THE UNIT CELL AND SPACE GROUP OF ORPIMENT

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Abstract

An x-ray study of orpiment has been made using the equi-inclination Weissenberg method. The monoclinic character of this crystal is confirmed by x-ray evidence. The dimensions of the reduced cell are:

$a = 11.47$Å
$b = 9.57$
$c = 4.24$
$\beta = 90°27'$.

This cell contains 4 As_2S_3. Its axes have the same orientation as the morphological axes adopted by Mohs, Stevanović, Palache, and Modell, but the lengths of the axes are different. The matrix of the transformation from the Mohs-Stevanović-Palache-Modell axes to the Buerger axes is

$$\begin{Vmatrix} 200 \\ 010 \\ 00\frac{2}{3} \end{Vmatrix}$$

The space group of orpiment is unequivocally determined as $P2_1/n$ (C_{2h}^5) for this cell.

Introduction: Orpiment is one of the few remaining sulfide minerals of simple composition for which there are no published x-ray crystallographic data. The reason for this is evidently that the crystals are so very plastic that it is difficult to obtain a single crystal which has not been bent or otherwise deformed in the process of removing it for study. The writer was fortunate in obtaining an excellent crystal of orpiment (from Mercur, Utah) from Dr. Harry Berman, who skillfully detached it from a protected cavity in a large specimen. While the point of attachment of the crystal had been injured, it retained a perfect, undistorted termination.

Orpiment, formerly believed to be orthorhombic,[1] is now regarded as monoclinic. The lower symmetry has been confirmed by studies and measurements of morphological development,[2,3] by the results of etching experiments,[2] and by optical observations.[3] Nevertheless, the departures of both angular and optical measurements from orthorhombic character are so slight that the results of an x-ray crystallographic study are of considerable interest.

Method: A somewhat elongated crystal having a single perfect termination can only be rotated about its axis of elongation if the distorted part is to be kept out of the x-ray beam. For this reason, a set of equi-

[1] Mohs, Friedrich (translated by William Haidinger), *Treatise on Mineralogy* (Archibald Constable and Co., Edinburgh, 1925), vol. **3,** pp. 47–49.

[2] Stevanović, S., Auripigment von Allchar in Macedonien: *Zeits. Krist,* **39,** 14–18 (1904).

[3] Palache, Charles, and Modell, David, Crystallography of stibnite and orpiment from Manhattan, Nevada: *Am. Mineral.,* **15** (1930) especially 371–374.

inclination Weissenberg photographs was taken with the orpiment crystal for rotations about the c-axis only. The length of the c-axis permitted taking zero, first, second, and third level photographs with copper radiation.

Symmetry: The symmetry of the zero level Weissenberg photograph is C_{2l}, while the symmetry of each of the several n-levels is C_l (see Fig. 1). This is consistent with a monoclinic character of orpiment, but is inconsistent with an orthorhombic character. The inferior symmetry of the n-levels is displayed only by the intensities of the spots on the film; the position symmetry of the spots on the n-levels is so close to C_{2l} that a departure from this position symmetry can be detected only by refined measurements.

Unit Cell: Inspection of the several c-axis Weissenberg photographs revealed the facts that the patterns of the several reciprocal lattice levels normal to c are identical, and that furthermore the cell types are rectangular. This indicates[4] that orpiment is based upon a primitive lattice.

The length of the c-axis was measured from the layer spacings of a rotation photograph. Each of two levels gave a value of 4.24 Å. These consistent results were obtained by placing the undeformed tip of the tiny crystal in the center of the beam, and then making layer line spacing measurements from tip to tip of the resulting reflections.

The a^* and b^* translations for the reduced reciprocal cell were determined by making x-measurements of the pinacoid reflections on the c-axis, zero layer photograph. These values were refined by extrapolation according to the method of Bradley and Jay.[5] Utilizing the refined value of b^* as found by this method, the crystallographic angle, β, was found by the method of dome offsets.[6] These several measurements establish the following reduced, simple monoclinic cell:

	ratio
$a=11.47$ Å	1.195
$b=9.57$	1
$c=4.24$	.442
$\beta=90°27'$	

[4] Buerger, M. J., The application of plane groups to the interpretation of Weissenberg photographs: *Zeits. Krist.*, (A) **91** (1935) especially 257–264.

[5] Bradley, A. J., and Jay A. H., A method for deducing accurate values of the lattice spacing from x-ray powder photographs taken by the Debye-Scherrer method: *Proc. Phys. Soc.*, **44**, 563–579 (1932).

[6] Buerger, M. J., The x-ray determination of lattice constants and axial ratios of crystals belonging to the oblique systems: *Am. Mineral.*, **22** (1937), especially 425–428.

It is known that the axes recorded above correspond in orientation with the axes of Palache and Modell, who adopted Stevanović's axial

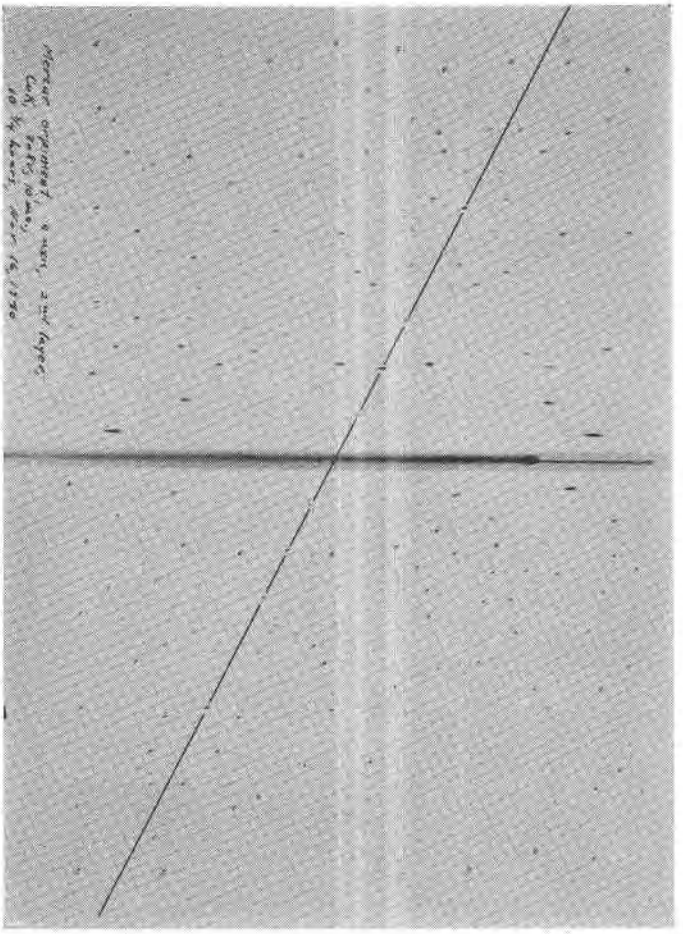

FIG. 1. Equi-inclination Weissenberg photograph of orpiment; c-axis, 2nd level, copper radiation. The only symmetry displayed by the photograph is the line shown, indicating the symmetry C_1 for the level.

ratio. This ratio, and the new one determined by x-ray methods compare as follows:

	Stevanović	relation	Buerger
a	.5962	($\times 2 = 1.1928$)	1.195
b	1		1
c	.6650	($\times \frac{2}{3} = .4421$)	.442

Accordingly the matrix of the transformation from the axes of Stevanović to those of Buerger is

$$\begin{Vmatrix} 2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \frac{2}{3} \end{Vmatrix}$$

Stevanović determined the density of the orpiment from Allchar, Macedonia as 3.49. Using this value, the orpiment cell contains 4 As_2S_3. For the cell constants given above, the computed value of the density is 3.48.

Space Group: The c-axis, zero level Weissenberg photograph displays doubled reciprocal cell translations along the central [010]* line. Comparison of the photographs of the several levels shows that the only other systematic multiple translations of the reciprocal lattice are all the [101]* translations in central (010)*. These two conditions indicate respectively a two-fold screw axis $\| b$ and a diagonal glide $\|$ (010). Taking into account the symmetry discussed above, the space group is unequivocally determined as $P2_1/n$ (C^5_{2h}).