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The Ferric Ion Distribution and Hydrogen Bonding in Epidote: a Neutron Diffraction Study at 15 K

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Abstract

The crystal structure of epidote, $Ca_2Al_{2\cdot2}Fe_{0\cdot8}Si_3O_{13}H$, at 15 K, $M_r = 477\cdot5$, $P2_1/m$, $a = 8\cdot893\,(2)$, $b = 5\cdot630\,(3)$, $c = 10\cdot150\,(2)$ Å, $\beta = 115\cdot36\,(1)^\circ$, $V = 459\cdot2$ Å^3, $Z = 2$, $D_m = 3\cdot482$ g cm^{-3}, $\mu = 0\cdot186$ cm^{-1}, was determined at the Brookhaven National Laboratory High Flux Beam Reactor using a neutron wavelength of 1·15948 (12) Å. 2409 reflections were used in least-squares refinement resulting in a final $R(F^2)$ of 0·0246 and $wR(F^2) = 0\cdot0331$. Anharmonic displacement tensors of up to order four for the H atom were refined. The analysis assigned 0·757 (3) Fe^{3+} ions to the larger octahedral site and 0·015 (3) Fe^{3+} to one of the other octahedral sites. The H atom is uniquely located on the O(10) atom with a bonding distance of 0·975 (1) Å and is involved in a bent hydrogen bond to O(4) [O(10)···O(4) 2·922 (1), H···O(4) 1·964 (1) Å, O(10)–H···O(4) 166·9 (1)°]. The bending of the bond is associated with the electrostatic repulsion from the Fe^{3+} [Fe···H 2·728 (1) Å] and Ca^{2+} ions [Ca(2)···H 3·0043 (14) Å]. The Fe/Al interchange in the octahedral site causes some structural reorganization, primarily a rotation of the Si(2) tetrahedron around its central atom and changes in the hydrogen-bond geometry.

I. Introduction

The epidote group of minerals, a common and complex family of rock-forming silicates, raises unresolved challenges to petrologists, chemists and geophysicists. The group may be represented by the chemical formula

$$Ca_2Al_{3-p}Fe_pSi_3O_{13}H \qquad (0 < p < 1\cdot0).$$

Fe^{3+} ions substitute for Al in this range and the different minerals are commonly referred to as zoisite or clinozoisite (orthorhombic and monoclinic) for low Fe

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content ($p < 0{\cdot}04$) and as epidote for higher degrees of substitution.

Considerable interest has been focused on the preferential location of the Fe atoms in the epidote structures (Dollase, 1971; Gabe, Portheine & Whitlow, 1973; Nozik, Kanepit, Fykin & Makarov, 1979; Carbonin & Molin, 1980). Furthermore, spectroscopic studies by Langer & Raith (1974) indicate a coupling between the hydrogen-bond strength and the Fe concentration. The O—H infrared absorption frequency increases from 3260 to 3370 cm^{-1} with increasing Fe content ($0 < p < 0{\cdot}85$). Changes of stretching frequency of this magnitude are attributed to a decrease in hydrogen-bond strength. To date, the lack of precise structural data on the H atom has prevented a detailed understanding of these observations.

The aim of this study is to provide precise information on the location of the Fe^{3+} ions as well as on the H atom. In order to obtain the most reliable data on the displacements of the atoms, the neutron diffraction study was performed at 15·0 (5) K, where the thermal motion essentially is reduced to zero-point vibrations, allowing the displacement parameters to be analyzed in terms of disorder contributions connected with the Fe/Al interchange. Closely related to this study is a neutron diffraction study at 15 K of the Fe-free orthorhombic form of zoisite (Smith, Pluth, Richardson & Kvick, 1987).

II. Experimental

A pale-green prismatic crystal of epidote (Untersulzbachtal, Salzburg, Austria, University of Chicago Mineral Collection, No. UC640) with composition $(Ca_{1.98}Mn_{0.02})(Fe_{0.81}Al_{2.19})Si_3O_{13}H$ determined by electron microprobe analysis was used for the neutron diffraction data collection at the Brookhaven National Laboratory High Flux Beam Reactor (beam line *H*6). Crystal and experimental data are summarized in Table 1. The crystal was mounted on a four-circle diffractometer with its crystallographic *b* axis approximately parallel to the φ axis and cooled to 15·0 (5) K with a Displex CS-202 (Air Products and Chemicals Inc.) closed-cycle refrigerator. Neutrons of wavelength 1·15948 (12) Å were obtained with a Ge(220) monochromator calibrated by least-squares fit of 32 $\sin^2 2\theta$ values from a standard KBr crystal at 295 K [$a_0 = 6{\cdot}6000\,(1)$ Å]. The cell dimensions at 15 K for epidote were obtained by least-squares fit of 31 $\sin^2 2\theta$ values ($39 < 2\theta < 60°$).

Table 1. *Crystal data and experimental details*

Chemical formula	$Ca_2Al_{2.2}Fe_{0.8}Si_3O_{13}H$
Crystal size	1·0 × 1·4 × 2·4 mm
Crystal habit	Prismatic, 8 faces of forms {100}, {010}, {001}, {101}, {201} and {111} Long direction along the *b* axis
Range of transmission values	0·970–0·984
Wavelength	1·15948 (12) Å, Ge(220) monochromator
Max. $(\sin\theta)/\lambda$	0·692 Å^{-1}
Number of reflections	2625 (recorded), 2409 (used in LS refinements)
Number of parameters varied	132
$R(F^2)$ (%)	2·46
$wR(F^2)$ (%)	3·31
$R(F)$ (%)	2·85
S (goodness of fit)	0·78

2625 reflections ($-12 \leq h \leq 12$, $0 \leq k \leq 7$, $-13 \leq l \leq 13$) out to a maximum $(\sin\theta)/\lambda = 0{\cdot}692$ Å^{-1} were collected using $\omega/2\theta$ step scans [$\Delta 2\theta = 2{\cdot}80°$ for $2\theta < 60°$ and $\Delta 2\theta = (-0{\cdot}5 + 5{\cdot}63\tan\theta)°$ for $60 < 2\theta < 107°$]. The background was taken as five times the first and last tenth of the scans. Lorentz and absorption corrections (8 × 8 × 8 Gaussian grid) were made. Two standard reflections monitored every 50 reflections showed a slight intensity increase, probably due to a small change in extinction, over the course of the data collection. The data were corrected as a function of time *t* (hours) by the averaged scaling function $I = I(\text{obs.}) \times [1 + 0{\cdot}9295 \times 10^{-4} \times t)$.

The least-squares refinements minimizing $\sum w(F_o^2 - F_c^2)^2$ where $w^{-1} = \sigma(F_o^2) + (0{\cdot}02F_o^2) + 0{\cdot}05$ were initiated using the atomic parameters of Nozik *et al.* (1979). Refinements of the occupancy factors for the cation sites [from here on denoted Al(1), Al(2), Fe, Si(1), Si(2), Si(3), Ca(1) and Ca(2)] assuming neutron-scattering lengths according to the atomic notations of the sites only revealed deviations larger than 2σ away from unit occupancy for the Al(1) and Fe sites. All remaining occupancy factors were thus kept fixed to full occupancy in the final LS cycles. The refinements converged at $R(F^2) = 0{\cdot}0246$ with all shifts smaller than $0{\cdot}01\sigma$. 132 parameters were varied in the final cycles including positional and anisotropic displacement parameters, occupancy factors for Al(1) and Fe, one scale factor and six anisotropic extinction factors (type I, Lorentzian mosaicity) (Becker & Coppens, 1974). No averaging of equivalent reflections was done since anisotropic extinction refinement was performed.

Four reflections with extinction corrections larger than 1·3 were given zero weight. The largest absolute residual in the final difference Fourier synthesis corresponded in scattering power to less than 1·8% of an O atom.

Inclusion of displacement tensors up to fourth order (see *International Tables for X-ray Crystallography*, 1974, § 5.2.3) for the H atom in the least-squares refinement did not significantly decrease the *R* factor. $wR(F^2)$ was lowered from 0·0331 to 0·0330 with an increase in the number of parameters from 132 to 147. The displacement tensors were restricted to the point-group symmetry *m* and the values for the third- and fourth-order terms were all smaller than 2σ. The displacement factors refined corresponded to a Gram–Charlier expansion of the probability density function.

Neutron-scattering lengths were taken from Koester, Rauch, Herkens & Schroeder (1981) with the exception of the scattering lengths for Ca, where the value

Table 2. *Positional* ($\times 10^5$), *equivalent isotropic* (Å^2) *and anisotropic thermal parameters* (Å$^2 \times 10^5$)

	x	y	z	B_{eq}	G
Al(1)	0	0	0	0·20 (3)	0·513 (3)
Al(2)	0	0	50000	0·17 (3)	0·500
Fe	29367 (4)	25000	22375 (3)	0·19 (1)	0·422 (1)
Ca(1)	75738 (7)	75000	15180 (6)	0·31 (1)	0·500
Ca(2)	60663 (7)	75000	42524 (6)	0·29 (1)	0·500
Si(1)	33978 (8)	75000	4818 (7)	0·15 (1)	0·500
Si(2)	68397 (8)	25000	27497 (7)	0·20 (1)	0·500
Si(3)	18377 (8)	75000	31840 (7)	0·17 (1)	0·500
O(1)	23435 (4)	−501 (6)	4190 (3)	0·36 (1)	
O(2)	30358 (4)	−1724 (7)	35511 (3)	0·21 (1)	
O(3)	79469 (4)	1316 (6)	34012 (3)	0·40 (1)	
O(4)	5187 (6)	25000	12964 (5)	0·26 (1)	0·500
O(5)	4109 (6)	75000	14531 (5)	0·25 (1)	0·500
O(6)	6675 (6)	75000	40696 (5)	0·29 (1)	0·500
O(7)	51549 (6)	75000	18136 (5)	0·34 (1)	0·500
O(8)	52512 (6)	25000	30915 (6)	0·56 (1)	0·500
O(9)	62775 (6)	25000	9925 (5)	0·51 (1)	0·500
O(10)	8203 (6)	25000	42787 (5)	0·27 (1)	0·500
H	5362 (13)	25000	32379 (10)	1·29 (2)	0·500

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Al(1)	201 (36)	221 (41)	231 (35)	33 (24)	68 (24)	−4 (25)
Al(2)	250 (27)	148 (32)	232 (25)	−8 (25)	67 (22)	3 (25)
Fe	196 (18)	324 (19)	177 (17)	0	46 (12)	0
Ca(1)	423 (23)	421 (25)	407 (22)	0	243 (19)	0
Ca(2)	285 (22)	611 (25)	168 (21)	0	43 (18)	0
Si(1)	239 (25)	167 (26)	142 (23)	0	59 (20)	0
Si(2)	308 (25)	258 (27)	179 (23)	0	84 (20)	0
Si(3)	163 (25)	309 (28)	178 (23)	0	66 (20)	0
O(1)	301 (12)	354 (15)	501 (12)	49 (11)	163 (10)	36 (12)
O(2)	397 (12)	521 (15)	411 (12)	−151 (11)	193 (10)	−88 (11)
O(3)	361 (12)	329 (15)	477 (12)	33 (11)	−85 (10)	8 (12)
O(4)	314 (18)	315 (21)	280 (18)	0	69 (15)	0
O(5)	246 (18)	396 (20)	269 (18)	0	80 (15)	0
O(6)	389 (19)	386 (20)	443 (19)	0	303 (16)	0
O(7)	229 (18)	630 (20)	306 (17)	0	−10 (15)	0
O(8)	742 (21)	727 (22)	987 (20)	0	681 (17)	0
O(9)	790 (21)	908 (22)	330 (18)	0	321 (16)	0
O(10)	403 (19)	285 (20)	397 (20)	0	238 (16)	0
H	2141 (43)	1880 (45)	925 (38)	0	692 (32)	0

The form of the temperature factor is $\exp[-2\pi^2(U_{11}h^2a^{*2}\cdots + 2hkU_{12}a^*b^* + \cdots]$.

4·65 fm from Kvick, Ståhl & Smith (1985) was used. Substitution of Mn for Ca was ignored. All calculations were performed on a VAX computer using programs by Lundgren (1983). The final atomic parameters are given in Table 2.*

III. Discussion

The general features of the epidote structure type are well known (Dollase, 1971; Gabe *et al.*, 1973). In summary the structure may be described as consisting of a single chain of octahedra [Al(1)] cross linked by SiO_4 and Si_2O_7 groups to a second zigzag chain composed of central Al(2) and outer Fe octahedra. The cavities between the chains and cross links are occupied by the Ca atoms. Selected bond distances and angles are given in Table 3.

Table 3. *Interatomic distances* (Å) *and angles* (°)

The number in the first parentheses gives the number of identical bonds. The e.s.d.'s are given in the parentheses after the value.

Al(1)–O(1)	(2) 1·9407 (6)	Al(2)–O(3)	(2) 1·8533 (5)
–O(4)	(2) 1·8454 (7)	–O(6)	(2) 1·9249 (7)
–O(5)	(2) 1·9566 (7)	–O(10)	(2) 1·8726 (7)
Mean	1·9142		1·8836
Fe(Al)–O(1)	(2) 2·2164 (8)	Si(1)–O(1)	(2) 1·6536 (9)
–O(2)	(2) 1·9871 (8)	–O(7)	1·5684 (8)
–O(4)	1·9435 (8)	–O(9)	1·6409 (9)
–O(8)	1·8601 (8)		
Mean	2·0351		1·6291
Si(2)–O(3)	(2) 1·6209 (9)	Si(3)–O(2)	(2) 1·6283 (8)
–O(8)	1·5924 (9)	–O(5)	1·6695 (9)
–O(9)	1·6332 (9)	–O(6)	1·6408 (8)
Mean	1·6169		1·6417
Ca(1)–O(1)	(2) 2·4608 (9)	Ca(2)–O(2)	(2) 2·5193 (9)
–O(3)	(2) 2·3272 (9)	–O(2)	(2) 2·8007 (9)
–O(5)	2·5519 (10)	–O(3)	(2) 2·6412 (9)
–O(6)	2·8590 (10)	–O(7)	2·2508 (9)
–O(7)	2·2957 (9)	–O(8)	(2) 3·0177 (16)
–O(9)	(2) 3·0019 (16)	–O(10)	2·5206 (10)
Mean	2·5874		2·6729
O(10)···O(4)	2·9222 (10)	Fe···H	2·7285 (12)
O(10)–H	0·9753 (10)	Ca(2)···H	3·0043 (14)
H···O(4)	1·9640 (11)		
O(1)–Al(1)–O(4)	86·43 (2)	O(3)–Al(2)–O(6)	89·70 (2)
O(1)–Al(1)–O(5)	89·31 (2)	O(3)–Al(2)–O(10)	88·26 (2)
O(4)–Al(1)–O(5)	84·13 (4)	O(6)–Al(2)–O(10)	84·02 (4)
O(1)–Fe–O(1)	80·75 (4)	O(2)–Fe–O(2)	98·43 (2)
O(1)–Fe–O(2)	89·69 (4)	O(2)–Fe–O(4)	92·96 (2)
O(1)–Fe–O(4)	76·82 (2)	O(2)–Fe–O(8)	88·00 (2)
O(1)–Fe–O(8)	102·08 (2)	O(4)–Fe–O(8)	178·54 (3)
O(1)–Si(1)–O(1)	113·05 (6)	O(3)–Si(2)–O(3)	110·71 (5)
O(1)–Si(1)–O(7)	111·86 (3)	O(3)–Si(2)–O(8)	110·59 (3)
O(1)–Si(1)–O(9)	106·45 (3)	O(3)–Si(2)–O(9)	107·09 (3)
O(7)–Si(1)–O(9)	106·65 (5)	O(8)–Si(2)–O(9)	110·65 (5)
O(2)–Si(3)–O(2)	107·18 (6)	O(10)–H···O(4)	166·9 (1)
O(2)–Si(3)–O(5)	111·64 (3)	H–O(10)–Al(2)	117·38 (4)
O(2)–Si(3)–O(6)	112·40 (3)	H–O(10)–Ca(2)	110·49 (7)
O(5)–Si(3)–O(6)	101·65 (5)	H···O(4)–Al(1)	127·42 (2)
		H···O(4)–Fe	88·58 (4)

Fe *distribution*

The non-stoichiometric Fe content in the epidote system $Ca_2Al_{3-p}Fe_pSi_3O_{13}H$ raises interesting questions about the preferential occupation of the three available octahedral sites by the Fe atom. Neutron diffraction is well suited for a study of partial occupancy by Fe and Al since the neutron-scattering lengths differ by a factor of 2·8 ($b_{Al} = 3{\cdot}449$ and $b_{Fe} = 9{\cdot}54$ fm). The independence of scattering lengths and $(\sin\theta)/\lambda$ allows a precise separation of substitutional and thermal-motion effects. The low-temperature experiment further increases the precision in the obtained atomic parameters.

In this study, by refining the occupancy factors, we conclude that there is no Fe in the Al(2) site and a small amount of Fe in the Al(1) site [1·5 (3)%]. The bulk of the Fe ions is found in the third site, which in this crystal contains 75·7 (3)% Fe and 24·3 (3)% Al. The crystallographically determined chemical formula can thus be expressed as $Ca_2Al_{2\cdot2}Fe_{0\cdot8}Si_3O_{13}H$ in satis-

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* A list of structure factors has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44773 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

factory agreement with the microprobe analysis. Our findings are in essential agreement with the previous crystallographic findings by Nozik *et al.* (1979), Gabe *et al.* (1973), and with spectroscopic studies (Burns & Strens, 1967; Bancroft, Maddock & Burns, 1967) which conclude that very little Fe can be found in the Al(1) and Al(2) sites.

Dollase (1971) compared epidote structures with differing Fe content and concluded that the average metal–oxygen distance in the Fe octahedron increases as a function of Fe content. This can, of course, be rationalized in terms of the different ionic radii for Fe and Al. Shannon & Prewitt (1969) have estimated these radii to be 0·645 and 0·530 Å respectively. In Fig. 1 we illustrate the Fe coordination sphere. The mean coordination distance of 2·0351 Å is considerably longer than the value of 1·9517 Å for the equivalent octahedron in the Fe-free zoisite structure also determined at 15 K (Smith, Pluth, Richardson & Kvick, 1987). In the present structure, the Al(1) and Al(2) octahedra also have considerably smaller mean values (1·9142 and 1·8836 Å, respectively) than the value found for the Fe octahedron. The substitution of Fe for Al gives rise to subtle changes in the structure and the precision of this study makes it possible to follow the reorganization by analysis of the displacement ellipsoids.

The principal axes of the r.m.s. components of displacement listed in Table 4 suggest that some atoms are considerably more affected than others. In particular, large differences in the values of the principal axes are found for atoms O(3), O(8) and O(9), which are the O atoms associated with the Si(2) tetrahedron. The ratio $R3/R1$ for these O atoms is 2·00, 1·91 and 1·94 respectively whereas the ratio is only 1·35 for the central Si(2) atoms. The smallest values are generally about 0·04–0·05 Å and represent the direction along the covalent M—O bonds. An analysis of these trends strongly suggests that the major reorganization due to Fe-site substitution is a rotation of the Si(2) tetrahedron around the Si(2) atom, and that translation plays a secondary role. The nature of the distortions appears to be similar to the ones observed in the analysis of epidotes with varying Fe content (Gabe *et al.*, 1973). The direction of the rotation of the tetrahedron is clearly illustrated by the displacement ellipsoids of atoms Si(2), O(3), O(8) and O(9) in Fig. 1. A slight translation of the tetrahedron in the direction of the Fe site is suggested by the Si(2) ellipsoid.

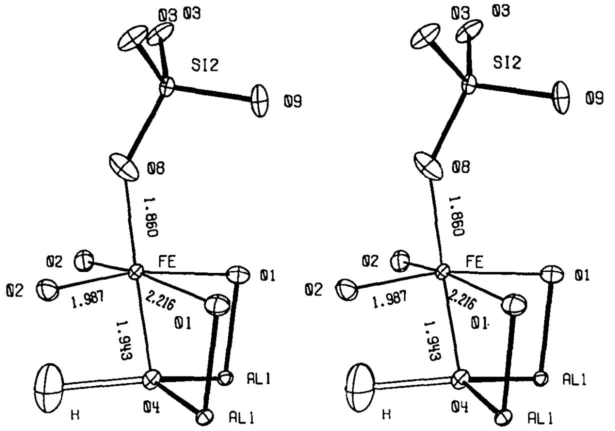

Fig. 1. The coordination around the Fe octahedral site. The displacement ellipsoids are illustrated at the 95% probability level. Distances in Å.

Table 4. *Root-mean-square components of displacement along the three principal axes* (Å)

	*R*1	*R*2	*R*3
Al(1)	0·042 (5)	0·047 (4)	0·053 (4)
Al(2)	0·038 (4)	0·046 (3)	0·055 (3)
Fe(Al)	0·040 (2)	0·050 (2)	0·057 (2)
Ca(1)	0·055 (2)	0·065 (2)	0·068 (2)
Ca(2)	0·040 (3)	0·059 (2)	0·078 (2)
Si(1)	0·038 (3)	0·041 (3)	0·052 (2)
Si(2)	0·042 (3)	0·051 (3)	0·057 (2)
Si(3)	0·040 (3)	0·043 (3)	0·056 (2)
O(1)	0·052 (1)	0·061 (1)	0·072 (1)
O(2)	0·054 (1)	0·062 (1)	0·079 (1)
O(3)	0·047 (1)	0·058 (1)	0·094 (1)
O(4)	0·050 (2)	0·056 (2)	0·063 (2)
O(5)	0·048 (2)	0·056 (2)	0·063 (2)
O(6)	0·044 (2)	0·062 (2)	0·071 (1)
O(7)	0·042 (2)	0·070 (1)	0·079 (1)
O(8)	0·055 (2)	0·085 (1)	0·105 (1)
O(9)	0·049 (2)	0·089 (1)	0·095 (1)
O(10)	0·053 (2)	0·053 (2)	0·067 (1)
H	0·092 (2)	0·137 (2)	0·148 (1)

H-*atom position and hydrogen bonding*

Our study shows that the H atom is confined to one position since no significant negative areas could be found in the final difference Fourier map. The H atom is covalently bonded to O(10) at a distance of 0·9753 (10) Å and the position is very similar to the unique H-atom position found in zoisite [O(10)—H 0·986 (2) Å] (Smith *et al.*, 1987). There is a rather weak hydrogen-bond interaction to O(4) [O(10)···O(4) 2·9222 (10); H···O(4) 1·9640 (11) Å] and the bond is bent with an O(10)—H···O(4) angle of 166·9 (1)°. The virtually linear hydrogen bond in zoisite [angle O(10)—H···O(4) 176·4 (2)°] is considerably stronger with an O(10)···O(4) distance of 2·742 (2) Å and an H···O(4) distance of 1·757 (2) Å. The hydrogen-bond environment in epidote is illustrated in Fig. 2 and it can be observed that the H atom is displaced away from the Fe and Ca(2) ions. The Fe···H distance is 2·7285 (12) Å; the Ca(2)···H distance is 3·0043 (14) Å; and the electrostatic repulsion between the atoms is the likely reason for the bending of the hydrogen bond.

The replacement of the Al^{3+} by the Fe^{3+} ion increases the O(10)···O(4) distance from 2·742 (2) Å in zoisite (15 K) to 2·9222 (10) Å in the present compound which indicates a weakening of the hydrogen bond with increasing Fe content. This is consistent with the observation that O—H stretch frequencies also increase with Fe content. Langer & Raith (1974) quote a stretch frequency of 3260 cm^{-1} for the Fe-free zoisite structure and their frequency *vs* Fe content correlation predicts 3363 cm^{-1} for our epidote concentration ($p = 0{\cdot}8$).

The repulsive forces between the positively charged atoms play an important role in the structure. As discussed above, the hydrogen bond becomes longer and nonlinear. It is well known that hydrogen bonding increases the net negative charges on the acceptor and donor O atoms, whereas the H atom receives a net positive charge (Kvick, 1974, and references therein), and this charge redistribution is reflected in the change in the IR frequencies. A lowering of the repulsive interactions discussed above is thus favored by a decrease in the hydrogen-bond strength.

Al *octahedra*

The Al—O distances vary between 1·8454 (7) Å for the Al(1)—O(4) bond and 1·9566 (7) Å for the Al(1)—O(5) bond. Differences of this magnitude may qualitatively be understood in terms of the formal bond strength of the participating O atoms.

Si *tetrahedra*

The two shortest Si—O bonds [1·5684 (8), 1·5924 (9) Å] correspond to O atoms with low formal bond strength and the longest bonds [1·6695 (9), 1·6536 (9) Å] are associated with high formal bond strength. It may be noticed that the distance of O(8) to Fe is quite short [1·8601 (8) Å; the sum of the effective radii of these atoms is 2·05 Å according to the compilation of Shannon & Prewitt (1969)]. This O atom is a corner-sharing atom between the Fe octahedron and the Si(2) tetrahedron and the short distance is responsible for the sensitivity of the tetrahedron to substitutional changes in the octahedron.

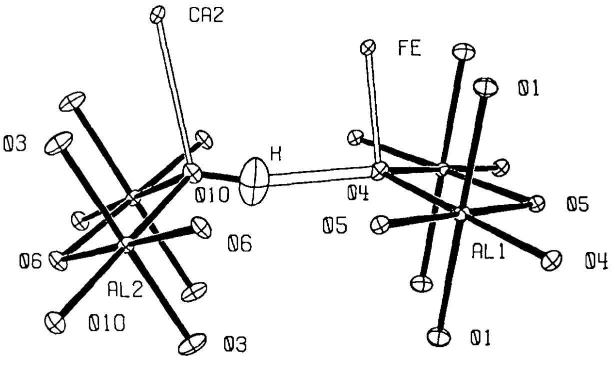

Fig. 2. A view of the hydrogen-bond environment. The displacement ellipsoids are illustrated at the 95% probability level.

IV. Concluding remarks

The epidote structure has one H-atom position, in a bent hydrogen bond. The hydrogen-bond strength is inversely correlated to the Fe content in the Fe octahedron and the bond bending appears to be related to the Fe—H and Ca—H repulsions. The Fe/Al interchange in the octahedral site causes some structural reorganization, which may be described primarily as a rotation of the Si(2) tetrahedron. The difference in location for this tetrahedron is apparent in the anisotropic displacement parameters.

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