

## THE CRYSTAL CHEMISTRY OF THE AMPHIBOLES: IV. X-RAY AND NEUTRON REFINEMENTS OF THE CRYSTAL STRUCTURE OF TREMOLITE

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### ABSTRACT

Three-dimensional counter-collected X-ray and neutron single-crystal data have been used to refine the crystal structure of a tremolite ( $\text{Na}_{0.388}\text{K}_{0.118}\text{Ca}_{1.802}(\text{Mg}_5)(\text{Al}_{10.228}\text{Si}_{7.787})\text{O}_{22}(\text{OH}_{1.337}\text{F}_{0.660}\text{Cl}_{0.012})$ ;  $a$  9.863(1)  $b$  18.048(2),  $c$  5.285(1) Å,  $\beta$  104.79(1)°,  $Z=2$  in the space group  $C2/m$ . The final  $R$ -factors of 3.2% (X-ray) and 2.1% (neutron) were obtained for 1376 and 709 observed reflections respectively.

The neutron study confirmed the position of the hydrogen atom proposed by Papike *et al.* (1969); the O(3)-H distance of 0.960(6) Å is typical for hydroxyl anion and the principal stretching frequency of 3684  $\text{cm}^{-1}$  indicates little or no hydrogen bonding with the chain-bridging anions. Comparison of the positional parameters obtained from both refinements shows that the positional parameters obtained in the X-ray study are not significantly affected by bonding effects. On the other hand, differences do occur between the corresponding thermal parameters; the X-ray R.M.S. thermal displacements are systematically larger than the neutron displacements, indicating a significant contribution from electron delocalization. In both studies, the amount of vibrational anisotropy is related to the coordination number. The orientation of the vibration ellipsoids is related to the disposition of the surrounding atoms; the minimum vibration direction is generally sub-parallel to the strongest bond, whereas the maximum vibration direction is generally oriented so as to involve the minimum bond stretching.

### SOMMAIRE

Les données recueillies sur monocristal par diffraction de rayons-X et de neutrons avec compteurs tridimensionnels ont été utilisées pour affiner la structure cristalline de tremolite  $\text{Na}_{0.388}\text{K}_{0.118}\text{Ca}_{1.802}(\text{Mg}_5)(\text{Al}_{10.228}\text{Si}_{7.787})\text{O}_{22}(\text{OH}_{1.337}\text{F}_{0.660}\text{Cl}_{0.012})$ ;  $a$  9.863(1),  $b$  18.048(2),  $c$  5.285(1) Å,  $\beta$  104.79(1)°,  $Z=2$  dans le groupe spatial  $C2/m$ . Les derniers indices  $R$  de 3.2% pour les rayons-X et 2.1% pour les neutrons ont été obtenus pour 1396 et 709 réflexions observées, respectivement. L'étude par neutrons a confirmé la position de l'atome d'hydrogène, proposée par Papike *et al.* (1969); la distance O(3)-H de 0.960(6) Å est typique pour l'anion hydroxyl et

la principale fréquence d'allongement de 3684  $\text{cm}^{-1}$  indique essentiellement aucun lien de l'hydrogène avec les anions qui lient les chaînes. Une comparaison entre les coordonnées de position atomique obtenues dans les deux affinements démontre que les paramètres de position obtenus par rayons-X ne sont pas affectés de façon significative par les effets de lien. Par contre, il y a des différences entre les paramètres thermiques correspondants; les déplacements thermiques R.M.S. déterminés par rayon-X sont systématiquement plus grands que ceux déterminés par neutrons, ce qui indique une contribution provenant de la délocalisation des électrons. Dans les deux études, le degré d'anisotropie vibrationnelle est fonction de la coordination des atomes. L'orientation des ellipsoïdes de vibration est en rapport avec la disposition des atomes environnants; la direction de la vibration minimum est généralement sub-parallèle au lien le plus fort, tandis que la direction de vibration maximum est généralement orientée de façon à entraîner un allongement minimum des liens.

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### INTRODUCTION

The past few years have seen an increase in the number of X-ray structure refinements of minerals at high temperatures, and considerable attention has been focused on the behavior of the atomic thermal parameters. It is well known that the anisotropic thermal parameters derived from X-ray data often absorb deviations from spherical symmetry of the atomic charge cloud, and thus temperature factors obtained in this way may be systematically in error due to bonding effects. This effect is not present when the diffraction experiment is performed with neutrons as an atom may be accurately represented by a point scatterer in this case. Thus a comparison of the results of these two experiments gives an indication of the systematic error inherent in the derived X-ray model. This has been shown to be considerable for atoms from the first row of the periodic table (Coppens 1974), to the extent that the positional parameters are also significantly affected. In order to assess this effect for (geologically) more relevant atoms, the crystal structure of a slightly edenitic tremolite has been investigated by both methods. This also has the additional advantage

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TABLE 1. CRYSTAL DATA &amp; DATA COLLECTION INFORMATION FOR TREMOLITE

Chemical Analysis		Unit Cell Contents <sup>1</sup>		Miscellaneous		
SiO <sub>2</sub>	56.57	Si	7.767	a = 9.863(1) Å	Space Group	C2/m
TiO <sub>2</sub>	0.01	Al <sup>IV</sup>	<u>0.228</u>	b = 18.048(2) Å	Density <sub>calc</sub>	2.964
Al <sub>2</sub> O <sub>3</sub>	1.41	Tetrahedral	<u>7.995</u>	c = 5.285(1) Å	Z	2
Fe <sub>2</sub> O <sub>3</sub>	0.01	Al <sup>VI</sup>	—	β = 104.79(1)°		
FeO	0.08	Ti	0.001		X-Ray	Neutron
MnO	0.03	Fe <sup>3+</sup>	0.001	Linear absorption coefficient (cm <sup>-1</sup> )	14.3	0.004
MgO	24.41	Fe <sup>2+</sup>	0.009	Crystal size (mm)	0.05x0.15x0.26	5x7x8
CaO	12.25	Mn	0.003	Radiation/Monochromator	Mo/C	—
Na <sub>2</sub> O	1.44	Mg	<u>4.995</u>	Crystal Axis for data collection	—	10 $\bar{1}$
K <sub>2</sub> O	0.68	Octahedral	<u>5.009</u>	No. of non-equivalent  F <sub>obs</sub>   > 4σ	1376	709
H <sub>2</sub> O	1.46	Ca	1.802	Final R (observed)	3.2%	2.1%
Cl	0.05	Na	0.383	Final R (all reflections)	4.4%	2.3%
F	1.52	K	<u>0.119</u>	Final R (all reflections)	4.4%	2.3%
		Large Cation	<u>2.304</u>	Standard deviation of unit weight observation	1.83	0.22
		OH	1.337	Extinction coefficient	1.4(1)x10 <sup>-6</sup>	3.2(2)x10 <sup>-4</sup>
		F	0.660	Final R <sub>w</sub> (observed)	3.5%	2.7%
		Cl	0.012	Final R <sub>w</sub> (all reflections)	4.6%	3.2%
Temperature factor form used:	$\exp - \left[ \sum_{i=1}^3 \sum_{j=1}^3 h_i h_j \beta_{ij} \right]$		$R = \frac{\sum ( F_{obs}  -  F_{calc} )}{\sum  F_{obs} }$ $R_w = \frac{(\sum w( F_{obs}  -  F_{calc} )^2 / \sum w F_{obs}^2)^{1/2}}{w = 1}$			

<sup>1</sup> Calculation based on 24(O,OH,F,Cl).

of providing accurate positional parameters for the hydrogen atom adjacent to O(3) in the structure.

The crystal structure of tremolite was determined by Warren (1929) and a two-dimensional refinement was presented by Zussman (1959). A full three-dimensional X-ray refinement was performed by Papike *et al.* (1969) on a fairly pure tremolite from the Gouverneur district of New York; this work approximately located the position of the hydrogen atom in the structure.

#### EXPERIMENTAL

The crystal used in this study was from the McMaster University mineral collection, and was originally collected from the Gouverneur district, New York, although the exact location is unknown. The original sample was a large single crystal measuring 10×4×2cm, elongate along Z and with the form {110}. Optical examination of both polished and thin sections showed it to be free of inclusions and apparently unzoned.

All single-crystal X-ray precession photographs of small fragments displayed diffraction symmetry 2/mC— consistent with space groups C2, C $\bar{m}$  and C2/m. Following previous work (Zussman 1959; Papike *et al.* 1969), the space group C2/m was assigned. Unit-cell parameters were determined from fifteen intense reflections aligned automatically on a four-circle diffractometer; the values obtained from a least-squares refinement (Table 1) were confirmed by repeating this procedure on several different crystals. Subsequent to the collection of the neutron data, the crystal used for the collection of neutron intensities was broken in half, crushed and analyzed (Table 1).

#### Neutron study

An equidimensional crystal of volume ~0.3 cm<sup>3</sup> was cut from the centre of the large crystal. This was mounted with epoxy on an aluminium pin and aligned by X-ray precession photography such that the  $\bar{1}01$  direction was coincident with the spindle axis. Intensity data were collected

on a semi-automatic four-circle diffractometer<sup>1</sup> in the McMaster University nuclear reactor. The incident neutron beam was obtained from the (220) face of a single crystal of aluminium in the transmission geometry. Because of the mosaic spread in the aluminium crystal, the wavelength of the incident beam was variable across its width. The wavelength was measured at the sample crystal position during the orientation procedure; the value obtained, 1.05926 Å, indicates that secondary contamination is very small. The crystal was aligned manually, and several peak profiles were examined to ensure that the mosaic spread of the sample crystal was not excessive. Diffracted intensities were measured with a helium-3 counter using  $\omega$ -scans and operating in the step-scan mode. The scan range was a step-function of two-theta and was wide enough to include several background counts on either side of the peak. To negate the effect of flux variations, counting time was controlled by a fixed-count monitor on the incident beam. Diffractometer settings were calculated using the program MACDIF, written by Martin Anderson and modified by Frank Hawthorne. Data collection was controlled by paper tape input through an on-line teletype. Reflections were collected up to  $100^\circ$   $2\theta$  ( $\sin \theta/\lambda = 0.723$ ) over one asymmetric unit. Due to the low intensity of the incident beam, the rate of data collection was slow ( $\sim 10$  reflections per day). To avoid collecting many unobserved reflections, approximate neutron intensities were calculated from the atomic parameters of preliminary X-ray refinement results ( $R=6\%$ ), and the neutron reflections were collected in sets of approximately equal intensity. As the intensities of the collected reflections decreased, the incident beam monitor count interval was increased in order to maintain good counting statistics. One standard reflection was examined each day ( $\sim$  once per 10 reflections) to ensure constancy of crystal alignment. The peak profile of each reflection was examined and those showing any irregularity were re-collected.

A total of 731 unique reflections was collected, corrected for background and the Lorentz effect and reduced using the program DIFDAT, written by Martin Anderson and modified by Frank Hawthorne. The resulting structure factors were classed as unobserved if their magnitude fell below that of four times the standard deviation based on counting statistics; this re-

sulted in 709 observed reflections. Because of the extremely small absorption coefficient for neutrons, no absorption corrections were performed.

#### X-ray study

A regular cleavage fragment of dimensions  $0.5 \times 0.15 \times 0.26$  mm was used to collect the intensity data. The crystal was mounted on a Syntex P1 automatic four-circle diffractometer operating in the  $\theta$ - $2\theta$  scan mode with variable scan rates from  $2.0$ – $24.0^\circ/\text{min.}$ , depending on the peak count through an angle of  $2^\circ$  and the  $\alpha_1$ - $\alpha_2$  separation. Graphite-monochromated  $\text{MoK}\alpha$  radiation ( $\lambda=0.71069 \text{ \AA}$ ) was used, and background counts were made at the beginning and end of each scan. Two standard reflections were monitored every 50 reflections; no significant change in their intensities was observed during the data collection. A total of 3191 reflections was measured over two asymmetric units out to a  $2\theta$  value of  $65^\circ$  ( $\sin \theta/\lambda = 0.754$ ). The data were corrected for absorption, using an eight-point gaussian quadrature integration for polyhedral crystal shape, for background, Lorentz and polarization effects. Equivalent reflections were averaged to produce an asymmetric set and converted to structure factors. The resulting  $|F_{\text{obs}}|$  were classed as observed if their magnitude exceeded that of four standard deviations based on counting statistics. Of the 1640 unique reflections produced, 1376 were classed as observed.

#### REFINEMENT

Crystal-structure refinement was carried out using the least-squares program RFINE (Finger 1969). Quoted  $R$ -factors are of the forms given in Table 1 and are expressed as percentages; anisotropic temperature factors are of the form given in Table 1.

#### Neutron

Coherent neutron scattering amplitudes were taken from Bacon (1972). Atomic coordinates and isotropic temperature factors for tremolite (Papike *et al.* 1969) were used as the initial model. One cycle of least-squares refinement varying the atomic positions resulted in an  $R$ -factor of 11.4%, and a further cycle varying the isotropic temperature factors gave an  $R$ -factor of 4.1%. An additional cycle of refinement varying positions and isotropic temperature factors converged to an  $R$ -value of 3.8%.

Difference fourier sections in the vicinity of the  $A$ -site revealed a splitting of the alkali atoms (Papike *et al.* 1969; Hawthorne & Grundy 1972, 1973a,b); using the split  $A$ -site positions

<sup>1</sup>Built by Martin Anderson, Dept. of Physics, McMaster University.

TABLE 2. ATOMIC PARAMETERS FOR TREMOLITE\*

Atom	x	y	z	$B_{equiv.}$
O(1)	0.1112(2)	0.0858(1)	0.2184(3)	0.52(2)
	0.1114(1)	0.08570(7)	0.2182(3)	0.44(2)
O(2)	0.1189(2)	0.1706(1)	0.7247(3)	0.55(2)
	0.1187(1)	0.17067(6)	0.7251(3)	0.46(2)
O(3)	0.1072(3)	0	0.7152(5)	0.76(3)
	0.1082(2)	0	0.7154(4)	0.62(3)
O(4)	0.3646(2)	0.2482(1)	0.7931(3)	0.70(2)
	0.3642(2)	0.24818(7)	0.7928(3)	0.61(2)
O(5)	0.3466(2)	0.1341(1)	0.1003(3)	0.77(3)
	0.3467(1)	0.13391(7)	0.0998(3)	0.64(2)
O(6)	0.3437(2)	0.1183(1)	0.5913(3)	0.69(2)
	0.3437(1)	0.11805(7)	0.5910(3)	0.62(2)
O(7)	0.3386(3)	0	0.2913(5)	0.76(4)
	0.3380(2)	0	0.2921(4)	0.75(3)
T(1)	0.28005(7)	0.08417(3)	0.2979(1)	0.43(1)
	0.2799(2)	0.08424(4)	0.2974(4)	0.32(2)
T(2)	0.28803(7)	0.17132(4)	0.8050(1)	0.42(1)
	0.2882(2)	0.17133(8)	0.8056(4)	0.37(3)
M(1)	0	0.08821(7)	1/2	0.54(2)
	0	0.0883(1)	1/2	0.37(3)
M(2)	0	0.17678(6)	0	0.51(2)
	0	0.1770(1)	0	0.39(3)
M(3)	0	0	0	0.53(2)
	0	0	0	0.35(4)
M(4)	0	0.27797(4)	1/2	0.72(2)
	0	0.2779(1)	1/2	0.72(3)
A(m)	0.0407(23)	1/2	0.0887(42)	2.1(3)
	0.0450(40)	1/2	0.1030(76)	1.4(4)
A(2)	0	0.4901(19)	0	2.1(3)
	0	0.4897(38)	0	1.4(4)
H	-	-	-	-
	0.2088(6)	0	0.7628(14)	-

\* In Tables 2 and 3, the upper set of figures are for the X-ray data, the lower set of figures for the neutron data.

TABLE 3. ANISOTROPIC TEMPERATURE FACTOR COEFFICIENTS\*

	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
O(1)	167(15)	34(4)	503(53)	2(6)	76(22)	3(12)
	111(11)	34(3)	436(44)	-5(4)	30(17)	-9(8)
O(2)	145(14)	49(4)	494(52)	-10(6)	90(21)	-2(12)
	98(10)	44(3)	448(45)	-6(4)	74(18)	-19(8)
O(3)	281(23)	46(6)	657(77)	0	129(33)	0
	181(17)	45(4)	598(67)	0	105(28)	0
O(4)	273(16)	30(4)	623(56)	-32(7)	178(24)	-27(12)
	216(10)	36(3)	627(53)	-32(5)	116(18)	-14(9)
O(5)	217(16)	70(5)	587(56)	0(7)	102(24)	74(13)
	160(11)	66(3)	368(43)	-6(5)	78(17)	76(9)
O(6)	219(16)	58(4)	545(55)	13(7)	140(23)	-71(12)
	154(10)	56(3)	553(42)	3(5)	90(17)	-58(10)
O(7)	249(24)	24(6)	1037(88)	0	146(36)	0
	193(16)	30(4)	1067(75)	0	88(27)	0
T(1)	153(6)	29(2)	361(20)	-5(2)	87(8)	-9(4)
	99(14)	25(4)	263(52)	2(6)	47(22)	-8(10)
T(2)	138(6)	31(2)	346(19)	-5(2)	78(8)	-6(4)
	100(14)	26(4)	379(55)	-5(6)	47(24)	-11(10)
M(1)	198(11)	39(1)	397(36)	0	113(15)	0
	130(16)	23(4)	328(61)	0	64(26)	0
M(2)	191(11)	30(3)	439(36)	0	100(15)	0
	100(16)	34(5)	343(64)	0	64(26)	0
M(3)	208(15)	28(4)	432(52)	0	67(22)	0
	139(22)	16(6)	319(84)	0	62(36)	0
M(4)	273(7)	40(2)	783(23)	0	302(10)	0
	248(20)	44(5)	873(81)	0	340(32)	0
H	-	-	-	-	-	-
	254(52)	218(18)	2455(236)	0	5(90)	0

\*  $B_{ij} \times 10^5$

TABLE 4. SELECTED INTERATOMIC DISTANCES IN TREMOLITE

Atoms	X-Ray	Neutron	Atoms	X-Ray	Neutron
T(1)-O(1)	1.611(2)Å	1.607(2)Å	T(2)-O(2)	1.613(2)Å	1.617(2)Å
T(1)-O(3)	1.637(2)	1.637(2)	T(2)-O(4)	1.589(2)	1.586(2)
T(1)-O(6)	1.639(2)	1.637(2)	T(2)-O(5)	1.662(2)	1.658(2)
T(1)-O(7)	1.629(1)	1.628(2)	T(2)-O(6)	1.675(2)	1.681(2)
Mean	1.629	1.627	Mean	1.635	1.635
M(1)-O(1)	2.061(2)	2.063(1)	M(3)-O(1)	2.071(2)	2.070(1)
M(1)-O(2)	2.071(2)	2.072(2)	M(3)-O(3)	2.047(2)	2.054(2)
M(1)-O(3)	2.082(2)	2.087(2)	Mean	2.063	2.065
Mean	2.071	2.074	M(4)-O(2)	2.415(2)	2.413(2)
M(2)-O(1)	2.143(2)	2.146(2)	M(4)-O(4)	2.336(2)	2.337(2)
M(2)-O(2)	2.091(2)	2.087(1)	M(4)-O(5)	2.766(2)	2.770(2)
M(2)-O(4)	2.018(2)	2.018(2)	M(4)-O(6)	2.548(2)	2.552(2)
Mean	2.084	2.084	Mean	2.516	2.518
A(m)-O(5)	2.94(1)	2.95(2)	A(2)-O(5)	2.83(3)	2.82(5)
A(m)-O(5)	3.10(1)	3.11(2)	A(2)-O(5)	3.12(3)	3.12(5)
A(m)-O(6)	2.78(1)	2.73(3)	A(2)-O(6)	3.03(2)	3.02(4)
A(m)-O(6)	3.56(1)	3.62(3)	A(2)-O(6)	3.27(2)	3.27(5)
A(m)-O(7)	2.49(2)	2.49(4)	A(2)-O(7)	2.486(4)	2.495(6)
A(m)-O(7)	2.58(2)	2.63(4)	A(2)-O(7)	3.684(3)	3.681(4)
A(m)-O(7)	3.19(2)	3.11(4)	Mean for 12	3.070	3.068
A(m)-O(7)	4.10(2)	4.11(4)	Mean for 8	2.867	2.864
Mean for 12	3.09	3.10	A(2)-O(5)	2.973(2)	2.968(1)
Mean for 8	2.84	2.84	A(2)-O(6)	3.148(2)	3.146(1)
A-O(5)	2.973(2)	2.968(1)	A-O(7)	2.480(3)	2.488(2)
A-O(6)	3.148(2)	3.146(1)	A-O(7)	3.680(4)	3.676(3)
A-O(7)	2.480(3)	2.488(2)	Mean for 12	3.067	3.065
A-O(7)	3.680(4)	3.676(3)	T(1)-T(2)	3.091(1)	3.095(3)
Mean for 12	3.067	3.065	through O(6)		
T(1)-T(2)	3.091(1)	3.095(3)	T(1)-T(2)	3.061(1)	3.057(3)
through O(6)			through O(5)		
T(1)-T(2)	3.061(1)	3.057(3)	T(1)-T(1)	3.038(1)	3.041(3)
through O(5)			across mirror		
T(1)-T(1)	3.038(1)	3.041(3)	M(1)-M(1)	3.184(2)	3.186(4)
across mirror			M(1)-M(2)	3.088(1)	2.090(2)
M(1)-M(1)	3.184(2)	3.186(4)	M(1)-M(3)	3.085(1)	3.086(1)
M(1)-M(2)	3.088(1)	2.090(2)	M(1)-M(4)	3.425(1)	3.422(3)
M(1)-M(3)	3.085(1)	3.086(1)	M(2)-M(3)	3.191(1)	3.195(2)
M(1)-M(4)	3.425(1)	3.422(3)	M(2)-M(4)	3.121(1)	3.209(2)
M(2)-M(3)	3.191(1)	3.195(2)	O(3)-H	--	0.960(6)
M(2)-M(4)	3.121(1)	3.209(2)			

TABLE 5. POLYHEDRAL EDGE LENGTHS IN TREMOLITE

Atoms	X-Ray	Neutron	Atoms	X-Ray	Neutron
T(1) Tetrahedron			T(2) Tetrahedron		
0(1)-O(5)	2.697(2)Å	2.696(2)Å	0(2)-O(4)	2.742(2)Å	2.740(2)Å
0(1)-O(6)	2.682(2)	2.680(2)	0(2)-O(5)	2.675(2)	2.675(2)
0(1)-O(7)	2.671(3)	2.664(2)	0(2)-O(6)	2.663(2)	2.670(2)
0(5)-O(6)	2.618(3)	2.620(2)	0(4)-O(5)	2.656(3)	2.656(2)
0(5)-O(7)	2.632(3)	2.632(1)	0(4)-O(6)	2.562(2)	2.566(2)
0(6)-O(7)	2.652(2)	2.644(2)	0(5)-O(6)	2.698(3)	2.697(2)
Mean	2.659	2.656	Mean	2.666	2.667
M(1) Octahedron			M(3) Octahedron		
0(1 <sup>III</sup> )-O(2 <sup>IV</sup> )	2.817(2)	2.817(2)	0(1 <sup>III</sup> )-O(1 <sup>IV</sup> )	2.752(3)	2.753(2)
0(1 <sup>III</sup> )-O(2 <sup>IV</sup> )	3.067(2)	3.072(2)	0(1 <sup>III</sup> )-O(1 <sup>IV</sup> )	3.097(3)	3.093(2)
0(1 <sup>III</sup> )-O(3 <sup>IV</sup> )	2.747(3)	2.756(2)	0(1 <sup>III</sup> )-O(3 <sup>IV</sup> )	2.747(3)	2.756(2)
0(1 <sup>III</sup> )-O(3 <sup>IV</sup> )	3.057(3)	3.056(2)	0(1 <sup>III</sup> )-O(3 <sup>IV</sup> )	3.069(3)	3.068(2)
0(2)-O(2)	2.884(3)	2.884(3)	Mean	2.914	2.916
0(2)-O(3)	3.081(2)	3.082(1)	M(4) Anti-prism		
0(3)-O(3)	2.685(5)	2.697(4)	0(2)-O(2)	2.884(3)	2.884(3)
Mean	2.926	2.928	0(2 <sup>IV</sup> )-O(4 <sup>IV</sup> )	3.144(2)	3.147(2)
M(2) Octahedron			0(2 <sup>IV</sup> )-O(4 <sup>IV</sup> )	3.005(2)	3.005(2)
0(1)-O(1)	2.752(3)	2.753(2)	0(2 <sup>IV</sup> )-O(5 <sup>IV</sup> )	3.638(3)	3.640(2)
0(1 <sup>III</sup> )-O(2 <sup>IV</sup> )	2.817(2)	2.817(2)	0(4 <sup>IV</sup> )-O(5 <sup>IV</sup> )	3.444(3)	3.448(2)
0(1 <sup>III</sup> )-O(2 <sup>IV</sup> )	3.043(2)	3.040(2)	0(4 <sup>IV</sup> )-O(6 <sup>IV</sup> )	2.562(2)	2.566(2)
0(1)-O(4)	3.007(2)	3.010(2)	0(5 <sup>IV</sup> )-O(6 <sup>IV</sup> )	2.618(3)	2.620(3)
0(2)-O(4)	3.005(2)	3.005(2)	0(5 <sup>IV</sup> )-O(6 <sup>IV</sup> )	3.082(3)	3.090(3)
0(2 <sup>IV</sup> )-O(4 <sup>IV</sup> )	2.909(2)	2.906(2)	0(6)-O(6)	3.457(3)	3.455(3)
0(4)-O(4)	2.992(4)	2.999(3)	Mean	3.084	3.086
Mean	2.942	2.942			

of ferrotschermakite (Hawthorne & Grundy 1973a), refinement of all variables for an isotropic thermal model resulted in convergence at an  $R$ -factor of 3.2%. At this stage, temperature factors (except those of the split  $A$ -site) were converted to anisotropic and a correction for isotropic extinction (Zachariassen 1968) was introduced into the refinement. Several cycles of least-squares refinement gradually increasing the number of variables resulted in convergence at an  $R$ -factor of 2.1%. There is a substantial difference between the scattering amplitudes of aluminium and silicon, and thus the site-occupancies of the tetrahedral sites were considered as variable with the bulk chemistry of the site constrained to be the same as that given by the chemical analysis. The following site-occupancies were obtained:  $T(1)=0.06(4)\text{Al}+0.96\text{Si}$ ;  $T(2)=0.00\text{Al}+1.00\text{Si}$ ; in view of the fact that the Al occupancy of  $T(1)$  is within  $2\sigma$  of zero, this result cannot be considered as significant.

### X-ray

Analytic scattering curves for neutral atoms were taken from Cromer & Mann (1968) with anomalous dispersion coefficients from Cromer & Lieberman (1970). Proceeding as for the neutron refinement, one cycle of least-squares

varying the positional parameters gave an  $R$ -factor of 6.0%, and a further cycle varying the isotropic temperature factors resulted in an  $R$ -factor of 5.6%. An additional cycle varying all parameters for an isotropic thermal model resulted in an  $R$ -factor of 5.2%. This was further reduced to 4.8% by positionally disordering the  $A$ -site and further refinement. At this stage, temperature factors were converted to anisotropic and a variable extinction correction was introduced. The hydrogen parameters from the neutron refinement were inserted at this stage, but were not allowed to vary. Several cycles of least-squares refinement gradually increasing the number of variables resulted in convergence at an  $R$ -factor of 3.1%\*.

Final atomic positions and equivalent isotropic temperature factors are presented in Table 2 and anisotropic temperature factors in Table 3. Interatomic distances and angles, and the magnitudes and orientations of the principal axes of the thermal ellipsoids, were calculated

\*Tables of structure factors can be obtained from: the Depository of Unpublished Data, National Science Library, National Research Council of Canada, Ottawa, Ontario, Canada.

TABLE 6. SELECTED INTERATOMIC ANGLES IN TREMOLITE

Atoms	X-Ray	Neutron	Atoms	X-Ray	Neutron
<b>T(1) Tetrahedron</b>			<b>T(2) Tetrahedron</b>		
0(1)-T(1)-0(5)	112.3(1)*	112.4(1)*	0(2)-T(2)-0(4)	117.8(1)*	117.6(1)*
0(1)-T(1)-0(6)	111.2(1)	111.4(2)	0(2)-T(2)-0(5)	109.5(1)	109.5(1)
0(1)-T(1)-0(7)	111.1(1)	110.9(1)	0(2)-T(2)-0(6)	108.2(1)	108.1(1)
0(5)-T(1)-0(6)	106.1(1)	106.3(1)	0(4)-T(2)-0(5)	109.6(1)	109.9(2)
0(5)-T(1)-0(7)	107.4(1)	107.5(1)	0(4)-T(2)-0(6)	103.4(1)	103.5(1)
0(6)-T(1)-0(7)	108.6(1)	108.2(2)	0(5)-T(2)-0(6)	107.9(1)	107.7(1)
Mean	109.5	109.5	Mean	109.4	109.4
<b>M(1) Octahedron</b>			<b>M(3) Octahedron</b>		
0(1 <sup>u</sup> )-M(1)-0(2 <sup>u</sup> )	95.8(1)	96.0(1)	0(1 <sup>u</sup> )-M(3)-0(1 <sup>u</sup> )	96.8(2)	96.7(2)
0(1 <sup>u</sup> )-M(1)-0(2 <sup>d</sup> )	85.9(1)	85.9(1)	0(1 <sup>u</sup> )-M(3)-0(1 <sup>d</sup> )	83.2(2)	83.3(2)
0(1 <sup>u</sup> )-M(1)-0(3 <sup>u</sup> )	95.1(1)	94.8(1)	0(1 <sup>u</sup> )-M(3)-0(3 <sup>u</sup> )	96.2(1)	96.1(1)
0(1 <sup>u</sup> )-M(1)-0(3 <sup>d</sup> )	83.1(1)	83.2(1)	0(1 <sup>u</sup> )-M(3)-0(3 <sup>d</sup> )	83.8(1)	83.9(1)
0(2)-M(1)-0(2)	88.2(1)	88.2(1)	Mean	90.0	90.0
0(2)-M(1)-0(3)	95.8(1)	95.7(1)	<b>M(4) Anti-prism</b>		
0(3)-M(1)-0(3)	80.3(1)	80.5(1)	0(2)-M(4)-0(2)	73.3(2)	73.3(2)
Mean	90.0	90.0	0(2 <sup>u</sup> )-M(4)-0(4 <sup>d</sup> )	78.6(1)	78.5(1)
<b>M(2) Octahedron</b>			0(2 <sup>u</sup> )-M(4)-0(4 <sup>u</sup> )	82.9(1)	83.0(1)
0(1)-M(2)-0(1)	79.9(1)	79.8(1)	0(2 <sup>u</sup> )-M(4)-0(5 <sup>u</sup> )	89.0(2)	89.0(2)
0(1 <sup>u</sup> )-M(2)-0(2 <sup>u</sup> )	91.9(1)	91.8(1)	0(4 <sup>u</sup> )-M(4)-0(5 <sup>d</sup> )	84.5(1)	84.5(1)
0(1)-M(2)-0(2 <sup>d</sup> )	83.4(1)	83.4(1)	0(4 <sup>u</sup> )-M(4)-0(6 <sup>u</sup> )	63.0(1)	63.1(1)
0(1)-M(2)-0(4)	92.5(1)	92.5(1)	0(5 <sup>u</sup> )-M(4)-0(6 <sup>d</sup> )	71.0(1)	70.9(1)
0(2 <sup>u</sup> )-M(2)-0(4 <sup>u</sup> )	90.1(1)	90.1(1)	0(5 <sup>u</sup> )-M(4)-0(6 <sup>u</sup> )	58.8(1)	58.8(1)
0(2 <sup>u</sup> )-M(2)-0(4 <sup>d</sup> )	94.0(1)	94.1(1)	0(6)-M(4)-0(6)	85.5(1)	85.2(1)
0(4)-M(2)-0(4)	95.5(2)	95.9(2)	Mean	75.9	75.9
Mean	90.0	90.0	<b>Tetrahedral Chain</b>		
<b>A Polyhedron*</b>			T(1)-0(5)-T(2)	136.2(1)	136.1(1)
0(7)-0(7)-0(7)	65.8(1)	65.9(1)	T(1)-0(6)-T(2)	137.8(1)	137.7(1)
Δ	0.269	0.268	T(1)-0(7)-T(1)	137.8(2)	138.2(2)
0(3 <sup>1</sup> )-0(3)-H	---	90.4(2)	0(5)-0(6)-0(5)	167.6(1)	167.6(1)
			0(5)-0(7)-0(6)	166.4(1)	166.6(1)

\* Δ = (90° - ∠ 0(7)-0(7)-0(7))/90°.

TABLE 7. ELLIPSOIDS OF VIBRATION FOR TREMOLITE

	R.M.S. Displacement $\text{\AA}^2$		Angle to a-axis in degrees		Angle to b-axis in degrees		Angle to c-axis in degrees	
	X-Ray	Neutron	X-Ray	Neutron	X-Ray	Neutron	X-Ray	Neutron
O(1)	0.075(4)	0.068(4)	94(15)	47(15)	7(23)	64(17)	95(28)	66(13)
	0.081(4)	0.077(3)	79(28)	119(31)	95(28)	29(26)	174(28)	88(39)
	0.088(4)	0.080(4)	12(27)	124(28)	85(15)	103(37)	94(28)	24(13)
O(2)	0.075(4)	0.065(4)	144(21)	10(14)	107(15)	87(9)	45(29)	114(18)
	0.082(4)	0.074(4)	114(27)	96(19)	112(20)	117(10)	135(28)	146(14)
	0.092(4)	0.088(3)	64(13)	83(6)	152(16)	152(10)	86(15)	66(10)
O(3)	0.087(5)	0.086(8)	90	132(36)	0	90	90	27(36)
	0.092(5)	0.086(6)	77(10)	90	90	0	179(10)	90
	0.113(5)	0.093(4)	13(10)	41(31)	90	90	91(10)	63(31)
O(4)	0.070(5)	0.066(3)	63(6)	57(4)	27(6)	34(6)	96(14)	106(8)
	0.084(4)	0.084(4)	70(8)	68(7)	100(13)	113(7)	168(8)	156(7)
	0.121(3)	0.109(2)	35(4)	41(4)	115(3)	114(3)	80(5)	72(6)
O(5)	0.074(5)	0.063(4)	102(9)	108(7)	121(4)	119(3)	31(4)	30(3)
	0.100(4)	0.086(3)	166(8)	158(6)	90(9)	91(5)	90(8)	97(6)
	0.117(3)	0.114(2)	97(9)	102(4)	31(3)	29(3)	60(4)	61(3)
O(6)	0.061(5)	0.071(4)	114(5)	115(10)	56(4)	56(4)	37(4)	37(5)
	0.101(4)	0.085(3)	148(12)	153(10)	86(15)	98(7)	107(11)	101(9)
	0.110(3)	0.106(3)	109(16)	98(6)	146(4)	145(4)	59(7)	55(4)
O(7)	0.063(7)	0.071(5)	90	90	0	0	90	90
	0.106(5)	0.094(4)	177(20)	165(7)	90	90	72(20)	91(7)
	0.117(5)	0.121(4)	87(20)	105(7)	90	90	18(20)	1(7)
T(1)	0.065(2)	0.057(6)	106(8)	105(23)	63(20)	65(27)	27(20)	25(27)
	0.069(2)	0.065(5)	69(8)	105(69)	30(19)	33(51)	116(21)	114(30)
	0.085(2)	0.068(5)	27(4)	21(51)	102(5)	70(64)	83(4)	97(36)
T(2)	0.065(2)	0.062(5)	112(7)	67(31)	84(14)	35(24)	9(7)	73(23)
	0.071(2)	0.069(5)	109(9)	156(31)	161(8)	71(47)	85(15)	62(68)
	0.081(2)	0.073(5)	30(6)	86(67)	108(8)	118(34)	81(5)	34(62)
M(1)	0.068(3)	0.061(5)	111(5)	90	90	0	6(5)	90
	0.080(3)	0.065(7)	90	73(20)	0	90	90	178(20)
	0.096(3)	0.078(5)	21(5)	17(20)	90	90	84(5)	88(20)
M(2)	0.070(3)	0.065(7)	90	125(38)	0	90	90	20(38)
	0.074(3)	0.072(5)	71(6)	145(38)	90	90	176(6)	110(38)
	0.094(3)	0.074(5)	19(6)	90	90	0	86(6)	90
M(3)	0.068(5)	0.052(9)	90	90	0	0	90	90
	0.076(5)	0.064(9)	87(8)	78(23)	90	90	168(8)	178(23)
	0.099(4)	0.080(6)	3(8)	12(23)	90	90	102(8)	92(23)
M(4)	0.072(2)	0.064(7)	136(1)	143(4)	90	90	31(1)	38(4)
	0.081(2)	0.085(5)	90	90	0	0	90	90
	0.123(1)	0.126(4)	46(1)	53(4)	90	90	59(1)	52(4)
H	---	0.108(11)	---	16(6)	---	90	---	89(6)
	---	0.185(9)	---	74(6)	---	90	---	179(6)
	---	0.189(8)	---	90	---	0	---	90

with the program ERRORS (L. W. Finger, pers. comm.), and are presented in Tables 4-7.

#### DISCUSSION

The general topology of the amphiboles has been discussed in detail elsewhere (e.g. Papike & Clark 1968; Papike & Ross 1970) and will not be repeated here. Figure 1 illustrates the  $C2/m$  amphibole structure and may be used in the interpretation of Tables 2-7. A comparison of the mean metal-oxygen distances obtained from this study with those obtained by Papike *et al.* (1969) is given in Table 8. The  $[T(1)-O]$  distance is significantly larger in this study, in-

dicating that the small amount of tetrahedral aluminium present is strongly ordered into the  $T(1)$  site in accord with previous studies (Papike & Clark 1967; Robinson *et al.* 1973; Hawthorne & Grundy 1973a,b, 1976). The  $[M(1)-O]$  and  $[M(3)-O]$  distances are slightly less in this study due to the partial occupancy of O(3) by fluorine. Using the regression equations of Hawthorne (in prep.) mean bond lengths of 2.067(8) $\text{\AA}$  and 2.060(7) $\text{\AA}$  are forecast for  $M(1)$  and  $M(3)$ , in good agreement with the experimental values. The  $[M(2)-O]$  distance is slightly larger than that observed by Papike *et al.* (1969); this arises from the small amount of octahedral

TABLE 8. MEAN METAL-OXYGEN DISTANCES FOR TREMOLITE.

	T(1)-O	T(2)-O	M(1)-O	M(2)-O	M(3)-O
Papike <i>et al.</i> (1969)	1.620Å	1.632Å	2.075Å	2.077Å	2.066Å
X-ray (this study)	1.629	1.635	2.071	2.084	2.063
Neutron (this study)	1.627	1.635	2.074	2.084	2.065

aluminium that occurs in the hydroxy-tremolite and which presumably orders into the  $M(2)$  site. For complete  $M(2)$  occupancy by magnesium, the regression equations of Hawthorne (in prep.) forecast a mean  $M(2)$  bond length of 2.084(5)Å, in exact agreement with the value obtained in this study.

It is well known that anisotropic thermal parameters derived from X-ray data can absorb deviations from spherical symmetry of the atomic charge cloud (Coppens 1968), and thus temperature factors obtained by X-ray crystal-structure refinement using spherical atomic form factors are systematically in error because of bonding effects. This effect is not present in a neutron crystal-structure refinement, and the derived anisotropic thermal parameters closely represent the vibrational behavior of the atoms

provided anharmonic effects are negligible. Thus a comparison of the results obtained from each experiment should give an indication of the systematic error in the derived X-ray structure model. In principal, these effects could also affect the atomic positions; however, this appears to be negligible for all except the lightest atoms of the first row of the periodic table. Half-normal probability plot analysis of the two sets of results shows that, whereas the atomic positions correspond very closely, significant systematic differences occur between the anisotropic temperature factors.

Delocalization of electron density will cause an increase in the temperature factors obtained from the X-ray refinement, and examination of Table 2 shows that, in general, the X-ray equivalent isotropic temperature factors are larger by 10 to 50% than the corresponding neutron values. The two exceptions to this are the  $M(4)$  and  $O(7)$  sites where the equivalent isotropic temperature factors are equal; this may result from positional disorder of the Ca and Na on the  $M(4)$  site and a reaction of  $O(7)$  to positional disorder on the  $A$  site.

A comparison of the magnitudes of the prin-

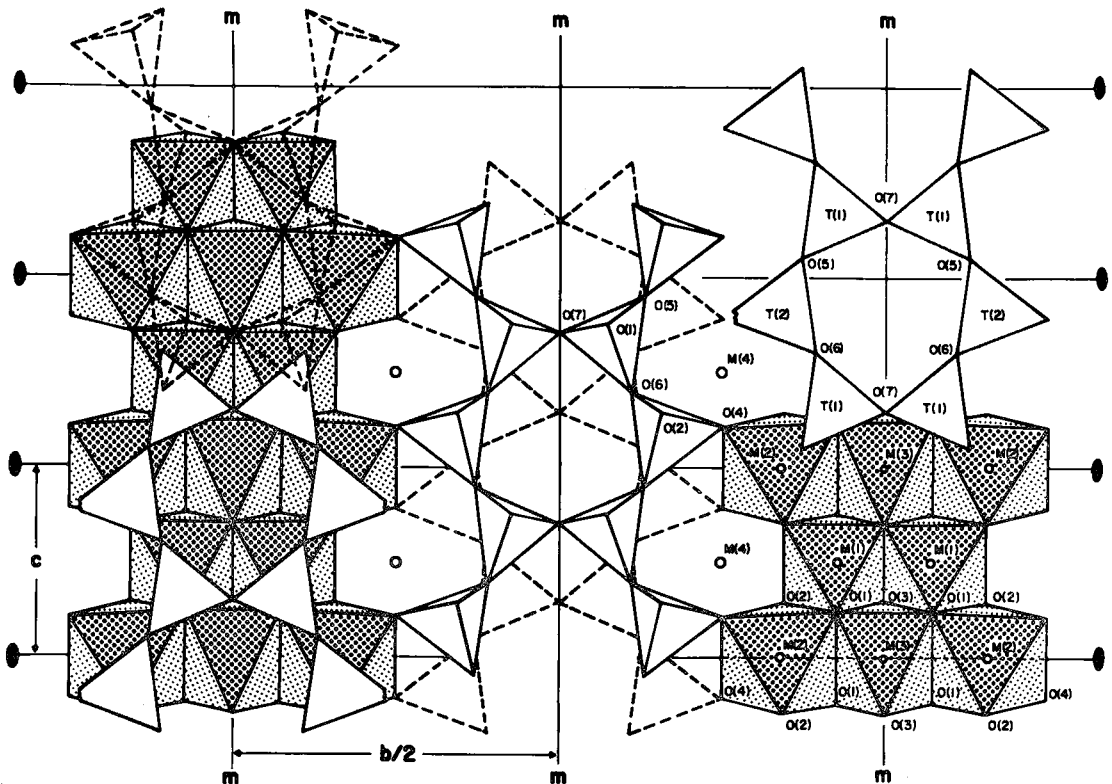


FIG. 1. The  $C2/m$  clino-amphibole structure projected down  $a^*$  (after Hawthorne & Grundy 1973a).

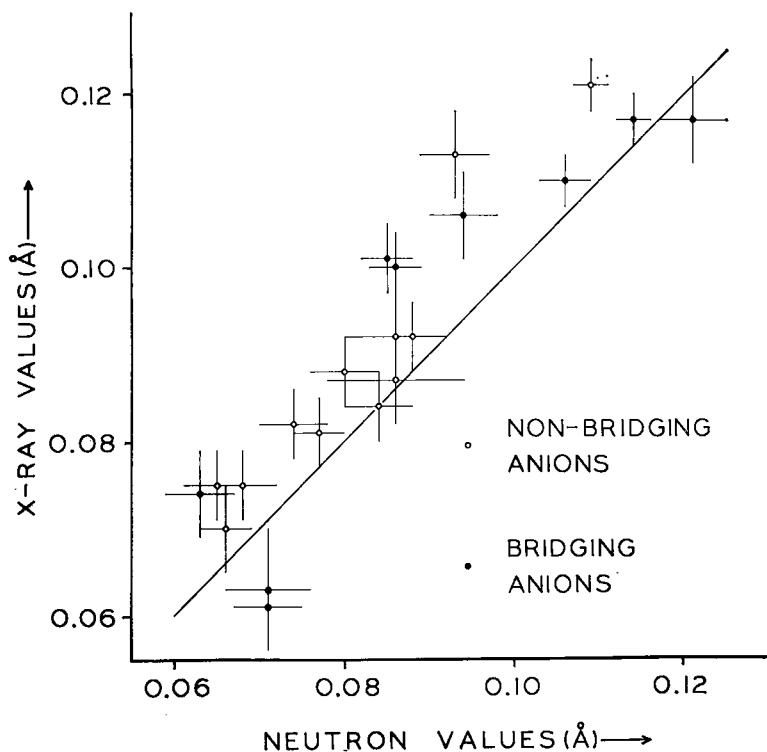


FIG. 2. Comparison of the magnitudes of the principal axes of the thermal ellipsoids of the anions in tremolite from the X-ray and neutron refinements.

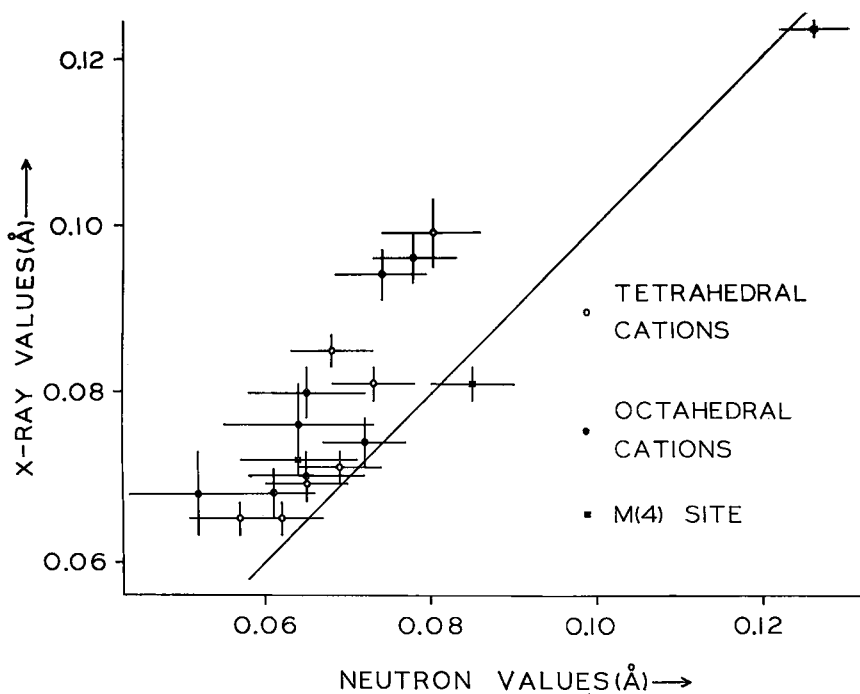


FIG. 3. Comparison of the magnitudes of the principal axes of the thermal ellipsoids of the cations in tremolite from the X-ray and neutron refinements.



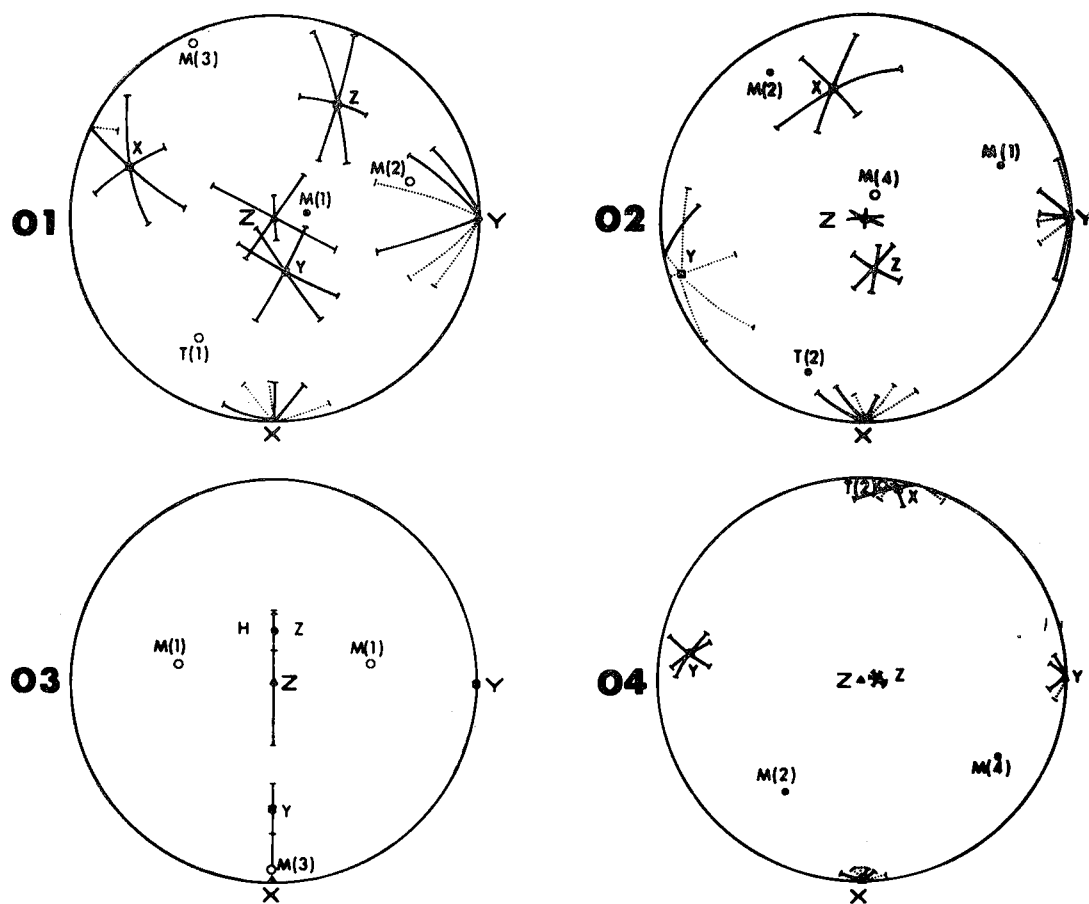


FIG. 4. Comparison of the orientations of the principal vibration axes of the anions in tremolite derived from X-ray and neutron data.

principal axes of the thermal ellipsoids (Figs. 2, 3) shows that the X-ray values generally exceed the neutron values as expected. The amount of anisotropy is generally less for the neutron results, but it is apparent from both studies that this is affected by the coordination number of the atom (Figs. 2, 3). For the anions, the mean difference between the magnitude of the maximum and minimum principal vibration axes changes from 0.054 Å (X-ray) and 0.050 Å (neutron) for two-fold coordination, to 0.048 Å and 0.032 Å for three-fold coordination, to 0.019 Å and 0.014 Å for four-fold coordination. Similarly, values for the cations change from 0.018 Å and 0.011 Å for four-fold coordination, to 0.028 Å and 0.017 Å for six-fold coordination, 0.051 Å and 0.062 Å for eight-fold coordination.

The orientations of the thermal ellipsoid principal axes are compared in Figures 4 and 5. The principal axes of O(1) are only slightly

anisotropic. The neutron values approximate a slightly oblate spheroid with X as the characteristic axis; this axis is sub-parallel to T(1)-O(1), the strongest bond to the O(1) anion. The X-ray vibration axes do not correspond closely to the neutron values; however, the X-ray values are not well-defined as the amount of anisotropy is small. For the O(2) anion, both studies indicate a slightly prolate spheroid with Z as the characteristic axis. The minimum vibration direction (neutron) is sub-parallel to T(2)-O(2), the strongest bond to the O(2) anion. The correspondence between the axis orientations in both studies is quite close. For O(3), the neutron results indicate an almost isotropic behavior whereas the X-ray results show strong anisotropy that approximates a prolate spheroid with Z as the characteristic axis. Examination of Figure 4 shows that the Z axis is parallel to the O(3)-H bond, and it is apparent that delocalization of electron-density along this bond has significantly

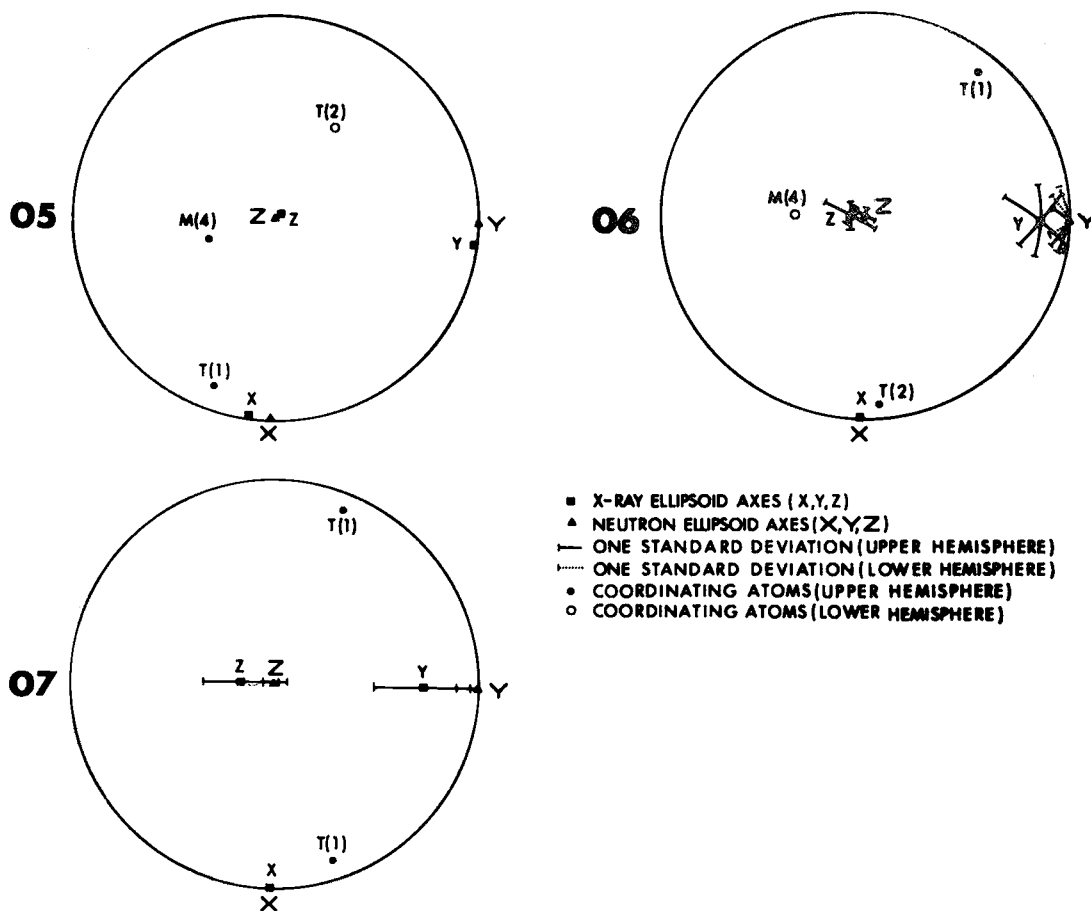


FIG. 4. See caption on page opposite.

affected the temperature factor values in the X-ray refinement. For the O(4) anion, both studies indicate that the principal axes correspond to triaxial ellipsoids whose orientations are statistically identical.

As with O(1) and O(2), the minimum principal vibration direction is sub-parallel to the bond formed with the coordinating tetrahedral cation. For the chain-bridging anions O(5), O(6) and O(7), both studies indicate significant anisotropic behavior. All principal axes from the neutron study are triaxial ellipsoids whereas, from the X-ray study, O(5) is a triaxial ellipsoid but O(6) and O(7) are approximate oblate spheroids. For these atoms, identical orientations of the thermal ellipsoids were obtained from both studies (Fig. 4). The minimum vibration directions are always sub-parallel to the tetrahedral bonds whereas the intermediate and maximum principal vibration directions are approximately perpendicular to the tetrahedral bonds in all cases. This is as expected since the

bond-stretching moments are considerably larger than the bond-bending moments, and it agrees with the infrared spectrum (unpublished data) which shows strong Si-O-Si bending modes. The neutron results for the tetrahedral sites T(1) and T(2) (Fig. 5), show their vibration to be statistically isotropic. The X-ray results show a slight anisotropic behavior, the principal vibration axes approximating oblate spheroids with X as the characteristic axis. For the octahedral sites, the neutron results indicate that the M(2) vibration is essentially isotropic whereas the M(1) and M(3) vibrations are slightly anisotropic with the principal vibration axes corresponding to prolate spheroids with Z as the characteristic axis. The principal vibration axes for M(1) and M(3) are normal to the octahedral faces and hence the maximum vibration involves the minimum possible bond-stretching. For the M(1) site, the X-ray results indicate principal vibration axes corresponding to a triaxial ellipsoid with essentially the same orientation as that

obtained in the neutron study (the reversal of the  $X$  and  $Y$  axes is not significant due to the spheroidal nature of the neutron vibration ellipsoid). From the X-ray results, the  $M(2)$  and  $M(3)$  vibration ellipsoids approximate prolate

spheroids with  $Z$  as the characteristic axis. Both studies show that the  $M(4)$  vibration is strongly anisotropic with the principal vibration axes approximating a prolate spheroid with  $Z$  as the characteristic axis. The orientation of the prin-

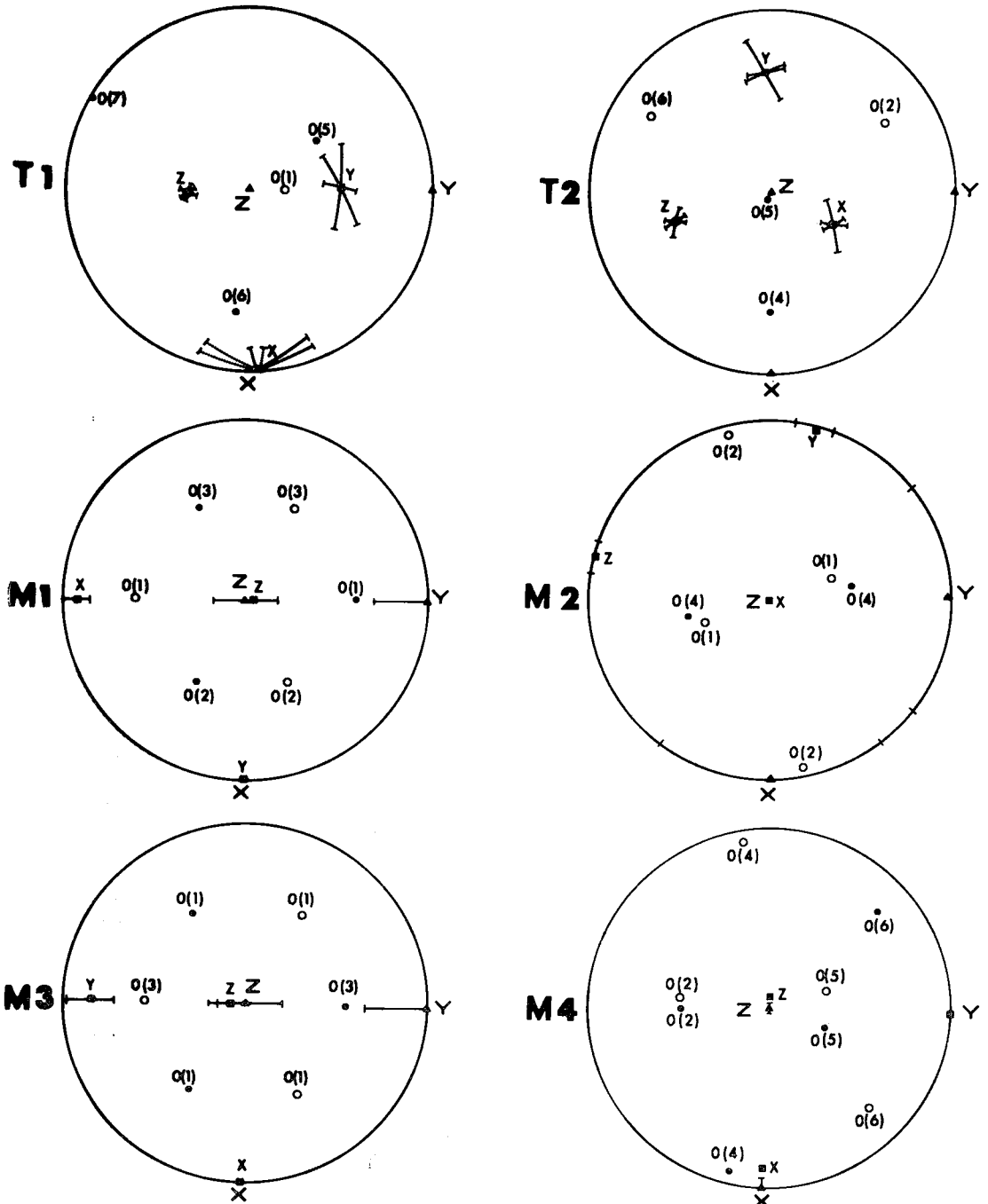


FIG. 5. Comparison of the orientations of the principal vibration axes of the cations in tremolite derived from X-ray and neutron data. Legend as for Figure 4.

cipal axes is the same in both studies; the minimum vibration direction is sub-parallel to  $M(4)-O(4)$ , the strongest bond, whereas the maximum vibration is perpendicular to this bond and bisects the angle between the  $M(4)-O(2)$  and  $M(4)-O(5)$  bonds.

It is apparent that the disposition of bonds around an atom strongly controls both the degree of anisotropy in its vibration and the orientation of the principal vibration directions. The minimum vibration direction tends to be oriented along the strongest bond with the maximum vibration direction bisecting the angle between the weaker bonds. As the coordination becomes more regular, this tendency decreases and the vibrations become more isotropic.

The magnitudes of the principal axes of the thermal ellipsoids are systematically larger for the X-ray refinement, indicating some contribution from bonding and ionization effects. The orientations of the principal axes of the thermal ellipsoids can be related to the strength and orientation of the bonds to the coordinating atoms. The minimum vibration direction is generally sub-parallel to the strongest bond; this becomes less apparent as the coordination and the strengths of the bonds become more regular.

The present neutron study confirms the hydrogen position in tremolite found by Papike *et al.* (1969). The  $O(3)-H$  bond length of  $0.960(6)\text{\AA}$  is fairly typical for a hydroxyl and shows that little or no hydrogen bonding with the chain-bridging anions occurs. This is supported by the infrared spectrum which shows a single narrow transition at  $3684\text{cm}^{-1}$ . This value agrees well with the relationship proposed by Hamilton & Ibers (1968) relating principal OH stretching frequency to nearest-neighbor anion distance. The vibration ellipsoid of the hydrogen is an oblate spheroid with its three principal axes parallel to  $a^*$ ,  $b$  and  $c$ . Because of the site-symmetry of the hydrogen position ( $m$ ), one principal axis is constrained to be parallel to the  $b$ -axis and the other two to lie in the mirror plane. The direction of minimum vibration is parallel to  $a^*$  and the  $O(3)-H$  bond. This orientation, together with the significant anisotropy of the hydrogen vibration, is to be expected as bond-stretching moments are much larger than bond-bending moments.

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