THE STRUCTURES OF HERDERITE, DATOLITE AND GADOLINITE DETERMINED BY DIRECT METHODS

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(Translated from: Kristallografiya, Vol. 4, No. 3, pp. 324-340)

(Original article submitted February 23, 1959)

The direct methods developed at the Institute of Crystallography and at Gorkii University have proved exceptionally powerful in solving the structures of the three minerals named in the heading; we give a detailed exposition of the solution with illustrations of the use of Harker-Kasper inequalities and of statistical analysis by Zachariasen's methods.

Herderite $CaBePO_4F$ [1-3] is of special interest because it contains beryllium (15.3 wt. % BeO, as against 14% BeO in beryl). Strunz [4] has supposed that herderite has a structure very like that of datolite $CaBSiO_4(OH)$, which Ito and Mori have examined [5] by the (half) heavy-atom method; the two should form a good example of how ions of equal size but different valency, having the same sum of all valencies for the groups (pairs), may replace one another to give the same structure:

$$CaBSiO_4(OH)$$
$$CaBePO_4F.$$

Gadolinite contains also $Fe^{\cdot\cdot}$: datolite is $Ca_2B_2(OH)_2Si_2O_8$, while gadolinite is $Fe^{\cdot\cdot}Y_2Be_2O_2Si_2O_8$.

The heredite crystal (from the Mineralogical Museum, Academy of Sciences of the USSR) had a largest dimension of about 1 mm; it had no faces, so the axes were found from Laue patterns by the Umanskii-Kvitki method [6]. The rotation patterns were used to confirm Strunz's parameters $a = 9.80$ A, $b = 7.68$ A, $c = 4.80$ A, $\beta = 90°06'$, $a : b : c = 1.276 : 1 : 0.625$ and the space group $C_{2h}^5 = P2_1/a$. This group is one of the commonest for organic and inorganic substances, and is convenient in that it contains a center of symmetry. The density (3.00 g/cm^3) and volume of the cell show that the cell contains four $CaBePO_4F$ units (molecules). The four pairs of centers of symmetry (duplicated positions without parameters) are the only points in the cell that are not in general positions with three parameters.

The x-ray patterns included three rotation photographs and Weissenberg photographs of the equatorial layer lines rotated about $\underline{a}$, $\underline{b}$, and $\underline{c}$, and of the 1st, 2nd, 3rd and 4th layer lines rotated about $\underline{c}$. The Mo-radiation produced many reflections, which are of value when direct methods of either kind are used.

Mamedov has used Harker-Kasper inequalities with Zachariasen's statistical methods to determine the signs of the reflections from the oscillation photograph for one layer line only in the case of $6CaSiO_3 \cdot H_2O = Ca_6[Si_6O_{17}](OH)_2$

(monoclinic) [7]. Rumanova [8] has developed similar methods for use with epidote (monoclinic). These methods have been much simplified to give the signs of the amplitudes for herderite.

The xy projection corresponds to the shortest repeat period (4.8 A). The $\underline{c}$ oscillation photograph had 167 independent hk0 reflections not equal to 0, whose intensities were estimated from the blackening [9]. The amplitudes were referred to the absolute scale (as is needed if the Harker-Kasper inequalities are to be used by Wilson's [11] and Vainshtein's [12, 13] methods. Both methods consider only the squares of the amplitudes and need no preliminary model. Wilson's method is statistical and demands reflection derived from the whole volume of the reciprocal lattice. We followed Mamedov in using only hk0 reflection, which is equivalent (see [14]) to assuming that the mean intensities are the same for all layers. The reflections, including the zero F_{hk0}, were related to the $\sin\vartheta/\lambda$ values by division into intervals 0.1-0.2, 0.2-0.3, 0.3-0.4, etc., i.e., into concentric rings with $(\sin\vartheta_1/\lambda - \sin\vartheta_2/\lambda) = 0.1$ in the equatorial section of the reciprocal lattice. All the reflections within a ring were used to find the means $\overline{F^2_{hk0}}$ and the sums of the squares of the mean atomic factors $\sum\limits_i \overline{f_i}^2$ from

$$\overline{F^2_{hk0}} : \sum_i \overline{f}_i^2 = K^2 \exp(-2B \sin^2 \vartheta / \lambda^2),$$

where K is the factor for passing from the experimental amplitude to the absolute ones. The curves $\log \Sigma \overline{f_i^2} / \overline{F^2_{hk0}}$ vs $\sin^2\vartheta/\lambda^2$ gave K^2 as 184, i.e., K = 13.6, for B = 0.58. We also used only the hk0 reflections in Vainshtein's method:

$$\frac{1}{S} \sum |F_{hk0}|^2 = \sum_i g'_i,$$

where S = (ab) is the area of that face of the cell. We must be given B and must allow for overlap between atoms in order to find K from this formula. Vainshtein's table [13] shows that B does not exceed one for herderite. We may expect that overlap is improbable along the very short axis c = 4.8 A; because the mean intensities of layer lines 0-4 are almost equal, the Vainshtein's formula has $g'_i = 0.38 \cdot Z^{2.37}$ with B = 1 without allowance for overlap.

The calculated g' and $\Sigma |F_{hk0}|^2$ gave $K^2 = 194$, i.e., that K = 13.9. The values agree well enough for us to assume that no exceptional errors are present.

The next step is to find the absolute unit structure amplitudes from

$$|U_{hk0}| = |F_{hk0}| : \sum_i f_i,$$

where f_i is the atomic factor of the i-th atom. These $|U_{hk0}|$ included 15 with values > 0.5, so in establishing the signs we could use the simplest inequality:

$$|U_{hkl}|^2 \leqslant \frac{1}{2} + \frac{1}{2} U_{2h,\, 2k,\, 2l}, \tag{1}$$

which gives the result quickly when $|U_{2h,\,2k,\,2l}|$ and $|U_{hkl}|$ are both larger than 0.5. But the only reflection found at once to have a positive sign was 24.0.0 ($U_{24.0.0} = 0.65$ and $U_{12.0.0} = 0.50$).

To find the signs of the other hk0 reflections, we used the basic inequalities

$$(U_H + U_K)^2 \leqslant (1 + U_{H+K})(1 + U_{H-K}), \tag{2}$$

$$(U_H + U_K)^2 \leqslant (1 - U_{H+K})(1 - U_{H-K}), \tag{3}$$

where H represents (hk$l$), etc.

We pick out amplitudes with $|U| \geq 0.45$ and use a simplified reciprocal grid to select many $|U_{hk0}|$ triplets for which (2) and (3) give the sign relations $S_{H \pm K} = S_H \times S_K$, where S is the sign of an amplitude. Let us consider some particular examples of the use of (2) and (3). In the list of unit amplitudes we find:

$$|U_{640}| = 0.64; \quad |U_{10.\bar{3}.0}| = 0.66; \quad |U_{16.1.0}| = 0.63; \quad |U_{\bar{4}70}| = 0.49.$$

The corresponding inequalities are

$$(U_{640} + U_{10.\bar{3}.0})^2 \quad (1 + U_{16.1.0}) \cdot (1 + U_{\bar{4}70}), \tag{2'}$$
$$(U_{640} - U_{10.\bar{3}.0})^2 \quad (1 - U_{16.1.0}) \cdot (1 - U_{\bar{4}70}). \tag{3'}$$

The four possible values of the RHS for the four meaningful combinations of the signs to $U_{16.1.0}$ and $U_{\bar{4}70}$ are

$$(1 + 0.63) \cdot (1 + 0.49) = 2.43$$
$$(1 + 0.63) \cdot (1 - 0.49) = 0.83$$
$$(1 - 0.63) \cdot (1 + 0.49) = 0.55$$
$$(1 - 0.63) \cdot (1 - 0.49) = 0.19.$$

The signs of the two items on the left must be either the same or different. If $S_{640} = S_{10.\bar{3}.0}$, the LHS in (2') is $(0.64 + 0.66)^2 = 1.69$. The inequality is satisfied if the RHS is 2.43. For this to be so we must have $S_{16.1.0} = S_{\bar{4}70} = +$, i.e., we must have both positive. If $S_{640} = -S_{10.\bar{3}.0}$, we see from (3') that the LHS is still 1.69, but that on the RHS the signs of the 16.1.0 and $\bar{4}70$ reflections must both be minus, i.e., that $S_{16.1.0} = S_{\bar{4}70} = -$. We cannot say which of these two contrary results is correct, since we do not know whether S_{640} and $S_{10.\bar{3}.0}$ have the same sign or different signs, though both give the consistent result

$$S_{16.1.0} = S_{\bar{4}70} = S_{640} \cdot S_{10.\bar{3}.0},$$

i.e. 16.1.0 and of $\bar{4}70$ have the same sign, which is the product of the signs of 640 and $10.\bar{3}.0$. This expresses the fact that 16.1.0 and $\bar{4}70$ have the same sign if 640 and $10.\bar{3}.0$ also have the same sign.

Consider a case in which the three amplitudes are large (≥ 0.5) and the fourth is nearly zero:

$$|U_{14.3.0}| = 0.67; \quad |U_{800}| = 0.51; \quad |U_{22.3.0}| = 0.57; \quad |U_{630}| = 0.07.$$

Again we have

$$(U_{14.3.0} + U_{800})^2 \quad (1 + U_{22.3.0}) \cdot (1 + U_{630}), \tag{2"}$$
$$(U_{14.3.0} - U_{800})^2 \quad (1 - U_{22.3.0}) \cdot (1 - U_{630}). \tag{3"}$$

The four possible values for the RHS are

$$(1 + 0.57) \cdot (1 + 0.07) = 1.68$$
$$(1 + 0.57) \cdot (1 - 0.07) = 1.46$$
$$(1 - 0.57) \cdot (1 + 0.07) = 0.46$$
$$(1 - 0.57) \cdot (1 - 0.07) = 0.40.$$

The maximum value for the LHS is $(0.67 + 0.51)^2 = 1.39$.

Again we suppose that $S_{14.3.0} = S_{800}$. Then (2") is satisfied if the RHS is 1.68, i.e., if $S_{22.3.0} = S_{630} = +$ (a). But it is satisfied also if the RHS is 1.46, which is possible if $S_{22.3.0} = +$, $S_{630} = -$ (b).

If we compare (a) and (b), we see that the sign of 630 stays undefined. If now we suppose that $S_{14.3.0} = -S_{800}$, (3") then gives us that $S_{22.3.0} = S_{630} = -$, when the RHS is 1.68, and that $S_{22.3.0} = -$, $S_{630} = +$, when the RHS is 1.46; i.e., S_{630} is still undefined. Thus, we conclude that $S_{22.3.0} = S_{14.3.0} \times S_{800}$, and that we can draw no conclusion about the sign of 630.

Interesting examples occur when the signs of two of the reflections are related symmetrically. Thus we have

$$|U_{640}| = 0.64; \quad |U_{\bar{6}40}| = 0.64; \quad |U_{12.0.0}| = 0.50; \quad |U_{080}| = 0.39.$$

The symmetry of group $P2_1/a$ implies that the signs of amplitudes related by the mirror plane must be the same when $h + k = 2n$, i.e., that $S_{640} \cdot S_{6\bar{4}0} = +1$. We use (2) directly. This is satisfied when the LHS is 1.64 and the RHS is 2.08, whereupon $S_{080} = S_{12.0.0} = +$, i.e., both signs are plus. It would be contrary to the symmetry of the group to suppose that 640 and $6\bar{4}0$ have different signs. Thus,

$$S_{080} = S_{12.0.0} = S_{640} \cdot S_{6\bar{4}0} = +.$$

Now for $h + k = 2n + 1$ the symmetry of $P2_1/a$ demands that $hk0$ and $h\bar{k}0$ have different signs, i.e. that reflections from planes related by the mirror plane should have different signs (and hence equal moduli). For example, $|U_{10.3.0}| = 0.66$; $|U_{10.\bar{3}.0}| = 0.66$; $|U_{20.0.0}| = 0.44$; $|U_{060}| = 0.45$. Then we have $S_{10.\bar{3}.0} = -S_{10.3.0}$.

But (3) is satisfied if the LHS is 1.74 and the RHS is 2.09, i.e., if

$$S_{20.0.0} = S_{060} = -.$$

The symmetry of the group prevents 10.3.0 and $10.\bar{3}.0$ from having the same sign. These relations between the signs, dependent on the symmetry, are of great assistance in finding the signs. It is clear that some inequalities give us either only the relations between the signs of two reflections or (if both indices are even) that the sign is plus. The relations implied by the symmetry can give also a minus sign (again, only for reflections whose two indices are even).

These useful ways of finding the sign relations can be to a large extent mechanized with the graphs given in [15]. In all we found 45 confirmations of the sign relations $S_{H \pm K} = S_H \cdot S_K$ for the following sets of three:

$(\overline{10}.11.0)$	$22.\bar{3}.0$	$16.\bar{7}.0 \times 640$
$(\bar{4}10)$	$16.7.0$	$10.3.0 \times 640$
$(\bar{8}10)$	$20.7.0$	$14.3.0 \times 640$
$(\overline{55}0)$	$17.13.0$	$11.9.0 \times 640$
$(\bar{6}40)$	$18.4.0$	$12.0.0 \times 640$
$(5\bar{8}0)$	$7.16.0$	$1.12.0 \times 640$
$(\overline{10}.5.0)$	$22.3.0$	$16.\bar{1}.0 \times 640$
$(\bar{4}70)$	$16.1.0$	$10.\bar{3}.0 \times 640$
(080)	$12.0.0$	$6\bar{4}0 \times 640$
$(\overline{12}.8.0)$	$24.0.0$	$18.\bar{4}.0 \times 640$
	$18.\bar{4}.0$	$12.\bar{8}.0 \times 640$
$(0.14.0)$	$12.\bar{6}.0$	$6.\overline{10}.0 \times 640$
$(1.14.0)$	$11.\bar{6}.0$	$5.\overline{10}.0 \times 640$
	$5.16.0$	$\bar{1}.12.0 \times 640$
$(\bar{5}70)$	$15.13.0$	$10.3.0 \times 5.10.0$
$(17.\bar{5}.0)$	$\bar{5}.13.0$	$\overline{11}.9.0 \times 640$
$(\overline{11}.11.0)$	$17.5.0$	$14.\bar{3}.0 \times 380$
$(\overline{11}.11.0)$	$21.9.0$	$16.\bar{1}.0 \times 5.10.0$
	$7.16.0$	$\bar{4}70 \times 11.9.0$
$(\bar{2}30)$	$22.3.0$	$12.0.0 \times 10.3.0$
$(\bar{4}60)$	$24.0.0$	$14.\bar{3}.0 \times 10.3.0$
(060)	$20.0.0$	$10.\bar{3}.0 \times 10.3.0$
$(14.\bar{4}.0)$	$6.10.0$	$\bar{4}70 \times 10.3.0$

	$5.13.0$	$\bar{5}.10.0 \times 10.3.0$
	$20.0.0$	$800 \times 12.0.0$
	$22.3.0$	$800 \times 14.3.0$
$(10.10.0)$	$18.\bar{4}.0$	$4\bar{7}0 \times 14.3.0$
$(\bar{6}20)$	$6.10.0$	640×060
$(\overline{12}.6.0)$	$12.6.0$	$12.0.0 \times 060$
	$10.3.0$	$10.\bar{3}.0 \times 060$
	$5.16.0$	$5.10.0 \times 060$
	$\bar{5}.16.0$	$\bar{6}40 \times 1.12.0$
	$\overline{11}.12.0$	$12.0.0 \times 1.12.0$
$(\bar{2}30)$	$10.11.0$	640×470
$(\bar{8}70)$	$16.7.0$	$12.0.0 \times 470$
	$10.3.0$	$6\bar{4}0 \times 470$
	800	$470 \times 4\bar{7}0$
	$13.11.0$	$10.3.0 \times 380$
$(\bar{4}.13.0)$	$16.7.0$	$10.\bar{3}.0 \times 6.10.0$
	$1.14.0$	$6\bar{4}0 \times 7.10.0$
$(\bar{2}40)$	$14.4.0$	800×640
$(6.10.0)$	$18.2.0$	$12.6.0 \times 6\bar{4}0$
	$21.9.0$	$15.5.0 \times 640$
	$15.5.0$	640×990
	$19.\bar{2}.0$	$15.5.0 \times 4\bar{7}0$

If the signs S_H and S_K are denoted by different letters in these relations, the sign of $S_{H \pm K}$ is the product of those letters. The inequalities enabled us to express many of the letters (whose number initially was rather large) in terms of products of two letters; ultimately there remained only a, b, and ab. Thus, we compiled a reference group from the 56 reflections (33%) which had signs. The sign of any amplitude having both indices even could be found directly. The simplest case was that of 24.0.0.; the signs of 18 other reflections of this type were deduced in a more complicated way. All amplitudes having $h = 2m$, $k = 2n + 1$ had signs denoted by a, whereas those having $h = 2m$, $k = 2n$ had ones denoted by ab, and those having $h = 2m+1$, $k = 2n + 1$, had ones of b.

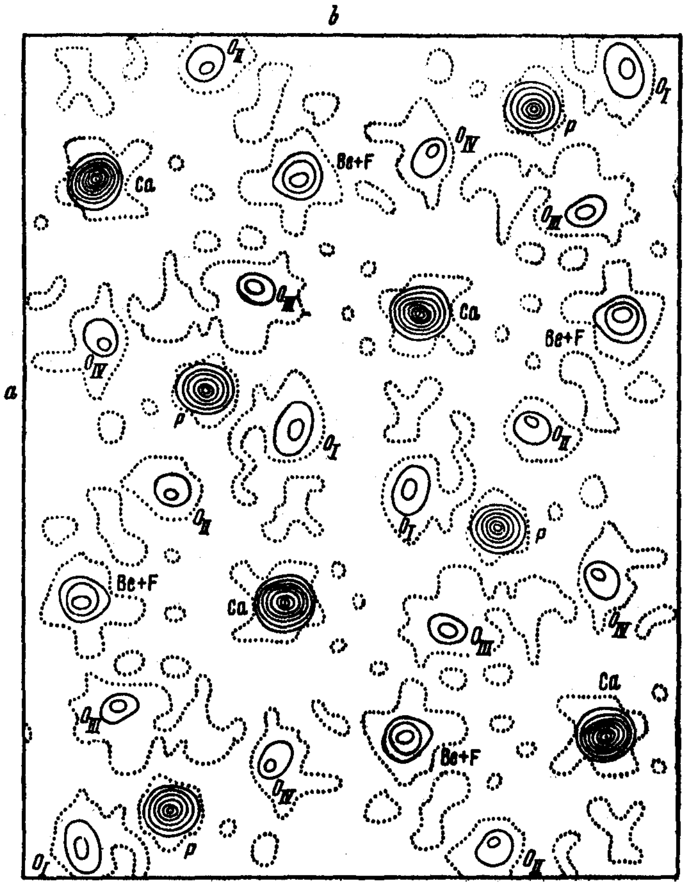

Fig. 1. The xy projection of the electron-density contours for herderite.

In a primitive lattice we may [8] assign arbitrarily three signs for the three-dimensional case, or two for a projection, subject to the condition that these signs are given to reflections falling in different groups. We have only two letters, so we may make them both plus.

The signs of the 56 reference reflections were checked by Zachariasen's method [16], and were used to find the signs of the other F_{hk0} by purely statistical methods. This process was successful for 84 amplitudes, i.e., of the 167 signs we established 140 with a "probability" (ratio of number of pairs implying that sign to the total number of pairs) not less than 70%. The number of defining pairs per F_{hk0} was 20-24.

The electron-density pattern constructred from the 140 (of the 167) F_{hk0} gave a well-resolved picture with large peaks, which we naturally equated to Ca atoms; the next most important peak fell at the centers of alternating squares and triangles formed by the less obvious peaks. The distances between the atoms, corresponding to these peaks were such as to indicate that the squares were projections of the PO_4 tetrahedra, and that the triangles were projections of BeO_4 tetrahedra standing on their bases; the central Be atom is covered by the fourth 0 (of F). The xy projection of the electron density agrees well with the corresponding Patterson diagram, which we constructed intially, but which gave no useful results. The divergence coefficient (R) at this stage was 24%, and only two of the F_{hk0} calculated from the atomic coordinates had signs, the reverse of those given by the direct method. A second xy projection, which included the remaining 27 F_{hk0} (with calculated signs), gave R = 14.9% without the zero reflections, and 20.4% with them (for all F_{hk0} up to $\sin\vartheta/\lambda = 1.1$); Fig. 1 shows this second projection; Fig. 2 compares the calculated and experimental structure amplitudes. The experimental values were numberd in accordance with the condition $\Sigma F_0 = \Sigma F_T$, which showed that the previous deduction of the absolute values was in error by not more than about 5%, i.e., could not interfere with the inequalities.

The $\underline{z}$ coordinates were deduced from the xz projection, which also checked the $\underline{x}$ and $\underline{y}$. The oscillation photograph on $\underline{b}$ for the equatorial layer had 116 non-zero h01, all with h = 2n on account of the glide plane, which halves the x axis. The h values for all reflections have been divided by 2 to conform to the smaller cell. The signs were again found by using the inequalities and statistical methods. There were 21 reflections with $|U_{h0l}| \geq 0.5$, so conditions were even more favorable; we were able to show that the relation $S_{H \pm K} = S_H \cdot S_K$ was correct for the following 60 sets of amplitudes:

	109	105×004		1200	$90\bar{3}$×303
	404	400×004	$(\bar{3}09)$	$90\bar{3}$	$60\bar{6}$×303
$(\bar{6}04)$	604	600×004		602	$30\bar{1}$×303
$(\bar{9}03)$	905	901×004		409	400×009
	$\bar{3}05$	$\bar{3}01$×004	(006)	600	$30\bar{3}$×303
$(30\bar{1})$	$\bar{3}09$	305×004	(008)	$60\bar{2}$	$30\bar{5}$×303
(602)	$\bar{6}06$	$\bar{6}02$×004		$30\bar{1}$	$00\bar{4}$×303
	703	$70\bar{1}$×004	$(\bar{2}02)$	10.02	602×400
(303)	309	$\bar{3}03$×006	$(\bar{2}04)$	10.04	604×400
(606)	$\bar{6}06$	$\bar{6}00$×006		$90\bar{3}$	$50\bar{3}$×400
$(\bar{6}08)$	604	$60\bar{2}$×006		$90\bar{5}$	$50\bar{5}$×400
	705	$70\bar{1}$×006		$70\bar{1}$	$30\bar{1}$×400
	404	$40\bar{2}$×006	(105)	$70\bar{5}$	$30\bar{5}$×400
(309)	$\bar{3}03$	$\bar{3}0\bar{3}$×006	$(\bar{2}06)$	10.02	$60\bar{2}$×404
(506)	$\bar{5}$.0.12	$\bar{5}03$×009		703	$\bar{3}01$×404
(304)	$\bar{3}$.0.14	$\bar{3}05$×009	(109)	$70\bar{1}$	$30\bar{5}$×404
$(\bar{5}05)$	705	105×600		705	$30\bar{1}$×404
	$\bar{2}08$	$\bar{3}03$×105	(004)	12.0$\bar{4}$	$60\bar{4}$×600
	$\bar{3}05$	400×105	(303)	$90\bar{3}$	$30\bar{3}$×600
	404	$30\bar{1}$×105	(305)	$90\bar{5}$	$30\bar{5}$×600
	602	$50\bar{3}$×105	(901)	303	$\bar{3}01$×602
$(\bar{5}07)$	703	$60\bar{2}$×105	(1200)	004	602×$60\bar{2}$
$(\bar{3}01)$	905	602×303	(307)	$90\bar{3}$	$30\bar{5}$×602
	703	400×303		$50\bar{3}$	$\bar{1}0\bar{5}$×602
$(\bar{3}05)$	901	$60\bar{2}$×303	$(60\bar{2})$	6.0.$\overline{10}$	006×604
	12.0.$\bar{4}$	$50\bar{3}$×701	$(90\bar{7})$	303	$\bar{3}05$×$60\bar{2}$
	404	$\bar{3}01$×703		12.0.$\bar{4}$	$50\bar{5}$×707
(406)	10.04	$30\bar{1}$×705		$30\bar{9}$	$00\bar{9}$×300
	901	004×903		12.0.$\bar{4}$	$60\bar{2}$×$\bar{6}06$
(301)	$90\bar{5}$	$30\bar{3}$×$60\bar{2}$		12.0.0	$50\bar{5}$×705

TABLE 1

Atomic Coordinates for Herderite, Datolite, and Gadolinite (as hundredths of the a, b and c axes). Datolite I gives the Japanese Results; Datolite II Gives our Data

Atoms	Herderite			Datolite I			Datolite II			Gadinolite	
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*
Ca — Y	33.0	11.3	99.5	33.8	10.3	99.0	33.9	10.8	99.0	32.7	10.8
P — Si	7.9	26.9	47.5	8.3	26.5	47.5	8.6	26.2	47.1	7.7	28.3
Be — B	33.3	40.8	55.8	34.0	40.0	60.0	34.0	41.0	57.6	33.4	40.5
O_I	4.1	39.7	25.0	4.0	39.5	25.0	4.0	39.5	24.2	2.1	39.6
O_{II}	45.6	27.8	65.0	46.0	30.0	69.0	46.0	30.4	67.1	44.4	28.2
O_{III}	19.5	34.3	67.3	21.0	33.0	70.0	21.0	32.7	67.6	20.1	33.4
O_{IV}	14.1	11.1	33.3	14.0	8.5	32.0	14.2	9.2	32.0	15.7	10.7
F — OH	33.0	41.7	20.9	33.5	41.5	27.5	33.6	41.5	25.8	33.5	40.5
$Fe^{\cdot\cdot}$	—	—	—	—	—	—	—	—	—	0	0

But here the result was to leave three letters instead of two (a, b, and c) and the products ab, ac, bc, and abc. Many (14) of the amplitudes with both indices even were shown to be positive, but about half of this type were represented by the letter b. The xy projection enabled us to choose between b = + and b = − because it

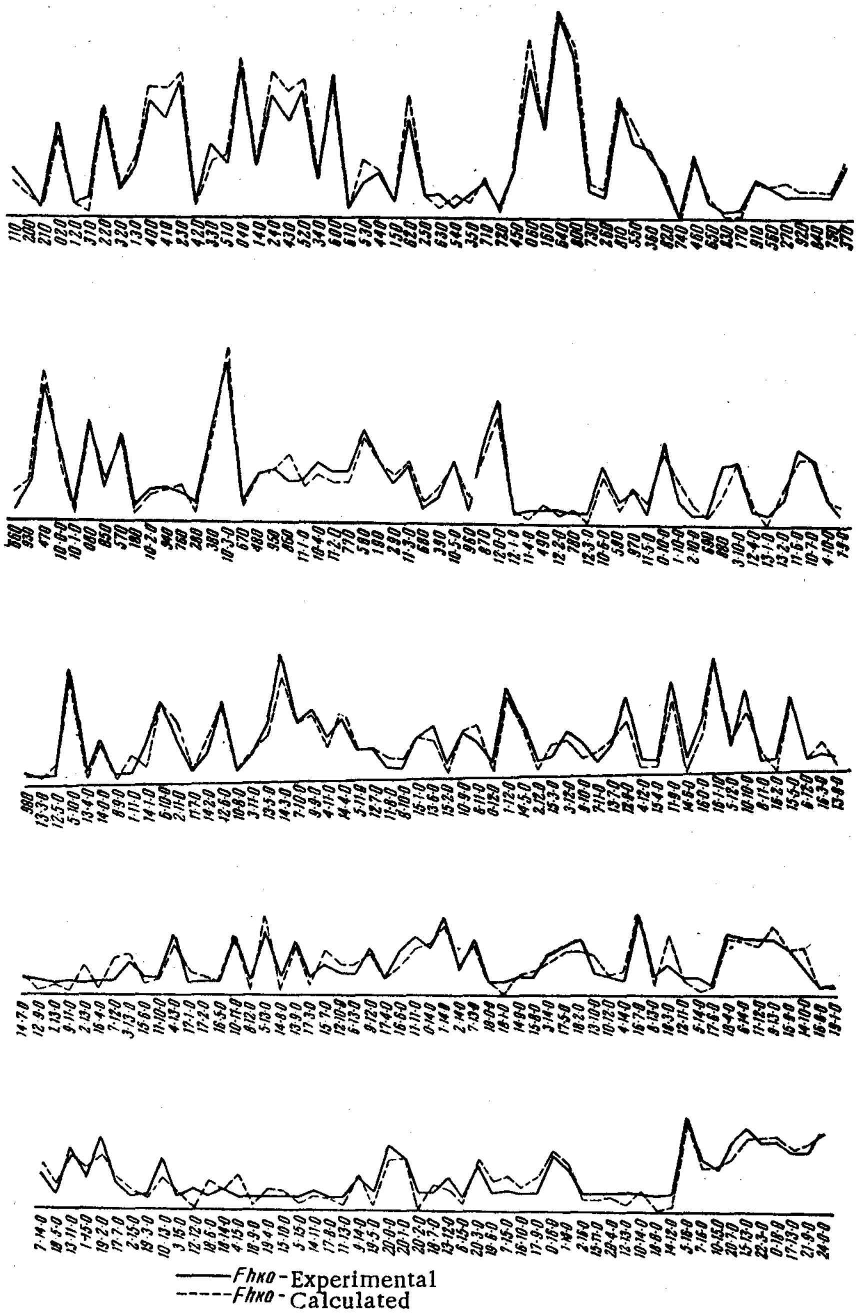

Fig. 2. Agreement between the calculated and experimental | Fhk0 | for herderite.

had good R (20.4%). The sign of the common reflection 800 was negative in that projection, whereas in the xz one the sign of 800 (400) was b. Hence b = — *, and the other signs are defined by a, c, and ac. If we had solved the xz projection independently, we could have chosen a and c arbitrarily (e.g. could have made them plus), but we can choose only three signs arbitrarily [8], and two had been used up in the xy projection; so if we were to put a = c = +, we had to ensure that this agreed with the first projection, as in the case of b. The appropriate reflection for a and c is 300 (600), which has a plus sign in xy, and here has the sign ac; hence a and c must have the same sign. We put a = c = + and took 10,h00 amplitudes whose signs had been defined in xy, and thereby

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* This could be expected a priori, since in any other case all the signs of the h = 2m, k = 2n group would be plus.

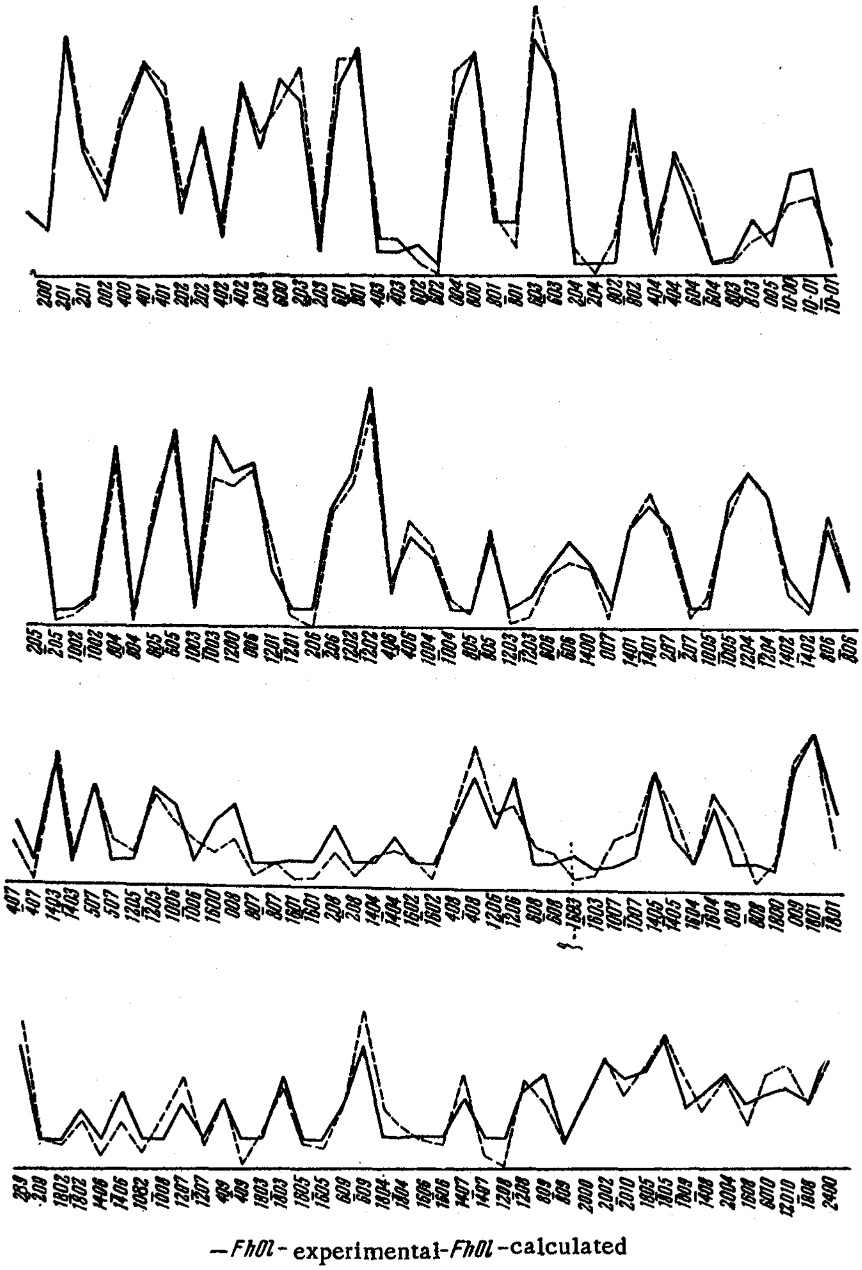

Fig. 3. Agreement between the calculated and experimental $|F_{h0l}|$ for herderite.

obtained a reference group of 61 reflections. Statistical methods with numbers of defining pairs up to 16 gave the rest of the signs. The mode was as before; the probability was 100% for the minimum number of pairs (3), and was not less than 70% when the number was large. There were 26 signs left in xz, which were not given by the first projection; these were calculated. The convergence coefficient for the repeated xz projection was 14.3% without the experimental zero reflections, or 19.7% with the 60 zero reflections, again for all F_{h0l} up to $\sin\vartheta/\lambda = 1.1$. Figure 3 shows how well the theoretical and experimental $|F_{h0l}|$ agree.

The xz projection (Fig. 4) shows few peaks; but they are sharp, being the Be atoms we took to be covered by O(F) in the xy projection.

Again, we checked the coordinates from the oscillation photograph on a (9.80 A) for the zero layer which had 67 nonzero reflections. The y and z coordinates from the xy and xz projections were used to calculated the

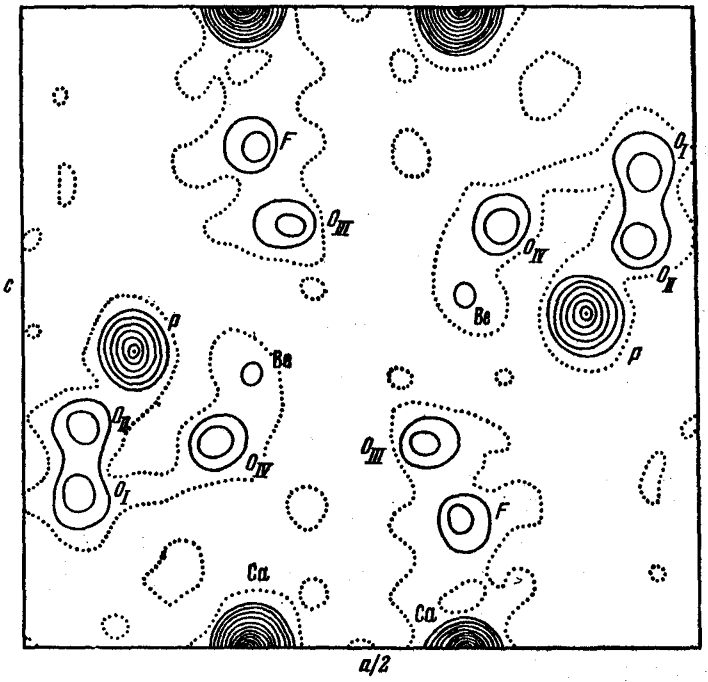

Fig. 4. The xz electron-density contours in projection for herderite.

F_{0kl} , which were compared with the experimental values. Here R = 17.4% for the 67 nonzero reflections and 19% for 83 reflections with 16 zeros up to ϑ/λ = 0.85

Table 1 gives the coordinates derived from the xy and xz projections. The atoms all lie in fourfold position, i.e. there are 24 independent parameters for the eight atoms in a formula unit.*

We used Vainshtein's method [13] to calculate the probable error in the coordinates by using the theoretical and experimental F_{hkl} ; the value for Ca was 0.004 A; for P, 0.006 A; for Be, 0.033 A; for O, 0.015 A; and for F, 0.013 A. As usual, these errors are determined by the errors made in estimating the intensities, and are increased by the errors introduced by interpolation.

Figure 5 shows that herderite contains infinite pseudotetragonal nets, consisting of PO_4 and BeO_3F tetrahedra, which species have different orientations. The nets consist of centrosymmetric rings made up from the two species of tetrahedron, which rings alternate with closed centrosymmetric octagons made up from the same two species. This pattern occurs in feldspar and in other closely allied aluminosilicates [17]. In Fig. 5 the atoms are given their z coordinates as hundredths of c; we see that the structure has two layers. Figure 6 shows the two layers separately as Pauling's polyhedra. The lower layer is made of slightly distorted cubes (Ca), which are typical of Ca in garnet, or of Cu in $CuAl_2$ [18]. The upper layer is a pseudotetragonal network of PO_4 tetrahedra (with one orientation) and of BeO_3F tetrahedra (with another).

Table 2 gives the interatomic distance. The P – O distances do not fall outside the range 1.51-1.57 A, while the O – O edges in the PO_4 tetrahedron range from 2.43 to 2.56 A. Other distances are: Be – O = 1.55-1.67 A and Be – F = 1.67 A, with O – O(F) = 2.52 - 2.73 A. The eight distances Ca – O = 2.40 - 2.70 A, most of them being close to the lower figure. The PO_4 tetrahedra are much smaller than SiO_4 ones, but the BeO_3F tetrahedra are almost the same size as SiO_4 ones.

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* The x coordinates have been reduced by 0.50a relative to those found by assigning the signs arbitrarily, which has been allowed for in the xy projection (Fig. 4), and in calculating the theoretical F. The origin has been moved in order to facilitate comparing our results with Ito's. This displacement is used in all following illustrations.

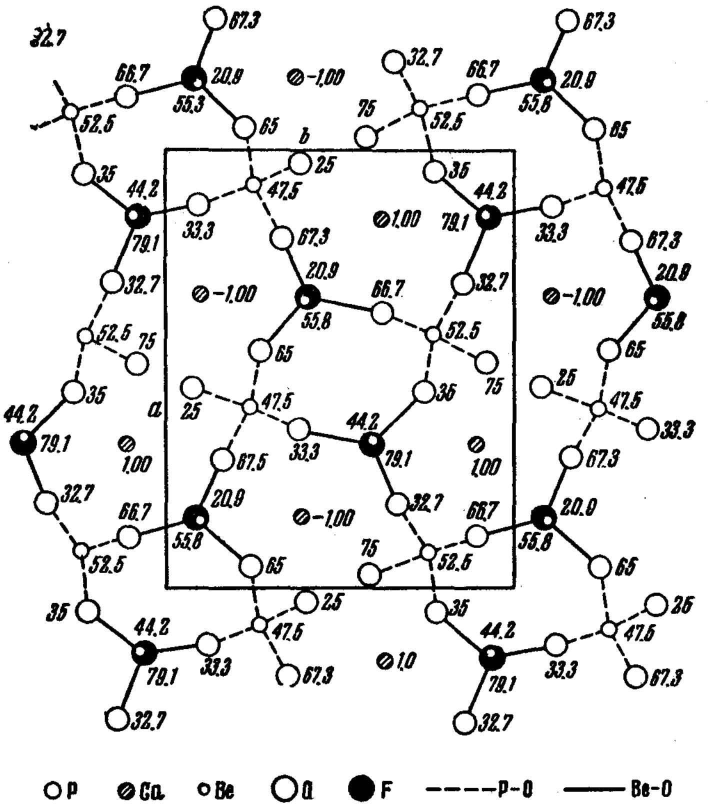

Fig. 5. The xy projection of the structure of herderite. The numbers are the atomic coordinates in hundredths of the axis c = 4.80 A.

TABLE 2

Atomic Distances in Herderite (A)

Tetrahedron		Tetrahedron		Polydedron	
$P-O_{I}$	1.51	$Be-O_{II}$	1.64	$Ca-O_{I}^{*}$	2.40
$P-O_{II}^{**}$	1.52	$Be-O_{III}$	1.55	$Ca-O_{I}^{*}$	2.40
$P-O_{III}$	1.57	$Be-O_{IV}^{*}$	1.67	$Ca-O_{II}$	2.44
$P-O_{IV}$	1.51	$Be-F$	1.67	$Ca-O_{III}$	2.61
$O_{I}-O_{II}^{**}$	2.49	$O_{II}-O_{III}$	2.52	$Ca-O_{III}^{*}$	2.70
$O_{I}-O_{III}$	2.56	$O_{II}-O_{IV}^{*}$	2.73	$Ca-O_{IV}$	2.44
$O_{I}-O_{IV}$	2.43	$O_{II}-F$	2.68	$Ca-F$	2.71
$O_{II}^{**}-O_{III}$	2.51	$O_{III}-O_{IV}^{*}$	2.62	$Ca-F^{**}$	2.58
$O_{II}^{**}-O_{IV}$	2.53	$O_{III}-F$	2.64		
$O_{III}-O_{IV}$	2.46	$O_{IV}-F$	2.67		

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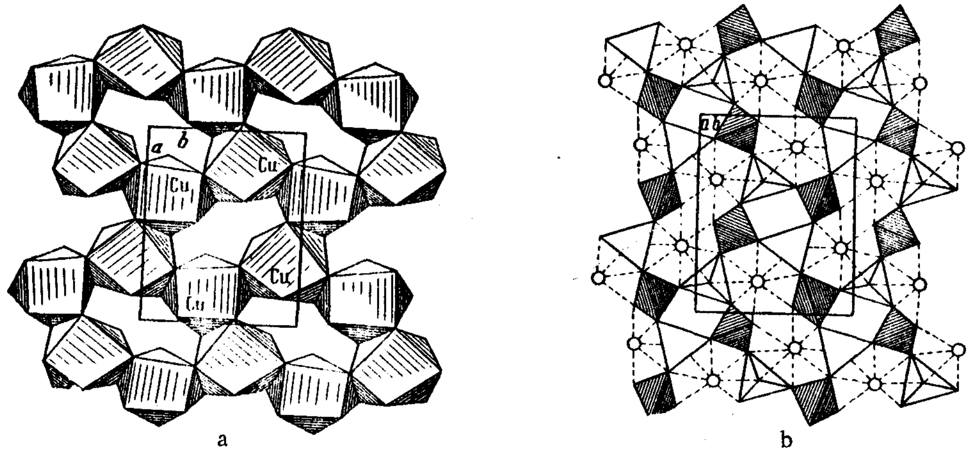
* Atoms related to the corresponding basic ones by the symmetry elements of the group.

** Atoms in adjacent cells.

Table 3 gives the sums of the valences compiled in accordance with Pauling's second rule for the common O-corners of the polyhedra. The balances are not satisfied exactly for O_I and O_{III}, but the lack of 1/4 at O_I and the same excess at O_{III} account for only 12.5% of the oxygen valences.



a b

Fig. 6. The structure of herderite in coordination polyhedra. a) Layer of twisted cubes with Ca atoms; b) second stage with grid of PO_4 tetrahedra (in projection, as squares) and of BeO_3F tetrahedra (in projection, as triangles).

TABLE 3

Valence Balance for Herderite

Anion	Cation			Sum of valences
	Ca	Be	P	
O_I	$2\cdot{}^1/_4$	—	$1\cdot{}^5/_4$	${}^7/_4 = 2 - {}^1/_4$
O_{II}	$1\cdot{}^1/_4$	$1\cdot{}^1/_2$	$1\cdot{}^5/_4$	2
O_{III}	$2\cdot{}^1/_4$	$1\cdot{}^1/_2$	$1\cdot{}^5/_4$	${}^9/_4 = 2 + {}^1/_4$
O_{IV}	$1\cdot{}^1/_4$	$1\cdot{}^1/_2$	$1\cdot{}^5/_2$	2
F	$2\cdot{}^1/_4$	$1\cdot{}^1/_2$	—	1
			Check	9.0

The structure of datolite $CaBSiO_4(OH)$ (a = 9.62, b = 7.60, c = 4.84 A; β = 90°; same space group) has been given by Ito and Mori. They used the xy Patterson projection to find the x and y coordinates of the Ca and Si atoms, from which they calculated the signs of the F_{hk0}. They used the 30 strongest F_{hk0} to construct the xy projection of the electron density, which revealed, in addition to the known Ca and Si, three peaks due to O atoms, which confirmed 55 signs as reliable; then a second synthesis was made, and then from 95 F_{hk0}, a third. The resulting coordinates were taken as final. The z coordinates were deduced from the chemical crystallography of the substance and were refined from a Fourier projection of the xy plane; the z coordinate of the B atom, which overlaps OH, was found from a section taken along [001].

The structure shows certain differences from that of herderite, especially in relation to the coordinates of the Ca atom (Table 1). In datolite the y for Ca is 10.3, whereas in herderite it is 11.3; the z for B is 60, whereas the one for the analogous Be in herderite is 55.8; the z values for O_{II} and O_{III} are 69 and 70 and 65 and 67.3, respectively. In datolite OH has z = 27.5, whereas in herderite F has z = 20.9. We have revised the coordinates of datolite by determining the structure afresh by the direct methods presented above.

For the xy projection we had 158 nonzero F_{hk0} (Mo radiation), as against 95 in the Japanese work. Wilson's method gave K = 13.3, and all the amplitudes were transferred to the absolute scale with B = 0.5 and were calculated to $|U_{hk0}|$ form; then they included 12 which were greater than 0.5. Then (2) and (3) were used to confirm that $S_{H \pm K} = S_H \cdot S_K$ was true for the sets listed below, which were selected from those with $|U_{hk0}| \geq 0.40$.

	22.4.0	14.3.0×810		24.0.0	$10.\bar{3}.0\times 14.3.0$
	20.7.0	$12.\bar{6}.0\times 810$		$14.\bar{3}.0$	060×14.3.0
	16.0.0	$8\bar{1}0\times 810$	$(18.\bar{4}.0)$	10.10.0	$\bar{4}70\times 14.3.0$
	24.0.0	$16.\bar{1}.0\times 810$	(16.7.0)	$\bar{4}.13.0$	$\overline{10}.3.0\times 6.10.0$
	$14.\bar{3}.0$	$6\bar{4}0\times 810$	(16.10.0)	$\overline{16}.10.0$	16.0.0×0.10.0
	$12.\bar{6}.0$	$4\bar{7}0\times 810$		$\bar{1}.17.0$	$\bar{7}.13.0\times 640$
	10.10.0	$2.\overline{11}.0\times 810$		$1.\overline{12}.0$	$\bar{7}.\overline{13}.0\times 810$
	$6.\overline{10}.0$	$\bar{2}.\overline{11}.0\times 810$		11.12.0	6.10.0×520
$(12.\bar{6}.0)$	12.6.0	$0\bar{6}0\times 12.0.0$	$(\bar{5}\bar{8}0)$	15.12.0	10.10.0×520
	6.10.0	$\bar{6}.10.0\times 12.0.0$		7.13.0	2.11.0×520
(230)	22.3.0	12.0.0×10.3.0		15.5.0	10.3.0×520
$(16.\bar{1}.0)$	470	$\bar{6}40\times 10.3.0$		1.12.0	$6.10.0\times\bar{5}20$
	6.10.0	$\bar{4}70\times 10.3.0$	(21.9.0)	$\bar{1}.15.0$	$\overline{11}.12.0\times 10.3.0$
	$10.\bar{3}.0$	$0\bar{6}0\times 10.3.0$		990	470×520
	$22.\bar{3}.0$	$12.\bar{6}.0\times 10.3.0$		$\bar{6}.10.0$	$\overline{12}.6.0\times 640$
	$\bar{6}40$	$\bar{4}70\times 10.3.0$	[(16.1.0)	$\bar{4}70$	$\overline{10}.3.0\times 640$
$(6\bar{2}0)$	6.10.0	060×640		$\bar{6}40$	$\overline{12}.0.0\times 640$
(080)	12.0.0	$6\bar{4}0\times 640$		$16.\bar{1}.0$	$4\bar{7}0\times 12.6.0$
$(\bar{8}70)$	20.1.0	$14.\bar{3}.0\times 640$		24.0.0	$12.\bar{6}.0\times 12.6.0$
(2.11.0)	10.3.0	$4\bar{7}0\times 640$	$(\bar{6}20)$	18.10.0	12.6.0×640
(0.14.0)	$12.\bar{6}.0$	$6.\overline{10}.0\times 640$	$(\bar{4}60)$	12.8.0	810×470
	640	$\bar{6}40\times 12.0.0$		580	060×520
$(10.\bar{4}.0)$	22.4.0	640×16.0.0		10.10.0	6.10.0×400
$(12.\bar{7}.0)$	20.7.0	470×16.0.0	$(\bar{4}\bar{1}0)$	4.13.0	470×060
$(8\bar{1}0)$	20.7.0	640×14.3.0	$(\overline{16}.6.0)$	6.16.0	16.0.0×060
	10.10.0	$\bar{6}.10.0\times 16.0.0$	$(\bar{2}90)$	14.11.0	8.1.0×6.10.0
	24.0.0	$8\bar{1}0\times 16.1.0$	(800)	0.14.0	470×470
	$22.\bar{3}.0$	$6\bar{4}0\times 16.1.0$			

The signs of all those amplitudes whose two indices are positive were determined directly; those with h = 2m + 1, k = 2n were denoted by c, those with h = 2m, k = 2n + 1 by a, and those with both odd, by ac. Both letters were assumed to be plus. The inequalities gave the signs of 47 reflections, which gave us a reference group from which to find the other F_{hk0} by statistical methods; this gave us the signs of a further 90 reflections. The probabilities were as before with numbers of defining pairs up to 20. The 137 F_{hk0} were used to construct the xy projection of the electron density. The signs of all the F_{hk0} were calculated from the coordinates given by this projection; in seven cases the signs were reversed. The new xy projection (from all 158 amplitudes) gave the

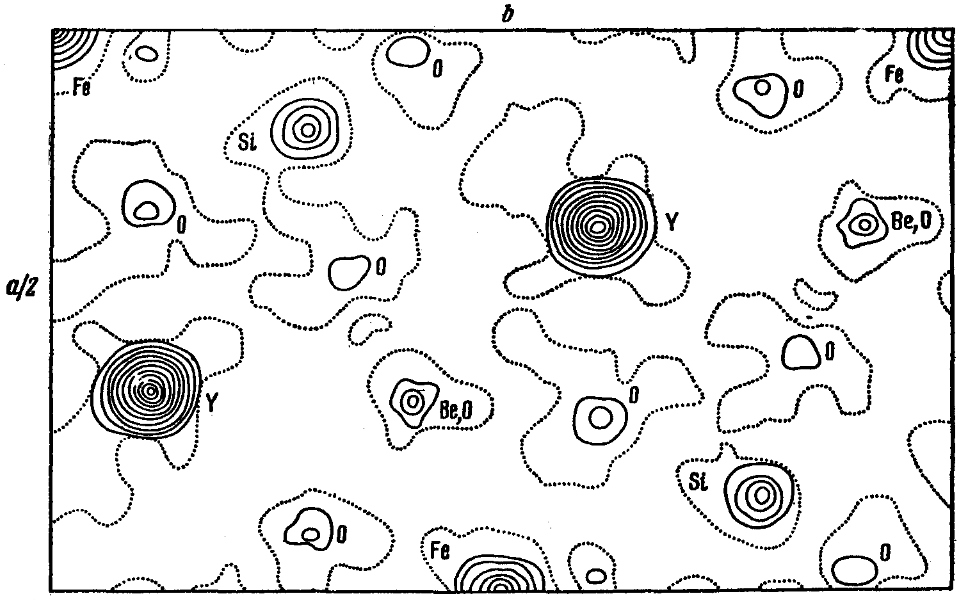


Fig. 7. The xy electron-density projection for gadolinite.

final x and y coordinates. The divergence coefficient (neglecting zeros) was 17.9%. The zeros up to $\sin\vartheta/\lambda =$ $= 1.1$ raised R to 22.4%.

We use the h0l reflection to find the z coordinates. The Weissenberg photograph (on b) for the zero-layer line gave 154 nonzero reflections, of which 22 had $|U_{h0l}|$ exceeding 0.5. The a plane again enabled us to halve the h. The h0l reflections complied with $S_{H\pm K} = S_H \cdot S_K$ in the sets

	$\bar{5}03$	800×303		$\bar{5}09$	500×009
$(30\bar{1})$	307	004×303	$(\bar{8}09)$	809	800×009
$(20\bar{4})$	4010	004×303	$(\bar{6}07)$	6.0.11	602×009
	707	404×303	$(\bar{7}07)$	907	800×107
$(\bar{3}0\bar{1})$	907	604×303	(604)	$\bar{4}010$	$\bar{5}03\times107$
$(\bar{6}02)$	1204	901×303	(705)	$\bar{5}09$	$\bar{6}02\times107$
$(30\bar{6})$	3012	009×303	(703)	$\bar{5}011$	$\bar{6}04\times107$
(901)	$\bar{9}05$	$\bar{6}02\times303$	(602)	0.0.12	$\bar{3}05\times307$
$(11.0.\bar{1})$	$\bar{5}07$	$\bar{8}04\times303$	(3.0.11)	303	$00\bar{4}\times307$
$(11.0.\bar{3})$	$\bar{5}09$	$\bar{8}06\times303$		12.0.4	800×404
	$\bar{2}08$	$\bar{5}05\times303$	(1006)	$\bar{2}02$	$\bar{6}0\bar{2}\times404$
(10.1.1)	$50\bar{5}$	$20\bar{8}\times303$		903	$50\bar{7}\times404$
	$60\bar{2}$	$30\bar{5}\times303$	(1.0.10)	11.0.4	$50\bar{3}\times607$
$(\bar{2}.0.10)$	$80\bar{4}$	$50\bar{7}\times303$	(11.0.1)	107	$\bar{5}03\times604$
$(\bar{2}06)$	800	$50\bar{3}\times303$	(008)	12.0.0	$60\bar{4}\times604$
	1200	$90\bar{3}\times303$	(12.0.0)	004	$602\times\bar{6}02$
	6011	607×004	(103)	1.0.11	107×004
$(\bar{9}01)$	907	903×004	$(50\bar{7})$	707	107×600
$(\overline{12}.0.4)$	12.0.4	$12.0.0\times004$	$(30\bar{3})$	903	303×600
(501)	$\bar{5}07$	$\bar{5}03\times004$	$(30\bar{7})$	907	307×600
	$\bar{5}09$	$\bar{5}05\times004$		$11.0.\bar{5}$	$50\bar{5}\times600$
$(50\bar{3})$	$\bar{5}.0.11$	$\bar{5}07\times004$		0.0.12	009×003
	$\bar{8}04$	$\bar{8}00\times004$	$(\bar{1}0\bar{9})$	$\overline{11}05$	$\bar{5}07\times602$
(905)	$\bar{9}03$	$\bar{9}0\bar{1}\times004$	(301)	905	$30\bar{3}\times60\bar{2}$
	$\bar{6}02$	$\bar{6}0\bar{2}\times004$	(600)	006	$\bar{3}03\times303$
(3.0.11)	$\bar{3}03$	$\bar{3}0\bar{7}\times004$		406	103×303
$(\bar{6}06)$	602	$60\bar{2}\times004$		0.0.12	$\bar{3}09\times303$
	901	$90\bar{3}\times004$		6011	308×303
	6.0.11	602×009	$(12.0.\bar{2})$	$\bar{6}08$	$\bar{9}05\times303$
	$\bar{2}.0.11$	$\bar{2}02\times009$	$(\bar{6}04)$	12.0.2	$90\bar{1}\times303$
(607)	$\bar{6}.0.11$	$\bar{6}02\times009$		10.0.6	$10.0.2\times004$

Then we found that all the reflections appearing in the inequalities could be expressed in terms of three letters. Amplitudes with h = 2m, k = 2n were either plus or b. The signs of amplitudes with h = 2m, k = 2n + 1 were c and bc. Also, those with h = 2m + 1, k = 2n had signs of ac or abc. If both indices were odd, the signs were a and ab.

We used the known and checked signs for the hk0 reflections (for which R was small) to find the absolute sign of b (=−), i.e., that sign which does not depend on the choice of origin, since this letter defines the sign of 16.0.0 ($U_{16.0.0}$), which is known to be minus from the xy projection. Thus, the signs of the amplitudes with h = 2m, k = 2n were found to be both plus and minus, while the other amplitudes were defined by a, c and ac. We checked that a = c = + was correct from 10.0.0, which is common to the xy and xz projections (its sign in xy was minus, and here was abc with b = −1, so a = c); this gave us a reference group of 79 reflections. Zachariasen's method gave a further 66 signs. The xz electron-density projection was constructed from 145 reflections; here the B peak was sharper than was the Be peak for herderite, and was also displaced further towards the base of its tetrahedron (relative to Be), which agrees with the tendency of B to compromise between fourfold and threefold coordination [19]. The signs of three F_{h0l} were changed in the recalculation. A repeat Fourier synthesis (with 154 amplitudes) gave a more regular relation between the peak heights; some of the peaks were displaced slightly. R for the 154 nonzero h0l was 12.9%; or 16.5% with the 100 zero ones, again up to $\sin\vartheta/\lambda = 1.1$.

Table 1 gives the atomic coordinates derived from the xy and xz projections and also gives Ito and Mori's results, which differ from ours by up to 0.025 (0.12 in the z coordinates. The two kinds of tetrahedron are much

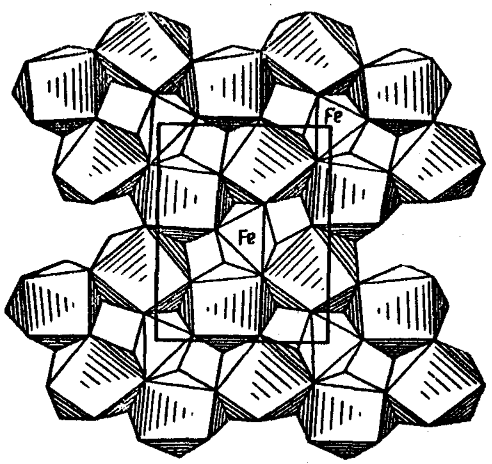


Fig. 8. The xy projection for gadoline in Pauling's polyhedra. The lower layer has the Y polyhedra; the Fe octahedra are at the centers of symmetry 000 and ½ ½ 0.

more regular; the distances are Si – O = 1.57, 1.58, 1.63, 1.63 A; all three B – O = 1.48 A (as against 1.45, 1.44, 1.47, in Ito's paper); Ca – O falls within the limits 2.35–2.66 A. The different O – OH distances (2.35, 2.52) given by Ito are replaced by 2.46 A, B – OH = 1.54 A.

The structure of the beryllophosphate (herderite) is related to that of the borosilicate (datolite) in such a way that the replacement of $Be^{2+}P^{5+}$ by $B^{3+}Si^{4+}$ corresponds to a change from the smaller PO_4 tetrahedron (edge about 2.50A) to the larger SiO_4 one (edge about 2.61 A), which change is balanced by the change from the large BeO_3F tetrahedron (edge about 2.64 A) to the smaller $BO_3(OH)$ one (edge about 2.45 A).

The same direct methods were used to solve for the structure of the not entirely isostructural rare-earth mineral gadolinite. The formula is derived from that of datolite, $CaBOHSiO_4$, by replacing $Ca^{2+}B^{3+}$ by $Y^{3+}Be^{2+}$ and by inserting at the centers of symmetry in the unit cell (which contains four "datolite" molecules) two extra $Fe^{\cdot\cdot}$ ions (in Fig. 7 the $Fe^{\cdot\cdot}$ octahedra are shown with the Y polyhedra), which insertion is compensated by replacing four OH by O. The resulting formula is $Fe^{\cdot\cdot}Y_2Be_2O_2Si_2O_8$ with two such molecules in the cell (a = 9.89, b = 7.52, c = 4.71 A; β = 90°33'). Ito gives no atomic coordinates; he demonstrates the structural similarities only by comparing in a general way the strengths of ten Debye lines and certain other lines.

Gadolinite is appreciably radioactive, which was checked on our samples; the cause is that thorium replaces the rare earths isomorphously, which results in the mineral's becoming metamict (i.e., to a large extent semi-amorphous), and which made the x-ray patterns of very poor quality. It is possible to analyze the structure, but the intensities could be estimated only for the hk0 reflections (111 nonzero), which gave 16 with $|U_{hk0}|$ larger than 0.5. Taking those initial $|U_{hk0}|$ larger than 0.40, we had 28 inequalities, which were strong ones, and which gave a group of 40 reference signs. The statistical treatment then left only 12 signs undefined. The resulting electron-density pattern (Fig. 7) was very clear. Table 1 gives the $\underline{x}$ and $\underline{y}$ coordinates. These are fairly accurate (R = 18.2%, neglecting the zero reflections, or 22.9%, taking account of them up to sin θ/λ = 0.8) and may be used to examine the differences between gadolinite and datolite, which arise mainly from the extra $Fe^{\cdot\cdot}$ ions at the empty centers of symmetry in the Ca polyhedra in the first layer (Fig. 8). The Ca has also been replaced by the smaller Y, and the B by the larger Be, of course. Table 1 shows that the two structures differ very much in the coordinates of O_I, O_{II}, O_{IV}, Si and Y. The Fe – O distances calculated for gadolinite from the data for datolite are $Fe^{\cdot\cdot} - O = 1.79$, $Fe^{\cdot\cdot} - O_{IV} = 2.03$ and $Fe^{\cdot\cdot} - O_V = 1.74$ A. Except for $Fe^{\cdot\cdot} - O_{IV} = 2.03$ A, the distances are clearly impossible for silicates (the sum of the ionic radii of Fe^{2+} and O^{2-} is 0.80 + 1.32 = 2.12 A), and so the $\underline{z}$ coordinates must differ considerably between the two structures, the more so since the replacement of Ca^{2+} by Y^{3+} ($r_Y = 0.97$ A, $r_{Ca} = 1.04$ A) must reduce the Y – O distance of gadolinite relative to the Ca – O distance of datolite, whereas the $Fe^{\cdot\cdot}$ ions at the centers of the four-rings must push the nearby O atoms sufficiently to give acceptable $Fe^{\cdot\cdot}$–O distances. This appears as the displacement of O_{II} and O_{IV} from the center, which is visible even in the xy projection. The interatomic distances may be calculated from the coordinates taken from the projection of gadolinite, but with our $\underline{z}$ coordinates taken from datolite, which at once gives more reasonable distances, namely, $Fe^{\cdot\cdot} - O_{II} = 1.92$, $Fe^{\cdot\cdot} - O_{IV} = 1.98$ and $Fe^{\cdot\cdot} - O_V = 2.18$ A.

In the structures of herderite and datolite we find grids with strong bonds (P, Si, B) alternating with ones with weak bonds (Ca polyhedra with large distances between cation and anion), whereas in gadolinite the second grids are stronger because Ca^{2+} replaces Y^{3+}, and also because Fe (which absorbs light strongly) is present. The result is that gadolinite is much harder and is optically positive, whereas herderite and datolite are optically negative.

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