

The Infra-red Spectrum of Afwillite, $\text{Ca}_3(\text{SiO}_3\text{OH})_2 \cdot 2\text{H}_2\text{O}$, in Relation to the Proposed Hydrogen Positions

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The infra-red absorption spectrum of afwillite, $\text{Ca}_3(\text{SiO}_3\text{OH})_2 \cdot 2\text{H}_2\text{O}$, has been examined in the region $2000\text{--}3500\text{ cm.}^{-1}$ in powdered material and in thin sections of a single crystal cut parallel to (100), (010) and (10 $\bar{1}$). Using unpolarized radiation and powdered afwillite, two very broad bands were observed centred at about 2400 and 2800 cm.^{-1} and two less broad bands close to 3130 and 3340 cm.^{-1} . The polarization properties of the bands at 3130 and 3340 cm.^{-1} were studied using the thin sections. These bands appear only when the electric vector has a component perpendicular to the crystallographic y axis, and it is found that the band at 3340 cm.^{-1} actually consists of two overlapping bands with a frequency difference of approximately 60 cm.^{-1} . These results confirm that both long and short hydrogen bonds are present in the afwillite structure. There is a fair correlation between the polarization directions of the absorption bands and those predicted from the X-ray structure analysis for the OH and H_2O groups.

Introduction

The structure of afwillite, $\text{Ca}_3(\text{SiO}_3\text{OH})_2 \cdot 2\text{H}_2\text{O}$, has been worked out by Megaw (1952) using X-ray techniques. The arrangement of the calcium, silicon and oxygen atoms was determined directly. The position of the hydrogen atoms was inferred from a consideration of the exact interatomic dimensions, the coordination of the oxygens and the requirements of Pauling's electrostatic valency rule. It was concluded that hydrogen is present both in water molecules and in hydroxyl groups, and that both long and short hydrogen bonds exist.

The work outlined in this paper was undertaken in the hope that infra-red data might give direct evidence as to the direction and length of the hydrogen bonds and thus serve as a check on the model proposed by Megaw. Preliminary measurements of the infra-red absorption of the powdered material had been made by Mr D. E. Bethell, but no work had been done with single crystals.

Experimental techniques

Afwillite has monoclinic symmetry, and the crystals are elongated and striated parallel to the y axis, with a perfect cleavage parallel to (10 $\bar{1}$) and an imperfect one parallel to (100) (referred to the axes chosen by Megaw). The material used by us came from a single clear colourless crystalline fragment with prominent cleavage faces from Kimberley (S. Africa), kindly provided by the late Mr A. F. Williams. Sections of area

approximately $10\text{ mm.} \times 6\text{ mm.}$ were cut parallel to the (10 $\bar{1}$) and (100) cleavage planes and then each was ground to a thickness of approximately $0\cdot03\text{ mm.}$ It proved impossible to obtain a single piece parallel to (010) of sufficient area, so a composite section was made up using two slightly overlapping pieces arranged optically to have the same orientation. The composite section was approximately $8\text{ mm.} \times 5\text{ mm.}$ in area and $0\cdot03\text{ mm.}$ thick. For spectroscopic measurements the crystal sections were held in place on a fluorite plate by a capillary layer of Nujol. The spectra were studied with a Hilger D209 double-beam spectrometer equipped with a 30° CaF_2 prism.

Experimental results

Fig. 1(a) shows the spectrum obtained with powdered afwillite. It consists of two very broad absorption bands centred at approximately 2400 and 2800 cm.^{-1} , of half-width $300\text{--}600\text{ cm.}^{-1}$, and two less broad bands at 3130 and 3340 cm.^{-1} of half-width $100\text{--}200\text{ cm.}^{-1}$. These same bands were observed previously by Bethell.

In each of the crystal sections studied nearly 100% absorption was observed in the region $2200\text{--}2950\text{ cm.}^{-1}$, and the intensity did not vary with the direction of polarization of the incident light to a sufficient extent to be readily measurable. The following discussion is therefore confined to the absorption bands at frequencies higher than 3000 cm.^{-1} .

Fig. 1(b) shows the spectrum obtained with the beam incident normally on the section cut parallel to the (10 $\bar{1}$) cleavage plane. With the incident electric vector \mathbf{E} perpendicular to the y axis, the two absorption bands at 3130 and 3340 cm.^{-1} have strong maxima

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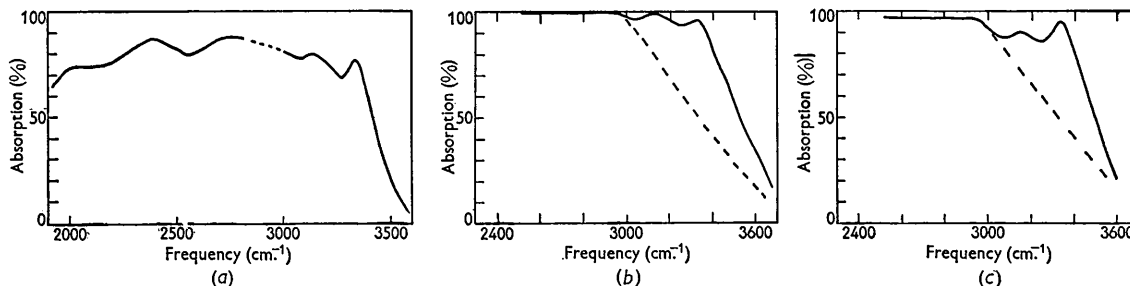


Fig. 1. (a) Infra-red spectrum of powdered afwillite. (b) Polarized infra-red spectrum of afwillite with the incident beam perpendicular to $(10\bar{1})$. The incident electric vector E is parallel (broken line) or perpendicular (full line) to the y axis. (c) Polarized infra-red spectrum of afwillite with the incident beam perpendicular to (100) . The incident electric vector E is parallel (broken line) or perpendicular (full line) to the y axis.

with 99 and 96% absorption respectively. With E parallel to the y axis no maxima could be detected at these frequencies, the observed absorptions of 78 and 50% respectively corresponding to a tail of absorption extending from the low-frequency region of near 100% absorption. Intermediate spectra were obtained for other orientations; these were identical for pairs of orientations of E making equal angles with the y axis.

The analogous spectrum obtained with the incident beam normal to the (100) section are shown in Fig. 1(c). Once again the absorption bands at 3130 and 3340 cm^{-1} have their maximum intensity (91 and 96% absorption respectively) when E is perpendicular to

the y axis, and no absorption peaks can be detected for E parallel to y (73 and 50% absorption). The plot of absorption in these two bands against the orientation of E is once again symmetrical with respect to the y direction.

Fig. 2(a)-(h) shows some of the spectra obtained with the incident beam normal to the (010) section and with various orientations of E relative to the (100) cleavage trace, which is the direction of the z axis. The variation in strength, with varying orientation of E , of the two absorption bands near 3100 and 3300 cm^{-1} is less marked than for the previous sections. The band at 3130 cm^{-1} has its maximum intensity when E is at 80° to the (100) cleavage trace (i.e. parallel to the $(10\bar{1})$ cleavage trace). The intensity of the band centred near 3300 cm^{-1} varies little with the orientation of E , but the maximum varies in position between the extremes of 3270 and 3340 cm^{-1} . It appears that there are overlapping absorption bands of comparable intensity at these two frequencies which normally combine to give a composite maximum. With the help of polarized radiation they have been separated experimentally by virtue of their different directional properties. The direction of maximum absorption associated with each frequency is recorded in Table 1, together with that of the band at 3130 cm^{-1} .

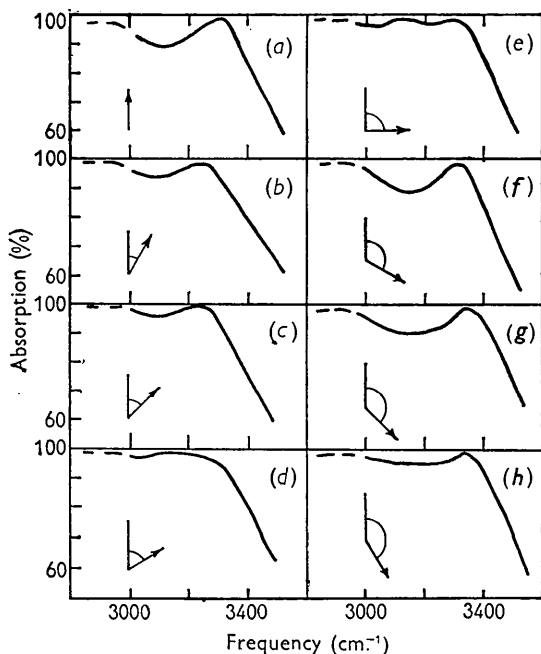


Fig. 2. Polarized infra-red spectrum of afwillite with the incident beam perpendicular to (010) . The angle between the electric vector E and the z axis is represented by the small figures on the lower left-hand corner of each diagram, in which the z axis is vertical and the $(10\bar{1})$ cleavage trace and the x axis are at 80° and 135° to it, respectively, in a clockwise direction.

Table 1. Direction of maximum absorption in (010) plane

Frequency (cm^{-1})	Angle from z axis to direction of maximum absorption (angle reckoned positive if measured towards x axis)	Estimated limits of experimental error
3130	$+ 80^\circ$	$\pm 15^\circ$
3270	$+ 35$	± 15
3340	$+ 135$	± 10

Discussion

Afwillite belongs to the class C_s-m ; this is characterized by a plane of symmetry parallel to (010) (perpendicular to the y axis). For each lattice point, the unit cell contains a pair of formula-units* related

* The four formula-units in the crystallographic unit cell illustrated in Fig. 4 are related in pairs by the translational

by the symmetry plane, all atoms being in general positions; thus we have to consider two pairs of equivalent OH groups and two pairs of equivalent H_2O molecules.

The vibrations of atoms in general positions of a structure of class m are all infra-red-active, and of symmetry class A' or A'' , according to whether the direction of dipole change involved is parallel or perpendicular to the symmetry plane. The discussion that follows is concerned solely with the OH-bond stretching vibrations (ν OH) of the OH and H_2O groups in the unit cell. The other vibrations of the unit cell have much lower frequencies.

A pair of equivalent OH groups in class m gives rise to two modes of vibration of the lattice. When they vibrate in-phase the dipole change lies in the (010) plane, along the projection of the OH bond (symmetry A'); when they vibrate out-of-phase, the dipole change is perpendicular to the plane (symmetry A''). Since the OH groups of an equivalent pair are well separated in the unit cell, they will not interact appreciably, and their two vibrations are expected to have closely similar frequencies. The absorption intensity of the A' relative to the corresponding A'' band will be greater the more nearly the OH bond lies parallel to the symmetry plane.

An isolated H_2O molecule has two ν OH modes of vibration, in which the dipole changes lie along the

two bisectors of the H-O-H angle, as in Fig. 3. A pair of equivalent H_2O molecules in class m gives rise, for each of these, to two vibrations of symmetries A' and A'' .

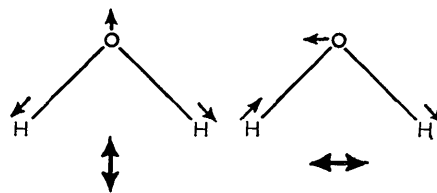


Fig. 3. Diagrammatic representation of the vibrational motions of an isolated water molecule. Light arrows represent the (exaggerated) atomic displacements during ν OH vibrations; heavy arrows represent the directions of the associated dipole changes.

If one atom of each equivalent pair is taken as representative, there are two independent OH's, each associated with two ν OH vibrations, and two independent H_2O 's, each associated with four ν OH vibrations, making twelve such vibrations in all for the unit cell. Half are of symmetry A' and half of symmetry A'' .

The frequencies of the ν OH vibrations will depend on whether the hydrogen atom is involved in a strong or a weak hydrogen bond. Strong bonds, corresponding to short O-O distances, are usually associated with broad absorption bands in the region 3000-2000 cm^{-1} , weak bonds with sharper bands in the region 3500-3000 cm^{-1} (Rundle & Parasol, 1952; Lord & Merri-

operation of a C -face-centred lattice. The spectroscopic properties of a crystal are not affected by translational operations.

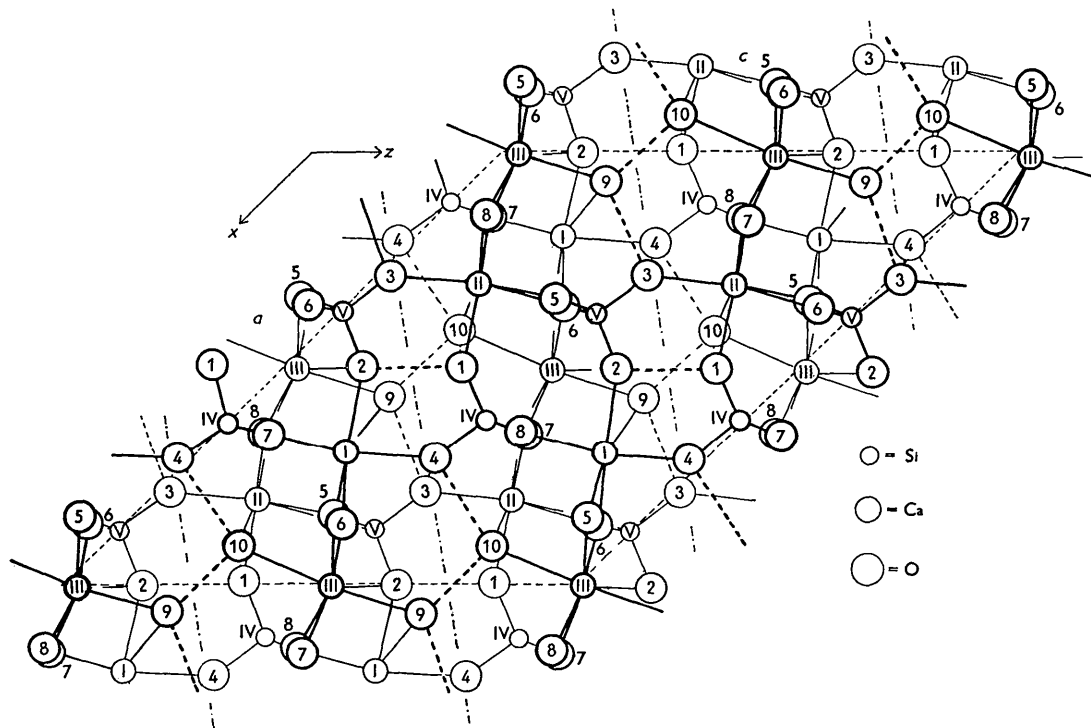


Fig. 4. Projection of the unit cell of awillite on (010), according to X-ray structure determination. Numbering of oxygen atoms as in text.

Table 2

Reference number of bond	Kinds of groups involved	Length (s.d. = $\pm 0.035 \text{ \AA}$)	Angle between bond and indicated crystallo- graphic axis (to nearest degree)	
			y axis (normal to (010))	z axis (trace of (100) cleavage)*
9 \rightarrow 3	$\text{H}_2\text{O} \rightarrow \text{O}$	2.73 \AA	85°	+69°
10 \rightarrow 1	$\text{H}_2\text{O} \rightarrow \text{O}$	2.71	21	+85
10 \rightarrow 4	$\text{H}_2\text{O} \rightarrow \text{OH}$	2.70	83	+55
2 \rightarrow 1	$\text{OH} \rightarrow \text{O}$	2.56	86	-2
4 \rightarrow 3	$\text{OH} \rightarrow \text{O}$	2.49	23	+103
9 \rightarrow 10	$\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}$	2.52	88	+135
Bisectors of angle 3-9-10	$\begin{cases} a_1 \\ a_2 \end{cases}$		86	+102
			87	+12
Bisectors of angle 1-10-4	$\begin{cases} b_1 \\ b_2 \end{cases}$		59	+63
			33	+40

* Angles measured towards x axis reckoned positive.

field, 1953). The presence of both types of absorption band in the spectrum of powdered awillite (Fig. 1(a)) confirms the presence of both types of bond in the structure.

The structure of awillite, as determined by the X-ray investigation, is shown in Fig. 4 in projection on (010). There are six independent hydrogen bonds. They are listed in Table 2, which shows their lengths and the angles they make with fixed directions in the structure. (The reference numbers given to the atoms are those used in the original description of the structure.) Three of the bonds are long ($\approx 2.7 \text{ \AA}$) and three short ($\approx 2.5 \text{ \AA}$).

It is necessary at this point to consider the nature of the experimental evidence and the postulates involved in using it. Three points should be noted.

First, the X-ray study gives a direct determination of the bond length O-O. It is generally assumed that the length is short for a strong bond and longer for a weak bond, and we shall accept this as a working rule. There may be exceptions, however, since a short distance between two oxygens could conceivably result from forces exerted on them by other neighbours which are themselves strongly bonded into position; if this effect is appreciable, the O-O distance will not give a true measure of the OH-O attractive force. There is evidence from sodium sesquicarbonate that such an effect may influence the thermal expansion (Candlin, 1956). In awillite, it may possibly influence the 9-10 distance, because these atoms are more or less clamped into position by their neighbours.

Secondly, the X-ray study shows the direction of the O-O joining line, but gives no direct information about the position of the hydrogen atom. In the present work we adopt the assumption, commonly made in the literature, that the hydrogen atom lies on the O-O line. Cases are known, however, where it can lead to errors of 15-20° in fixing the O-H direction (see for instance Ambrose, Elliott & Temple, 1951), and such deviations may well occur in awillite.

Thirdly, the X-ray study shows that the H_2O groups are not always equidistant from the two oxygen atoms towards which their hydrogen atoms are directed. If the two hydrogen bond strengths are different, the assumption that the dipole changes lie along the bisectors of the H-O-H angle no longer holds rigidly. Further, the oxygen of one water molecule also serves as negative end for another hydrogen bond, and this may give rise to disturbing effects, for which no theoretical treatment is available.

On these three points, therefore, simplifying assumptions have to be made which are founded neither on experimental evidence nor on accepted theory. Nevertheless they represent the most reasonable starting point for an attempted correlation of structure and infra-red behaviour in the existing state of knowledge.

Table 2 shows that both independent OH groups (labelled 2 and 4) are associated with short O-O distances, and one water molecule (10) with two long distances. These are expected to give rise to absorption at frequencies below and above 3000 cm^{-1} respectively. The second water molecule (9) is associated with one long distance and one short, and its vibrations may cause absorption at frequencies on either side of 3000 cm^{-1} .

As stated above, the absorption bands of the thin crystal section at frequencies below 2950 cm^{-1} are so strong that no quantitative measurements of their polarization properties are possible. Nevertheless, the fact that absorption is very great whether the plane of polarization is parallel or perpendicular to (010) would point to the existence of strong hydrogen bonds (short O-O distances) with appreciable components parallel and perpendicular to the plane. That this is in qualitative agreement with the X-ray structure can be seen from Table 2.

It is interesting to note that the OH groups, as identified by the X-ray work, are associated with short O-O distances and low-frequency broad ν OH bonds. In both these respects they are analogous to

the OH groups in the ions H_2PO_4^- and HCO_3^- in KH_2PO_4 and NaHCO_3 respectively (Miller & Wilkins, 1952; Bethell & Sheppard, unpublished), although in these two compounds the hydrogen atom is randomly displaced to either side of the centre of each O-O bond, while in afwillite it is associated with one of the two O's and is not statistically interchangeable. The resemblance of the infra-red spectra suggests that the OH groups have essentially a covalent linkage to the central Si atom. If they had been ionic, as in the alkali and alkaline earth hydroxides, the ν OH vibrations would have been expected to give sharp bands at frequencies in the range $3500\text{--}3700\text{ cm.}^{-1}$ (Jones, 1954; Busing, 1953; Mara & Sutherland, 1953; Petch, unpublished). No bands of this type were observed.

The specific absorption bands observed at frequencies above 3000 cm.^{-1} must all correspond to vibrations of symmetry A' , since the maximum absorption in each case occurs in a direction parallel to (010). This implies that the majority of the weak hydrogen bonds (long O-O distances) lie nearly in (010); their components perpendicular to the plane must be small. From Table 2, it can be seen that two of the long O-O distances, 9-3 and 10-4, lie nearly in (010), but the third, 10-1, is inclined steeply to it. Hence it would have been expected that one absorption band associated with water molecule 10 should have had considerable strength perpendicular to (010). This is an apparent discrepancy between deductions from the X-ray and infra-red results. It is possible, however, that the missing A'' component is simply masked by the strong general absorption in the region between 3000 and 3300 cm.^{-1} , which is due to the tail of the very intense bands of lower frequency.

The three absorption bands associated with particular directions in the (010) plane are of considerable interest. These must be derived from water molecules only, since the OH groups are both involved in strong bonds and hence give absorption in the lower-frequency range. The vibration directions may be calculated with the help of the assumptions mentioned earlier. They are plotted in Fig. 5(a) together with the observed directions of maximum absorption. Rough quantitative estimates of the intensities expected have been made by considering the inclination of the directions to the (010) plane; they are indicated by lengths of lines in the figure.

In Fig. 5(a) the observed vibration direction α may be correlated with either of the calculated directions a_2 or b_2 , the observed β with calculated b_1 ; the differences are not much outside the estimated limits of experimental error of $10\text{--}15^\circ$ in the observed directions. The third observed direction, γ , must be correlated with the calculated a_1 , and here the difference is 33° . The discrepancy is greater than the purely experimental error, but is not outside the possible combined errors due to experiment and to the simplifying assumptions that have to be made in connection with the theoretical calculations. It should be noted that the calculated

direction a_1 is associated with the water molecule 9 and that the long and short O...O distances associated with this (corresponding to a weak and a strong

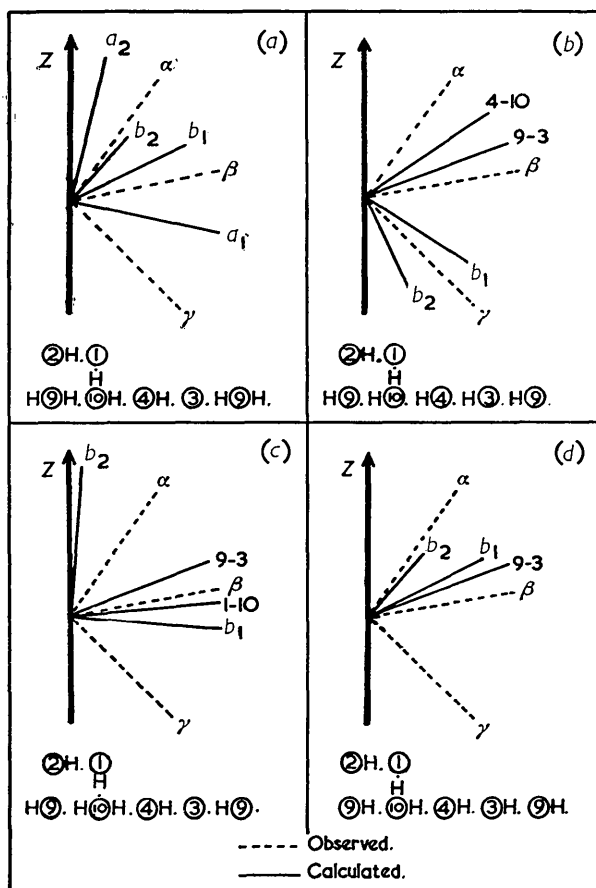


Fig. 5. Comparison between observed and calculated directions of ν OH absorption bands, at frequencies higher than 3000 cm.^{-1} , polarized in the plane (010), (a) for the original arrangement of hydrogen atoms assumed by Megaw, (b)–(d) for alternative arrangements of hydrogen atoms. The assumed arrangements are represented schematically in the figure.

Observed directions of absorption bands are marked α (3270 cm.^{-1}), β (3130 cm.^{-1}) and γ (3340 cm.^{-1}). Absorption directions expected from water molecule based on oxygen 9 are marked a_1, a_2 , those from water molecule based on oxygen 10, b_1, b_2 ; O-H...O bond directions are numbered according to the atoms concerned in them. Lengths of lines indicate approximate relative strength of expected bands.

hydrogen bond) make the theoretical treatment of this molecule as an isolated water molecule particularly unsatisfactory. Thus although the agreement between the observed and calculated directions is not as clear as might have been wished, it is not unreasonable.

Although the allocation of hydrogen atoms which has been assumed in the above discussion seems strongly to be preferred on the basis of the X-ray results, it was thought to be advisable to see whether any closely related alternative allocation might give better agreement with the spectroscopic measure-

ments. The total number of ways of interchanging hydrogen atoms is large, but it was considered that the crystal structure indicates very strongly that (a) oxygen atom 10 represents a water molecule, and (b) oxygen atoms 1, 3 and 4 represent only OH or O groups but not water molecules. The first assumption follows from the fact that 10 is the oxygen atom with the greatest number (three) of hydrogen-bonded neighbours, the second from the fact that 1, 3 and 4 are directly bonded to silicon atoms.

In Fig. 5(b)–(d) the observed directions of absorption bands are compared with the calculated directions for each of the remaining possible hydrogen arrangements consistent with the above assumptions. In each case the arrangement of hydrogen atoms is shown schematically. It should be noted that no change will occur in the predicted spectrum if the hydrogen atom is shifted from one oxygen atom to another in an $\text{OH} \cdots \text{O}$ unit in which water molecules are not involved; such alternative arrangements have not been represented separately. On comparing the four diagrams of Fig. 5 it is seen that the agreement between experiment and theory is least satisfactory for Fig. 5(c) and Fig. 5(d), but that there seems to be little to choose between Fig. 5(a), already considered above, and Fig. 5(b). The latter gives a better correlation with the observed absorption band γ , but the former accounts more satisfactorily for the observed band α . It therefore appears that the spectroscopic results alone do not provide reasons for preferring an alternative arrangement of hydrogen atoms, and the detailed arguments previously advanced for the original arrangement from the X-ray results still militate in its favour.

It should be noted that there are only three calculated directions of absorption shown in Fig. 5(d) whereas there are four in the other cases. This is because the arrangement of hydrogen atoms assumed in calculating Fig. 5(d) shows the 9–10 distance as associated with an OH group and not a water molecule. As this is a short distance corresponding to strong hydrogen bonding the corresponding absorption frequency would most probably lie below 3000 cm^{-1} . As noted earlier, however, the short 9–10 distance may be due to steric forces rather than hydrogen bonding and in this case the absorption band could

appear above 3000 cm^{-1} . The 9–10 direction is in fact almost coincident with the direction of absorption band γ , and if this band were included much the best agreement of all would be obtained between theory and experiment. This point should perhaps be borne in mind in future studies of the problem of location of hydrogen atoms, but the agreement may be fortuitous and cannot be given great weight at this stage.

It must therefore be concluded that the observed polarized infra-red spectrum of awillite is only moderately in agreement with that predicted from the allocation of hydrogen atoms indicated by X-ray studies. However, the combined errors involved in the experimental measurements and the theoretical predictions are considerable, and, within the limits set by them, the spectroscopic and X-ray data are consistent. The differences in detail between the results of observation and calculation draw attention to questions of general interest about the behaviour of 'water of crystallization', which are most likely to be answered from detailed studies of a variety of materials by different techniques.

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References

- AMBROSE, E., ELLIOTT, A. & TEMPLE, R. (1951). *Proc. Roy. Soc. A*, **206**, 192.
 BUSING, W. R. (1953). *J. Chem. Phys.* **23**, 933.
 CANDLIN, R. (1956). *Acta Cryst.* In the Press.
 JONES, L. H. (1954). *J. Chem. Phys.* **22**, 217.
 LORD, R. C. & MERRIFIELD, R. E. (1953). *J. Chem. Phys.* **21**, 166.
 MARA, R. T. & SUTHERLAND, G. B. B. M. (1953). *J. Opt. Soc. Amer.* **43**, 1100.
 MEGAW, H. D. (1952). *Acta Cryst.* **5**, 477.
 MILLER, F. A. & WILKINS, C. H. (1952). *Analyt. Chem.* **24**, 1253.
 RUNDLE, R. E. & PARASOL, M. (1952). *J. Chem. Phys.* **20**, 1487.