

Refinement of the Alum Structures.

I. X-Ray and Neutron Diffraction Study of $\text{CsAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, a β Alum*

BY DON T. CROMER

*Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico, U.S.A.
and Puerto Rico Nuclear Center, Mayaguez, Puerto Rico*

M. I. KAY

Puerto Rico Nuclear Center, Mayaguez, Puerto Rico

AND ALLEN C. LARSON

Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico, U.S.A.

(Received 15 December 1965 and in revised form 31 January 1966)

The structure of $\text{CsAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, a β alum, has been refined from three-dimensional X-ray diffraction data and neutron diffraction data from the $hk0$ zone. The maximum shift in atom positions from those given by Lipson (1935) is only 0.04 Å. Criteria for classifying alums as α , β or γ types are discussed.

Introduction

The alums are a large class of double salts having the general formula $\text{A}^+\text{B}^{3+}(\text{RO}_4)_2 \cdot 12\text{H}_2\text{O}$ where A can be NH_4 , CH_3NH_3 , Na, K, Rb, Cs; B can be Al, Ga, Cr, Fe, V; and R can be S, Se or Te. BeF_4^{2-} alums are also known. These compounds are cubic, space group $P\bar{a}3$, although this symmetry can only be achieved statistically with the ammonium and substituted ammonium alums. The alums were all thought to be isomorphous until the X-ray work of Lipson (1935) showed that there are three different types which he named α , β and γ , in the order of their discovery.

The type of alum formed depends on the size of the monovalent cation. If the cation is small the γ alum forms. The only known representative of this class is $\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. The β alum forms if the cation is large and the α alum, which is by far the most common type, occurs if the cation is of intermediate size. In all the alums there are two crystallographically different water molecules, each associated exclusively with either the monovalent or trivalent cation. The trivalent cation is always surrounded by six water molecules in a nearly regular octahedron but the orientation of the octahedron with respect to the cell axes is different in each of the three types. The monovalent cations in the α and γ alums also have six water molecules. In γ alum these water molecules form a nearly regular octahedron. In α alum the octahedron is distorted by compression along the threefold axis.

The large cation in β alums can accommodate 12 oxygen neighbors. To attain this large coordination number the water octahedron is compressed along the

threefold axis and stretched out normal to this axis until it is nearly planar. The two ends of the resulting trigonal antiprism are separated by only about 0.06 Å. The sulfate groups at each end of this antiprism are then moved along the threefold axis toward the central cation until six sulfate oxygen atoms are about the same distance from the cation as are the water molecules. A slightly distorted cubic close packed array of oxygen atoms thus surround the cation.

In the γ structure six water molecules approach the small sodium cation much more closely than in the α structure. This motion cannot take place unless the hydrogen bonding system changes. The most striking result is that the sulfate groups become oppositely oriented along the threefold axis.

Discussions of the relations among the three structures have been given by Lipson (1935) and by Jona & Shirane (1962). None of the alums has been investigated by modern counting techniques although Okaya, Ahmed, Pepinsky & Vand (1957) have studied methylammonium aluminum sulfate dodecahydrate (MASD) by photographic methods and refined the structure by least squares. Okaya *et al.* (1957) do not classify MASD in a particular structure type because 'the difference between α and β alum types is not adequately defined structurally'. On the other hand we believe that the three structure types may be clearly distinguished and that MASD is a member of the β alums. The characteristic that distinguishes the γ alums from the α and β alums is the orientation of the sulfate group. In the γ alums this group is oriented opposite to its orientation in the α and β alums. The β alums have twelfold and the α alums have sixfold coordination of oxygen about the central monovalent cation. Okaya *et al.* (1957) probably overlooked this difference in coordination because the distances which they state are from the

* Work performed under the auspices of the U.S. Atomic Energy Commission.

center of gravity of the CH_3NH_3^+ ion are actually from the nitrogen or carbon atoms of the disordered ion.

We have investigated several of the alums by both X-ray and neutron diffraction methods. The present paper concerns the structural refinement of $\text{CsAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, an example of the β alum type.

Experimental

Crystals for the X-ray study were grown from a water solution. Well formed octahedra, sometimes with small $\{100\}$ and $\{110\}$ forms developed, were readily obtained, and spheres were ground in a Bond sphere grinder. A sphere 0.16 mm in diameter was used in obtaining the intensity data. The lattice constant was measured with a carefully aligned single-crystal orienter on a General Electric XRD-5 X-ray diffraction unit and found to be 12.352 ± 0.003 Å (Mo $K\alpha_1 = 0.70926$ Å) in reasonable agreement with 12.358 ± 0.002 Å reported by Lipson & Beevers (1935). Mo $K\alpha$ radiation and Zr-Y balanced filters were used in measuring the intensities within the range $2\theta \leq 50^\circ$ by both the fixed crystal, fixed counter method and the 2θ scan method. One-fourth of the hemisphere was measured by the former technique and one-sixth by the latter. Thus, equivalent reflections were measured three times by the fixed crystal method and twice by the 2θ scan method. No absorption corrections were necessary ($\mu R = 0.19$). The internal consistency of the data was estimated by forming the indices $R_F = \Sigma |F_i - (\bar{F}^2)^{\frac{1}{2}}| / \Sigma (\bar{F}^2)^{\frac{1}{2}}$ and $R_{F^2} = \Sigma |F_i^2 - \bar{F}^2| / \Sigma \bar{F}^2$ where the summations were taken over all reflections observed more than once. These values and the number of observations are given in Table 1. The internal consistency is better with the 2θ scan data but this is partly the consequence of comparing only two equivalent reflections rather than three. If the assumptions are made that the measurements are normally distributed, and that for the case of three equivalent measurements the mean is equal to the median, then R_F for two measurements should be about 1.5 times that for three measurements (Dixon & Massey, 1957).

Table 1. Summary of observed X-ray data

	Number of non-equivalent reflections measured	Number observed	R_F	R_{F^2}
Fixed crystal	557	362	0.0199	0.0242
2θ Scan	557	320	0.0097	0.0111

Reflections were considered observed if $(I - \text{Background}) \geq 3.0 \times (I + \text{Background})^{\frac{1}{2}}$. Because the contrast between the intensity and the background is greater for the fixed crystal method more reflections are observed by this technique.

For neutron diffraction studies larger crystals are necessary. Fine wires were suspended in a supersaturated solution of cesium alum and numerous small crystals formed on these wires. Most of the crystals were

scraped from the wires and the remainder were suspended in a saturated solution which was then allowed to evaporate slowly. An octahedron, 4 mm on an edge, was selected for study. The fine wire remaining inside the crystal was assumed to have a negligible effect on the neutron scattering. The crystal was briefly immersed in liquid nitrogen to increase its mosaic nature and thus reduce the effects of extinction. The neutron diffraction intensities of the $hk0$ zone were measured with the single-crystal spectrometer at the Puerto Rico Nuclear Center. A wavelength of 1.06 Å was used, and non-equivalent reflections within the range $2\theta \leq 90^\circ$ were measured by step scanning. Of these, 64 were observed according to the criterion $(I - \text{Background}) \geq 2.0 \times (I + \text{Background})^{\frac{1}{2}}$. Because of the large incoherent scattering of hydrogen, absorption corrections were applied. The linear absorption coefficient for cesium alum is 4.31 cm^{-1} . Calculated transmission factors were between 0.292 and 0.353.

Refinement of the structure with X-ray data

The atomic positions given by Lipson (1935) were used as starting values for a full-matrix least-squares refinement of all non-hydrogen parameters. Anisotropic thermal parameters were used in the form

$$\exp [-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$$

The scattering factors of Cromer & Waber (1965) were used for cesium, aluminum and sulfur, and that given in *International Tables for X-ray Crystallography* (1962) was used for oxygen. Since the anomalous dispersion for cesium is small, no correction was made. The quantity minimized was $\Sigma w(F_o - F_c^*)^2$. Two weighting systems were used, $w = w_E$ and $w = w_E / (F_o + 0.02F_o^2)$ where w_E is the weight based on counting statistics as given by Evans (1961).

$$F_c^* = \frac{KF_c}{\left\{ 1 + g \left[\frac{2(1 + \cos^4 2\theta)}{(1 + \cos^2 2\theta)^2} \right] \text{Lp} F_c^2 \right\}^{\frac{1}{2}}}$$

where K is a scale factor, g is an extinction parameter (Zachariasen, 1963), Lp is the Lorentz and polarization factor, and F_c is the ordinary calculated structure factor. For unobserved reflections $w = 0$. At the end of the refinements $\Delta\xi_i / \sigma(\xi_i) < 10^{-3}$ for all parameters ξ .

Both sets of data were refined with both weighting systems and nearly identical results were obtained. However, when the modified weights, *i.e.* $w = w_E / (F_o + 0.02F_o^2)$, were used the standard deviations were about 40% smaller, the S-O bond lengths were more nearly the same and the parameters obtained from the two different data sets were in closer agreement. With either data set the maximum parameter difference as a function of weighting system was about one standard deviation but for most parameters was considerably less.

The values of the residuals, R , with unobserved reflections omitted are given in Table 2 for both the fixed crystal and 2θ scan methods. To our knowledge, no

detailed comparison of these two experimental techniques has appeared in the literature, at least not for a crystal as complex as a β alum. Cromer, Larson & Roof (1960) compared results for CeCu_6 obtained by the Evans (1953) method, which is a scan by moving the Weissenberg dial angle, ω , and by the fixed-crystal,

fixed-counter method. For various reasons, however, the CeCu_6 data did not provide a good comparison of the fixed crystal and scan techniques. Consequently it is of interest to report here in detail the results obtained by using both of these experimental techniques.

Table 2. *R* values for different sets of data

	$R = \Sigma \Delta F / \Sigma F_o $	$R_w = \Sigma w \Delta F / \Sigma w F_o $
Fixed crystal		
$w = w_E$	0.0394	0.0380
$w = w_E / (F_o + 0.02F_o^2)$	0.0354	0.0528
2 θ Scan		
$w = w_E$	0.0418	0.0356
$w = w_E / (F_o + 0.02F_o^2)$	0.0375	0.0501
Neutron data		
$w = w_E / (F_o + 0.02F_o^2)$	0.0744	0.0590

Table 3 gives the final least-squares parameters for the two sets of data. In nearly all cases the parameter differences are smaller than a standard deviation. The thermal parameters obtained from the fixed crystal data, however, are systematically slightly larger, probably because at higher angles a small portion of the intensity is lost because of α_1 - α_2 separation. This effect is not nearly as pronounced with the alum as it was with CeCu_6 because with the alum the data were limited to 50° 2θ whereas with CeCu_6 the data extended to 90° 2θ . It is clear that the fixed-crystal method gives

Table 3. *Least-squares parameters for* $\text{CsAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ *from X-ray diffraction data*

The upper numbers are from the fixed crystal data and the lower numbers from the 2θ scan data. $w = w_E / (F_o + 0.02F_o^2)$ in both cases

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{11} \times 10^5$	$B_{22} \times 10^5$	$B_{33} \times 10^5$	$B_{12} \times 10^5$	$B_{13} \times 10^5$	$B_{23} \times 10^5$
Cs	0.5	0.5	0.5	428 ± 7	B_{11}	B_{11}	-88 ± 10	B_{12}	B_{12}
	0.5	0.5	0.5	404 ± 7	B_{11}	B_{11}	-84 ± 15	B_{12}	B_{12}
Al	0.0	0.0	0.0	218 ± 15	B_{11}	B_{11}	54 ± 36	B_{12}	B_{12}
	0.0	0.0	0.0	186 ± 15	B_{11}	B_{11}	18 ± 50	B_{12}	B_{12}
S	0.32867 ± 15	<i>x</i>	<i>x</i>	217 ± 9	B_{11}	B_{11}	59 ± 22	B_{12}	B_{12}
	0.32865 ± 19	<i>x</i>	<i>x</i>	211 ± 11	B_{11}	B_{11}	60 ± 31	B_{12}	B_{12}
O _s (1)	0.25955 ± 40	<i>x</i>	<i>x</i>	402 ± 34	B_{11}	B_{11}	-220 ± 66	B_{12}	B_{12}
	0.25935 ± 48	<i>x</i>	<i>x</i>	384 ± 38	B_{11}	B_{11}	-241 ± 87	B_{12}	B_{12}
O _s (2)	0.27893 ± 42	0.34108 ± 42	0.43637 ± 40	486 ± 43	340 ± 41	250 ± 38	143 ± 70	313 ± 67	91 ± 65
	0.27869 ± 53	0.34096 ± 55	0.43681 ± 49	484 ± 53	338 ± 54	212 ± 47	150 ± 93	331 ± 81	133 ± 82
O _w (1)	-0.15928 ± 43	0.05065 ± 43	0.28465 ± 40	323 ± 40	366 ± 40	401 ± 39	10 ± 70	116 ± 69	25 ± 70
	-0.15917 ± 57	0.05129 ± 54	0.28488 ± 52	285 ± 53	358 ± 50	390 ± 50	-6 ± 89	162 ± 90	-5 ± 86
O _w (2)	0.15236 ± 41	-0.00199 ± 37	0.00001 ± 40	203 ± 34	329 ± 38	399 ± 42	40 ± 69	103 ± 63	-3 ± 63
	0.15261 ± 44	-0.00209 ± 50	-0.00138 ± 56	187 ± 38	308 ± 42	385 ± 45	21 ± 101	50 ± 86	54 ± 91
<i>g</i>	$1.74 \pm 31 \times 10^{-7}$								
	$1.58 \pm 32 \times 10^{-7}$								

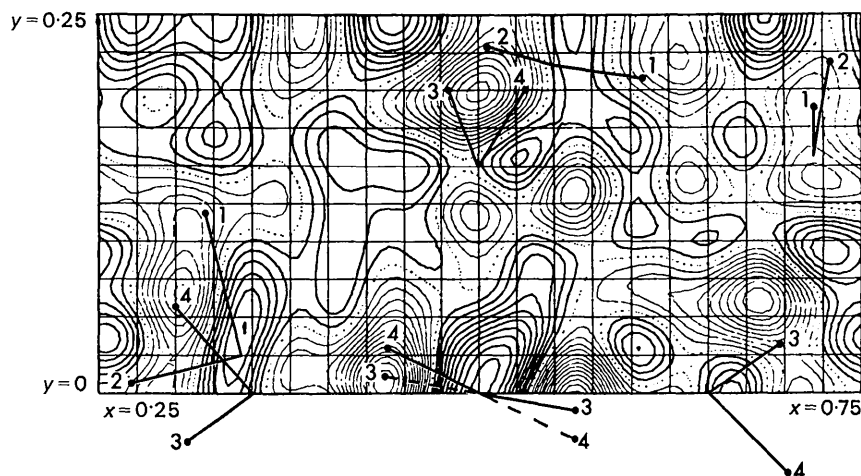


Fig. 1. Neutron diffraction difference Fourier synthesis showing hydrogen atoms only. Contours are at equal arbitrary units. Heavy lines are positive contours, light lines negative and the zero contour is dotted.

Table 4. Observed and calculated structure factors for CsAl(SO₄)₂ · 12H₂O

The column headings are k, 10|F_o|/K, and 10F_c*/K (see text). If |F_o| is negative the minus sign means 'less than'.

Table with 6 columns: h, k, 10|F0|/K, 10Fc*/K, l, and another l. It contains multiple rows of data for various hkl reflections, with values for observed and calculated structure factors.

data that are quite satisfactory and, unless accurate thermal parameters are of particular interest, we prefer this method. More reflections are observed and thus the standard deviations of atomic positions are smaller. Also, the fixed crystal method is much faster. It takes perhaps one-fifth the time required by the scan method, although if a fully automated system is used this time differential may be unimportant.

Table 4 gives the observed and calculated structure factors for the fixed crystal data. A similar table for the 2θ scan data can be obtained from the authors.

Refinement of the structure with neutron diffraction data

Structure factors were calculated by using the parameters obtained from the X-ray analysis but without any hydrogen contribution. The structure factors were initially scaled so that ΣF_o=ΣF_c and a difference Fourier synthesis was calculated. Approximate hydrogen positions were obtained and a least-squares refinement minimizing Σw(F_o-KF_c)² was calculated where w= w_E/(F_o+0.02F_o²), the symbols having the same meanings as given above. Parameters in this refinement were isotropic temperature factors for each crystallographically different atom, the scale factor and coordinates of the hydrogen atoms. The sulfur and oxygen atoms were not allowed to move. Table 5 gives the final parameters, and Table 6 gives the observed and calculated structure factors. The R indices are in Table 2. Fig. 1 is a difference Fourier synthesis showing hydrogen atoms only.

Table 5. Least-squares parameters for CsAl(SO₄)₂ · 12H₂O from neutron diffraction data

Equivalent isotropic thermal parameters from X-ray data are in parenthesis.

Table with 5 columns: Atom, B, x, y, z. It lists parameters for atoms H(1), H(2), H(3), H(4), Cs, Al, S, O_s(1), O_s(2), O_w(1), O_w(2).

Discussion

The interatomic distances and bond angles are given in Table 7. The errors were computed by using the entire variance-covariance matrix and include the trivial effect of lattice constant error. However, the errors in distances and angles involving hydrogen assume no error in the heavy atom positions. The anisotropic thermal parameters were transformed to obtain the thermal ellipsoid parameters which are given in Table 8.

The isotropic thermal parameters computed from the neutron data, except those for cesium and alumi-

Table 7. *Interatomic distances and angles in CsAl(SO₄)₂ · 12H₂O from fixed crystal and neutron diffraction data*

Standard deviations, in parentheses, apply to the rightmost digit			
Distances corrected for thermal motion are in parentheses			
Al-6O _w (2)	1.882 (5) Å		
Cs-6O _w (1)	3.367 (5)		
-6O _s (2)	3.454 (5)		
The sulfate group			
S-O _s (1)	1.479 (9)	< O _s (1)-S-O _s (2)	109.9 (2)°
	(1.496)	< O _s (2)-S-O _s (2)	109.0 (2)
S-3O _s (2)	1.473 (5)	< O _s (2)-O _s (2)-O _s (2)	60.0
	(1.485)	< O _s (2)-O _s (2)-O _s (1)	60.2 (1)
O _s (1)-3O _s (2)	2.417 (8)	< O _s (2)-O _s (1)-O _s (2)	59.5 (3)
O _s (2)-2O _s (2)	2.399 (8)		
Water molecules			
O _w (1)-H(1)	0.941 (26)	< H(1)-O _w (1)-H(2)	107.6 (24)
	(0.955)		
O _w (1)-H(2)	0.963 (29)		
	(0.968)		
O _w (2)-H(3)	0.974 (26)	< H(3)-O _w (1)-H(4)	107.2 (20)
	(0.974)		
O _w (2)-H(4)	0.984 (36)		
	(0.995)		
Hydrogen bonds			
O _s (1)-3O _w (1)	2.822 (6)	< O _s (1)-H(1)-O _w (1)	165 (2)
O _s (1)-3H(1)	1.902 (25)		
O _s (2)-O _w (1)	2.766 (7)	< O _s (2)-H(2)-O _w (1)	171 (3)
O _s (2)-H(2)	1.811 (29)		
O _s (2)-O _w (2)	2.648 (7)	< O _s (2)-H(3)-O _w (2)	166 (3)
O _s (2)-H(3)	1.692 (27)		
O _w (1)-O _w (2)	2.615 (7)	< O _w (1)-H(4)-O _w (2)	163 (3)
O _w (1)-H(4)	1.657 (33)		
Miscellaneous angles			
Al-O _w (2)-H(3)	121 (2)°	< H(1)-O _s (1)-H(1)	102 (1)
Al-O _w (2)-H(4)	130 (2)	< H(1)-O _s (1)-S	116 (1)
H(3)-O _w (2)-H(4)	107 (2)		
H(1)-O _w (1)-H(4)	109 (2)	< H(2)-O _s (2)-H(3)	101 (1)
H(2)-O _w (1)-H(4)	116 (2)	< S-O _s (2)-H(2)	119 (1)
H(1)-O _w (1)-H(2)	108 (3)	< S-O _s (2)-H(3)	131 (1)

Table 8. *Thermal ellipsoids in CsAl(SO₄)₂ · 12H₂O, fixed crystal data*

Atom	r.m.s. amplitude	B _i	Direction angles relative to crystal axes		
			α	β	γ
Cs	0.162 ± 3 Å	2.08 ± 7 Å ²	54.7°	54.7°	54.7°
	0.191 ± 2	2.88 ± 5	—	—	—
	0.191 ± 2	2.88 ± 5	—	—	—
Al	0.145 ± 11	1.66 ± 25	54.7	54.7	54.7
	0.122 ± 7	1.17 ± 14	—	—	—
	0.122 ± 7	1.17 ± 14	—	—	—
S	0.146 ± 7	1.68 ± 15	54.7	54.7	54.7
	0.120 ± 5	1.14 ± 9	—	—	—
	0.120 ± 5	1.14 ± 9	—	—	—
O _s (1)	0.119 ± 22	1.11 ± 42	54.7	54.7	54.7
	0.199 ± 10	3.13 ± 32	—	—	—
	0.199 ± 10	3.13 ± 32	—	—	—
O _s (2)	0.214 ± 9	3.63 ± 29	33 ± 5	72 ± 7	64 ± 4
	0.155 ± 10	1.91 ± 25	108 ± 9	19 ± 7	95 ± 13
	0.118 ± 12	1.10 ± 23	116 ± 6	93 ± 13	26 ± 5
O _w (1)	0.150 ± 10	1.78 ± 25	28 ± 14	89 ± 28	118 ± 13
	0.168 ± 9	2.22 ± 25	96 ± 28	11 ± 28	99 ± 28
	0.183 ± 9	2.66 ± 27	63 ± 13	79 ± 27	30 ± 14
O _w (2)	0.120 ± 11	1.15 ± 21	16 ± 9	98 ± 14	104 ± 8
	0.160 ± 9	2.02 ± 23	83 ± 15	8 ± 14	94 ± 22
	0.178 ± 9	2.51 ± 26	76 ± 8	88 ± 22	14 ± 10

Table 9. Translation and torsional vibration matrices for the sulfate group relative to the unit cell axes

$$\tau = \begin{pmatrix} 0.0160 & 0.0015 & 0.0015 \\ & 0.0160 & 0.0015 \\ & & 0.0160 \end{pmatrix} \text{ \AA}^2$$

$$\omega = \begin{pmatrix} 29.2 & -8.8 & -8.8 \\ & 29.2 & -8.8 \\ & & 29.2 \end{pmatrix} \text{ deg}^2$$

$$\sigma\tau = \begin{pmatrix} 0.0020 & 0.0017 & 0.0017 \\ & 0.0020 & 0.0017 \\ & & 0.0020 \end{pmatrix} \text{ \AA}^2$$

$$\sigma\omega = \begin{pmatrix} 5.1 & 3.9 & 3.9 \\ & 5.1 & 3.9 \\ & & 5.1 \end{pmatrix} \text{ deg}^2$$

atoms and the sulfur atom thus surrounds O(1). H(2) on $O_w(1)$ and H(3) on $O_w(2)$ are bonded to $O_s(2)$. These hydrogen atoms and the sulfur atom are nearly coplanar with $O_s(2)$. H(4) on $O_w(2)$ is bonded to $O_w(1)$. The angles involving H(1), H(2) and H(4) about $O_w(1)$ are nearly tetrahedral.

Hamilton (1962) has given an empirical relation between O-O hydrogen bond lengths and O-H bond lengths or O-H---O angles. His empirical functions and the present experimental values are plotted in Fig. 2. The present O-H distances are systematically smaller than predicted but the differences are within the standard deviation of the measurement and the standard deviation of the prediction of the empirical function. There is no systematic trend in the O-H---O angles, all of which are nonlinear, but again the differences between the present experimental values and the empirical curve are not significant.

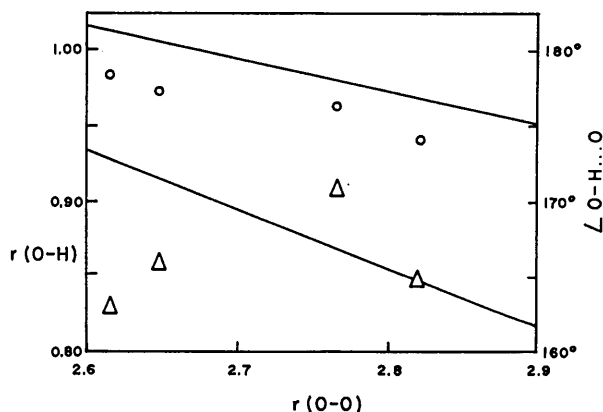


Fig. 2. Plot of O-H distance vs O-O, the hydrogen bond distance (circles) and O-H---O angle vs O-O distance (triangles). The upper line is the empirical function for O-H distance and the lower line is the empirical function for O-H---O angle (Hamilton, 1962).

Although the present results are of considerably greater accuracy than those of Lipson (1935), the maximum shift in atomic position is only 0.04 Å.

Except as noted, all calculations were performed on an IBM 7094 computer using codes written by Larson, Roof & Cromer (1963, 1964, 1965). Fig. 1 was drawn by an SC-4020 microfilm plotter.

References

- BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142.
 CROMER, D. T., LARSON, A. C. & ROOF, R. B., JR. (1960). *Acta Cryst.* **13**, 913.
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.
 CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 754.
 DIXON, W. J. & MASSEY, F. J., JR. (1957). *Introduction to Statistical Analysis* p.405, Table 8b(2). New York: McGraw-Hill.
 EVANS, H. T. (1953). *Rev. Sci. Instrum.* **24**, 156.
 EVANS, H. T. (1961). *Acta Cryst.* **14**, 689.
 HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609.
 HAMILTON, W. C. (1962). *Ann. Rev. Phys. Chem.* **13**, 28. *International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
 JONA, F. & SHIRANE, G. (1962). *Ferroelectric Crystals*. International Series of Monographs on Solid State Physics, Vol. I., 335. Oxford: Pergamon Press.
 LARSON, A. C. (1965). *Acta Cryst.* **18**, 717.
 LARSON, A. C., ROOF, R. B., JR. & CROMER, D. T. (1963, 1964, 1965) Los Alamos Scientific Laboratory Reports, LA-2974, 3043, 3233, 3198, 3259, 3309, 3310.
 LIPSON, H. (1935). *Proc. Roy. Soc.* **A151**, 347.
 LIPSON, H. & BEEVERS, C. A. (1935). *Proc. Roy. Soc.* **A148**, 664.
 OKAYA, Y., AHMED, M. S., PEPINSKY, R. & VAND, V. (1951). *Z. Kristallogr.* **109**, 367.
 TRUEBLOOD, K. N. (1962). *I.U.Cr. World List of Computer Programs*. 1st ed. Groningen.
 ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139.