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REFINEMENT OF THE CRYSTAL STRUCTURE OF APOPHYLLITE

I. X-RAY DIFFRACTION AND PHYSICAL PROPERTIES

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Abstract

The crystal structure of apophyllite, with $a=8.963(2)$, $c=15.804(2)$, $P4/mnc$, $Z=2$, has been refined ($R=0.042$) by least squares with 546 independent intensities collected with a diffractometer. Apophyllite is a sheet structure with the bridging Si-O bond lengths 1.619(3), 1.631(3), and 1.626(3)Å, while the non-bridging bond length Si-O(3) is 1.589(3)Å. The two independent Si-O-Si angles are 139.9(2) and 140.6(2) degrees. The mean Si-O bond length is 1.616Å. As it was not possible to locate unequivocally the hydrogen ions with the X-ray data, the interpretation of the role of the water in the structure was based on the charge balance approach of Donnay and Allman (1970). Assuming that the fluorine ion is bonded to the calcium ion, the water oxygen, O(4), is hydrogen bonded to O(3), while the second proton appears to form a bifurcated hydrogen bond with O(2) and O(3). The D.T.A. and T.G.A. curves show that the water loss is discontinuous and results in a weight loss of 16 percent. The infrared absorption spectra show O-H stretching vibration bands at 3560 cm^{-1} and 3070 cm^{-1}; and single crystal infrared data show strong absorption bands using a cleavage flake with (001) oriented 70 and 90 degrees from the infrared beam.

Introduction

Apophyllite is an unusual sheet structure with space group $P4/mnc$ (Taylor and Náray-Szabó, 1931). Rings of four silicon-oxygen tetrahedra surround the four-fold axes and form parts of rings with eight tetrahedra resulting in a layered structure. The unshared oxygens in the adjacent four-fold rings point approximately along the $+c$ and $-c$ crystallographic axes respectively. The coordination of the interlayer ions is also unusual; the potassium ion is surrounded by eight water molecules, the calcium ion is bonded to two water molecules (shared with K^+) and four oxygen ions, forming a trigonal prism. The fluorine ion has been considered to be part of the Ca-polyhedron; however, E. Prince, 1970, hereafter referred to as Part II, finds that fluorine is part of an HF group. The fluorine ion is surrounded by a planar group of four Ca ions.

A number of interesting aspects of the structure and physical properties prompted us to embark on a refinement of the crystal structure. We were curious about the precise average bond length that would be found in a four-unit sheet structure with pure silicon oxygen tetrahedra. Gillespite, $BaFeSi_4O_{10}$, (Pabst, 1959) and isostructural compounds such

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as "Egyptian blue," $CaCuSi_4O_{10}$, (Pabst, 1959) have a comparable silicate sheet. In these structures, there is more overlap in adjacent four-fold rings resulting in a smaller value for the *a* cell edge. For example, in apophyllite $a = 8.96$ Å while in gillespite $a = 7.50$ Å (if the sheet were unwrinkled completely then $a = 10.4$ Å).

In addition, a recent refinement of a related structure, datolite, (Pant and Cruickshank, 1967) showed large variations in the silicon-oxygen bond distances within a single tetrahedron, with the nonbridging silicon-oxygen distances significantly shorter than the bridging distances. Apophyllite has a similar structure and might be expected to show similar large variations in bond lengths, particularly since the interlayer calcium ions have low electronegativity (this is reflected in the perfect cleavage on (001)).

The position of the protons belonging to the water molecule and their effect on the physical properties have been a problem for some time. In the original determination of the structure (Taylor and Náray-Szabó, 1931), the data were adequate to note one short interatomic distance between the oxygen of the water molecule and another oxygen (the active oxygen, O(3)) in the silicon tetrahedron. A consideration of bond strengths led them to the conclusion that the oxygen (water) position is occupied by an OH^- which is linked to O(3) by a proton. Recent differential thermal analysis curves reported for apophyllite generally agree that the water loss is discontinuous. For example, Kostov (1962) noted two distinct endotermic peaks at 300 and 390°C.

In order to augment the structure determination, we have included data from infrared absorption, differential thermal analysis, and thermogravimetric analysis.

EXPERIMENTAL

The material selected for this study is from the Phoenix Mine, Keweenaw Peninsula, Michigan, where it occurs in fractures in basalt flows. The microprobe and chemical analyses are compared in Table 1. A microprobe scan indicated that no other elements are present besides those reported here. Some minor differences are apparent between the two analyses, with the microprobe analysis, in general, giving relatively lower percentages of the major elements; however, both of them show that the deviation from ideal composition only involves sodium replacing potassium. The formula used in the refinement was

$$(Na_{0.16}K_{0.84})Ca_4(Si_8O_{20})F \cdot 8H_2O.$$

The cell constants and the calculated density at 20°C are:

$a = 8.965(2)$Å $c = 15.768(2)$Å calculated density $= 2.370$gm.cm.$^{-3}$

$Z = 2$ Volume $= 1268.8(6)$Å^3

The error in brackets refers to the last digit. These parameters were computed from a least-squares treatment of observed 2θ; values obtained from a powder diffractometer chart. The

Table 1. Microprobe and Chemical Analyses of Phoenix Mine Apophyllite

	Microprobe			Chemical		
Oxide	Wt. percent[a]	Formula[c]		Wt. percent[b]	Formula[c]	
SiO_2	50.60	Si: 7.84	7.89	51.98	Si: 7.83	7.90
Al_2O_3	0.30	Al: 0.05		0.36	Al: 0.07	
K_2O	4.20	K: 0.83	0.98	4.45	K: 0.85	1.02
Na_2O	0.50	Na: 0.15		0.61	Na: 0.17	
CaO	23.80	Ca: 3.95		25.10	Ca: 4.05	
F	2.30	F: 1.13		2.20	F: 1.05	
H_2O	(16.25) 97.95	H: (16.4)		16.25 100.95	H: 16.2	
O for F	-1.00 96.95			-0.92 100.03		

a. Analysis by P. H. Ribbe

b. Analysis by P. M. Black

c. Atoms per formula, based on 29 (O,OH,F)

radiation was nickel-filtered Cu, the scanning rate was 1/2 degree/min., and the internal standard was synthetic quartz. The computer program used is a self-indexing least-squares program (Evans, Appleman, and Handwerker, 1963). A total of 12 reflections were used in the refinement.

In order to corroborate the space group determination (Taylor and Náray-Szabó, 1931), levels of (001)* with (0-*n*-4) precession photographs were taken. The observed reflections were in agreement with Laue group $4/mmm$. In a complex-twinned yellow apophyllite from Korsnas, Finland, Th. G. Sahama (1965) describes optical properties which are not consistent with tetragonal symmetry. In addition, he noted the existence of reflections hhl with $l \neq 2n$. As a result of this investigation, Sahama concludes that the apophyllite from Korsnas is pseudotetragonal, possibly belonging to space group $Pnna$ or $Pnnm$. In view of this, the precession photographs were searched for evidence of these reflections, but none were found for the Phoenix Mine apophyllite. Later during the refinement, as an additional check on the symmetry, 51 pairs of reflections (F_{hkl} vs. F_{khl}) from three levels were measured. The agreement between these reflections

$$\left[\frac{1}{n}\;\frac{(F_{hkl}-F_{khl})}{F_{hkl}}\right]$$

was 0.049, which is comparable to the agreement factor ($R=0.042$) of the subsequent refinement of the structure. The possibility still exists that this apophyllite is pseudotetragonal; however, we believe the ultimate precision of the refinement justifies the use of space group $P4/mnc$.

The crystal used was roughly cylindrical in shape with mean radius 0.14 mm. and length 0.25 mm. A total of 546 intensities were collected from six levels about a using MoKα

radiation, an equi-inclination Weissenberg single-crystal goniometer, a scintillation detector, and strip chart recording. Each curve was integrated twice with a disc-type polar planimeter and the values averaged. The precision of measurement averaged about one percent. The intensities were corrected for Lorentz and polarization factors. Absorption corrections were not significant since $m_{\mu}r=0.10$. The refinement was carried out with a least-squares program (Busing, Martin, and Levy (1962)) on the IBM 360/91. During the first cycle of refinement, the atomic positions of Taylor and Náray-Szabó were used. Form factors were taken from International Tables Vol. III (Ibers, 1962). The temperature factor for the silicon ions was set at 0.5 Å^2 while 1.0 Å^2 was used for the other ions. Varying the atomic parameters and one scale factor and holding the isotropic temperature factors constant led to a residual R of 0.15. In the second cycle of refinement, all the parameters were varied and the T-value was 0.054. A subsequent anisotropic refinement gave $R=0.042$. All of the measured intensities were included in the final refinement and are given in Table 2.[1] Table 3 shows the final atomic positions and the anisotropic temperature factors.

In an attempt to find the positions of the protons in the water molecule, $F_{\text{obs.}}$ and ΔF Fourier maps were calculated. The resolution was insufficient to locate hydrogen ions with certainty. The area of highest electron density was in a reasonable position, between the oxygen of the water molecule and O(3), halfway along the shortest oxygen distance of 2.75 Å. This position was tested by including this hydrogen ion position in the least-squares refinement, but the large shifts in the atomic parameters of the hydrogen ion indicated that the least-squares treatment was not able to verify this position.

The important bond distances and angles are presented in Table 4. These were calculated with the function and error program (ORFFE) (Busing, Martin, and Levy (1964)). The errors were calculated using the errors in the cell parameters and the correlation matrix from the least-squares refinement.

Discussion of the Structure

The structure of apophyllite is shown in Figure 1. In the tetrahedral layers, only the unshared oxygen, O(3), is bonded to the interlayer calcium ions. (Table 5). It can be seen that the oxygen, O(4), of the water molecule occupies a strategic position in the structure. The potassium ion is coordinated by eight O(4) ions in the form of a squat tetragonal prism. Each O(4) is shared with a Ca ion which, in turn, includes two O(4) ions among its six nearest neighbors forming a trigonal prism.

Theoretical studies of bond length and bond angle variations in silicates (Pant and Cruickshank, 1967; Brown and Gibbs, 1969) can be tested against apophyllite data. As predicted by Pauling (1929) and later authors, the bridging Si-O bonds (mean length = 1.625 Å) should be, and are, longer than the nonbridging Si-O(3) bonds of 1.589 Å. If appreciable π bonding is responsible for the short bond, the bond angles subtended at silicon by the tetrahedral edges and involving O(3) should be affected. They are indeed, with angles 112 to 113°, whereas the angles subtended

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[1] To obtain a copy of Table 2, order NAPS Document #01482 from National Auxiliary Publications Service of the A.S.I.S., c/o CCM Information Corporation, 909 Third Avenue, New York, New York 10022; remitting $2.00 for microfiche or $5.40 for photocopies, in advance payable to CCMIC-NAPS.

Table 3. Atomic Positions and Thermal Parameters for Apophyllite

	$\underline{x}$	$\underline{y}$	$\underline{z}$	$\underline{B}_{11}^{c}$	$\underline{B}_{22}$	$\underline{B}_{33}$	$\underline{B}_{12}$	$\underline{B}_{13}$	$\underline{B}_{23}$
F	0	0	0	.55(12)	.55(12)	2.89(40)	0	0	0
K	0	0	1/2	2.00(12)	2.00(12)	4.98(20)	0	0	0
Ca	.1102(1)[a]	.2460(1)	0	.58 (3)	.68 (3)	.60(10)	.064 (3)	0	0
Si	.2258(2)	.0864(2)	.1900(1)	.55 (3)	.55 (3)	.80(10)	-.03 (3)	-.17 (6)	.00 (6)
0(1)	.3635(6)	.1365(6)	1/4	.80 (9)	.80 (9)	.60(20)	-.10 (12)	-.23 (6)	-.23 (6)
0(2)	.0843(3)	.1899(2)	.2177(2)	.68 (9)	1.03 (9)	1.78(10)	.32 (9)	-.06(10)	-.34(10)
0(3)	.2642(3)	.1020(3)	.0923(2)	.97 (9)	1.00 (9)	1.00(10)	.10 (9)	-.23(10)	-.11(10)
0(4)[b]	.2128(4)	.4498(4)	.0900(2)	2.64(20)	1.13 (9)	1.50(20)	-.13 (12)	-.06(10)	-.40(10)

a. Standard error in brackets refers to the last digit.

b. 0(4) belongs to the water molecule.

c. The form of the temperature factor is $\exp[-(1/4)(\underline{h}^2\underline{a}^{*2}\underline{B}_{11} + \underline{k}^2\underline{b}^{*2}\underline{B}_{22} + \ell^2\underline{c}^{*2}\underline{B}_{33} + 2\underline{hk}\underline{a}^*\underline{b}^*\underline{B}_{12} + 2\underline{h\ell}\underline{a}^*\underline{c}^*\underline{B}_{13} + 2\underline{k\ell}\underline{b}^*\underline{c}^*\underline{B}_{23})]$

Table 4. Bond Lengths and Angles for Apophyllite

Bond Lengths (Angstroms)

Tetrahedron (Si-O)

Si - O(1)	1.619(3)[a]
Si - O(2)	1.631(3)
Si - O(2)1[c]	1.626(3)
Si - O(3)	1.589(3)
mean	1.616

Tetrahedron (O-O)

O(1) - O(2)	2.596(3)
O(1) - O(2)1	2.571(3)
O(1) - O(3)	2.666(3)
O(2) - O(2)1	2.632(4)
O(2) - O(3)	2.672(4)
O(2)1- O(3)	2.680(4)
mean	2.636

Ca-Polyhedron (Ca-O)

Ca - O(3)	2.387(3)
Ca - O(3)1	2.404(3)
Ca - O(4)	2.491(3)
mean	2.427

Ca-Polyhedron (O-O)

O(3) - O(3)1	3.588(4)
O(3) - O(4)	3.151(5)
O(3)1- O(4)	3.283(5)
O(4) - O(4)2	2.848(8)
O(3) - O(3)2	2.916(7)

K-Polyhedron

K - O(4)	2.972(3)
O(4) - O(4)1	3.690(5)

O(4)[b] - O

O(4) - O(3)1	2.750(5)
O(4) - O(2)	3.173(5)

Si-Si

Si - Si(1)	3.065(2)
Si - Si(2)	3.043(3)

Bond Angles (degrees)

Tetrahedron (O-Si-O)

O(1) - Si - O(2)	106.1(2)
O(1) - Si - O(2)1	104.7(2)
O(2) - Si - O(2)1	107.9(2)
O(1) - Si - O(3)	112.4(3)
O(2) - Si - O(3)	112.3(2)
O(2)1- Si - O(3)	112.9(2)

Si - O - Si

Si - O(1) - Si	139.9(1)
Si - O(2) - Si	140.6(3)

[a] Standard error in brackets refers to the last digit

[b] O(4) belongs to H_2O

[c] The symmetry transforms are numbered as follows:
1. $y,\bar{x},z$; 2. $x,y,\bar{z}$.

by the edges made of the bridging oxygens range from 105 to 108° (Table 4).

Table 5 shows the bond lengths and the estimated bond valences using

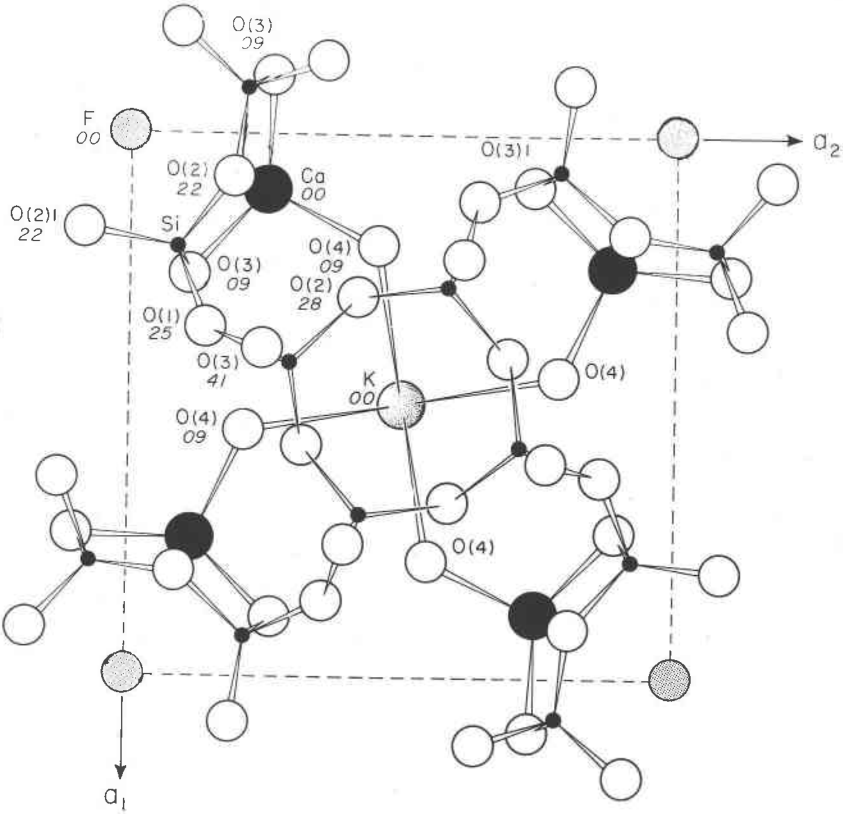

FIG. 1. Structure of apophyllite viewed along [001].

the method of Donnay and Allman (1970). It is instructive to calculate the valences using the model that would have been assumed from X-ray diffraction data alone, namely, that the fluorine ion is part of the calcium polyhedron. Table 5 also includes values for the maximum bond length, $L_{max.}$, the mean bond length, $\overline{L}$, and p used in the calculations. The only complication is the assignment of an "ideal value" for v for the calcium ion. The regular square of calcium ions surrounding the fluorine ion at the origin suggests an approach analogous to the one taken for bultfonteinite (Donnay and Allman, 1970). We consider the cation polyhedron about $^{IV}F^-$ and assign bond valence $\frac{1}{4}$ to each Ca-F bond. The v_i value for calcium then becomes $(2-\frac{1}{4})/6$ or $7/24$, so that the ideal valence sum will equal: $6\times 7/24+\frac{1}{4}=2$. When this is done, the valence sums over the anions for the given cations, $\Sigma_A v$, are close to the ideal values. The deviations $\Sigma_c v$ from their ideal values indicate the presence

Table 5. Bond Lengths (Å) and Estimated Bond Valences in Apophyllite, $(K_{0.84}Na_{0.16})\ Ca_4(Si_4O_{10})_2F\cdot 8H_2O$

Anions (numbered)	$K_{0.84}Na_{0.16}$ 2(b)	Ca 8(h)	Si 16(i)	ΣV_a(v.u.)	Anion Chemistry	ΣV_a corrected for H bonds	Short Oxygen-Oxygen Distances and Estimated Hydrogen-Bond Valences		
							Acceptor \ Donor	$H_2O(4)$	ΣV_H
O(2) 8(a)			1.619/0.994	1.988	$O^=$	1.988			
O(2) 16(i)			1.631/0.973 1.626/0.980	1.953	$O^=$	2.023	O(2)	3.17/0.07	0.07
O(3) 16(i)		$2.384/0.31^2$ $2.404/0.30^2$	1.589/1.054	1.664	$O^=$	1.924	O(3)	2.75/0.19 3.15/0.07	0.26
O(4) 16(i)	$2.972/0.125^8$	$2.500/0.27^2$		0.395	H_2O	0.065	ΣV_a	0.33	
O(5) 2(a)		2.416/0.25		1.00	F^-	1.00			
ΣV_c(v.u.)	1.000	2.01	4.01						
$\bar{L}$(Å)	2.972	Ca-O:2.429 Ca-F:2.416	1.616						
$L_{max.}$(Å)	3.30	Ca-O:3.25	2.13						
p	9.061	Ca-O:2.955	3.144						
v_i	1/8	Ca-F: 1/4 Ca-O: 7/24	1.00						

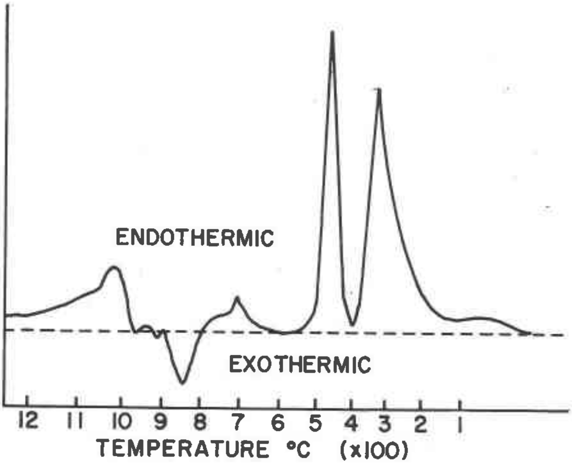

FIG. 2. Differential thermal analysis curve for apophyllite.

of hydrogen bonding. The columns on the far right of Table 5 show the oxygen-oxygen approaches that bear on hydrogen bonding together with the estimated hydrogen bond valence strengths. When these latter values are added to the previous $\Sigma_c v$ data, the sums are near the ideal values. The interpretation follows that O(4) is hydrogen bonded to O(3) and is also bonded to O(2) and O(3) with a weak bifurcated hydrogen bond. These results should be compared to those of Table 4, Part II, in which the hydrogen positions are known and the hydrogen bond strengths can be determined accurately. Also see Figure 1, Part II, for the detailed geometry of the hydrogen bonding around O(4). D.T.A. and T.G.A. curves (Figs. 2 and 3) were run for apophyllite. The D.T.A. curve shows two distinct endothermic peaks roughly centered at 325 and 450°C with the lower temperature peak quite broad and the higher

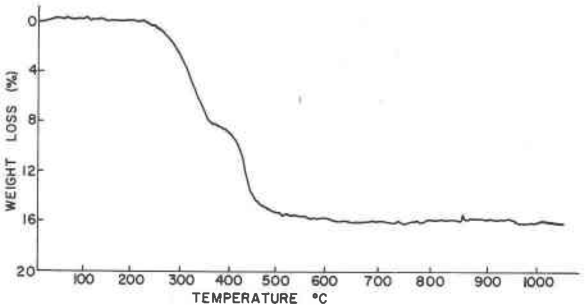

FIG. 3. Thermogravimetric analysis curve for apophyllite.

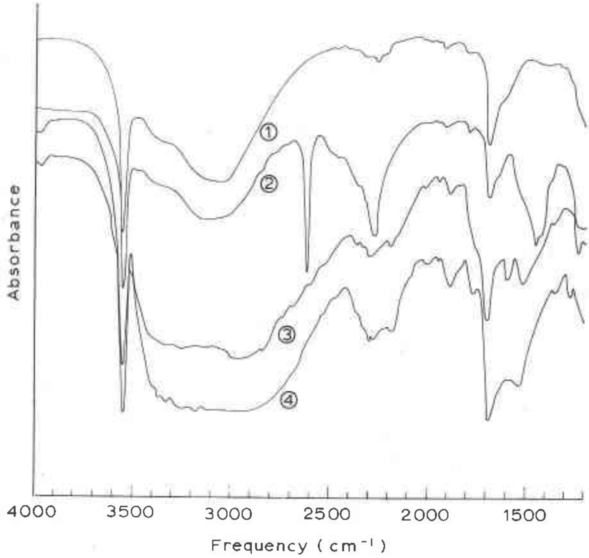

FIG. 4. Infrared absorption spectra for apophyllite.

(1) Apophyllite, KBr disc, dilution 0.001 gm. in 0.20 gm. KBr.
(2) Apophyllite—partially deuterated, KBr disc, dilution 0.001 gm. in 0.20 gm. KBr.
(3) Apophyllite (001) cleavage flake oriented at 90° to beam and
(4) Same sample oriented at 70° to infrared beam.

temperature peak relatively sharp. The T.G.A. curve corroborates this and shows that water loss starts at about 225°C and continues to a discontinuity between about 375 and 400°C; then dehydration is more rapid until 16 percent total weight loss has been reached at 600°C. The first broad peak can be attributed to loss of H_2O while the second may be due to loss of HF (see Part II for details).

The O-H stretching vibration region of the infrared spectra of apophyllite is shown in Figure 4-1. The spectra shows a sharp absorption band at 3560 cm^{-1} and a broad band at 3070 cm^{-1}. Examination of the infrared absorption spectra of some thirty different apophyllite specimens showed identical spectra with two O-H stretching bands similar in position and in their ratios of absorbence to those figured. To sharpen the absorption bands and to eliminate the possibility of there being more than two O-H bands present, the specimen was partially deuterated. Figure 4-2 shows the positions of the two pairs of O-H and O-D bands. Work on hydrogen-bonded compounds has shown that the O-H stretching frequency is an almost linear function of the O-H. . .O bond distance (Nakamoto, *et al.*, 1955). The sharp 3560 cm^{-1} absorption band is slightly less energetic than the characteristic free O-H frequency at c. 3700 cm^{-1} and indicates a weak hydrogen bond while the 3070 cm^{-1} band indicates a stronger hydrogen bond and a shorter O-H. . .O bond distance. A 0.005 mm. thick (001) cleavage flake of apophyllite was oriented at 90° and 70° to the infrared beam (Figure 4-3, 4). Both O-H absorption bands appeared with considerable intensity in the spectra. Because of the perfect (001) cleavage, it was not possible to study the absorption spectra of a slice parallel to *c*.

SUMMARY

A refinement of the structure of apophyllite has given precise values for the variation of Si-O bond lengths and for the mean Si-O distance in this sheet structure. It has also provided data on the coordination geometry of Ca^{2+} and K^{+}. O(4) is found to belong to a water molecule; the positions of hydrogen bonds between oxygen ions have been determined by applying the principle of local charge neutralization in a quantitative way. D.T.A., T.G.A., and infrared data can be explained on the basis of the refined structure.

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