THE UNIT CELL AND SPACE GROUP OF CHILDRENITE

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ABSTRACT

The unit cell constants and the space group of childrenite, $AlPO_4 \cdot Fe(OH)_2 \cdot 2H_2O$, have been determined by the Buerger precession method with the following results: $a = 10.38$Å, $b = 13.36$ Å, $c = 6.911$ Å; $a:b:c = 0.7766:1:0.5173$; $Z = 8$; calculated density = 3.186 g./cc.; space group *Bba*2.

INTRODUCTION

Crystals of childrenite, $AlPO_4 \cdot Fe(OH)_2 \cdot 2H_2O$, are orthorhombic with axial ratio, determined from morphological data (1), $a:b:c = 0.7780:1:0.52575$ and a specific gravity of 3.18–3.24. The specimens examined in the present study of the unit cell constants and space group were from the type locality of Tavistock, Devonshire, England. They were kindly supplied by Dr. Clifford Frondel from the Mineralogical Collection at Harvard University (specimen 80618).

Assuming the morphological axes to coincide with the corresponding structural ones, photographs were taken of the zero, first and second reciprocal lattice levels normal to each of the *a*, *b* and *c* axes using Professor M. J. Buerger's precession camera (2). Cone axis photographs (2) served as a guide to the reciprocal lattice spacings and hence as a check on the numerical labelling of the levels examined. Both copper (nickel foil filter) and molybdenum (zirconium oxide filter) were employed in the course of the investigation. Reciprocal lattice spacings and angles were measured with the instrument devised by Professor Buerger (3) for precession films. The approximate accuracy of the precession instrument and of the film measuring device was tested with cone axis and zero level photographs obtained with the *a* and *b* (orthohexagonal) axes of a (rather large) crystal of α-quartz as precession axes. A more rigid test of the precision attainable with the precession instrument will be described in another communication.

RESULTS

Space Group

Typical precession photographs of childrenite are reproduced in Figs. 1 to 6 inclusive. The geometry of all the levels examined is summarized in Fig. 7 in which the central areas of the plane nets for the zero, first and second reciprocal lattice levels normal to each of the *a*, *b*, and *c* axes are represented. In this diagram, extinctions not due specifically to space group symmetry elements as well as the relative intensities of the actual

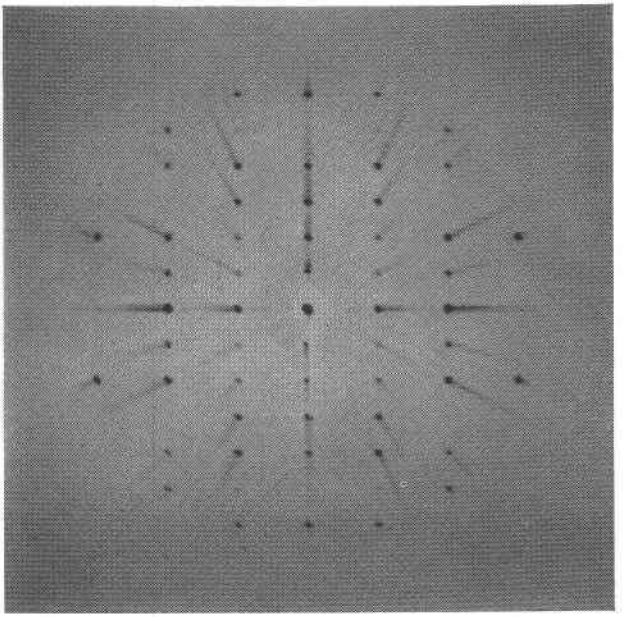

FIG. 1. Childrenite. *a* axis, zero level (Mo) (c^* horizontal).

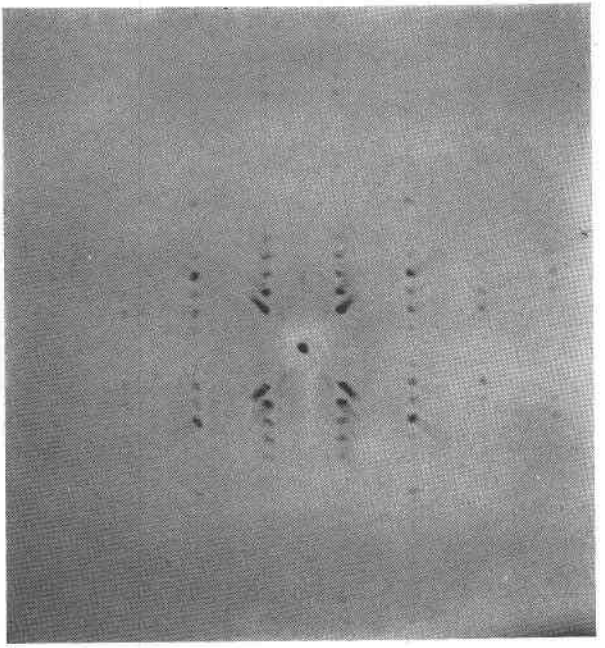

FIG. 2. Childrenite. *a* axis, first level (Mo) (c^* horizontal).

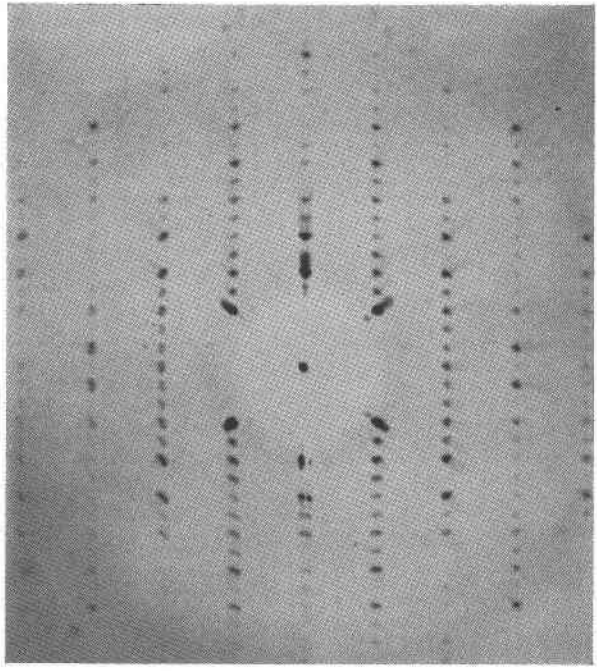

FIG. 3. Childrenite. *a* axis, second level (Mo) (c^* horizontal).

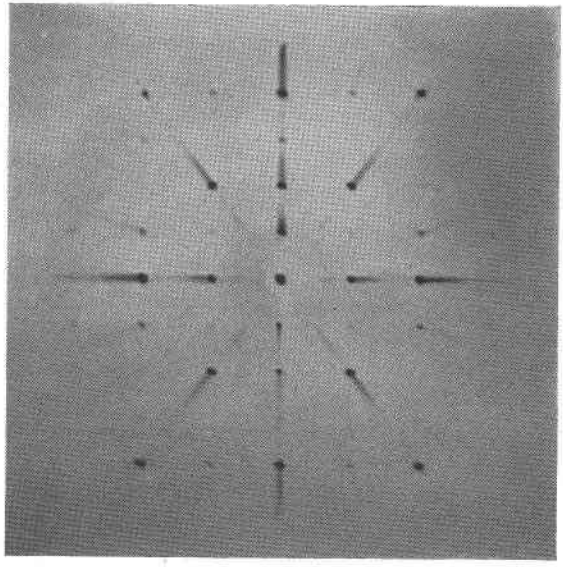

FIG. 4. Childrenite. *b* axis, zero level (Mo) (c^* horizontal).

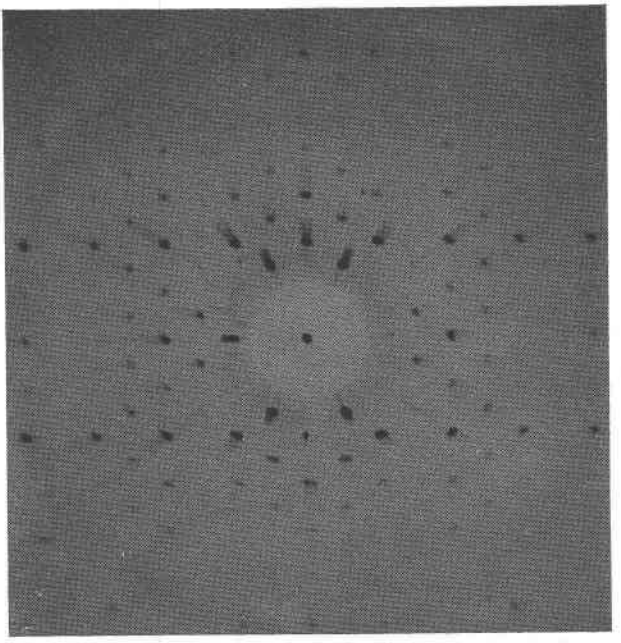

FIG. 5. Childrenite. b axis, second level (Mo) (c^* horizontal).

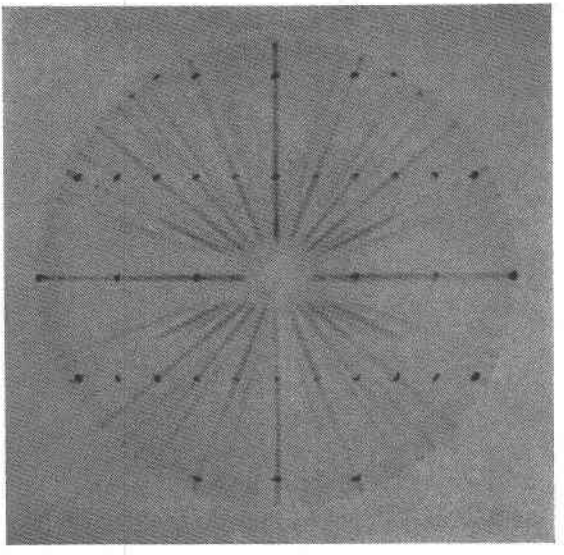

FIG. 6. Childrenite. c axis, zero level (Cu) (b^* horizontal).

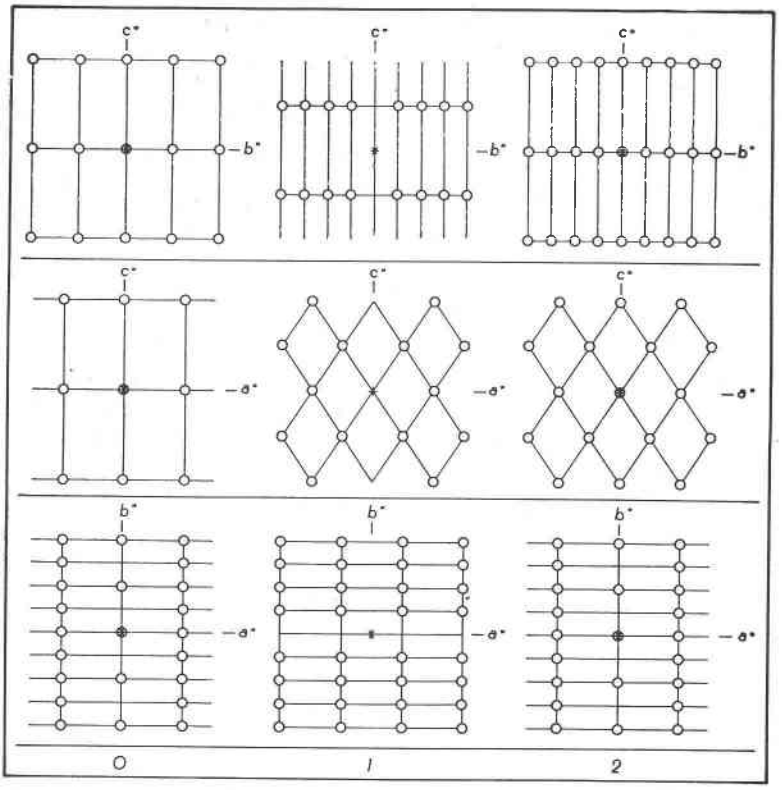

FIG. 7. 0,1,2 level reciprocal lattice nets shown by (top row)*a*, (middle row)*b*, (bottom row)*c* axis precession photographs of childrenite.

diffraction spots on the films have been ignored. The center of each net is marked with a star.

By simple inspection of the b^*c^* and a^*b^* nets it is apparent that the direct cell is *b*-side centered. The doubled spacing of the rows parallel to c^* in the zero level b^*c^* net indicates a glide plane of component $b/2$ perpendicular to the *a* axis. This glide plane also accounts for the 2_1 screw axis along *b* which produces the doubled translation along b^* in the zero level a^*b^* net. In the a^*c^* nets the change from the diamond net characteristic of the upper levels to the rectangular net shown by the zero level reveals a glide plane of component $a/2$ (or the equivalent $c/2$, since the cell is *b*-side centered) perpendicular to the *b* axis. In each two-dimensional net the directions of the two reciprocal axes are mutually perpendicular and are symmetry lines.

Thus the diffraction symmetry is *mmm* and the diffraction symbol is

mmmBba – so that the space group must be either *Bba*2 (C_{2v}^{17}) or *Bbam* (D_{2h}^{18}). The axes of the structural unit cell, therefore, are in harmony with those assigned from morphological data. Childrenite crystals were tested for piezoelectricity by Dr. Frondel and a small but positive effect was obtained. The centrosymmetrical space group, *Bbam*, thus is eliminated and childrenite must be assigned to the space group, *Bba*2.

Unit Cell Constants

The best *a*, *b* and *c* axis zero level precession photographs obtained with copper radiation were selected for measurement. In each case the angles between rows of the net parallel to the reciprocal axes were determined and confirmed the orthogonality of the lattice. The distances between successive pairs of rows parallel to a given axis were measured to 0.05 mm. and averaged. This value was divided by the magnification factor ($F = 6.00$ cm.) to give the spacing in reciprocal lattice units, or double the spacing where the reciprocal lattice translations were doubled due to space group extinctions.

The reciprocal lattice spacings are summarized in Table 1.

TABLE 1

Precession Axis	d_a^*	d_b^*	d_c^*
a	—	0.115_5	0.223_0
b	0.148_3	—	0.223_2
c	0.148_9	0.115_2	—
Average	0.148_6	0.115_4	0.223_1

Using the value 1.5418 Å (4) for λ (CuKα), the direct cell translations are:

$a = 1.5418/0.1486 = 10.38$ Å‡

$b = 1.5418/0.1154 = 13.36$ Å‡

$c = 1.5418/0.2231 = 6.911$ Å‡

and the axial ratio:

$$a:b:c = 0.7766:1:0.5173.$$

The volume (V) of the unit cell $= a \times b \times c = 958.0$ Å^3.

‡ The numerical values differ slightly from those reported at the 1947 Spring Meeting of The Crystallographic Society of America (5) because the direct lattice translations have been recomputed from the measured reciprocal lattice spacings in terms of the presently accepted Ångstrom unit instead of the kX unit.

Taking the specific gravity as 3.2, the formula weight (M) as 229.8 (Al, 26.97; P, 30.98; Fe, 55.85; 7O, 112.00; 4H, 4.032) chemical atomic mass units and the density (ρ) $= 1.6602ZM/V$(4), the number of formula units per cell

$$Z = \frac{3.2 \times 958.0}{1.660 \times 229.8} = 8.035 \approx 8.$$

With $Z=8$, the density calculated from the foregoing formula is 3.186 g./cc.

Work is continuing on eosphorite into which childrenite graduates by replacement of Fe by Mn. Delay has been occasioned by a change in laboratories and by the fact that the smallest crystals of eosphorite so far examined have turned out to be multiple growths with so many individual members that even precession photographs could not be measured accurately.

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REFERENCES

1. Dana's Textbook of Mineralogy (Wiley), N. Y. **1932,** p. 732.
2. BUERGER, M. J., The Photography of the Reciprocal Lattice, *A.S.X.R.E.D. Monograph* No. **1** (1944).
3. BUERGER, M. J., *Am. Mineral.*, **30,** 553 (1945).
4. *J. Sci. Instrum.*, **24,** 27 (1947); *R.S.I.*, **18,** 688 (1947); *Am. Mineral.*, **32,** 591 (1947).
5. *Am. Mineral.*, **32,** 685 (1947).