i>b</i>	<i>cd</i>	
7	<i>c</i>	<i>ab</i>	
8	<i>c</i>	<i>ad</i>	
9	<i>c</i>	<i>bd</i>	
10	<i>d</i>	<i>ab</i>	
11	<i>d</i>	<i>ac</i>	
12	<i>d</i>	<i>bc</i>	
13	<i>a</i>	<i>e</i>	} 8 one-parameter structures. Sulfurs on 2-fold rotation axes
14	<i>a</i>	<i>f</i>	
15	<i>b</i>	<i>e</i>	
16	<i>b</i>	<i>f</i>	
17	<i>c</i>	<i>e</i>	
18	<i>c</i>	<i>f</i>	
19	<i>d</i>	<i>e</i>	
20	<i>d</i>	<i>f</i>	
21	<i>a</i>	<i>g</i>	} 4 two-parameter structures Sulfurs on reflection planes
22	<i>b</i>	<i>g</i>	
23	<i>c</i>	<i>g</i>	
24	<i>d</i>	<i>g</i>	

24 possible structures

INTENSITY CONSIDERATIONS

PHASE FUNCTION OF  $V_k^{12}$ . The amplitude of a wave scattered by a set of atoms in a unit cell, as a function of the positions of the atoms, may be represented by

$$P = \sum_n e^{2\pi i(h'\theta_1 + k'\theta_2 + l'\theta_3)}$$

where,  $\sum_n$  indicates a summation over the  $n$  atoms considered in the cell  
 $e$  is the base of natural logarithms  
 $i = \sqrt{-1}$

$\theta_1, \theta_2, \theta_3$  are the phase coordinates of an atom  
 $h', k',$  and  $l'$  are the index numbers of the plane reflecting.

If the crystal considered has a center of symmetry, the phase function may be more conveniently put into the following form by summing over half the total number of atoms, taking the coordinates in centrosymmetrical pairs:

$$P = \sum_{n/2} 2 \cos (h'\theta_1 + k'\theta_2 + l'\theta_3).$$

The particular form of the phase function for  $V_k^{12}$  is then obtained by substituting the coordinates of general positions 1, 2, 6, and 7 (each one with its centrosymmetrical derivative understood) in this relation, which gives:

$$P = 2 \left\{ \begin{aligned} &\cos (h'\theta_1 + k'\theta_2 + l'\theta_3) + \cos (-h'\theta_1 - k'\theta_2 + l'\theta_3) \\ &+ \cos (h'[\pi - \theta_1] + k'[\pi + \theta_2] + l'[\pi - \theta_3]) \\ &+ \cos (h'[\pi - \theta_1] + k'[\pi + \theta_2] + l'[\pi + \theta_3]) \end{aligned} \right\},$$

using space group orientation. This may be reduced to:

$$P = \begin{cases} 8 \\ 4 \\ 2 \end{cases} \cos (h\theta_a) \cdot \cos (k\theta_b) \cdot \cos (l\theta_c), \text{ where } h+k+l \text{ is even,}$$

and

$$P = - \begin{cases} 8 \\ 4 \\ 2 \end{cases} \cos (h\theta_a) \cdot \sin (k\theta_b) \cdot \sin (l\theta_c), \text{ where } h+k+l \text{ is odd,}$$

transformed to marcasite coordinates.  $\begin{cases} 8 \\ 4 \\ 2 \end{cases}$  indicates that coefficient

8, 4, or 2 should be used corresponding to the number of atoms in the equivalent position considered.

REFLECTION INTENSITIES. The actual amplitude contribution of a set of atoms to the reflection of a plane is given by

$$s = F \cdot P$$

where  $P$  is the amplitude given previously and  $F$  is the scattering ability of the atom as a function of the angle between the incident and reflected beam. The  $F$  values used for the calculations involved in determining the structure of marcasite are given in Fig. 5. The

curve for iron has been drawn directly from the data of Bragg and West.<sup>18</sup> The sulfur curve has been calculated by the method indicated by these authors.<sup>19</sup> The sulfur curve probably does not

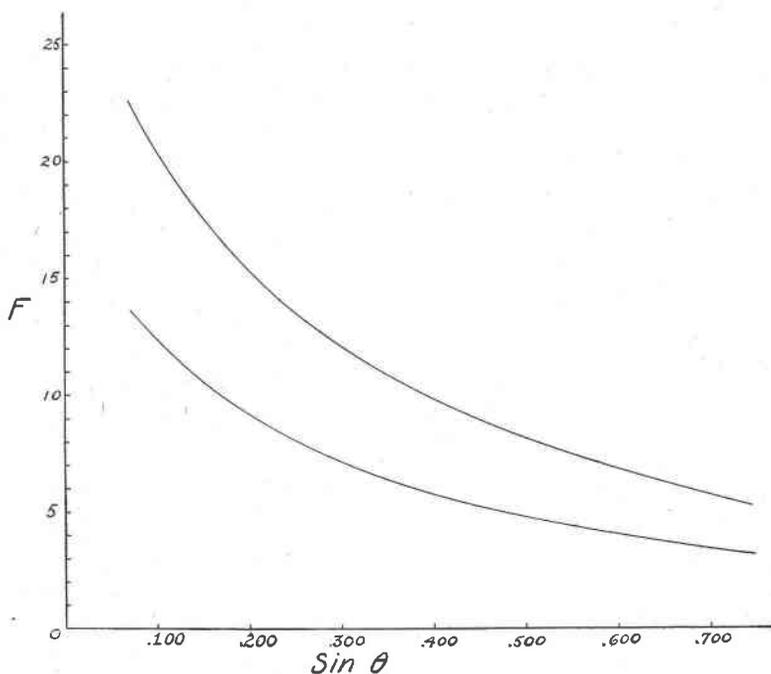


FIG. 5. The  $F$  values of iron (upper curve) and sulfur (lower curve) used in the determination of the structure of marcasite.

fall off as rapidly as it should, but for the relatively small values of  $\sin \theta$  employed in most of the calculations, it has given very satisfactory service.

The amplitude contribution of all the atom species to the plane, or the structure factor, is

$$S = \sum s = \sum FP = F_{\text{iron}} \cdot P_{\text{iron}} + 2F_{\text{sulfur}} \cdot P_{\text{sulfur}}$$

<sup>18</sup> W. Lawrence Bragg and J. West, A Technique for the X-ray Examination of Crystal Structures with many Parameters: *Zeit. für Krist.*, **69**, 1928-1929, p. 139.

<sup>19</sup> *Op. cit.*, p. 137.

summed over all the atom species, in this case over iron and sulfur. The intensity of the reflection of a plane is given by<sup>20</sup>

$$I = \frac{1}{K^2} \cdot \frac{1 + \cos^2 2\theta}{\sin 2\theta} \cdot S^2 = \frac{1}{K^2} \cdot \Theta \cdot S^2$$

where  $K$  is a constant for a given apparatus and crystal specimen.

#### ELIMINATION OF IMPOSSIBLE MARCASITE STRUCTURES

INTENSITY COMPARISONS. The iron atoms of marcasite occupy symmetry-fixed positions, and the sulfur atoms occupy positions of no more than two undetermined parameters. It is possible, therefore, to calculate the intensities of reflections of various orders to be expected from one pinacoid for the two parameter structures, for two pinacoids for the one parameter structures, and for all three pinacoids from the symmetry-fixed structures. Comparison with the intensities actually observed then allows structures to be eliminated which do not give sequences of intensities identical with those observed. The observed orders of intensities for the pinacoids are as follows:

200	>	400	>	600
strong		medium		weak
040	>	060	>	020
medium		weak		absent
002	>	006	>	004
strong		medium		absent

In Table II, the intensities (in the convenient form  $|K\sqrt{I}|$ ), calculated for the different possible arrangements, are compared with those observed. Only the two parameter structures,

21-24:  $\begin{vmatrix} a \\ b \\ c \\ d \end{vmatrix} \cdot g_{\text{sulfur}}$ , give intensity orders not in conflict with those  
iron

actually observed. Since all these structures are identical, they may be represented by the single structure  $a_{\text{iron}} \cdot g_{\text{sulfur}}$ .

<sup>20</sup> W. Lawrence Bragg and J. West, *op. cit.*, p. 125.

THE MARCASITE STRUCTURE. From the above considerations it is evident that the iron atoms occupy symmetry centers while the sulfurs lie in reflection planes. The structure can be represented by the following coordinates:

Irons at  $[[000]]$  and  $[[\pi\pi\pi]]$   
 Sulfurs at  $[[0\theta_b\theta_c]]$ ,  $[[0\theta_b\theta_c]]$ ,  $[[\pi, \pi - \theta_b, \pi + \theta_c]]$ ,  $[[\pi, \pi + \theta_b, \pi - \theta_c]]$ .

It remains now to determine the values of the parameters  $\theta_b$  and  $\theta_c$ .

DETERMINATION OF PARAMETERS

The two parameters,  $\theta_b$  and  $\theta_c$  have been fixed by independently finding a value of each, for which all planes not involving the other variable give calculated intensities in the same order as the observed intensities. All intensity comparisons, except as specifically

TABLE V. OBSERVED PINACOID INTENSITY ORDERS COMPARED WITH CORRESPONDING INTENSITIES CALCULATED FOR POSSIBLE MARCASITE STRUCTURES

Plane	Calculated Intensities $ K\sqrt{I} $			Observed Intensities
	Arrangements 1-12	Arrangements 13-20	Arrangements 21-24	
200	139	Variable with $\theta_a$	139	Strong
400	56		56	Medium
600	28		28	Weak
020	186	186	Variable with $\theta_b$	Absent
040	83	83		Medium
060	45	45		Weak
002	225	225	Variable with $\theta_c$	Strong
004	107	107		Absent
006	61	61		Medium

noted beyond, were made on a single  $c$  axis, complete rotation photograph using a cylindrical camera (Fig. 6). This allows all intensities to be compared with one another.

In a preliminary way, it is evident from the intensity order:

110	>	040	>	060	>	020,
very strong		medium		weak		absent

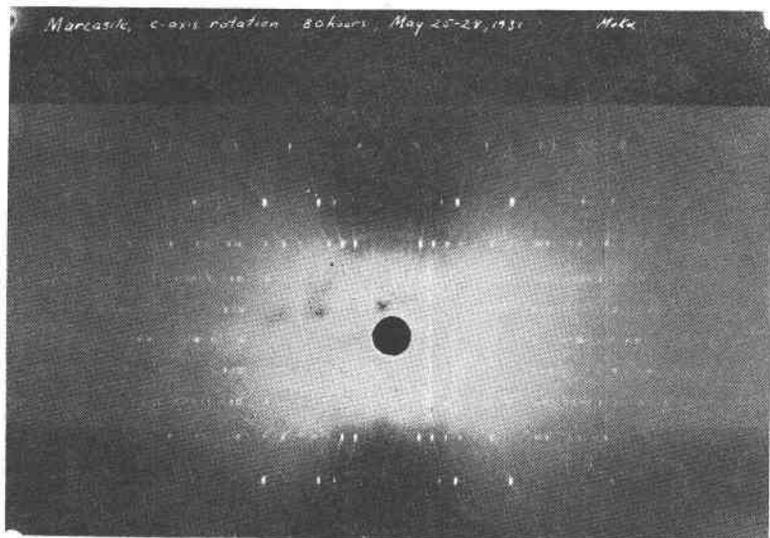


FIG. 6. Print of marcasite  $c$  axis rotation photograph. The fogging is due to  $x$ -rays scattered backward by the paper covering of the film during a very long exposure.

that  $\theta_b$  must lie in the general region near  $70^\circ$ , or in its centrosymmetrical region near  $290^\circ$ . The centrosymmetrical region may be temporarily neglected, since it simply indicates the position of the centrosymmetrical atom.

The variable  $\theta_b$  is more closely fixed as indicated in Fig. 7, where the intensities of all planes not involving the other parameter,  $\theta_c$ , are plotted as functions of the variable  $\theta_b$ . At the bottom of the figure, some of the intensity relations which tend to limit the value of the parameter are indicated.  $\theta_b$  is thus fixed at about  $73^\circ$  or  $74^\circ$  corresponding to  $u_b = .203$  or  $.205$ , to within less than a percent of the

total possible variation. It is interesting to note that this value is almost  $u_b = \frac{1}{2}$  within the limits of accuracy of fixing  $\theta_b$ .

As an indication of the correctness of the value of  $\theta_b$ , the intensities calculated (graphically) at  $\theta_b = 73^\circ$  are listed in Table VI in comparison with the order of intensities observed on the  $c$  axis rotation photograph. The check is very satisfactory.

An additional check is had by studying the list of planes indexed (Table I). By examining the columns corresponding to the pyramids ( $h5l$ ), a type permitted by the space group for all values of  $h, k, l, h+k, h+l, k+l$ , and  $h+k+l$ , it is evident that only such planes reflect as have  $h+k+l$  even. Out of at least ten chances for

TABLE VI. COMPARISON OF CALCULATED AND OBSERVED ORDERS OF INTENSITIES FOR ( $hk0$ ) PLANES, AT  $\theta_b = 73^\circ$

$ K\sqrt{I} $	Plane	Observed order	
272	110	110	Very Strong
		∇	
139	200	200	Strong
		∇	
115	150	150	Strong
99	310		
85	240	∇	
80	350	310, 240, 350, 040, 400	Medium
57	040		
56	400	∇	
52	550	550	Moderately Weak
34	190		
32	640	∇	
31	460		
29	710	190, 640, 460, 710, 600, 060	Weak
28	600		
26	060		
10	130		
6	330	∇	
4	020		
3	530		
2	220	130, 330, 020, 530, 220, 420, 620, 170	Absent
2	420		
0	620		
0	170		

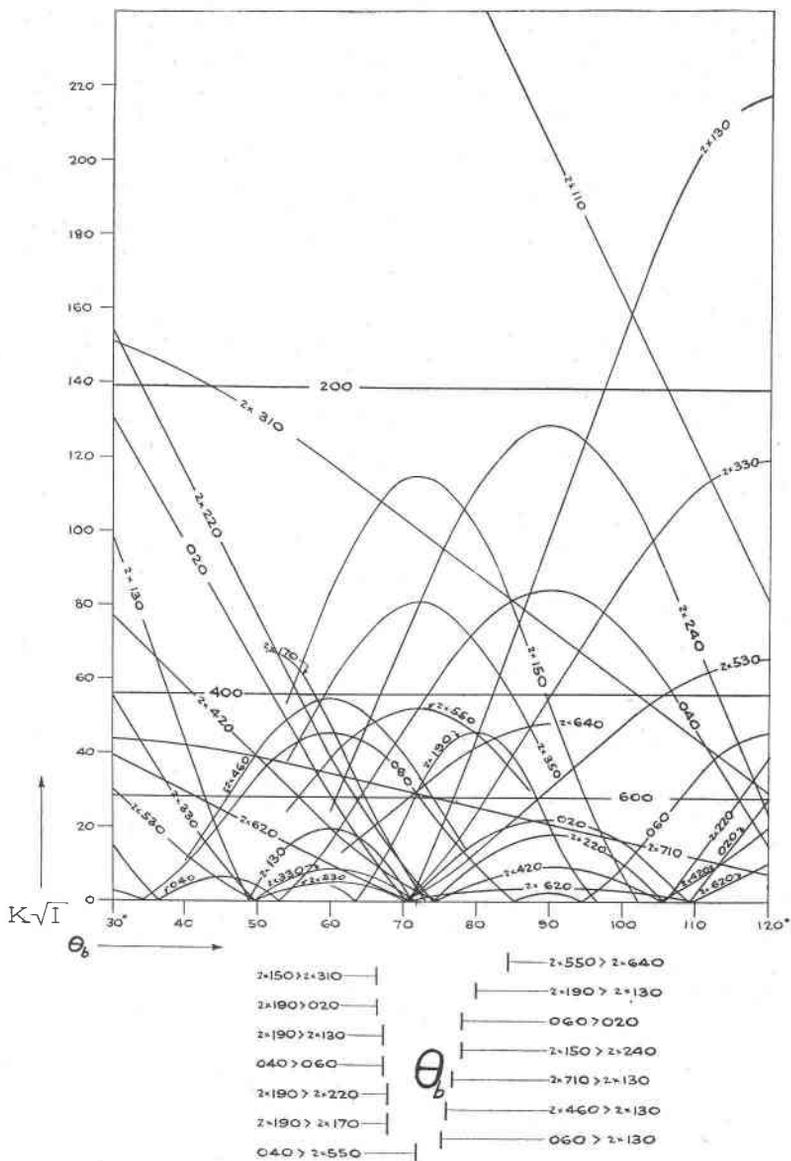


FIG. 7. The variations of intensity for all resolved planes within the dimensions of the apparatus for the  $c$  axis rotation and not involving  $\theta_c$ , plotted as functions of the parameter  $\theta_b$ . The notation  $2 \times hkl$  indicates that there are two pairs of planes in the form reflecting to the same spot on the photograph.

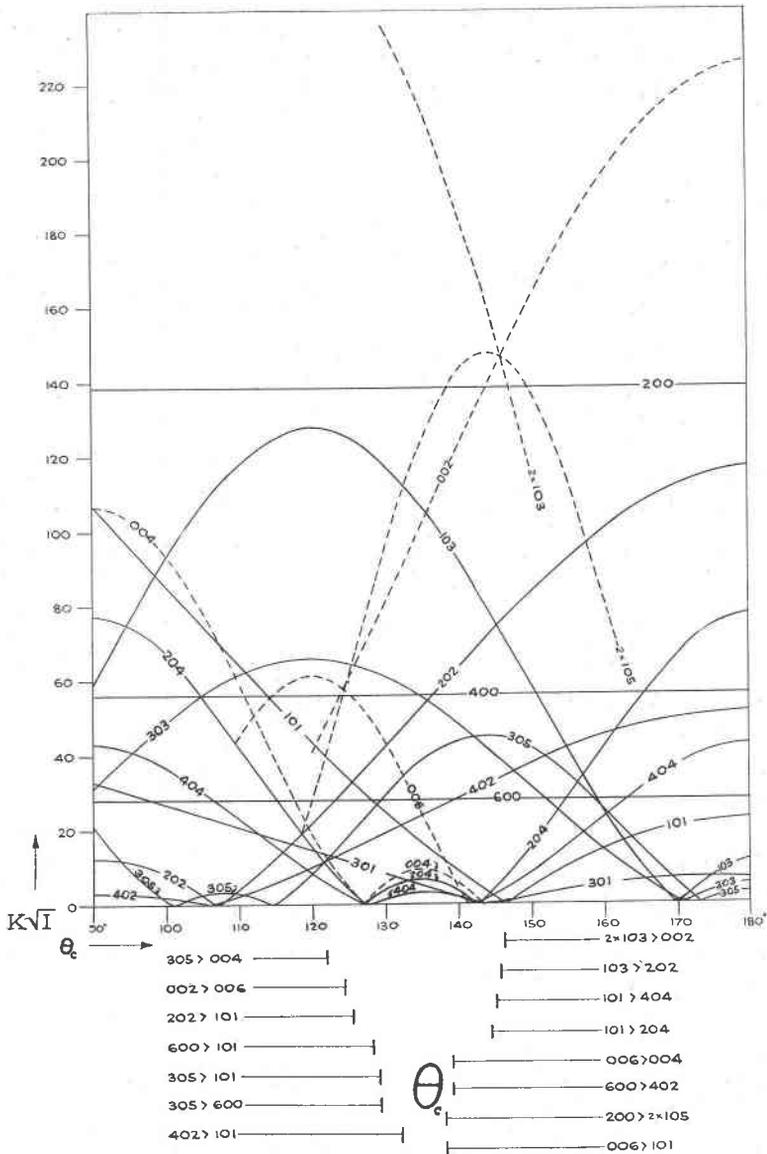


FIG. 8. The variations of intensity for all resolved planes within the dimensions of the apparatus for the  $c$  axis rotation, and not involving  $\theta_b$ , plotted as functions of the parameter  $\theta_c$ . The broken curves are additional intensity variations plotted for comparisons of the reflections of certain planes not appearing on the  $c$  axis rotation, but present on the  $a$  axis rotation. The notation  $2 \times h0l$  indicates there are two pairs of planes in the form reflecting to the same spot on the photograph.

planes with  $h+k+l$  odd to reflect, not one reflection is recorded. There is no contribution by iron atoms to the reflections for which  $h+k+l$  is odd, all diffracted radiation being due to the sulfur atoms. For marcasite, the phase function,  $P$ , for the sulfur atoms, takes the form:

$$P = -4 \sin(k\theta_b) \cdot \sin(l\theta_c).$$

For planes ( $h5l$ ), this is more specifically:

$$P = -4 \sin(5\theta_b) \cdot \sin(l\theta_c).$$

Evidently the right hand member vanishes for any value of  $\sin(5\theta_b)$  which is zero. This occurs when  $5\theta_b$  is  $0^\circ$ ,  $180^\circ$ ,  $360^\circ$ , etc., or when  $\theta_b$  is  $0^\circ$ ,  $36^\circ$ ,  $72^\circ$ ,  $108^\circ$ , etc. The  $72^\circ$  solution corresponds with the  $\theta_b$  determined graphically. Any value of  $\theta_b$  very near to  $72^\circ$  would give rise to a sulfur contribution corresponding to an intensity too small to be detected on the photograph.

The parameter,  $\theta_c$ , has been determined graphically (Fig. 8) in a manner similar to that used in the determination of  $\theta_b$ . In addition, Fig. 8 shows the variation of certain planes (dotted curves) not appearing on the  $c$  axis rotation photograph, and whose observed intensity orders have been obtained from an  $a$  axis rotation photograph. The parameter  $\theta_c$  is seen to be limited to  $135^\circ$ , corresponding to  $u_c = .375 = \frac{3}{8}$ , to within less than one percent of the total possible variation. As an indication of the correctness of  $\theta_c = 135^\circ$ , the calculated intensities at this point in comparison with the observed order are given in Table VII. The correspondence is very good, taking into consideration the following point: reflections from planes located near the center of the rotation photograph, and on high layer lines always appear too intense, compared with calculated intensities. This is a normal condition, caused, in part, by the greater thickness of the splinter shaped crystal traversed by these beams. In no case has this effect seriously impaired the closeness of parameter determination.

An additional check on the correctness of  $\theta_c$  is had by an inspection of the list of planes indexed (Table I). In the rows corresponding to ( $0k4$ ) and ( $hk4$ ), it is evident that only such planes reflect as have  $h+k+l$  even. Out of at least fourteen chances for planes with  $h+k+l$  odd to reflect, not one reflection is recorded. For this type

TABLE VII. COMPARISON OF CALCULATED AND OBSERVED ORDERS OF INTENSITIES FOR (h0l) PLANES, AT  $\theta_c = 135^\circ$

$ K\sqrt{I} $	Plane	Observed order	
		103	Very Strong
		∇	
139	200	200	Strong
107	103	∇	
56	400		
56	303	400, 303, 202, 305	Medium
52	202	∇	
38	305		
28	600	600, 402	Weak
24	402	∇	
16	101	101	Very Weak
7	204	∇	
5	301	204, 301, 404	Absent
3	404		

of plane, the total diffracted radiation is due to the sulfur atoms. In this case, the phase function takes the form

$$P = -4 \sin(k\theta_b) \cdot \sin(4\theta_c).$$

The right hand member vanishes for values of  $4\theta_c$  equal to  $0^\circ, 180^\circ, 360^\circ$ , etc., or for values of  $\theta_c$  equal to  $0^\circ, 45^\circ, 90^\circ, 135^\circ, 180^\circ$ , etc. The  $135^\circ$  solution is identical with the value of the parameter already determined.

As final checks on the proposed parameters, Table VIII shows the graphically calculated and the observed intensities of planes not involving  $\theta_c$ , and planes not involving  $\theta_b$ , both taken together for comparison, and Table IX shows the calculated intensities of all planes having values of  $\sin \theta$  less than .4, and not near the central portion of the photograph. To include planes of higher values of  $\sin \theta$  would be to push the proof of accuracy of the parameters beyond the order of accuracy of their determination. The checks are clearly satisfactory.

#### THE MARCASITE STRUCTURE

DESCRIPTION. The considerations just detailed lead to a complete description of the structure of marcasite, in the following terms:

Unit cell:  $a = 3.37 \text{ \AA}$   
 $b = 4.44 \text{ \AA}$   
 $c = 5.39 \text{ \AA}$

Space group:  $V_h^{12}$

TABLE VIII. COMPARISON OF CALCULATED AND OBSERVED ORDERS OF INTENSITIES FOR  $(hk0)$  AND  $(h0l)$  PLANES, AT

$\theta_b = 73^\circ$   
 $\theta_c = 130^\circ$

$ K\sqrt{I} $	Plane	Observed order	
272	110	110, 103	Very Strong
		∇	
139	200	200	Strong
		∇	
115	150	150	Strong
107	103		
99	310	∇	
85	240		
80	350		
57	040	310, 240, 350, 040, 400, 303, 202, 305	Medium
56	400		
56	303	∇	
52	202		
52	550	550	
38	305		
34	190	∇	
32	640		
31	460		
29	710	190, 640, 460, 710, 600, 060, 402	Weak
28	600		
26	060	∇	
24	402		
16	101	101	Very Weak
10	130		
7	204		
6	330	∇	
5	301		
4	020		
3	404	130, 204, 330, 301, 020, 404, 530,	
3	530	220, 420, 620, 170	Absent
2	220		
2	420		
0	620		
0	170		

Iron atoms (on symmetry centers) at:  $[[000]]$  and  $[[\frac{1}{2}\frac{1}{2}\frac{1}{2}]]$   
 Sulfur atoms (on reflection planes) at:  $[[0u_bv_c]]$ ,  $[[0\bar{u}_b\bar{v}_c]]$ ,

$[[\frac{1}{2},\frac{1}{2}-u_b,\frac{1}{2}+v_c]]$ , and  $[[\frac{1}{2},\frac{1}{2}+u_b,\frac{1}{2}-v_c]]$

$$\text{where } \begin{cases} U_b = .203 \pm .01 \\ V_c = .375 \pm .01 \end{cases}$$

$$\text{corresponding to } \begin{cases} u_b b = y_b = .900 \\ v_c c = z_c = 2.02 \end{cases}$$

TABLE IX. COMPARISON OF CALCULATED AND OBSERVED ORDERS OF INTENSITIES FOR ALL PLANES HAVING SIN  $\theta$  UNDER .4 AND POSITIONS NOT TOO NEAR CENTER OF PHOTOGRAPH, AT

$$\begin{cases} \theta_b = 73^\circ \\ \theta_c = 135^\circ \end{cases}$$

$ K\sqrt{I} $	Plane	Observed order	
272	110	110, 121	Very Strong
226	121		
151	231+041	231+041, 111, 200	Strong
147	111		
139	200	212, 321, (132+222), 031	Strong
113	212		
109	321	310, (131+221), 240, 211, 040, 311	Medium
102	132+222		
99	310	021, 032	Weak
89	131+221		
86	031	101	Very Weak
85	240		
83	211	130, 141, 301, 020, 220	Absent
60	311		
57	040		
37	021		
35	032		
16	101		
10	130		
8	141		
5	301		
4	020		
2	220		

for the marcasite studied. The coordinates are referred to the conventional marcasite orientation, taking the origin at a symmetry center.

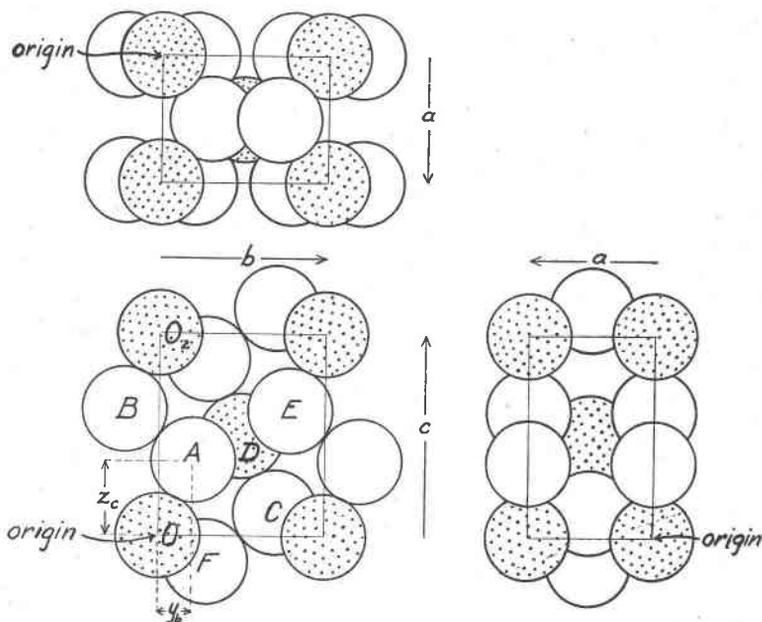


FIG. 9. (001)-plan (upper left), (100)-elevation (lower left), and (010)-elevation (lower right) of marcasite. The iron atoms (stippled) and sulfur atoms are drawn to scale. The relation between the sulfur pair and iron triad is well seen in the lower right (010) elevation. The bottom three irons form the triad, to which is attached, below and in back, the bottom two sulfurs. The axis of the sulfur pair slopes down and back away from the iron triad.

A unit cell of this structure, together with a few additional atoms to complete the picture, is shown in Fig. 9. The structure is identical with the one proposed by Huggins on grounds of atomic theory and shown in Fig. 2. From a certain point of view, it can be easily visualized as a stack of separate (100) planes; each plane consists of parallel strings of Fe-S-S-Fe-S-S- - - extending in the direction of the  $c$  axis with all the iron atoms in a straight line, but with the sulfur atom pairs nesting zigzag between these irons and causing the crooked appearance of the string. Adjacent threads have sulfur pairs pointing in the same direction, but adjacent planes have them pointing in reversed directions. Between (100) planes the fit

is made by contacting an iron atom of one plane with the nearest sulfur atoms of neighboring strings in the next plane.

GEOMETRICAL PROPERTIES. Various important geometrical properties of the structure of marcasite can be calculated as follows:

Paired sulfur distance:

$$AB = \sqrt{(2y_b)^2 + (c - 2z_c)^2} = 2.25\text{\AA}.$$

Unpaired sulfur distances:

$$AE = \sqrt{(b - 2y_b)^2 + (c - 2z_c)^2} = 2.96\text{\AA}$$

$$AC = \sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{b}{2}\right)^2 + \left(2z_c - \frac{c}{2}\right)^2} = 3.10\text{\AA}$$

$$AF = \sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{b}{2} - 2y_b\right)^2 + \left(\frac{c}{2}\right)^2} = 3.16\text{\AA}$$

$$AA' \text{ (two (100) sheets apart)} = a = 3.37\text{\AA}.$$

Iron—iron distances:

$$DD' \text{ (two (100) sheets apart)} = a = 3.37\text{\AA}$$

$$OD = \sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{b}{2}\right)^2 + \left(\frac{c}{2}\right)^2} = 3.88\text{\AA}$$

$$OO_2 = c = 5.39\text{\AA}$$

$$DD_2' = \sqrt{a^2 + b^2} = 5.52\text{\AA}$$

Iron—sulfur distances:

$$AO = \sqrt{y_b^2 + z_c^2} = 2.21\text{\AA}$$

$$AD = \sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{b}{2} - y_b\right)^2 + \left(\frac{c}{2} - z_c\right)^2} = 2.24\text{\AA}.$$

The structure displays 6-3 coordination. The iron atom, *D* is surrounded by six sulfurs at distances which are identical, within the accuracy of measurement: two sulfurs in the same plane, *C* and *G*, centrosymmetrical with respect to the iron; two in the plane in front, *A* and *E*; and two in the plane behind, centrosymmetrical with *A* and *E*. All these surround the iron at a distance of 2.21–2.24 Å. The sulfur atom, *A*, in turn, has three irons nearest it at this distance: *O*, in the same plane, and *D* and *D'* in the plane in front and behind.

The relation of the structure to other structures can best be visualized by separating a sulfur pair with its immediate iron environment. This group, as indicated in Fig. 1B, is a sulfur pair capped at each end by an iron triad. The triangles formed by the iron triads are rotated  $180^\circ$  with respect to one another. These triangles are not exactly equilateral, but are rather isosceles, as indicated by the distances:  $DD' = 3.37\text{\AA}$ ;  $OD$  and  $OD' = 3.88\text{\AA}$ ; the acute angle is about  $51\frac{1}{2}^\circ$  instead of the ideal  $60^\circ$ . The angle which the plane of the iron triad makes with the direction of the sulfur pair is very close to the ideal  $90^\circ$ . For the parameters given, it can be calculated as:

$$180^\circ - \tan^{-1}(b/c) - \tan^{-1}\left(\frac{yb}{c - z_c}\right) = 87^\circ.$$

#### RELATION TO OTHER STRUCTURES

**PYRITE.** These same units in the undistorted, ideally symmetrical condition are distinguishable in pyrite, and indeed it was on the assumption that these units carried over from pyrite to marcasite that Huggins<sup>21</sup> proposed a structure for marcasite. The difference between pyrite and marcasite is essentially one of a different linking of these units, at the same time satisfying the 6-3 coordination requirement.

In Table X certain geometrical properties of pyrite<sup>22</sup> are given in comparison with those of the marcasite structure, to bring out the essential identity of this common unit.

**RUTILE.** The rutile structure is a special case of the marcasite structure. The marcasite structure tends toward the rutile structure by decrease of the distance between the sulfur atom and the plane of the iron triad. When the sulfur atom actually occupies the plane of the iron triad, and the triad makes an angle of  $90^\circ$  with the sulfur pair, it is identical with the rutile structure type.

Proof of the close relation between the marcasite and rutile groups, as well as an excellent visual check on the general correctness of the marcasite structure, is offered in Fig. 10, in which stand-

<sup>21</sup> *Loc. cit.*

<sup>22</sup> Pyrite designations and distances taken from: P. P. Ewald and C. Hermann, *Strukturbericht*, 1913-1926, p. 153 (supplement to recent numbers of *Zeit. Krist.*).

ard crystal drawings of marcasite,<sup>23</sup> löllingite,<sup>24</sup> and rutile<sup>25</sup> are given in the same orientation for comparison. The tetragonaloid aspect of the marcasite group is obvious.

TABLE X. COMPARISON OF CERTAIN DIMENSIONS OF THE COMMON UNIT OF THE PYRITE AND MARCASITE STRUCTURES

	Pyrite	Joplin marcasite
Paired sulfur distances	$d = 2.10\text{Å}$	$AB = 2.25\text{Å}$
Iron-iron distances in triad	$\begin{cases} f = 3.82 \\ f = 3.82 \\ f = 3.82 \end{cases}$	$\begin{aligned} DD' &= 3.37 \\ OD &= 3.88 \\ OD' &= 3.88 \end{aligned}$
Distances from sulfur to irons in nearest triad	$\begin{cases} e = 2.26 \\ e = 2.26 \\ e = 2.26 \end{cases}$	$\begin{aligned} AO &= 2.21 \\ AD &= 2.24 \\ AD' &= 2.24 \end{aligned}$
Distance from apex of one iron triad to centrosymmetrical apex	$\begin{cases} a = 5.40 \\ a = 5.40 \\ a = 5.40 \end{cases}$	$\begin{aligned} c &= 5.39 \\ DD_2 &= 5.52 \\ DD_2 &= 5.52 \end{aligned}$
Angle between sulfur pair and iron triad	$90^\circ$	$\pm 87^\circ$

### THE CHEMICAL NATURE OF MARCASITE

RADII OF SULFUR AND IRON ATOMS. The geometrical properties listed indicate that the closest iron-sulfur approach is identical with the closest sulfur-sulfur approach, to within the limits of error of the determination. Slight changes in the parameters do not destroy the essential nature of this feature. Assuming that both the iron and sulfur atoms behave like rather hard spheres, it follows that they have the same radius, namely; about 1.12Å.

<sup>23</sup> Traced from: Victor Goldschmidt, *Atlas der Kristallformen*, Heidelberg, 1920, vol. 6.

<sup>24</sup> L. H. Bauer and H. Berman, Löllingite from Franklin, New Jersey, *Am. Mineral.*, 12, 1927, p. 40.

<sup>25</sup> Habit taken from *Dana's System*, (1914), p. 238, Fig. 4, but redrawn so that the rutile *c* axis direction corresponds with the marcasite and löllingite *a* axis direction, and the rutile *a*<sub>1</sub> and *a*<sub>2</sub> axial directions corresponding with the marcasite and löllingite *b* and *c* axial directions.

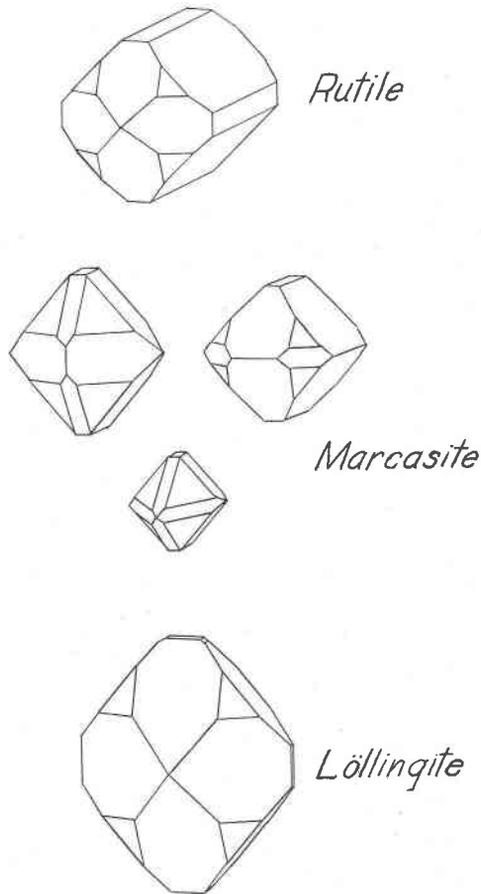


FIG. 10. Comparison of the habits of the rutile and marcasite groups. As redrawn, the rutile  $c$  axis is parallel with the marcasite and löllingite  $a$  axis direction. Other axes are parallel. Corresponding faces, referred to this orientation, have identical indices.

STATE OF IONIZATION. The probable state of ionization of the atoms in marcasite may be investigated without any chemical assumptions whatever by considering the sulfur-iron spacing to be expected from sulfur atoms and iron atoms in various states of ionization. The situation may be appreciated at a glance, thus:<sup>26</sup>

<sup>26</sup> Radii from: V. M. Goldsmidt, *Geochemische Verteilungsgesetze der Elemente*, vol. 7: *Skrifter utgitt av Det Norske Videnskaps-Akademi i Oslo I. Matem.-Naturvid. Klasse*, 1926, No. 2, pp. 26, 34, and 43.

	$S^{6+}$ , .34Å	$S^0$ , 1.04Å	$S^{2-}$ , 1.74Å
$Fe^0$ , 1.26Å	1.60Å	2.30Å	3.00Å
$Fe^{2+}$ , 0.83Å	1.17Å	1.87Å	2.57Å
$Fe^{3+}$ , 0.67Å	1.01Å	1.71Å	2.41Å

The figures are additions of the corresponding sulfur and iron radii. Evidently the only satisfactory chemical constitution for marcasite, from this geometrical criterion, is  $Fe^0S_2^0$ , which gives a sulfur-iron spacing of 2.30 Å, in rather good agreement with the observed spacing of 2.24 Å. The conclusion is that the sulfur and iron are in essentially the atomic state. The same situation also holds for pyrite, where this distance is 2.26 Å.

#### ACKNOWLEDGEMENT

It is a pleasure to acknowledge assistance from several sources. I am especially indebted to Prof. Palache of Harvard University for the gift of specimens of marcasite used in preliminary work, for placing at my disposal the use of the Harvard density determining apparatus, for permission to use the Harvard cylindrical camera for the rotating crystal method, and for many other courtesies rendered during the research. Mr. Berman of Harvard University also facilitated my work during the density determination.

I wish to thank my colleague, Prof. B. E. Warren, for permission to use the rotating crystal apparatus of the Department of Physics of the Massachusetts Institute of Technology, pending installation of suitable equipment in the Mineralogical Laboratories. Dr. Warren has also been kind enough to aid me at a number of points during my first working contact with the rotating crystal method.

This is the first of a series of papers dealing with the crystal structures of the marcasite group. The others, it is expected, will appear shortly.