THE UNIT CELL AND SPACE GROUP OF CUBANITE

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Abstract

Sudbury cubanite has been studied by the equi-inclination Weissenberg method. This investigation leads to the following information:

Centrosymmetrical symmetry: $mmm=D_{2h}$
Crystal system: orthorhombic
Unit cell:

	absolute	*ratio*
	$a=6.43$ Å	.582
	$b=11.04$	1.000
	$c=6.19$	.561
	$z=4$ $CuFe_2S_3$ per cell	

Diffraction symbol: $mmmPc-n$
Space group: Pna $(=C_{2v}^{9})$, or $Pcmn$ $(=D_{2h}^{16})$.

The axial ratio chosen by surface morphological study is referred to the correct structural cell.

Introduction

Peacock and Yatsevitch[1] have recently made a well coördinated study of cubanite from the Frood Mine, Sudbury, Ontario. The writer is indebted to Dr. Peacock and also to Professor Palache of Harvard University for the privilege of basing the present structural study on this well described material. The characteristics of this cubanite are as follows:

orthorhombic holohedral
$a:b:c=.5822:1:.5611$
axis of high magnetic susceptibility: [010]
$d^{27}=4.101$
analysis:

Cu	22.88%
Fe	41.41
S	35.35
	99.64

Some difficulty was experienced in obtaining a single crystal free from twinning and still having a sufficiently full form development to permit it to be easily oriented for rotations about the three crystallographic axes. A specimen was finally selected which was obviously a twin, but in which the twin boundary could be recognized. From this a rough small piece was removed which contained only one individual, and which was bounded by a few recognizable planes.

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[1] Peacock, M. A., and Yatsevitch, G. M., Cubanite from Sudbury, Ontario: *Am. Mineral.*, vol. **21**, pp. 55–62, 1936.

CELL CHARACTERISTICS

METHOD. The entire study was carried out by the equi-inclination Weissenberg method.[2] A specially constructed equi-inclination apparatus was used for this purpose.[3] The films were interpreted by the new inspective method,[4] without any indexing.

The cell characteristics were determined from films taken with the use of cobalt radiation, which is only slightly absorbed by iron bearing crystals and which is quite clean. These films include ordinary rotation photographs about each of the three crystallographic axes (the second two being superfluous except as checks on orientation and cell dimensions), Weissenberg resolutions of the equators of each of these rotations, and equi-inclination resolutions of the 1st, 2nd and 3rd layers for the c axis rotation, as well as the 3rd layer for the a axis rotation (chiefly for symmetry).

For the determination of parameters, it is desirable to have reflections of higher orders than can be recorded by the long wave-length cobalt radiation. Accordingly, a second set of equatorial Weissenberg photographs was made for the three axial rotations, using molybdenum $K\alpha$ radiation (zirconia screened).

SYMMETRY. The equi-inclination Weissenberg photographs for rotations about the three crystallographic axes, regardless of layer, are all equi-inclination projections of the plane symmetry C_{2l}. This fixes the centrosymmetrical point-group of the crystal as $mmm=D_{2h}$, and fixes the crystal system as orthorhombic, a conclusion in accord with the results of study of the surface morphological development of cubanite.

The equatorial photograph for the c axis rotation displays a pseudosymmetry extraordinarily close to C_{6l}, but the n layer photographs for the same rotation axis entirely lack this pseudo-symmetry. This plainly indicates that the crystal structure projected on the (001) plane is based upon some hexagonal framework.

SPACE LATTICE TYPE. The c axis 1st, 2nd, and 3rd layer equi-inclination photographs are all of type 11, corresponding with rectangular plane lattices having a point at the rotation axis. All photographs, when superposed, show an identical distribution of spots. The stacking sequence is therefore 9, coincident rectangles. This information together with the symmetry previously noted, fixes the space lattice type as primitive orthorhombic, $mmmP$.

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[2] Buerger, M. J., The Weissenberg reciprocal lattice projection and the technique of interpreting Weissenberg photographs: *Zeits. Krist.* (A), vol. **88**, pp. 356–380, 1934.

[3] Buerger, M. J., An apparatus for conveniently taking equi-inclination Weissenberg photographs: *Zeits. Krist.* (A), vol. **94**, pp. 87–99, 1936.

[4] Buerger, M. J., The application of plane groups to the interpretation of Weissenberg photographs: *Zeits. Krist.* (A), vol. **91**, pp. 255–289, 1935.

UNIT CELL. The cell dimensions were first roughly determined from the layer line spacing of the c axis rotation, plus Z measurements of the dome reflections on n layer equi-inclination photographs for the c axis rotation. These values were subsequently refined by X measurements of high order pinacoid reflections. The cell so determined is as follows:

Absolute	Ratios	
	Cell (Buerger)	Surface Morphology (Peacock and Yatsevitch)[1]
$a=6.43$Å	$.582_5$	.5822
$b=11.04$	1.	1.
$c=6.19$	.561	.5611
	$\frac{a}{c}=1.038$	1.038

The cell contents are obtained through the use of the relation:

$$\text{density}=\frac{\text{cell mass}}{\text{cell volume}}=\frac{N\times f\times 1.649\times 10^{-24}}{V} \qquad (1)$$

where N = the number of formula weights per unit cell
f = the formula weight.

The chemical analysis may be reduced as follows:

	Weight per cent	Atomic per cent	Atomic ratios	Excess for ideal $CuFe_2S_3$
Cu	22.88	3.600	.980	$-.020$
Fe	41.41	7.415	2.018	$+.018$
S	35.35	11.025	3.000	.000

It will be observed that the analysis indicates an excess of iron over that required by the ideal formula $CuFe_2S_3$. This excess is almost exactly balanced by a copper deficit. It is fairly apparent, therefore, that the analysis indicates that one metal is substituting for the other in proxy solid solution.[5] Without pushing the precision of the analysis too far, the formula for the Frood cubanite may thus be written[6]

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[5] Buerger, M. J., The pyrite-marcasite relation: *Am. Mineral.*, vol. **19**, pp. 53–58, 1934.

[6] Buerger, M. J., The temperature-structure-composition behavior of certain crystals: *Proc. Nat. Acad. Sci., U.S.A.*, vol. **20**, p. 446, 1934.

$$\left|\begin{matrix} Cu_{.98} \\ \\ Fe_{.02} \end{matrix}\right| Fe_2S_3$$

This has a formula weight of 271.3 as compared with 271.4 for the ideal compound.

Substituting this value of the formula weight, the cell volume, and the measured[1] density, 4.101, in relation (1) above, leads to a 4.02_5 formula weights per unit cell.

SPACE GROUP. Comparison of the reciprocal translations on the three zero layer photographs, with the reciprocal translations of the lattice as shown by the *n* layer photographs, reveals the following multiple translations in the zero levels of the reciprocal lattice:[4]

plane	doubled reciprocal translation
(100)	*c*
(010)	none
(001)	*a* and *b*

Some of the above space pattern characteristics were checked by Mr. Ely Mencher who graphically reconstructed[2] the reciprocal lattice.

These multiple translations indicate the following symmetry characteristics:

plane	glide components
(100)	$\frac{c}{2}$
(010)	----
(001)	$\frac{a}{2}+\frac{b}{2}$

The diffraction symbol is therefore *mmmPc-n*. This diffraction effect may be obtained from either of the space groups *Pcmn* (D_{2h}^{16}), or *Pc-n*, which transforms by axial interchange to *Pna-*=*Pna* (Mauguin) ($=C_{2v}^9$).

ACKNOWLEDGMENT. The writer is indebted to the International Nickel Co., Ltd., for permission to publish this study.