THE CRYSTAL STRUCTURE OF CUBANITE

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Abstract

The structure of cubanite has been uniquely determined with the aid of intensity data derived from Weissenberg photographs. The space group is *Pcmn* and the cell has the following dimensions: $a=6.45$, $b=11.095$, $c=6.221$ kX. This cell contains 4 $CuFe_2S_3$. The copper atoms and one-third of the sulfur atoms each occupy the equipoint 4*c* (reflection planes), while the iron atoms and the remaining two-thirds of the sulfur atoms are in the general position, 8*d*. The structure is defined by the following parameters (origin at inversion center):

	x	y	z
Cu	$\frac{7}{12}$	$(\frac{1}{4})$	.122
S_1	$\frac{11}{12}$	$(\frac{1}{4})$	.270
Fe	$\frac{1}{12}$	.083	.135
S_2	$\frac{5}{12}$	.083	.265

The x and z parameters are subject to some further slight refinement by three-dimensional Fourier synthesis.

The structure is based upon almost ideal, hexagonal close-packing of sulfur atoms. The metal atoms are each surrounded by four sulfur atoms in almost ideal tetrahedral coordination. The structure may be regarded as made up of slices of the wurtzite structure parallel to (010), joined to identical but inverted slices by means of the sharing of one of the edges of each iron coordination tetrahedron. This curious sharing of a tetrahedral edge is correlated with the ferromagnetic properties of cubanite.

Introduction

The structure of cubanite is of more than ordinary interest. In the first place cubanite shares with the native iron, magnetite, and pyrrhotite the distinction of being ferromagnetic. While the structures of iron and magnetite are known, it is doubtful whether the structure assigned to pyrrhotite is correct, at least in detail, for the true cell of pyrrhotite is a multiple of the cell of the assigned structure.[1] Thus a knowledge of the structure of cubanite might be expected to cast light on the nature of the weak ferromagnetism in iron-bearing sulfides.

In the second place cubanite is known to unmix from chalcopyrite,[2] giving rise to oriented[3] plates in the chalcopyrite matrix. It is known that

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[1] Buerger, M. J., The cell and symmetry of pyrrhotite: *Am. Mineral.*, **32,** 411–414 (1947).

[2] Schwartz, G. M., Intergrowths of chalcopyrite and cubanite; experimental proof of the origin of the intergrowths and their bearing on the geological thermometer: *Ec. Geol.*, **22,** 44–61 (1927).

[3] Buerger, N. W., and Buerger, M. J., Crystallographic relations between cubanite segregation plates, chalcopyrite matrix, and secondary chalcopyrite twins: *Am. Mineral.*, **19,** 289–303 (1934).

the segregation must arise from ordering of the atoms in a disordered high-temperature form of chalcopyrite,[4] but the character of the ordering mechanism cannot be known until the structure of cubanite is known.

In this paper an account is given of the determination of the structure of cubanite. While all the coordinates of all the atoms have not been highly refined, they have been determined closely enough to permit a contribution to an understanding of the problems mentioned above.

CELL AND SYMMETRY

In an earlier contribution,[5] the diffraction symbol of cubanite was shown to be *mmmPc-n*. This embraces the two space groups *Pcmn* and $Pc2_1n$. The cell dimensions were also reported. More accurate cell dimensions for cubanite from the Frood Mine, Sudbury, Ontario are as follows:

$$a = 6.45kX$$
$$b = 11.095$$
$$c = 6.221$$

These new values were obtained with the aid of a precision, back-reflection Weissenberg apparatus[6] but utilizing one radiation only. Unfortunately with this radiation the *h*00 reflections were too poorly disposed on the photographs to permit refining the *a* axis dimension.

The cubanite cell contains 4 $CuFe_2S_3$.

STRUCTURE DETERMINATION

Introduction.—The structure of cubanite was determined from intensity considerations, except that rough geometrical packing considerations guided the search for *z* parameters. As the structure became revealed it became evident that the only kind of Fourier method which would aid in the parameter determination was the method of sections. Since this required more quantitative intensity data than were at hand and could be obtained in a reasonable time, the refinement of the structure by Fourier methods was deferred until such data were at hand.

The intensities required for the determination of the structure as given in this paper were derived from zero-level Weissenberg photographs made with filtered Mo$K\alpha$ radiation. This provided the relative intensities of the *hk*0, *h*0*l*, and 0*kl* spectra.

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[4] Buerger, M. J., The temperature-structure-composition behavior of certain crystals: *Proc. Nat. Acad. Sci.*, **20**, 444–453 (1934).

[5] Buerger, M. J., The unit cell and space group of cubanite: *Am. Mineral.*, **22**, 1117–1120 (1937).

[6] Buerger, M. J., The precision determination of the linear and angular lattice constants of single crystals: *Zeits. Krist.*, (A) **97**, 433–468 (1937).

Equipoint Possibilities.—The cubanite cell contains 4 $CuFe_2S_3$. This necessitates finding equipoint combinations adding to 4, 8, and 12. Space group $Pc2_1n$ contains only the general equipoint, 4*a*. Space group *Pcmn* contains the general equipoint 8*d* as well as the special positions on sets of inversion centers, 4*a* and 4*b*, and on reflection planes, 4*c*. The correct equipoint combination for cubanite is determined by the following intensity analysis:

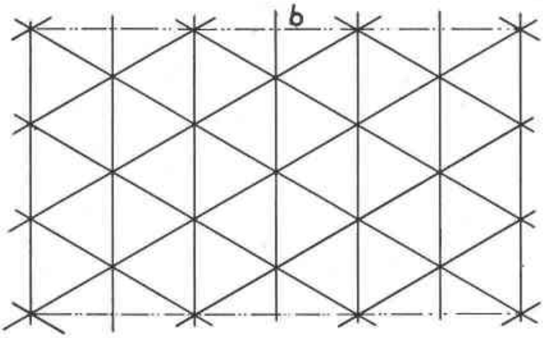

FIG. 1

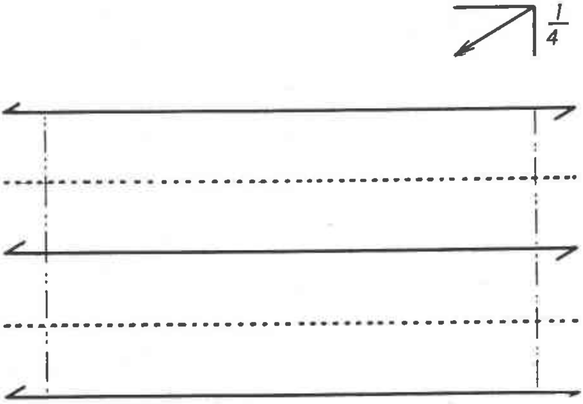

FIG. 2

Preliminary Intensity Considerations.—A conspicuous feature of the intensity distribution is the special intensity pattern of the *hk*0 reflections. Of the possible *hk*0 reflections permitted by both space groups, only a limited number appear (in a pattern to be discussed shortly), the rest being missing or very weak. This pattern of strong reflections is characterized by a regular decline of the orders of 060, and a regular decline of the orders of 330. The significance of this is that all atoms must be located on (010) sheets spaced $b/6$ apart and also on (110) sheets which divide a and b into thirds.

In Fig. 1 these two sets of intersecting sheets are shown projected on (001). In projection they constitute a net. The net must, of course, be made conformable with the symmetry elements of the space group. The symmetry elements of the two space groups, $Pc2_1n$ and $Pcmn$, which come up for consideration, are shown projected on (001) in Fig. 2. The net of Fig. 1 can be located in the symmetry common to the two space groups only in the one way shown in Fig. 3.

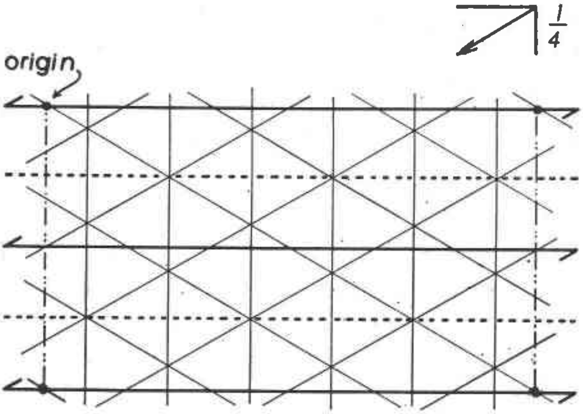

FIG. 3

Since, as pointed out above, all atoms must be confined to lines of the net in order to satisfy intensity requirements, each atom must be located on some node of the net. Very approximately, iron and copper have the same scattering power, so that the two kinds of metal atoms in cubanite are indistinguishable. There are only two ways of distributing the metals in the net of Fig. 3 so as to satisfy symmetry and also place the correct number in the cell. One is to place the metals on the nodes in the vertical glide planes, the other is to place them on the nodes next nearest to these glide planes. These schemes result in the metal distributions shown in Figs. 4 and 5, respectively. These possible locations have the x and y parameters given in Table 1.

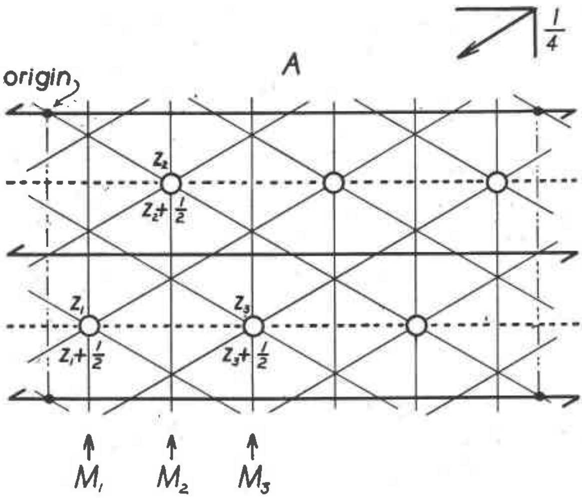

FIG. 4

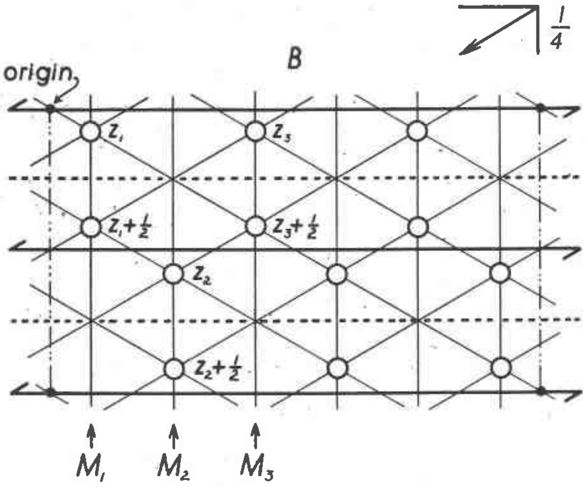

FIG. 5

TABLE 1. PERMISSIBLE x AND y COORDINATES OF ATOMS IN CUBANITE
(Origin is on a two-fold screw of $Pc2_1n$, or on an inversion center of $Pcmn$.)

Possibility A, Fig. 4.			Possibility B, Fig. 5.		
	x	y		x	y
M_1 (or S_1)	$\frac{3}{4}$	$\frac{1}{12}$	M_1 (or S_1)	$\frac{1}{12}$	$\frac{1}{12}$
M_2 (or S_2)	$\frac{1}{4}$	$\frac{1}{4}$	M_2 (or S_2)	$\frac{7}{12}$	$\frac{1}{4}$
M_3 (or S_3)	$\frac{3}{4}$	$\frac{5}{12}$	M_3 (or S_3)	$\frac{1}{12}$	$\frac{5}{12}$

Note: Coordinates are given for the less symmetrical space group $Pc2_1n$. For space group $Pcmn$, M_3 (or S_3) is symmetrically equivalent to M_1 (or S_1) and should be omitted.

Following the same argument, the sulfur atoms, which are equal in number to the metal atoms, must be distributed in one of the two ways shown in Figs. 4 and 5. This limits the structure to four possible projections. Using the abbreviations M for metal, S for sulfur, *A* for the distribution shown in Fig. 4 and *B* for the one shown in Fig. 5, these possible structures are M_AS_A, M_AS_B, M_BS_A, and M_BS_B.

Structure possibility M_AS_A projects on (010) as a simple plane lattice array. Hence, it would be characterized by regular declines of intensity in orders of all *hk*0 reflections. This is contrary to the observed intensity sequences, which are not regular declines for all order series. Thus combination M_AS_A can be eliminated from further consideration.

Combination M_BS_A can be eliminated on similar grounds: As a rather good approximation either of the metals Cu or Fe has twice the scattering power of S. Now arrangement *A* has two atoms (sulfur in this case) projected on each point, and arrangement *B* (metals in this case) has one atom projected on each point. The sum of both arrays is a lattice array of points. Furthermore the points have equal scattering powers, since a sulfur point has two sulfur atoms, each with half the scattering power of a metal point. Thus the composite array should scatter very approximately as a simple lattice array of points, which is characterized by a regular decline of intensity of the orders of all *hk*0 reflections. Since this is contrary to the observed intensity sequences, combination M_BS_A can be eliminated from further consideration.

This reasoning eliminates any structure containing sulfur atoms in S_A. The remaining combinations, M_AS_B and M_BS_B are of structural interest because S_B is also the projection of hexagonal close-packed sulfur atoms in which the remaining, z, parameter of sulfur is $\frac{1}{4}$. Close packing of the sulfur atoms is also consistent with the axial ratio of the cubanite cell, as shown by the following comparison:

AXIAL RATIOS

	Cubanite	Hexagonal close packing
a	.581	.577
b	1	1
c	.560	.549

The suggestion that the sulfur atoms are in close packing in cubanite is strong enough to serve as a useful guide in the subsequent exploration of parameters.

Relation between Remaining Structure Combinations.—An attempt is now called for to decide between arrangements M_AS_B and M_BS_B. For preliminary exploration, the following approximations are possible. If sulfur is assigned a scattering power of unity, then iron and copper each have scattering powers of approximately 2. Furthermore, because of the symmetry of the projections, amplitudes can be computed for *hk*0 spectra by means of the structure factor of space group *Pcmn* (see subsequent section).

Arrangement M_BS_B gives rise to a simple pattern of amplitudes (uncorrected for Lorentz, polarization, or *f* factors). This is shown in Table 2. Arrangement M_AS_B gives rise to the same absolute amplitudes, but with different signs for certain of the spectra for which *h* is odd. Since these phase differences cannot be distinguished, it follows that structure M_AS_B cannot be distinguished from structure M_BS_B by any criterion based upon the reflections *hk*0.

TABLE 2

	6	9		0		0		9		0		0		9
	5		0		3		0		0		3		0	
	4	3		0		0		3		0		0		3
h	3		0		9		0		0		9		0	
	2	3		0		0		3		0		0		3
	1		0		3		0		0		3		0	
	0	9		0		0		9		0		0		9
		0	1	2	3	4	5	6	7	8	9	10	11	12
								k						

The observed intensities of diffraction by cubanite follows the pattern of amplitudes shown in Table 2. This confirms that the structure of cubanite is indeed one of the combinations M_AS_B or M_BS_B. From the point of view of packing, the combination M_AS_B corresponds to a pyrrhotite type of packing. In this case, the copper atoms would merely substitute for certain iron atoms in the pyrrhotite structure, thus causing it to display superstructure characteristics. The combination M_BS_B is based upon a complication of the wurtzite packing and represents a structural type not previously observed.

Both structures suggested above have the same distribution of equipoints, but with different parameters. Their properties, so far as known to this point, are summarized in Table 3. (In this table, the initial sulfur atoms are differently chosen from those in Table 1 in order to give them *z* parameters nearer zero.)

TABLE 3. APPROXIMATE COORDINATES OF ATOMS IN POSSIBLE CUBANITE STRUCTURES
(z parameters based upon assumption that sulfur atoms are close packed and that metal atoms are in interstices.)

Space Group	Atoms	Equipoint	M_AS_B, Pyrrhotite-Like Structure			M_BS_B, Wurtzite-Like Structure		
			x	y	z	x	y	z
$Pc2_1n$	$M_1=Fe_1$	$4a$	$\frac{3}{4}$	$\frac{1}{12}$	0	$\frac{1}{12}$	$\frac{1}{12}$	$\frac{1}{8}$
	$M_2=Cu$	$4a$	$\frac{1}{4}$	$\frac{1}{4}$	0	$\frac{7}{12}$	$\frac{1}{4}$	$\frac{1}{8}$
	$M_3=Fe_2$	$4a$	$\frac{3}{4}$	$\frac{5}{12}$	0	$\frac{1}{12}$	$\frac{5}{12}$	$\frac{1}{8}$
	S_1	$4a$	$\frac{5}{12}$	$\frac{1}{12}$	$\frac{1}{4}$	$\frac{5}{12}$	$\frac{1}{12}$	$\frac{1}{4}$
	S_2	$4a$	$\frac{11}{12}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{11}{12}$	$\frac{1}{4}$	$\frac{1}{4}$
	S_3	$4a$	$\frac{5}{12}$	$\frac{5}{12}$	$\frac{1}{4}$	$\frac{5}{12}$	$\frac{5}{12}$	$\frac{1}{4}$
$Pcmn$	$M_1=Fe$	$8d$	$\frac{3}{4}$	$\frac{1}{12}$	0	$\frac{1}{12}$	$\frac{1}{12}$	$\frac{1}{8}$
	$M_2=Cu$	$4c$	$\frac{1}{4}$	$\frac{1}{4}$	0	$\frac{7}{12}$	$\frac{1}{4}$	$\frac{1}{8}$
	S_1	$8d$	$\frac{5}{12}$	$\frac{1}{12}$	$\frac{1}{4}$	$\frac{5}{12}$	$\frac{1}{12}$	$\frac{1}{4}$
	S_2	$4c$	$\frac{11}{12}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{11}{12}$	$\frac{1}{4}$	$\frac{1}{4}$

In passing, it should be noted that the more natural space group of cubanite is $Pcmn$ because the general position is just filled by the most abundant atom. Space group $Pc2_1n$ requires the same atomic species to be of two symmetrically unrelated varieties. This is equivalent to saying that if $Pc2_1n$ is the space group, the structure is identical with a corresponding structure in $Pcmn$ except for a distortion, and there appears to be no obvious reason for such a distortion.

Structure Factors.—The structure factors for the reflections from the several prism zones of $Pcmn$ and from the [010] zone of $Pc2_1n$ are listed in Table 4. It should be observed that the forms of the structure factor for the reflections $h0l$ (including $h00$ and $00l$) are identical for the two possible space groups. Thus the undetermined z parameters of the atoms may be explored in a single search by the utilization of these spectra.

TABLE 4. STRUCTURE FACTORS FOR PRISM-ZONE REFLECTIONS

Reflection	Class	Space Group $Pcmn$	Space Group $Pc2_1n$
$hk0$	h even, k even h odd, k odd	$8\cos 2\pi hx \cos 2\pi ky$ $-8\sin 2\pi hx \sin 2\pi ky$	
$h0l$	$h+l$ even $h+l$ odd	$8\cos 2\pi hx \cos 2\pi lz$ $-8\sin 2\pi hx \sin 2\pi lz$	$4\cos 2\pi hx \cos 2\pi lz$ $-4\sin 2\pi hx \sin 2\pi lz$
$0kl$	k even, l even k odd, l even	$8\cos 2\pi ky \cos 2\pi lz$ $-8\sin 2\pi ky \sin 2\pi lz$	

For the purposes of further parameter study the intensities have been computed according to a plan discussed elsewhere.[7]

Preliminary Search for Parameters of Metal Atoms.—In the preliminary search for parameters satisfying the intensity requirements, it is useful to assume that the sulfur atoms are close packed, as suggested by the z parameters in Table 3. The only question is then, in which set of interstices do the metals lie? If the metals are assumed to have the parameters given by the M_AS_B structure of Table 3, the computed $h0l$ intensities bear no relation to the observed intensities, even with reasonable variations from the ideal parameters. On the other hand, when the metals are assumed to have the parameters given by the M_BS_B structure of Table 3, there is a noteworthy correspondence between computed and observed intensities. The correspondence is considerably improved by increasing the z parameter of Fe to .135. The parameter values then reasonably explain the $00l$ and $h0l$ spectra.

Computations of the intensities of $0kl$ spectra using the structure factor for *Pcmn* then yield a set of intensities in good preliminary agreement with the observed intensities. These considerations thus confirm structure M_BS_B as based upon space group *Pcmn*. The space group $Pc2_1n$ thus comes up for consideration only as a possibly slightly generalized equivalent of *Pcmn*. Since further parameter refinement based upon *Pcmn* reproduces the spectra rather exactly, this may be regarded as the correct space group.

Refinement of y Parameters.—With the structure type, approximate parameters, and space group fixed, the number of variable y parameters reduce to two: one for Fe and one for S_2. These parameters can be fixed by studying the $0l0$ spectra, 14 even orders of which can be recorded by MoKα radiation. Only the higher orders not divisible by 6 are useful in this study, for those divisible by 6 form a series of very strong spectra of gradually declining intensity, and their intensities are insensitive to small variations in the y parameters from the neighborhood of the ideal $\frac{1}{12}$. The amplitudes of sensitive orders for the ideal parameters are as follows:

0·10·0	−2.2
0·14·0	−2.9
0·16·0	1.5
0·20·0	2.9
0·22·0	−1.9
0·26·0	−0.9
0·28·0	1.0

This series is already in good agreement with the observed intensities

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[7] Buerger, M. J., Numerical structure factor tables: *G. S. A. Special Publication No.* **33** (1941).

and it turns out that any variation of the two y parameters away from the ideal values spoils the correspondence. From this it may be concluded that the y parameters of both Fe and S_2 are very close to $\frac{1}{12}$.

Refinement of z and x Parameters.—Any further trial and error refinement of parameters is fraught with great difficulties. Furthermore, refinement of parameters by Fourier synthesis of the electron density projected on (100), (010), or (001) is useless. Both of these situations are primarily due to the fact that the structure presents such regularities that non-equivalent atoms project to very nearly the same points when the structure is projected on any pinacoid. The greatest resolution occurs in projection on the (100) plane, but even here the resolution is not very good, yet because there is some resolution, an intensity fit can be found for the $0kl$ reflections by varying the z parameters. A rather good fit occurs for

	y	z
Fe	.083	.135
Cu	.250	.122
S_1	.083	.270
S_2	.250	.265

The only possible way to refine the x and z parameters is to prepare, by Fourier synthesis, sections of the three-dimensional electron density distribution at y levels of $\frac{1}{12}$ and $\frac{1}{4}$, thus locating the Fe and S_2 in the first section and the Cu and S_1 in the second section. These syntheses require quantitative intensities for all reflections hkl. Since these intensities are not yet available on a quantitative basis, this project is temporarily deferred.

THE STRUCTURE

As a result of the foregoing analysis, it is evident that the space group of cubanite is *Pcmn*. The best coordinates found by a trial and error search are as follows:

	x	y	z
Cu in 4*c*	$\sim\frac{7}{12}$	$(\frac{1}{4})$	.122
S_1 in 4*c*	$\sim\frac{11}{12}$	$(\frac{1}{4})$	.270
Fe in 8*d*	$\sim\frac{1}{12}$	.083	.135
S_2 in 8*d*	$\sim\frac{5}{12}$	.083	.265

The x and z parameters should not be regarded as final, but merely as rather close. More precise values await a three-dimensional Fourier study.

The structure is based upon an almost ideal, hexagonal close-packed array of sulfur atoms. Each metal atom occurs in an interstitial space between sulfur atoms in such a way that the metal has an almost ideal tetrahedral sulfur coordination.

The structure, however, is not one which has hitherto been described.

Its unusual characteristics can be appreciated with the aid of Fig. 6. This diagrammatically shows a region of the structure with ideal parameters in the neighborhood of $z=0$, specifically $-\frac{1}{4}<z<\frac{1}{4}$. The structure can be seen to be composed of slabs of the wurtzite arrangement parallel to (010) and averaging $b/2$ wide. Since the wurtzite arrangement is polar, the metal coordination tetrahedra all point up, or else they all point down. In the cubanite structure, the wurtzite-like slabs are joined to one another by inversion centers so that neighboring slabs have their tetrahedral apex directions reversed. The central section of each slab is composed of copper tetrahedra and the sides of the slab are composed of iron tetrahedra. Since an inversion center occurs at the midpoint of an edge of the iron tetrahedron, it has the effect of joining all iron tetrahedra in pairs which share this edge.

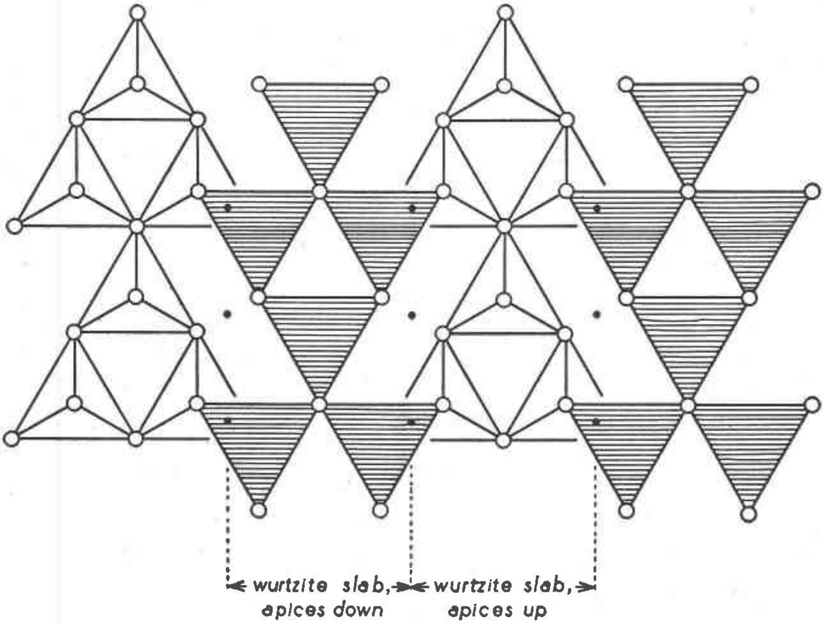

FIG. 6

The sharing of tetrahedral edges is most unorthodox, even in nonionic crystals. Since the sharing occurs for iron tetrahedra only, it is difficult to avoid the correlation of this curious feature with the unusual characteristic of ferromagnetism. The only other ferromagnetic sulfide is pyrrhotite, and there is a reasonable doubt about the correctness of the structure assigned to it, since pyrrhotite does not have the translation periods of the assigned structure.[1]

With the structure of cubanite known, the mechanism of the unmixing of cubanite from chalcopyrite can be studied. This is discussed in a subsequent contribution.