An accurate determination of the cell dimensions of bultfonteinite, $Ca_4Si_2O_{10}H_6F_2$.

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BULTFONTEINITE from Bultfontein mine, Kimberley, South Africa, is a hydrated fluorine-containing calcium silicate, of approximate composition $Ca_4Si_2O_{10}H_6F_2$. It was first described in 1932 by Parry, Williams, and Wright,[1] who gave an account of its morphology, optical properties, composition, and chemical relationships. It is triclinic but markedly pseudo-orthorhombic. The present work consists primarily of a determination of the unit-cell dimensions, involving a more accurate evaluation of the interaxial angles than the earlier one; this is followed by some tentative suggestions about the structure.

The material examined was kindly provided by the late Mr. A. F. Williams. Most of the crystals could be seen optically to be very much twinned, but it was possible to pick out small lath-shaped fragments, a few tenths of a millimetre in length, which showed uniform extinction over most of their area. X-ray observations were made on three fragments of this kind; crystal 3 had a uniform interference colour over its whole area, crystal 1 had a small stripe of a different colour near the edge, and crystal 2 was slightly wedge-shaped.

The approximation to orthorhombic symmetry made it easy to set the crystal. Oscillation photographs (with Cu-$K\alpha$ radiation) taken about two axes gave rough values of all three cell edges, which enabled all reflections to be indexed. The face of largest area was parallel to (100). Twinning was present in all three crystals, but it proved possible to interpret it and to establish the twin laws.

Twinning.

With the first crystal, oscillation photographs about the needle axis z gave reflections on layer lines only, showing that *all* twin components

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[1] J. Parry, A. F. Williams, and F. E. Wright, Min. Mag., 1932, vol. 23, p. 145.

had strictly parallel z-axes. In oscillation photograph about y, however, strong spots on the layer lines had weaker companions off the layer line but on the same row line, and also companions of about half their own intensity on the same layer line; these latter, if not too weak, had themselves row-line companions. This showed the presence of twinning about the normals to (100) and (010), the former giving rise to components more nearly equal in volume than the latter. However, there was no detectable vertical splitting of reflections $h00$, even for $h = 14$. This could only be true if the angle (100):(010) were very close to 90°; the splitting should have been observed if the difference was greater than 10′.

Crystal 2 showed the same kind of twinning; crystal 3 (optically the most uniform) showed twinning about the normal to (100) only. These results fit in with the optical observations if the composition plane is normal to the twin axis, since twinning about the normal to (100) would still lead to a uniform appearance of the crystal viewed through this face.

It is worth drawing attention at this point to the interaxial angles listed in table I. Since α^* differs from 90° more than does β^*, the difference of angle between the z^*-axes of the two components will be greater in a twin about the normal to (010) than in one about the normal to (100). Thus the twin law which is observed experimentally to be more prevalent is the one which involves the smaller geometrical misfit.

Accurate determination of spacings.

An ordinary Unicam cylindrical camera was used. The setting of the crystal with respect to the circle was found from ordinary oscillation photographs. Then a film was inserted in the van Arkel position, and the crystal was given appropriate oscillations so that selected high-angle reflections were recorded on the film on either side of the beam. The distance between the spots was measured on a simple comparator with vernier reading to $\frac{1}{10}$ mm.

The method used here may be compared with those of Farquhar and Lipson[1] and Weisz, Cochran, and Cole.[2] Essentially it combines the photographic technique of the former (in a simplified form which involves no special modifications to the camera) with the treatment of the data used by the latter in their 'θ-method'. Like the 'θ-method', it relies entirely on measurement of a few high-angle reflections, and its

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[1] M. C. M. Farquhar and H. Lipson, Proc. Physical Soc., 1945, vol. 58, p. 200.

[2] O. Weisz, W. Cochran, and W. F. Cole, Acta Cryst., 1948, vol. 1, p. 83. [M.A. 10-330.]

accuracy is about the same. It does not aim at the very high accuracy which can be attained in favourable cases, at the expense of much more labour, by graphical extrapolation from a large number of reflections.

Calculation and choice of reflections.

(i) *Oscillation about y-axis.*—For any reflection in the [010] zone, we have

$$\xi^2(h0l) = h^2a^{*2}+l^2c^{*2}+2hla^*c^*\cos\beta^* \tag{1}$$

where a^*, c^*, β^* are axial lengths and interaxial angle of the reciprocal lattice, and $\xi = 2\sin\theta$. Since ξ is directly determinable from the photographs, it is possible by measurement of a number of $h0l$ spacings to determine a^*, c^*, and β^* from equation (1). The choice of reflections to be used is determined primarily by the requirement that θ shall be nearly 90°, since this is necessary for accuracy; convenience of mathematical handling of the equations takes second place. For a crystal in which β^* is nearly 90°, it is an obvious choice to use pairs of reflections $h0l$, $h0\bar{l}$, since they occur at nearly the same value of θ. If the crystal is twinned about the normal to (100), they have the further advantage of appearing within the same oscillation range, so that one exposure serves to record both. Then

$$\xi^2(h0\bar{l}) = h^2a^{*2}+l^2c^{*2}-2hla^*c^*\cos\beta^*,$$

hence

$$\tfrac{1}{2}[\xi^2(h0l)+\xi^2(h0\bar{l})] = h^2a^{*2}+l^2c^{*2} \tag{2}$$

$$\tfrac{1}{2}[\xi^2(h0l)-\xi^2(h0\bar{l})] = 2hla^*c^*\cos\beta^*. \tag{3}$$

Thus $\cos\beta^*$ can be determined easily with high accuracy.

For bultfonteinite, 14,0,0 gave a reflection at about 80°, enabling a^* to be determined immediately. The pair of reflections 307, $30\bar{7}$ then could be used to evaluate c^* and β^*. Other reflections available were 207, $20\bar{7}$; 12,0,2, 12,0,$\bar{2}$. Comparison of the c^* values derived from these reflections of different θ (all greater than 60°), and from photographs with and without black paper between film and camera, enabled a check to be made of the effective camera radius (i.e. the radius of the shrunk film after development). It proved to be exactly 3 cm. when the black paper was used. If the paper was omitted, the relative error in the spacing amounted to only 2×10^{-4} for a reflection at $\theta = 80°$. Film shrinkage of 0·3 %, if not allowed for, would give an error of the same magnitude; variations of shrinkage from one film to another are likely to be much less than this. This emphasizes the usefulness, when accuracy is required, of concentrating on high-angle reflections.

Values of β^* were derived from the three pairs of planes mentioned above, using the known a^* and c^*, and the mean value was taken.

(ii) *Oscillation about z-axis.*—A crystal mounted to rotate about the z-axis was used to obtain b^* and γ^*, the former from 4,10,0, the latter from the pair 790, $7\bar{9}0$, by the method of successive approximations. In this, a rough value of b^* was used to find γ^* from 790, $7\bar{9}0$; this was then substituted in the expression for calculating b^* from 4,10,0, and the new value of b^* in its turn used to get an improved value of γ^*. This method leads in the end to better values for both quantities than the use of a single pair of reflections, since 4,10,0 is more sensitive to changes in b^*, than 790 and $7\bar{9}0$ to changes in γ^*; and it saves the extra work of measuring the spacing of $4,\overline{10},0$.

(iii) *Oscillation about x-axis.*—Finally, a crystal mounted about the x-axis was used to find α^* from the pair of reflections 056 and $05\bar{6}$ by the method of successive approximation. This pair had a lower value of θ than the reflections used in the other zones, and the results are correspondingly less accurate.

Results.

These are given in table I, with the morphological values for comparison. Several points should be noticed.

TABLE I. Lattice parameters of bultfonteinite.

	Present work.	Results of Parry, Williams, and Wright, 1932.
a	10·992±0·004 Å.	—
b	8·183±0·002	—
c	5·671±0·001	—
a:b:c ...	1·3433:1:0·6930	$\frac{1}{2}$(1·3512):1:0·6873
α	93° 57′	94° 17′
β	91 19	91 59
γ	89 51	90 44
α^*	86° 03′±18′	85° 41′
β^*	88 41 ±02	87 57
γ^*	90 04 ±01	89 07

(1) The true unit cell is double the morphological cell in the a direction. Thus, to transform the indices of Parry, Williams, and Wright to the new indices, all values of h must be doubled.

(2) The angles determined in the present work differ very considerably from the old values. The old values are likely to be less accurate, because of the difficulty of goniometric measurements referred to by Parry, Williams, and Wright; their limits of error are in fact not stated.

In the present method, the pseudo-orthorhombic symmetry made conditions especially favourable to the attainment of high accuracy.

(3) The sense of the axes cannot be chosen so as to make all interaxial angles greater than 90°. The choice actually made seems in best agreement with the older work.

Structural relationships.

The formula of bultfonteinite may be written

$$Ca_3[SiO_3(OH)]_2.2H_2O.CaF_2,$$

in comparison with the structural formula of afwillite[1]

$$Ca_3[SiO_3(OH)]_2.2H_2O.$$

Parry, Williams, and Wright draw attention to this relationship in composition, and give arguments from chemical evidence suggesting that it is significant. Evidence from the cell dimensions points in the same direction. The *c*-spacing of bultfonteinite, 5·67 Å., is very nearly the same as the *b*-spacing of afwillite,[1] 5·63 Å., and in both cases this is morphologically the fibre axis. In afwillite one can pick out units of composition $Ca_2Si_2O_8$ consisting of Si tetrahedra and Ca octahedra linked together by shared edges in the direction of the fibre axis, and forming infinite pillars in this direction. They are the units into which an afwillite crystal would be subdivided by operation of the two prominent cleavage planes. In afwillite they are linked laterally by the third Ca atom into sheets, which in turn are held together only by hydrogen bonds and a few weak Ca–O bonds. It seems quite possible that a rearrangement of these pillars gives rise to the bultfonteinite structure, the two remaining Ca ions being available to link them together sideways, as well as the fluorine atoms which may form O–H–F bonds. It cannot be taken for granted that the H_2O groups persist as such; there may be complete rearrangement of the hydrogen atoms.

It is hoped that further work on this structure may be possible.

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[1] H. D. Megaw, Acta Cryst., 1952, vol. 5, p. 477. [M.A. **12**–98.]