American Mineralogist, Volume 58, pages 218-223, 1973

A Reinvestigation of the Epidote Structure: Confirmation of the Iron Location

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Abstract

The crystal structures of two epidotes with compositions $Ca_2Al_{2.16}Fe_{0.84}Si_3O_{13}H$ and $Ca_2Al_{2.60}Fe_{0.40}Si_3O_{13}H$ have been refined with the aid of single-crystal X-ray diffractometer data. The final *R* values, based on four thousand structure amplitudes, are 0.026 and 0.031 respectively. The estimated standard deviations of the interatomic distances and angles are of the order of 0.0015 Å and 0.05°. These two structures together with the structure of clinozoisite ($Ca_2Al_{2.96}Fe_{0.04}Si_3O_{13}H$) provide geometric information over a wide range of iron substitution. The average distances in corresponding octahedral sites show clearly that the iron is substituted at *M*(3), in agreement with spectroscopic evidence. Further structural differences can be understood, to some extent, from the different size of the *M*(3) sites and the mobility of the structure as shown by thermal motion. An attempt to determine the hydrogen atom parameters was unsatisfactory. However, the results of bond-valence calculations are consistent with the hydrogen position as originally assumed.

Introduction

The isomorphous minerals of the clinozoisite-epidote-piemontite group have the general composition $Ca_2Al_{3-p}M_pSi_3O_{13}$ H, where *M* denotes Fe and/or Mn. Clinozoisite does not contain more than 0.3 Fe atoms per formula unit but in the other minerals up to 1.2 Fe atoms may be present (Strens, 1972, private communication). The name iron epidote will be used for samples having only Fe as a substituent.

The structure of epidote proposed by Ito (1950) was confirmed by Belov and Rumanova (1953) and Ito, Morimoto, and Sadanaga (1954), by X-ray analysis of samples having compositions close to $Ca_2Al_2FeSi_3O_{13}H$. The structure has three types of octahedral sites into which the trivalent cations can be placed. The Al^{3+} ions were assigned to the centrosymmetric *M*(1) and *M*(2) sites and the Fe^{3+} ions to the asymmetric *M*(3) site. In view of the relatively low accuracy of this earlier work, the size differences between the *M*(1), *M*(2) and *M*(3) sites are not significant and there remains some doubt about the *M*(3) assignment. Spectroscopic measurements of iron epidotes, with *p* less than 1.0 [optical absorption spectra (Burns and Strens, 1967) and Mössbauer spectra (Bancroft, Maddock, and Burns, 1967)] have subsequently shown that the amount of Fe^{3+} at the *M*(1) and *M*(2) sites cannot be large.

The increased accuracy now attainable by X-ray methods should allow the size differences between the three sites to be exploited in an attempt to establish the details of the Fe^{3+} assignment. In 1968 Dollase published the X-ray structure of an iron epidote with $p = 0.04$ (clinozoisite). The present work describes the structures of iron epidotes with *p* values of 0.4 and 0.8. With these three structures it is possible to compare geometric details over a large range of iron substitution. In a publication that appeared during the course of this work Dollase (1971) discussed this subject. Our results are not as extensive as those of Dollase, but they are more accurate and it has been possible to show that the iron substitution is at the *M*(3) site.

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Experimental

Epidote crystals were chosen from two samples originating from different localities in the Tyrol, Austria. The compositions given in Table 1 were determined by microprobe analysis. The sample with the higher amount of iron will be labelled HEP and that with the lower amount, LEP. Weight percentages of the oxides of the constituent elements are respectively 13.87 and 7.00 Fe_2O_3, 23.32 and 24.70 CaO, 37.96 and 39.36 SiO_2 and 22.91 and 29.32 Al_2O_3. Mg, Ti and Mn could not be detected.

The X-ray measurements were carried out on a pale-green sphere of HEP and a pinkish fragment of LEP. The crystals were mounted in random orientations on two different computer-controlled four-circle diffractometers using graphite-monochromatized molybdenum radiation. Least-squares procedures were used to obtain cell parameters (see Table 1) from angular measurements of 24 reflections with 2θ greater than 70°. The intensities of all independent reflections with 2θ less than 90° were collected with the $\theta/2\theta$-scan technique and background measurements taken at the ends of each scan range. The systematically absent reflections ($0k0$ for $k = 2n + 1$) are consistent with the space group $P\ 2_1/m$.

Absorption corrections for a sphere were applied to the HEP data, and for the LEP fragment the corrections were calculated with the aid of Gaussian quadrature (Gabe and O'Byrne, 1970). Structure amplitudes F_o and associated variances $\sigma^2(F_o)$ were derived as described by Gabe, Glusker, Minkin, and Patterson (1967). The arbitrary significance level of 5 percent [$I \leq 1.65\ \sigma(I)$ where I is the net intensity] was chosen as the criterion for unobserved reflections.

Both structures were refined by difference Fourier- and full-matrix least-squares methods. The quantity $\Sigma[1/\sigma^2(F_o)\ (F_o - k\ F_c)^2]$ was minimized, where F_c is the modulus of the calculated structure amplitude and k is a scale factor.

HEP Refinement. Refinement was carried out with programs of the XRAY system (Stewart, Kundell, and Baldwin, 1970), using the scattering factors of Doyle and Turner (1968) for the heavier atoms and the one of Stewart, Davidson, and Simpson (1965) for hydrogen. The values for neutral atoms were employed in all cases except for the $M(3)$ site where 0.9 times the scattering factor of Fe^{3+} was used. A peak in a difference map with a height of 0.6 eÅ^{-3} at a distance of 0.95 Å from O(10) was chosen as the location of the hydrogen atom. This is in agreement with Ito, Morimoto, and Sadanaga (1954).

TABLE 1. Crystal Data of Three Iron Epidotes, $Ca_2Al_{3-p}Fe_pSi_3O_{13}H$.* Space Group: $P2_1/m$, $Z = 2$, $\lambda(MoK\alpha_1) = 0.70926$ Å)

	HEP	LEP	Clinozoisite**
p	0.84	0.40	0.04
a (Å)	8.8877(14)	8.8802(10)	8.879(5)
b	5.6275(8)	5.6043(8)	5.583(5)
c	10.1517(12)	10.1511(13)	10.155(6)
β (°)	115.383(14)	115.455(12)	115.50(5)
ρ_{calc} (g cm^{-3})	3.464	3.391	
μ (cm^{-1})	31.8	25.5	
crystal size (cm)	0.033	0.021x0.018x0.014	
number of reflections:			
observed	3889	3738	
unobserved	169	297	

* *The numbers in parentheses are estimated standard deviations in terms of the last decimal.*

** *For reasons of comparison, the lattice parameters of clinozoisite (Dollase, 1968) are given.*

The H atom was included in the final cycles of the refinement but its parameters ($B = 1.0$ Å^2) were not varied. Regions of approximately -2 eÅ^{-3} at the cationic positions in the difference map diminished after an extinction correction of the form, F_o (corr) $= F_o(0.00133\ F_o + 0.97)$, was applied. Further efforts to reduce these negative regions by refinement of the cationic-site occupancies and by use of cationic scattering factors were unsuccessful. The final value of the conventional R index is 0.026 and the final parameter shifts are less than one quarter of the corresponding standard deviations.

LEP Refinement. In this refinement the LASL71 (Larson, Cromer, and Roof, 1965) system was used. The atomic scattering factors mentioned previously were expressed in the analytic form of Cromer and Waber (1965). The scattering function $(1 - q)f(\text{Al}) + q\ f(\text{Fe})$ was used for the composite atom at $M(3)$, where $f(\text{Al})$ and $f(\text{Fe})$ are the scattering factors of Al and Fe and q is a parameter of the refinement. The final value of q was 0.377(1) which is in agreement with the p value of 0.40. Anomalous dispersion terms were taken from Cromer and Liberman (1970). The extinction parameter g was included in the refinement as proposed by Larson and Cromer (1971) and converged to a value of 9.3(4) $\times 10^{-6}$.

In the later stages of the refinement a difference map showed that the only peak of any significance was one of 1.0 eÅ^{-3} at a distance of 0.85 Å from O(10). This was assumed to be the hydrogen atom and parameters were assigned accordingly. However, further refinement led to an unsatisfactory B value of 8.3(8) Å^2 and a distance of 0.88(3) Å to O(10). The final R index is 0.031 and the parameter shifts are less than one half of the standard deviations.

The final positional parameters of HEP and LEP as listed in Table 2 are similar to previously determined values for epidote structures. Standard deviations are of the order of 0.0015 Å for the interatomic distances and of 0.05° for the associated angles. The temperature parameters are given in Table 3 and it can be seen that the U_{11} and U_{22} values for HEP are in general somewhat larger than those for LEP. This effect, however, is probably of no significance.

In the final lists of structure amplitudes[2] it was noted that for the smallest F_o values F_c is systematically too small. This discrepancy is probably due to multiple diffraction, increasing the intensities of weak reflections. The effect will only be apparent as an enhancement of these weak reflections and even then only in cases where the temperature factor is low because such a diffraction phenomenon will be associated with approximately twice the temperature factor (Post, 1972).

Discussion

The epidote structure is well known and there does not seem to be any reason to redescribe it. There are, however, several points of interest about the present analysis which should be commented upon. The structural information for clinozoisite which is used extensively is taken from Dollase (1968). The *p* value of 0.04 (Dollase, 1971) places the structure in an almost ideal position as the end member of the series, HEP, LEP, clinozoisite. In the subsequent discussion it is helpful to refer continually to Table 4, where interatomic distances are compared, and to Figure 1, which gives the projection of the structure on (010).

1. The entry for *M*(3) in Table 4 shows a very

TABLE 2. Positional Coordinates of the Atoms in HEP and LEP in Fractions of the Cell Edges

	HEP	LEP	HEP	LEP	HEP	LEP
	x		*y*		*z*	
Ca(1)	0.75715(4)	0.75972(4)	3/4		0.15156(3)	0.15373(3)
Ca(2)	0.60486(4)	0.60660(4)	3/4		0.42399(4)	0.42363(3)
Si(1)	0.33959(5)	0.33880(5)	3/4		0.04766(5)	0.04804(4)
Si(2)	0.68429(5)	0.68054(5)	1/4		0.27454(5)	0.27507(4)
Si(3)	0.18393(5)	0.18304(5)	3/4		0.31837(5)	0.31686(4)
Al(1)	0		0		0	
Al(2)	0		0		1/2	
M(3)	0.29386(3)	0.29085(4)	1/4		0.22419(3)	0.22415(3)
O(1)	0.23425(9)	0.23427(8)	0.99441(14)	0.99603(13)	0.04150(9)	0.04377(7)
O(2)	0.30396(10)	0.30189(8)	0.98255(15)	0.98442(13)	0.35529(8)	0.35306(7)
O(3)	0.79503(10)	0.79037(8)	0.01341(15)	0.01259(13)	0.33935(9)	0.34346(7)
O(4)	0.05292(13)	0.05360(12)	1/4		0.12948(12)	0.13082(11)
O(5)	0.04158(13)	0.04009(12)	3/4		0.14534(12)	0.14389(11)
O(6)	0.06715(14)	0.06242(12)	3/4		0.40688(13)	0.40295(11)
O(7)	0.51486(14)	0.51600(12)	3/4		0.18053(13)	0.17858(11)
O(8)	0.52547(16)	0.51639(13)	1/4		0.30809(15)	0.30150(12)
O(9)	0.62769(17)	0.63540(14)	1/4		0.09895(14)	0.10181(12)
O(10)	0.08228(14)	0.07798(13)	1/4		0.42852(12)	0.42501(11)
H	0.043[a]	0.079(3)	1/4		0.325[a]	0.338(3)

[a] *Not refined.*

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[2] The final lists of structure amplitudes of HEP and LEP may be ordered as NAPS Document Number 02039. The present address is Microfiche Publications, Division of Microfiche Systems Corporation, 305 East 46th Street, New York, N. Y. 10017. Please remit in advance $1.50 for microfiche or $5.00 for photocopies. Please check the latest issue of this journal for the current address and prices.

TABLE 3. Temperature Parameters in Å^2($\times$ 10^5) for the Atoms in HEP and LEP*

	HEP	LEP	HEP	LEP	HEP	LEP	HEP	LEP	HEP	LEP	HEP	LEP
	U_{11}		U_{22}		U_{33}		U_{12}		U_{13}		U_{23}	
Ca(1)	1115(12)	1127(13)	770(11)	944(14)	855(11)	885(12)	0		665(9)	629(10)	0	
Ca(2)	993(12)	1032(13)	1667(15)	1609(16)	660(11)	721(12)	0		278(9)	333(10)	0	
Si(1)	434(14)	485(16)	411(15)	528(18)	490(14)	471(16)	0		186(12)	173(13)	0	
Si(2)	522(15)	595(17)	436(15)	560(18)	541(15)	502(17)	0		224(12)	202(14)	0	
Si(3)	399(14)	476(16)	483(15)	611(18)	468(14)	468(16)	0		204(12)	214(13)	0	
Al(1)	427(15)	557(17)	331(16)	471(19)	520(15)	581(17)	-234(13)	-48(15)	177(12)	197(14)	42(13)	-31(15)
Al(2)	459(15)	549(18)	390(17)	464(19)	618(16)	599(17)	0(13)	28(15)	204(13)	181(15)	-5(14)	17(15)
M(3)	482(8)	472(13)	643(9)	669(15)	625(9)	574(13)	0		182(7)	162(10)	0	
O(1)	591(24)	683(28)	536(27)	662(32)	1148(29)	1011(31)	85(22)	67(26)	403(22)	375(24)	48(23)	79(26)
O(2)	830(26)	838(29)	746(29)	926(34)	820(27)	728(29)	-293(23)	-268(26)	381(22)	390(24)	-82(23)	-133(27)
O(3)	726(26)	675(28)	566(28)	611(32)	1040(29)	1011(31)	55(23)	75(26)	-13(22)	-49(24)	-6(24)	-51(27)
O(4)	664(36)	691(40)	501(37)	620(45)	562(35)	430(39)	0		220(30)	222(33)	0	
O(5)	606(36)	634(40)	574(38)	609(44)	532(35)	407(38)	0		146(29)	186(33)	0	
O(6)	858(39)	792(42)	581(39)	604(45)	963(40)	734(43)	0		633(33)	511(35)	0	
O(7)	636(38)	640(42)	1055(46)	995(50)	816(40)	789(45)	0		67(32)	141(36)	0	
O(8)	1030(44)	1241(51)	1595(56)	1338(57)	1613(52)	1708(56)	0		984(41)	1108(45)	0	
O(9)	1745(55)	2130(63)	2118(65)	2206(70)	782(43)	855(50)	0		753(42)	944(47)	0	
O(10)	805(38)	916(44)	528(38)	609(46)	882(39)	699(43)	0		502(40)	544(36)	0	

* *The Debye-Waller factor is defined as* $\exp(-2\pi^2 \Sigma_{i,j} h_i h_j a_i^* a_j^* U_{ij})$.

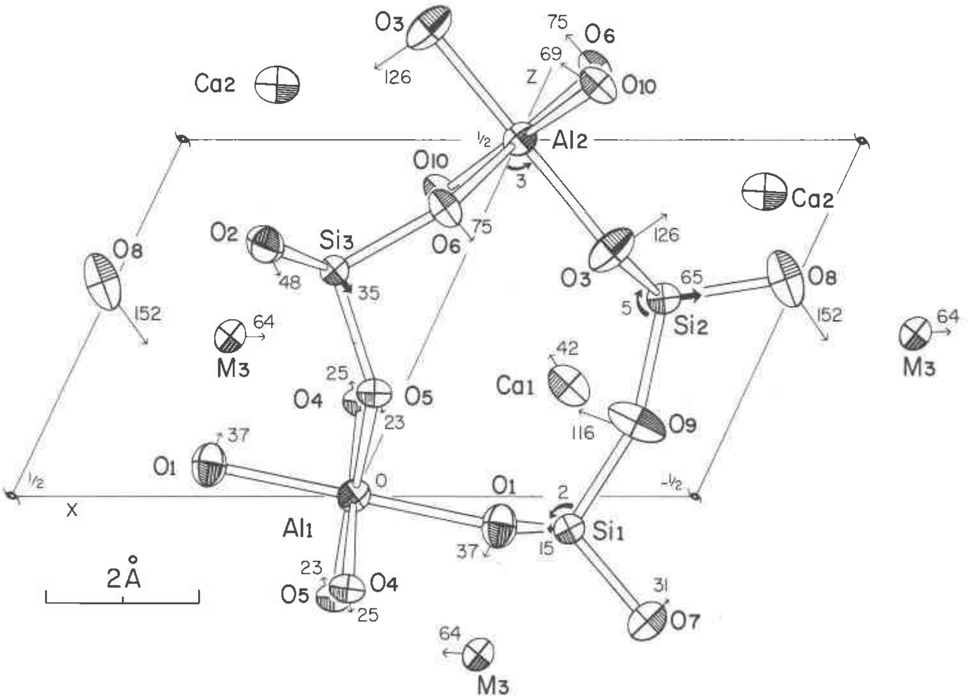

FIG. 1. ORTEP projection of the LEP structure on the (010) plane. The vibrational ellipsoids correspond to 95 percent probability density. The atom pairs O(1), O(3) and O(2) belonging to the Si(1), Si(2) and Si(3) tetrahedra are projected above each other. The magnitudes of the rotations and translations are shown with the corresponding arrows in degrees and Å units $\times$ 10^{-3}. The lengths of the translational arrows are on four times the indicated scale.

TABLE 4. Interatomic Distances (d) for HEP, LEP, and Clinozoisite* and Difference $\Delta d = d_{\mathrm{LEP}} - d_{\mathrm{HEP}}$

		d_{HEP} (Å)	d_{LEP} (Å)	Δd (10^{-3}Å)	d_{clin}** (Å)
Ca(1)-O(1)	x2	2.4585(10)	2.4780(9)	20	2.4909(37)
-O(3)	x2	2.3227(10)	2.3449(8)	22	2.3682(36)
-O(5)		2.5556(14)	2.5343(13)	-21	2.5224(54)
-O(6)		2.8612(12)	2.7893(10)	-72	2.7448(41)
-O(7)		2.2949(15)	2.2841(13)	-11	2.2834(56)
-O(9)	x2	2.9999(6)	2.9746(6)	-25	2.9524(29)
Average		2.5860	2.5781		2.5748
Ca(2)-O(2)	x2	2.7842(10)	2.8097(9)	26	2.8185(35)
-O(2)***	x2	2.5270(9)	2.5359(8)	9	2.5428(34)
-O(3)	x2	2.6528(11)	2.5754(9)	-77	2.5321(38)
-O(7)		2.2480(14)	2.2616(12)	14	2.2672(52)
-O(8)	x2	3.0146(6)	3.0294(6)	15	3.0445(29)
-O(10)		2.5307(12)	2.5509(11)	20	2.5746(45)
Average		2.6736	2.6713		2.6718
Si(1)-O(1)	x2	1.6499(9)	1.6523(8)	2	1.6525(36)
-O(7)		1.5635(11)	1.5619(9)	-2	1.5661(40)
-O(9)		1.6343(18)	1.6327(15)	-2	1.6270(62)
Average		1.6244	1.6248		1.6245
Si(2)-O(3)	x2	1.6184(9)	1.6190(7)	1	1.6198(33)
-O(8)		1.5876(18)	1.5916(15)	4	1.5934(56)
-O(9)		1.6315(15)	1.6272(13)	-4	1.6267(57)
Average		1.6140	1.6142		1.6149
Si(3)-O(2)	x2	1.6274(9)	1.6253(8)	-2	1.6287(34)
-O(5)		1.6676(11)	1.6669(10)	-1	1.6622(38)
-O(6)		1.6383(16)	1.6479(14)	10	1.6566(56)
Average		1.6402	1.6414		1.6441
Al(1)-O(1)	x2	1.9393(9)	1.9316(8)	-8	1.9304(30)
-O(4)	x2	1.8434(8)	1.8466(7)	3	1.8505(27)
-O(5)	x2	1.9559(9)	1.9433(8)	-13	1.9363(30)
Average		1.9129	1.9072		1.9057
Al(2)-O(3)	x2	1.8539(8)	1.8582(7)	4	1.8589(26)
-O(6)	x2	1.9269(11)	1.9262(9)	-1	1.9228(36)
-O(10)	x2	1.8696(10)	1.8642(11)	-5	1.8519(35)
Average		1.8835	1.8829		1.8779
M(3) -O(1)	x2	2.2241(9)	2.2000(8)	-24	2.1840(37)
-O(2)	x2	1.9855(9)	1.9563(8)	-29	1.9264(37)
-O(4)		1.9352(11)	1.9027(11)	-33	1.8614(45)
-O(8)		1.8600(14)	1.8100(12)	-50	1.7811(46)
Average		2.0357	2.0042		1.9772
O(10)-H		0.95	0.88(3)		0.77(8)

*Only those interatomic distances are quoted which are less than the $L_{\max}$ values (Donnay and Allmann, 1970) of the corresponding cations.

**Calculated from the parameters and estimated standard deviations of Dollase (1968).

***O(2) at: $1-x$, $y-\frac{1}{2}$, $1-z$

marked and consistent shrinkage of this site as the amount of iron is reduced. The average cation to anion distances for the Al(1), Al(2) and $M(3)$ sites of LEP are 0.006, 0.001, and 0.032 Å smaller than in HEP, and for clinozoisite they are 0.002, 0.005 and 0.027 Å smaller than in LEP. This may be considered as a geometric confirmation of the Fe^{3+} location. If a composite radius for the ion at $M(3)$ is calculated on the basis of the values of 0.645 and 0.530 Å for the radii of Fe^{3+} and Al^{3+} (Shannon and Prewitt, 1969) the shrinkages would be 0.051 and 0.041 Å, which agree reasonably well with the values found.

2. The values of the average interatomic distances, $\bar{d}$, of the $M(3)$ octahedra in HEP, LEP and clinozoisite satisfy the equation, $\bar{d} = (0.073p + 1.975)$ Å, where p is the atomic fraction of Fe^{3+}, as determined by microprobe analysis. For the three structures the deviation from equality is much less than the standard deviation of any of the distances used to find the average. This linear relation is significantly different from the one given by Dollase (1971, Fig. 3) as a straight line. However, it is difficult to make a comparison because the epidotes described here have only iron as a substituent.

3. The epidote structure is conveniently described as layers of Si and Al polyhedra, parallel to the bc plane, with Ca and $M(3)$ ions in the spaces between the layers. The layers consist of buckled nets of 5 membered rings, which are themselves made up of 3 Si tetrahedra and 2 Al octahedra. Any study of this type provides the opportunity to examine the structural changes produced by altering the substitution at a particular site. In this case, the geometric differences in the structure must be related to changes in the iron substitution at $M(3)$, and it is possible to explain these differences, to some extent, on this basis.

Figure 1 is an ORTEP (Johnson, 1965) plot of the structure of LEP, showing the Si/Al ring as the main feature. The figure also shows the main translational and rotational changes which occur between HEP and clinozoïsite. In all cases LEP lies between the two extremes. Thin arrows show the relative individual atomic translations projected onto the (010) plane, and thick curved arrows show the mean translations and rotations in the (010) plane, of the Si(1), Si(2), Si(3) and Al(2) polyhedra, considered as rigid bodies (see Δd column, Table 4).

Five of the six $M(3)$-O distances involve oxygen

TABLE 5. Valence Sums of the Oxygen Atoms in HEP and LEP in Valence Units*

	HEP	LEP
O(1)	1.92	1.86
O(2)	2.03	2.02
O(3)	2.08	2.08
O(4)	1.90	1.89
O(4)**	2.02	2.02
O(5)	2.05	2.08
O(6)	2.02	2.03
O(7)	1.90	1.92
O(8)	2.07	2.16
O(9)	2.12	2.14
O(10)	1.30	1.30
O(10)**	1.17	1.17

* *Expected values are 2.00 for O^{2-} and 1.00 for OH^{-}.*

** *Values corrected for the hydrogen bond.*

atoms associated with 5 membered rings of the same layer. The remaining distance is to O(8) which is part of the Si(2) tetrahedron. It can be seen, from the figure and Table 3, that this tetrahedron is the least rigid part of the structure. Therefore, as the size of the *M*(3) ion is decreased, firstly *M*(3) [and O(8)] moves towards the layer and secondly O(8) must move towards *M*(3). Thus it is reasonable that O(8) shows the largest shift. The Si(2) tetrahedron has the largest mean rotation and translation, which produces smaller opposite rotations in the adjacent Al(2) and Si(1) polyhedra. The mean translation of the Si(3) tetrahedron is consistent with the rotation of the Al(2) octahedron, and the rotation of the Al(1) octahedron caused by the rotation of the Si(1) tetrahedron. With this description it is possible to account for all the large Ca-O distance changes. Notably the shortening of the Ca(1)-O(6), Ca(1)-O(9) and Ca(2)-O(3) and the lengthening of Ca(2)-O(10) can be seen on the figure.

4. In neither HEP nor LEP has the position of the hydrogen atom been established beyond doubt. The assumption that the hydrogen is bonded to O(10) can be justified by bond-valence calculations according to Donnay and Allmann (1970). In Table 5 the valence sums for the oxygen atoms are given; for both structures the sum for O(10) is close to the expected value of 1.00 for a hydroxyl group. This is perhaps the strongest evidence that the hydrogen is attached to O(10). The O(4)-O(10) distances in the two structures are 2.933(2) and 2.900(2) Å, which are reasonable for a hydrogen bond. If it is assumed that O(4) is the acceptor, the valence sums are improved.

Acknowledgments

We wish to thank the Geological Survey of Canada for supplying the HEP sample, which originated from Untersulzbachtal in the Tyrol, and the Royal Ontario Museum for the LEP sample (M15525) from Zillertal. We also wish to thank Dr. D. C. Harris of the Department of Energy, Mines and Resources, for the microprobe data, and Dr. P. G. Manning of the Department of the Environment for originally suggesting the problem and for helpful discussions during the course of the work. J.C.P. gratefully acknowledges the Canada Council Fellowship and Travel grant.

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Manuscript received, August 28, 1972; accepted for publication, October 2, 1972.