

# The low-temperature behaviour of analcime. 1: High-resolution neutron powder diffraction

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## Abstract

The structure of a synthetic sample of analcime has been determined as a function of temperature between 30–300 K by high-resolution neutron powder diffraction. Although there are some reports of samples of analcime having non-cubic structures, the sample in our experiments remained cubic (space group  $Ia3d$ ), and hence disordered, down to low temperatures. The absence of phase transitions involving ordering of the orientations of the water molecules, ordering of the sodium positions, or a displacive instability as in leucite and related materials, is discussed. We speculate that part of the reason for the absence of ordering of the water molecules or sodium cations is associated with the Al/Si disorder, which cannot order at low temperatures. We also discuss the likely distribution of the orientations of the water molecules at low temperatures, and propose that the water diads lie close to any of the crystal diads with the H–H vectors lying close to the triads.

KEYWORDS: analcime, neutron diffraction, low-temperature behaviour.

## Introduction

THE mineral analcime,  $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ , has attracted a lot of interest recently for a number of reasons. In part some of the interest has arisen because of the similarities of its structure to leucite, and the displacive phase transitions in leucite and related materials are themselves a topic of current research (e.g. Phillips and Kirkpatrick, 1994; Palmer *et al.*, 1996, and references cited therein). One of the issues in the study of leucite has been the role of Al/Si ordering (Dove *et al.*, 1993). In the cubic phase of

leucite or analcime, there can be no long-range ordering that is consistent with the  $Ia3d$  space group. The issue of short-range Al/Si ordering in analcime has therefore received some recent attention (Phillips and Kirkpatrick, 1994; Dove and Heine, 1996).

This paper forms part of a sequence of papers on the low-temperature behaviour of analcime, focusing on the behaviour associated with the water molecules. The first paper (Line *et al.*, 1994) was concerned with a study of the rotational dynamics of the water molecules using incoherent quasielastic neutron scattering (IQNS) techniques. There can be no long-range orientational ordering of the water molecules consistent with the  $Ia3d$  space-group symmetry since the symmetry of the water site,  $23$ , is higher than the symmetry of the water molecule,  $2mm$ . Thus the individual water molecules reorient

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between the different allowed orientations to give the time-averaged cubic symmetry. The time-scale for reorientational motions was deduced as a function of temperature from the IQNS data, which allowed us to determine the activation energy for reorientation (Line *et al.*, 1994). One of the surprising results was that there was no sign in the IQNS data of a phase transition at low temperatures to a state with long-range orientational order and much slower rotational dynamics. A similar lack of ordering of water molecules was also found in hydrated cordierite (Winkler *et al.*, 1994; Winkler and Hennion, 1994). The possibility of the absence of an ordering phase transition in analcime has prompted the present study, which is concerned with using high-resolution neutron powder diffraction to examine the temperature-dependence of the structure of analcime at low temperatures. Indeed, we find that there is no phase transition to an ordered structure.

We will continue the theme of what actually happens in analcime at low temperatures in two papers that will be published separately. These will be concerned with the temperature dependence of the vibrational spectra studied using infrared spectroscopy and the temperature dependence of the water vibrations studied by inelastic neutron scattering. In these papers we will consider specifically the nature of the chemical binding of water molecules to the aluminosilicate framework. The present paper is mostly concerned with the behaviour of the crystal structure on cooling.

The structure of cubic analcime is given in Table 1. This has previously been studied by Ferraris *et al.* (1972) by neutron diffraction from a single crystal at room temperature. Because in the cubic  $Ia3d$  structure each tetrahedral site is equivalent by symmetry, we refer to this as the *T* site rather than distinguishing separate Al and Si sites. The average position of the oxygen in the water molecules are also fixed by symmetry. The sodium sites are only 2/3 occupied. Some samples of analcime appear not to be of cubic symmetry, (Mazzi and Galli, 1978; Pechar, 1988), but all the samples we have worked on have remained cubic at all temperatures (Line *et al.*, 1996; see also Line, 1995). In this respect it should be noted that we have

confirmed that the behaviour of the crystal structure of analcime reported here is also found in a number of other samples we have investigated. It is not clear why different samples can have slightly different structures, but it is important to note that the reported distortions of the cubic structure are much smaller than those reported for leucite (Palmer *et al.*, 1996).

The dehydration properties of analcime have also been studied recently. Line *et al.* (1995, 1996) report a number of different kinetics studies, and have determined the changes in the crystal structure that accompany dehydration. In actual fact the changes in the crystal structure are only slight: there is a small change in the cell parameter, but no change in the space group or in the aluminosilicate framework.

### Experimental method

The neutron powder diffraction experiments were carried out on the HRPD diffractometer at ISIS, Rutherford Appleton Laboratory (UK), the same instrument that was used to study the phase transitions in leucite (Palmer *et al.*, 1996). ISIS provides a pulsed source of neutrons, and the diffraction patterns are obtained by measuring the intensity of diffracted beams as a function of flight-time at fixed scattering angle. The use of high scattering angles and long flight path give an extremely high resolution, and the use of a large number of detectors all around the Debye-Scherrer cone ensure that the measured signal is of the highest possible intensity.

Because the  $^1\text{H}$  isotope of hydrogen has an extremely large cross-section for incoherent scattering (Bee, 1988; Sears, 1992), which in a diffraction measurement would lead to a very large background (see Line *et al.*, 1996, for an example of where this effect can be used in a diffraction experiment, and Line *et al.*, 1994, where this can be used for the study of rotational dynamics), it is preferable to use deuterated samples. Direct deuteration of analcime has proven to be difficult, or at least it is difficult to ensure that most of the water in the sample has been replaced by heavy water, and so we produced our deuterated samples of analcime by conversion from leucite. We heated leucite in a

TABLE 1. Crystal structure of analcime, space group  $Ia3d$

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy
Na	24 <i>c</i>	1/8	0	1/4	2/3
T	48 <i>g</i>	-1/8	0.161	-0.089	1
O	96 <i>h</i>	-0.116	0.145	0.031	1
Water O	16 <i>h</i>	1/8	1/8	1/8	1

solution of NaCl in D<sub>2</sub>O, and found that we could obtain nearly 100% conversion to analcime.

The sample was packed into a cylindrical vanadium can of volume 4 cm<sup>3</sup>. This was then cooled within a He-flow cryostat. We typically allowed for a period of about 15 minutes equilibration once the thermocouples registered that the sample had reached the target temperature, with the temperature being cooled in steps of 30 K. The data collection time was typically about 2 hours, dependent on the fluctuations in the intensity of the incident beam.

The diffraction patterns were obtained for *d*-spacings between 0.7–2.5 Å. A typical spectrum is shown in Fig. 1, where we compare the measured diffraction pattern and the fitted pattern. The crystal structures were obtained by Rietveld refinement using the program of David *et al.* (1992). A small

number of peaks in the diffraction patterns could not be accounted for, and these were excluded from the refinements. In the refinements we allowed the cell parameter, a background function, peak shape parameters, atomic fractional coordinates, and anisotropic temperature factors to vary.

The main problem we encountered in our refinements was in accounting for the disordered positions of the deuterium nuclei: this is discussed in more detail below. We should note now that we have tried a large number of models to describe the orientational distribution of the water molecules. Some work slightly better than others, but the calculated diffraction patterns are not very sensitive to the model. The different models have very little effect on the overall structure, such as the cell parameters and coordinates of the other atoms.

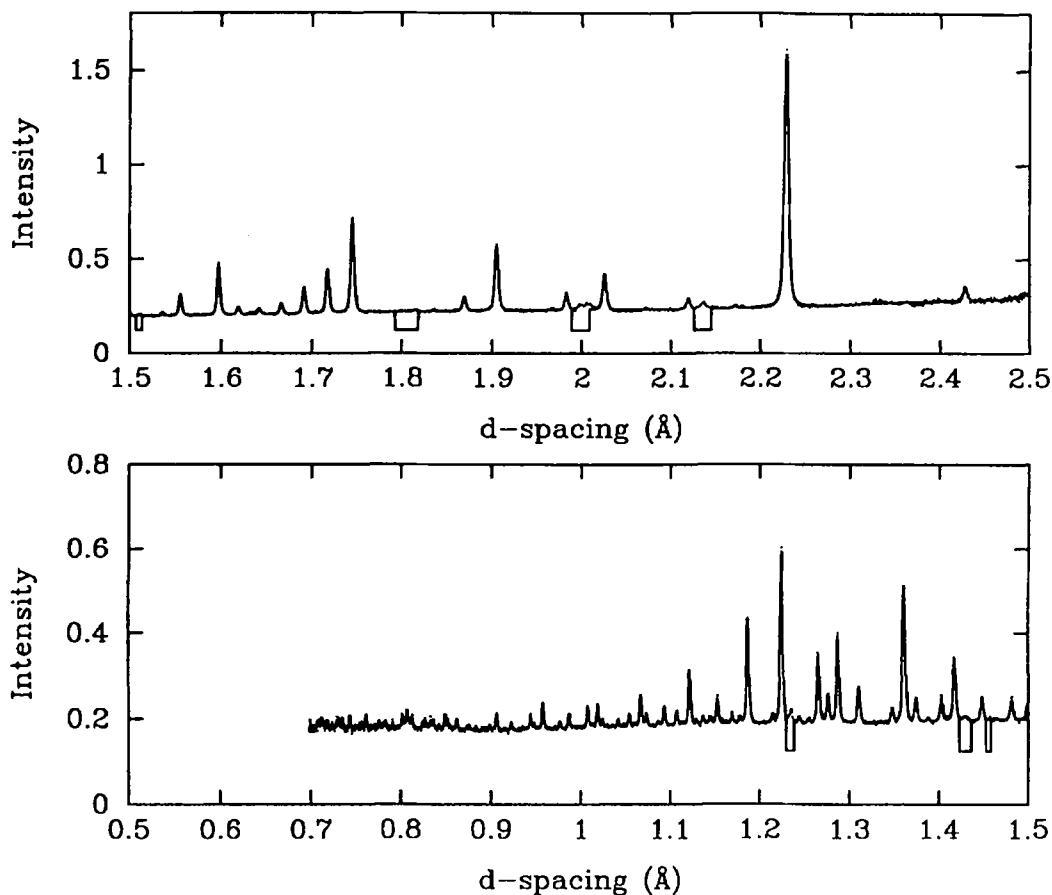


FIG. 1. Diffraction pattern from analcime at 30 K. The small points mark the experimental data, and the smooth curve is the fitted pattern from the Rietveld refinement. The regions where the fitted curve drops below the background level were excluded from the refinement.

Accordingly we can discuss many of the features of the structure as determined by the Rietveld refinements without having to reference any specific model for the water orientations.

We should comment on the accuracy of the refinements. The agreement between the observed and calculated diffraction patterns can be seen in Fig. 1. To quantify the agreement, we can consider a number of *R*-factors:

$$R = \frac{\sum |\text{obs} - \text{calc}|}{\sum \text{obs}}$$

$$R_b = \frac{\sum |\text{obs} - \text{calc}|}{\sum (\text{obs} - \text{back})}$$

$$R_w = \frac{\sum w \times \text{obs} - \text{calc}|}{\sum w \times \text{obs}}$$

$$R_{wb} = \frac{\sum w \times |\text{obs} - \text{calc}|}{\sum w \times (\text{obs} - \text{back})}$$

$$\chi^2 = \frac{1}{N - P} \sum w \times |\text{obs} - \text{calc}|^2$$

where 'obs' is an observed intensity, 'calc' is a calculated intensity, 'back' is the fitted background, *w* is the weighting on the observed intensity (taken to be the reciprocal of the variance of the measured intensity due to counting statistics, but we recognise that this neglects any systematic errors such as those due to incomplete powder averaging of all grain orientations), *N* is the number of observed points, and *P* is the number of fitted parameters. The summations are over all data points. The results of our refinements give values of *R* ~ 2–2.5, *R<sub>b</sub>* ~ 14–18, *R<sub>w</sub>* ~ 2.5–3, *R<sub>wb</sub>* ~ 2.3–4, and  $\chi^2$  ~ 2.3–4.7.

## Results

### Overall features of the crystal structure

We first focus on the overall features of the crystal structure of analcime as deduced by our neutron powder diffraction measurements, and leave the detailed distributions of the orientations of the water molecules to the following subsection. The results of the refinements of the cell parameters and atomic fractional coordinates, excluding the positions of the deuterium nuclei, are given in Table 2. The results of the refinements for the anisotropic temperatures of the Na and tetrahedral sites are given in Table 3, and the anisotropic temperatures for the framework oxygen and the isotropic temperature factor for the water oxygen are given in Table 4. The anisotropic temperature factors are defined as (taking account of the cubic symmetry):

$$-\left[\frac{1}{4a^2}\right](h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})$$

No account was taken of sample absorption, so the temperature factors reported in Tables 3 and 4 are probably only of limited significance.

The temperature dependence of the cell parameter, the two O–T bond lengths, and the T–O–T angles are given in Fig. 2. The important feature to note from any of the graphs shown in Fig. 2 is that there is no sign of any type of phase transition. We might have expected to see a phase transition associated with ordering of the orientations of the water molecules or the ordering of the positions of the sodium cations, or a phase transition involving a displacive instability as in leucite (Palmer *et al.*, 1996). In Fig. 3 we show portions of the diffraction patterns in more detail, where any sign of a phase transition might be expected to appear as a new peak or as a peak splitting. Given the high resolution of

TABLE 2. Crystal structure data from the present study

Temp (K)	<i>a</i> (Å)	O(x)	O(y)	O(z)	<i>T</i> (y)
30	13.69438(7)	–0.11524(9)	0.14501(8)	0.03077(9)	0.1609(1)
60	13.6959(1)	–0.1153(1)	0.1451(1)	0.0309(1)	0.1610(1)
90	13.6980(1)	–0.1151(1)	0.1451(1)	0.0308(1)	0.1611(1)
120	13.7009(1)	–0.1152(1)	0.1449(1)	0.0307(1)	0.1611(1)
150	13.7043(1)	–0.1154(1)	0.1449(1)	0.0307(1)	0.1611(1)
180	13.7078(1)	–0.1154(1)	0.1448(1)	0.0306(1)	0.1612(1)
210	13.7114(1)	–0.1153(1)	0.1448(1)	0.0306(1)	0.1613(1)
240	13.7150(1)	–0.1154(1)	0.1448(1)	0.0305(1)	0.1613(1)
270	13.7179(1)	–0.1154(1)	0.1446(1)	0.0305(1)	0.1613(1)
300	13.7206(1)	–0.1158(1)	0.14527(9)	0.0305(1)	0.1612(1)

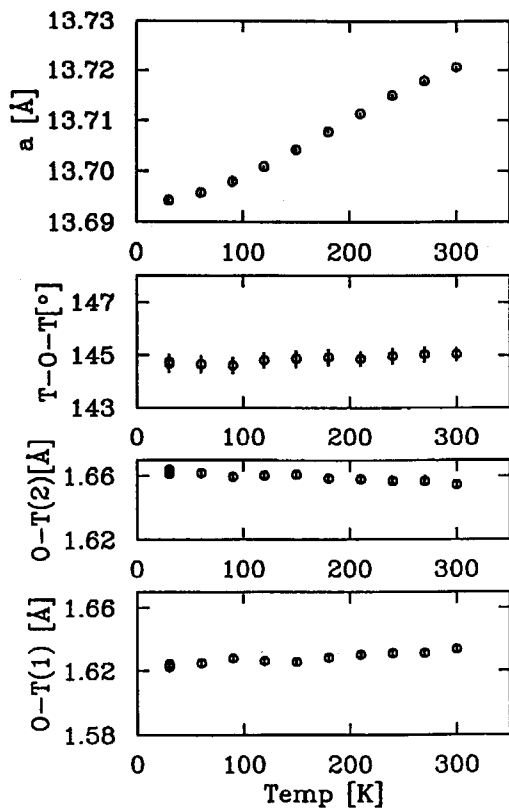


FIG. 2. Temperature dependence of the unit cell parameter, the T–O–T bond angle, and the two O–T bond lengths.

HRPD, the absence of any sign of a phase transition in the diffraction data vindicates the lack of any sign of a phase transition in the structural data in Fig. 2.

All that Fig. 2 shows is the typical behaviour associated with normal thermal expansion ( $7.3 \times 10^{-6} \text{ K}^{-1}$ ), taking account of the condition that the rate of change of the structure should be zero at  $T = 0 \text{ K}$ . The positive thermal expansion contrasts with the observation of a negative thermal expansion in dehydrated analcime, as we have discussed elsewhere (Line *et al.*, 1996).

#### Modelling the distribution of the orientations of the water molecules at low temperatures

The problem of locating (and then refining) the positions of the hydrogen atoms is non-trivial. The water molecules are orientationally disordered, which means that there may indeed not even be any specific sites for the hydrogen atoms, and if there are they will only be partially occupied. This is illustrated in Fig. 4, which shows a Fourier section passing through a water and sodium site. The peak associated with the nuclear density of the water molecule is asymmetric, but there are no distinct lobes due to the hydrogen atoms. The asymmetric peak is just-about broad enough to encompass the whole water molecule. Thus it is extremely difficult to model the precise nuclear density.

We have tried using a number of different models in the structure refinements. All these are described in Line (1995). Here we report the more successful models. Each used a fixed geometry for the water molecule. Model P1A had the O–H bond length of  $0.98 \text{ \AA}$  (as in free water, Soper, 1984) and the H–O–H angle of  $104^\circ$ , and the models IFA and TILT0 had the bond length of  $1 \text{ \AA}$  (as in ice, as given in Hobbs, 1974) and the same bond angle. For the models P1A and IFA we placed the molecular diad along the crystal diad, and rotated the molecule about the crystal diad. The starting point that defines zero rotation had the H–H vector along the triad passing

TABLE 3. Anisotropic temperature factors for the Na and T sites

Temp (K)	Na			T			
	$B_{11}$	$B_{22}$	$B_{23}$	$B_{11}$	$B_{22}$	$B_{23}$	$B_{13}$
30	1.7(3)	0.8(2)	-1.3(3)	-0.1(1)	0.47(8)	-0.26(9)	-0.02(8)
60	1.5(3)	1.2(2)	-1.5(2)	0.1(1)	0.51(8)	-0.22(9)	0.00(8)
90	1.9(3)	1.0(2)	-1.3(2)	0.1(1)	0.35(8)	-0.11(8)	0.05(8)
120	2.4(4)	0.9(2)	-1.4(2)	0.3(1)	0.37(7)	0.00(8)	0.10(7)
150	2.9(4)	1.1(2)	-1.7(3)	0.5(1)	0.37(7)	0.03(8)	0.20(8)
180	2.9(4)	1.1(2)	-1.3(3)	0.5(1)	0.39(8)	0.05(9)	0.19(8)
210	3.4(4)	1.1(2)	-1.4(3)	0.6(1)	0.39(7)	0.17(7)	0.20(7)
240	3.3(5)	1.4(2)	-1.2(3)	0.6(1)	0.38(7)	0.23(8)	0.17(7)
270	3.7(4)	1.3(2)	-1.4(3)	0.6(1)	0.35(7)	0.28(7)	0.15(7)
300	3.9(3)	1.7(2)	-1.4(2)	0.7(1)	0.41(6)	0.33(6)	0.22(6)

TABLE 4. Anisotropic temperature factors for the framework oxygen site, and isotropic temperature factor for the water oxygen site

Temp (K)	$B_{11}$	$B_{22}$	Framework O				Water O $B_{iso}$
			$B_{33}$	$B_{23}$	$B_{13}$	$B_{12}$	
30	2.9(1)	2.41(7)	0.06(6)	0.22(5)	0.26(6)	-0.55(5)	5.6(2)
60	2.9(1)	2.49(8)	0.07(6)	0.19(6)	0.28(6)	-0.62(5)	5.6(1)
90	2.8(1)	2.42(7)	0.07(6)	0.21(5)	0.19(6)	-0.50(5)	5.8(1)
120	2.98(9)	2.47(7)	0.06(5)	0.25(5)	0.18(5)	-0.48(5)	6.1(1)
150	3.05(9)	2.53(7)	0.06(6)	0.27(5)	0.12(6)	-0.45(5)	6.4(2)
180	3.0(1)	2.47(7)	0.07(6)	0.26(6)	0.16(6)	-0.40(5)	6.9(2)
210	3.10(8)	2.57(6)	0.06(5)	0.30(5)	0.05(5)	-0.40(4)	7.0(2)
240	3.06(9)	2.61(7)	0.06(6)	0.32(5)	-0.02(5)	-0.31(5)	7.4(2)
270	3.12(8)	2.64(7)	0.06(5)	0.34(5)	-0.02(5)	-0.30(5)	7.8(2)
300	3.22(7)	2.70(6)	0.05(5)	0.38(4)	-0.09(4)	-0.23(4)	8.3(1)

through the site. The operation of the crystal triads along  $\langle 111 \rangle$  generated 6 sites for the hydrogen atoms, there being only one triad and three diads passing through any water site. For the model TILTO we placed the molecular diad along the crystal diad at the best orientation given by the refinements of the IFA model, and then rotated the molecular diad away from the crystal diad towards the direction of the triad passing through the site. For the P1A and IFA models we were able to use anisotropic temperature factors, but in the TILTO model there is a doubling of

the number of hydrogen sites, and we found that we were only able to use isotropic temperature factors. In Fig. 5 we show the variation of the refinement  $R_b$ , defined above, with the rotation of the molecule in each case. (It should be appreciated that the lowest value of  $R_b$  for the TILTO model is higher than the lowest value of  $R_b$  for the IFA model because of the use of isotropic temperature factors in the TILTO model.)

The conclusion from these refinements is that the best model has the molecular diad pointing along the

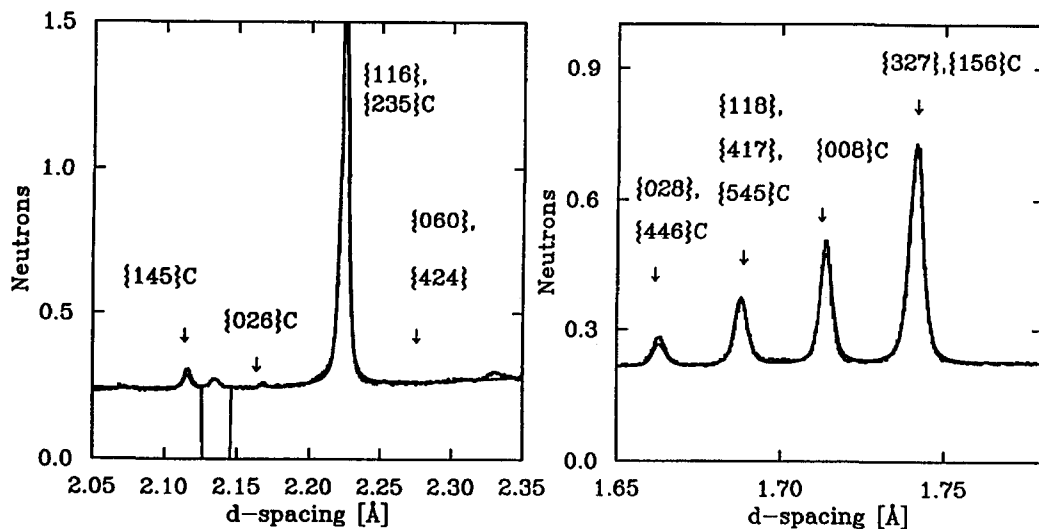


FIG. 3. Regions of the diffraction pattern at 30 K showing the absence of any peak splitting or new peaks that are forbidden by the  $Ia3d$  symmetry of the cubic phase. Peaks labelled with 'C' are those permitted by the  $Ia3d$  symmetry.

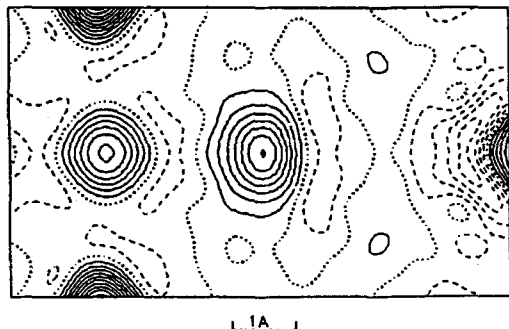


FIG. 4. Fourier map of the nuclear density of analcime, showing a  $(\bar{2} 1 1)$  section cutting through the water site, at 30 K. The horizontal axis is  $[0 \bar{1} 1]$ , and the vertical axis is  $[1 1 1]$ . The peak in the middle is the water molecule, the peak at centre-left is a sodium cation, the peaks on the top and bottom borders are framework oxygen atoms, and the peak on the far right is a tetrahedral cation. The asymmetric shape of the peak for the water molecule probably arises from the distribution of the hydrogen atoms.

crystal diads, and the H-H vector along the triad passing through the site. Because there are three diads passing through the site there are three possible orientations of the water molecule. Each water site is surrounded by three coplanar sodium sites, only  $2/3$  of which are occupied. The three diads passing through the water site also pass through the three sodium sites, and the triad is normal to the plane

containing the three sodium sites. If exactly two of these are occupied, it might be expected that the hydrogen atoms will be oriented away from the sodium cations, and thus point towards the empty sodium site. This may explain a tendency for the molecular diad to lie along the crystal diad which passes through the unoccupied sodium site. The tendency for the H-H vector to be vertical (i.e. parallel to the triad) ensures that the Na...D distance is the maximum possible. This distribution can be seen in the Fourier map shown in Fig. 4. The hydrogen atoms are seen as the lobes coming out of the top and bottom left hand side of the nuclear density at the water site, pointing towards the sodium site on the left. There would of course be other lobes coming out of the section along different directions related by symmetry.

We also tried the model reported by Ferraris *et al.* (1972). In this model there is an additional site for the hydrogen positions along the crystal diad. The quality of the refinements were not significantly different from the models described above, but the refined occupancy of the additional site was very low (6%), and the O-H bond length was refined to the unreasonably-large value of 1.57 Å.

Pechar (1988) has also given a model for the orientations of the water molecules in analcime, at least in a monoclinic sample that appears to have some degree of order. As a result of the symmetry of his sample being monoclinic, Pechar (1988) assigned the sodium atoms around the cage varying occupancies such that the sodium site was partially ordered with one site for each cage having a double occupancy. Because of the monoclinic symmetry,

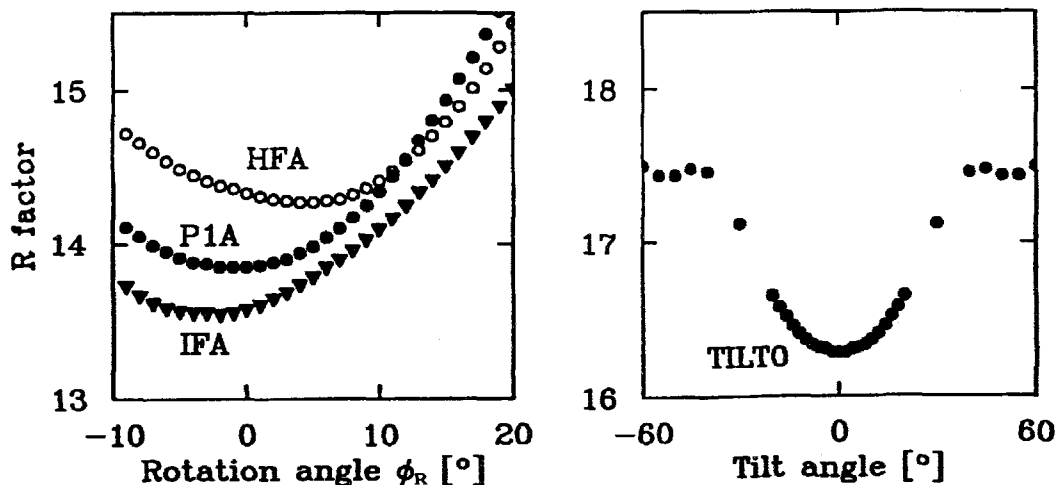


FIG. 5. The variation of the  $R$ -factor  $R_b$  (defined in the text) with the rotation angles for the three models described in the text.

one water orientation alone could be modelled for each site, and the refinement gave O–H bond lengths of 0.96 and 0.97 Å, and H–O–H bond angles of 103° and 107°, which are fairly close to the ideal values. The result of the refinement was that water was not oriented with respect to the sodium site in the manner that we have refined, but at an intermediate position with the molecular diad at 30° to the double-occupancy sodium site and 52° to the cage triad. It is possible that, just as with our study, the water could have been better modelled over several sites in addition to the one used. Since sodium disorder was modelled, one would expect there to be water disorder as well. The occupancies in that study were not refined, so it is difficult to make a comparison with our model. Nevertheless, the study showed that in principle it is possible to locate the hydrogen atoms in analcime, albeit to a limited extent.

### Discussion and conclusions

The interesting result from this study is that there is no phase transition on cooling. We might have expected three possible types of phase transition: a phase transition involving an ordering of the orientations of the water molecules, a phase transition involving ordering of the positions of the sodium cations, and a phase transition involving a displacive instability as in leucite. Clearly these could have occurred alone or in combination.

First let us consider the two possible ordering phase transitions. The absence of a phase transition involving ordering of the orientations of the water molecules is consistent with our previous study of the reorientational dynamics by incoherent quasielastic neutron scattering (Line *et al.*, 1994). It is, however, somewhat surprising, for it implies that analcime has some considerable degree of disorder at low temperatures (zero-point entropy). There are probably two factors involved. Firstly, there is always a kinetic factor, the same that leads to the absence of ordering of water molecules in pure hexagonal ice-Ih (Hobbs, 1974). This comes into play when the phase transition is expected to occur at a temperature  $k_{\text{B}}T_c$  that is small compared to the energy required for an individual molecule to reorient into an ordered orientation. Low transition temperatures arise when the interaction between neighbouring molecules is weak. In the present case, the direct dipole–dipole interaction will not lead to complete ordering, only ordering of the dipole directions. Complete ordering must involve quadrupole–quadrupole interactions, and the direct quadrupole–quadrupole interactions (which vary as  $r^{-5}$ ) will not be strong over the distance between neighbouring molecules. In many cases the ordering interactions can be mediated by the

lattice, whereby local lattice distortions that arise from the orientation of one molecule have an influence on neighbouring molecules. These indirect interactions have the same interaction range as direct dipole–dipole interactions,  $r^{-3}$ . The framework of the analcime/leucite structure is not easily distorted, since there are only a few lines of rigid unit modes (Dove *et al.*, 1995; Hammonds *et al.*, 1996), and so the indirect interactions might also be relatively weak. The same arguments might also explain the lack of an ordering phase transition in hydrated cordierite (Winkler *et al.*, 1994; Winkler and Hennion, 1994). But in analcime there is an additional factor. If the distribution of the positions of the sodium cations is not ordered, different water molecules will have different numbers of sodium neighbours, ranging from 0–3. The effect of having different sites will probably completely disrupt any interactions that can drive the ordering of the orientations of the water molecules. The question then has to shift to the issue of why there is no ordering of the sodium cation positions. It might be thought indeed that the interactions involved in this ordering will be stronger than the interactions involved in the ordering of the orientations of the water molecules, which might then lead to a reasonably high transition temperature. The reasons why the sodium cations do not order might be a simple kinetics problem, but given the small size of the sodium cation and its likely mobility, this might not be thought likely. Instead we suggest that one possible hindrance to the sodium ordering might be the Al/Si disorder. It is known that the transition temperatures for Al/Si ordering in analcime and leucite are low (Dove *et al.*, 1993, 1996); indeed, they appear to be so low that the timescale for ordering will be too long for it to occur on a laboratory timescale (Phillips and Kirkpatrick, 1994; Dove and Heine, 1996). Hence no long-range Al/Si ordering is expected to occur in the sample in our experiments. However, some degree of short-range Al/Si order occurs (Phillips and Kirkpatrick, 1994; Dove and Heine, 1996), and it is possible that the local arrangement of sodium cations, at least in the hydrated form, is influenced by the local Al/Si arrangement. Since this does not change on cooling, then maybe neither will the arrangement of sodium cations. Alternatively it might be that the local orientational disorder of the water molecules, which changes on a relatively slow time-scale (Line *et al.*, 1994), also disrupts any ordering interactions for the sodium cations. In this case, the sodium disorder and the water disorder will both disrupt the two ordering processes, either leading to an overall low transition temperature or to the disordered state being the equilibrium state at all temperatures.

We now turn to the issue of the absence of a displacive phase transition in analcime similar to the



those observed in leucite and analogous materials (Palmer *et al.*, 1996). We have noted elsewhere (Line *et al.*, 1996) that dehydrated analcime also does not undergo a similar displacive phase transition. The reason for this is that the displacive phase transitions in the alkali leucites appear to require the presence of a cation in the position of the water molecule in order to provide a driving force for the phase transition, as documented elsewhere (Dove *et al.*, 1996). The cation can pull the framework around it, overcoming forces (most notably those associated with the bending of the T–O–T bonds) that tend to prefer the cubic structure. This is unlike the case of quartz, where the distortions that accompany the phase transition do not involve bending of the Si–O–Si bonds. The absence of a cation in the middle of the cavities in either hydrated or dehydrated analcime means that there is no overall driving force for a displacive phase transition in these materials, so the cubic phase remains stable at all temperatures.

In conclusion, we have shown that the crystal structure of analcime remains cubic on cooling to low temperatures. There are no orientational ordering, sodium cation position ordering, or displacive phase transitions. The structure of analcime remains disordered at low temperatures.

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