# An X-ray Diffraction Determination of the Crystal Structure of Ammonium Hydrogen Sulphate above the Ferroelectric Transition

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The structure of ammonium hydrogen sulphate (AHS) has been determined from three-dimensional X-ray diffraction data collected at room-temperature. At this temperature AHS is non-ferroelectric. At $-3°C$ it is known to make a second-order transition to a ferroelectric phase in which the spontaneous polarization is parallel to the $c$ axis of the pseudo-orthorhombic monoclinic unit cell. This cell contains two symmetrically inequivalent formula units, which are found to be closely related by a pseudo-symmetry. The two inequivalent sulphate tetrahedra are distorted and they are linked by short hydrogen bonds into chains parallel to the $b$ axis. Additional information on the positions of the protons in these hydrogen bonds was obtained from neutron diffraction data collected in the ($h0l$) layer only: the $b$ axis is very short – 4·6 Å. Both the X-ray and the neutron analyses show that the hydrogen atoms are ordered onto acentric sites in these bonds. Both studies also agree in suggesting that the ammonium ions are executing pronounced thermal motion. The structure shows two features which are unusual in non-ferroelectric phases of ferroelectric materials: first the pseudo-symmetry of the structure, and secondly the ordering of the protons onto acentric sites in the short hydrogen bonds – bonds which are expected to play a rôle in the ferroelectric transition. These features of the structure are discussed in relation to the ferroelectric transition and the further work that they suggest. Some of the methods of analysis applied to the problems raised by the pseudo-symmetry of the structure are discussed.

## 1. Introduction

Ammonium hydrogen sulphate (AHS), $NH_4HSO_4$, was shown to be ferroelectric by Pepinsky, Vedam, Hoshino & Okaya (1958). It exhibits a large dielectric anomaly on passing from a non-ferroelectric to a ferroelectric phase at $-3°C$ (the 'upper transition') and another small but sharp anomaly on passing to a second non-ferroelectric phase at $-119°C$ (the 'lower transition').

The non-ferroelectric, room-temperature structure may be described on a pseudo-orthorhombic cell which contains 16 formula units. The space group of this cell is $B2_1/a$, and the cell dimensions are $a = 24·66 \pm 0·02$, $b = 4·60 \pm 0·01$, $c = 14·82 \pm 0·02$ Å, $\beta = 89·87 \pm 0·01°$. This cell is assumed throughout this paper: it greatly simplifies the description and discussion of many essential features of the structure. The ferroelectric phase and low temperature non-ferroelectric phase have pseudo-orthorhombic cells of similar dimensions to those given above and have space groups $Ba$ and $B1$ respectively (Pepinsky *et al.*, 1958).

It is the dielectric constant along the $c$ axis which exhibits the anomalies referred to. Those along the $b$ and $a$ axes are continuous through the transitions. Below $-3°C$ the spontaneous polarization along the $c$ axis increases, at first rapidly, and then more slowly, to 0·8 $\mu$C cm$^{-2}$ before dropping abruptly to zero at $-119°C$ (Pepinsky *et al.*, 1958).

The results obtained by Pepinsky *et al.* (1958) and more recently by Strukov, Koptsik & Ligasova (1962)

and Strukov & Danilycheva (1963) suggest that the upper transition is second order. The lower transition appears to be first order (Pepinsky *et al.*, 1958).

Since 1958 AHS has been the subject of several Raman scattering (Bazhulin, Myasnikova & Rakov, 1963), infrared absorption (Myasnikova, 1962; Myasnikova & Yatsenko, 1962; Oden, 1966) and nuclear magnetic resonance (n.m.r.) (Burns, 1961; Miller, Blinc, Brenman & Waugh, 1962) experiments, and also a neutron inelastic scattering experiment (Rush & Taylor, 1965). There is general agreement from this work that the internal vibrations of the $NH_4^+$ ion do not change in passing through the upper transition, though the lower transition may be associated with an ordering of these ions (Miller *et al.*, 1962). Both transitions appear to be accompanied chiefly by a change in the character of hydrogen bonding in the structure. The internal vibrations of the $SO_4^{2-}$ ions are reported to show no change at either transition (Myasnikova, 1962; Myasnikova & Yatsenko, 1962; Bazhulin *et al.*, 1963). Some recent deuteron magnetic resonance (d.m.r.) experiments on $ND_4DSO_4$ at the upper transition show weak changes in the signals from the $DSO_4^-$ ion, which have yet to be interpreted, and detect no change in those from $ND_4^+$ (Smith, 1968). The results of Rush & Taylor (1965) suggest that the rotational freedom of the $NH_4^+$ ion is quite high. The d.m.r. results are in agreement with this conclusion and, further, indicate that the ion is either unsymmetrical or has unequal lifetimes in its various configurations (Smith, 1968).

Some unsuccessful attempts have been made to

detect low frequency optical modes of AHS and some related ferroelectrics in spectra from Raman scattering and infrared absorption (Bazhulin et al., 1963; Myasnikova & Arefev, 1964).

The aim of the present X-ray diffraction study (Nelmes, 1969) was to determine the structure of the room-temperature non-ferroelectric phase. The only structural information available prior to the work reported here was an estimate of the coordinates for the rubidium atoms in $RbHSO_4$ (Bengtssen, 1941): AHS and $RbHSO_4$ are isomorphous (Pepinsky & Vedam, 1960). The ultimate aim of the project, of which the present study is the first part, is to relate the structural changes associated with the upper transition to a general microscopic theory of ferroelectric transitions (Cochran, 1960).

The methods of analysis applied to the problems posed by the pseudo-symmetry of the AHS structure, and other aspects of this feature of the structure, are discussed in some detail. Similar problems are to be expected in structural studies of most ferroelectrics (see Frazer, 1962).

## 2. Experimental

Crystals for the X-ray experiment were cut from AHS supplied in crystalline form by British Drug Houses Ltd. at laboratory reagent purity. The dimensions of the specimen were of the order of 0·25 mm; the calculated linear absorption coefficient (*International Tables for X-ray Crystallography*, 1962) was 6·4 cm⁻¹ for Mo $K\alpha$. For a subsidiary neutron diffraction experiment a crystal was obtained from aqueous solution.

Under normal laboratory conditions AHS is extremely deliquescent. A method of preserving specimens for X-ray work was developed which entailed enclosing them in thin-walled, transparent, spherical, fused-silica bulbs (Nelmes, 1970). This technique introduced only a small isotropic absorption of the incident and reflected beams. For neutron work soda-glass bulbs were used.

Full three-dimensional X-ray intensity data were collected on the Hilger and Watts Y230 Mk III four-circle diffractometer (Arndt & Willis, 1966), using zirconium filtered Mo $K\alpha$ radiation. Data were collected out to $\sin\theta/\lambda = 0\cdot81$ Å⁻¹ in the hemisphere $\pm h$, $k \le 0$, $\pm l$: the $-b$ axis was directed upwards with the $\chi$-shaft at datum.

The specimen instability and equipment failures led to the data being collected in three distinct sets. A total of 15,000 reflexions were measured, and were recorded as digitized profiles punched on paper tape. With overlap between data sets, these were reduced to the intensities and errors of 6500 symmetrically inequivalent reflexions with $h \ge 0$, $k \le 0$, $\pm l$ (DAT 1). These were used for the initial structure analysis and refinement. In the final stages of refinement the refined scaling factors for each of the sets were used to produce a single set of the intensities and errors of the 3720 reflexions
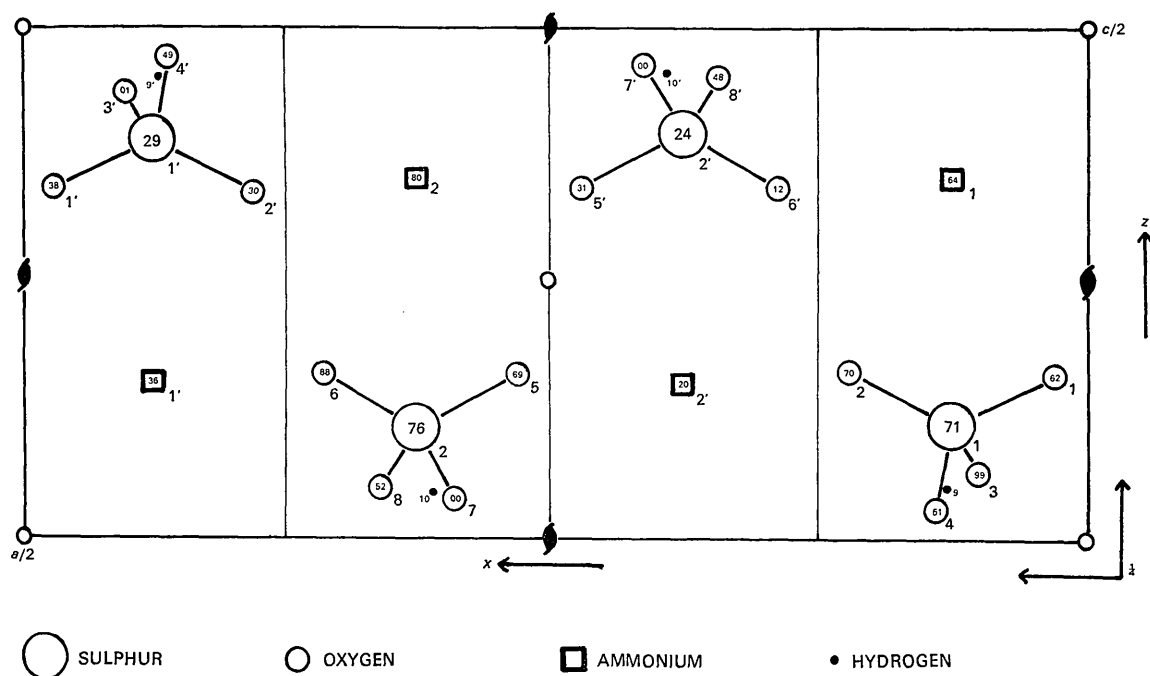


SULPHUR          OXYGEN          AMMONIUM          • HYDROGEN

Fig. 1. A diagram of the structure projected onto (010). A quarter of the unit cell is shown. The atoms of the asymmetric unit are unprimed and those related by symmetry are primed. Fractional $y$ coordinates ($\times 100$) are inscribed in each atom, except the hydrogen atoms, which are at heights 36, 64, 13 and 87 for hydrogen atoms 9, 9', 10 and 10' respectively. $B2_1/a$ symmetry elements are shown. The cell parameters are: $a = 24\cdot66$, $b = 4\cdot60$, $c = 14\cdot82$ Å; $\beta = 89\cdot87°$ (pseudo-orthorhombic cell).

with $h \geq 0$, $k \leq 0$, $\pm l$, and $\sin\theta/\lambda \leq 0\cdot81$ Å$^{-1}$ (DAT2). Of these, 435 were 'accidentally absent'.

Preliminary studies had shown the following systematic intensity distribution:

| in $h0l$ | $h = 4n$, strong |
| | $h = 4n + 2$, weak |
| | ($h$ or $l$ odd, space group absence); |
| in $h1l$, $h2l$, etc. | $h = 4n$, strong |
| | $h = 4n + 2$, weak |
| | $h$ odd, intermediate; |
| in $h00$, $h20$, etc. | $h = 8n$, very strong |
| | $h \neq 8n$, weak; |
| and in $h10$, $h30$, etc. | $h = 8n + 4$, very strong |
| | $h \neq 8n + 4$, weak; |

$n$ is any integer. In the data collection the systematically weak reflexions were measured separately with a longer counting time than the other reflexions.

A 'standard' reflexion was measured once every hour. Both the long and the short term fluctuations in its integrated intensity were of the order of $\pm 3\%$. This was taken as a measure of the irreducible instability in the experiment, and was included in the random error associated with each intensity.

There are several recognized sources of significant systematic error in measured integrated intensities. In the reduction of the AHS data corrections for only two of these – counting losses and the Lp factor – were applied. The errors associated with the linear truncation of background radiation affect mainly the atomic thermal parameters (Ladell, 1968); so also do those associated with thermal diffuse scattering (Cochran, 1969) and absorption (Srivastava & Lingafelter, 1966). The procedure adopted for reflexions affected by extinction was to omit from the final stages of the least-squares refinement those where the effect was greater than, or comparable with, the error in the reflexion intensity (Arndt & Willis, 1966, p. 251). Elimination of multiple reflexions (Coppens, 1968) was not attempted. However, space group absent reflexions were not significantly 'present', and at the end of refinement there was no indication of any significant systematic over-estimation of the observed intensities of weak reflexions (Post, 1969).

Neutron data collection was performed on the DIDO reactor at A.E.R.E. Harwell with the Hilger & Watts Mk. II four-circle diffractometer. The peak wavelength from the monochromating crystal was 1·04 Å. Data were collected in the ($h0l$) layer only, out to $\sin\theta/\lambda = 0\cdot78$ Å$^{-1}$. The 'weak' reflexions ($h = 4n + 2$) were again given a greater counting time.

The volume of the specimen was insufficient to give good 'weak' reflexion data in the time available: the intensities of 'weak' reflexions with $\sin\theta/\lambda > 0\cdot62$ Å$^{-1}$ were not significant. The data were reduced to one set of symmetrically inequivalent observed intensities and errors comprising 190 'strong' reflexions ($h = 4n$) and 120 'weak' reflexions. The 'standard' reflexion intensities showed significant long and short term variations of $\pm 4\%$.

The data were collected under less stringent conditions than in the X-ray experiment. The systematic errors to be expected in the data were similar. After removing the background the only other correction applied was the L factor. Counting losses and extinction effects were insignificant. The other sources of systematic error previously discussed have effects similar to the X-ray case.

## 3. Analysis and the pseudo-symmetry

The unit-cell contains 16 formula units, and $B2_1/a$ has 8 general positions. The two symmetrically inequivalent molecules in the unit cell will be taken to be those in the regions $(x,y,z)$ and $(x+\frac{1}{4},y,z)$, where $0 \leq x \leq a/8$, $0 \leq y \leq b$ and $0 \leq z \leq c/2$ (see Figs. 1 and 3).

The systematic intensity distribution previously noted indicates that the AHS structure is comprised of four closely similar subcells, of dimensions $a/4 \times b \times c$, which have a pseudo-symmetry higher than $B2_1/a$ (see Fig. 1). The intensity distribution implies that this pseudo-symmetry includes an $n$-glide plane perpendicular to $\mathbf{c}$, and a mirror plane perpendicular to $\mathbf{a}$.

In the (010) projection – down the helpfully short $b$ axis – the unit cell has dimensions $a/2 \times c/2$ and contains four formula units (see Fig. 1). This cell has the space group $p2$. The corresponding subcell has dimensions $a/4 \times c/2$, and its pseudo-symmetry is $pmg$ (note the similarity of the two halves of Fig. 1).

As already seen, the $h0l$ intensities may be divided into 'strong' ($h = 4n$) and 'weak' ($h = 4n + 2$) reflexions. Since $\varrho(x,z)$, the electron density at $(x,z)$, is centrosymmetric,

$$\varrho(x,z) = \frac{1}{A} \sum F(h0l) \cos 2\pi(hx + lz) .$$

Hence

$$[\varrho(x,z) + \varrho(x+\tfrac{1}{4},z)] = \frac{2}{A} \sum_{h=4n} F(h0l) \cos 2\pi(hx + lz) \quad (1)$$

and

$$[\varrho(x,z) - \varrho(x+\tfrac{1}{4},z)] = \frac{2}{A} \sum_{h=4n+2} F(h0l) \cos 2\pi(hx + lz) . \quad (2)$$

The 'weak' reflexions transform to the 'difference structure' [equation (2)]; the 'strong' reflexions transform to the 'average structure' [equation (1)]. The separation of the projected structure into these two elements proved helpful in the solution of this pseudo-symmetric structure. Similar techniques are likely to be helpful for any pseudo-symmetric structure (Qurashi, 1963).

The 'average structure' was readily solved from a Patterson synthesis of the 'strong' reflexions, considering the constraints imposed by the pseudo-symmetry. The structure was refined by the minimum residual method of Bhuiya & Stanley (1963). This method appeared ideally suited to the problems of

parameter correlation posed by the two-dimensional 'average structure' and 'difference structure' of AHS. Allowing individual isotropic temperature factors, the usual $R$ index, $\sum \Delta / \sum |F_o|$ $(\Delta = ||F_o| - |F_c||)$, was reduced to 9·5% for the 'average structure'.

At each atomic site of the true structure the 'average structure' has two atoms slightly displaced from each other [see equation (1)]. The 'difference structure' at the same site results from the 'subtraction' of one of these atoms from the other [see equation (2)], giving rise to a pair of positive and negative peaks (Qurashi, 1963). The atoms in the molecule at $(x,z)$ will be represented by the positive peaks and those of the molecule at $(x+\frac{1}{4},z)$ by the negative peaks. The problem of solving the 'difference structure' was thus that of correctly allocating the atoms in the 'average structure' between the two separate molecules of the true structure. Given the 'average structure' coordinates there were just 32 possible ways of making this allocation (the hydrogen atoms were ignored at this stage). None of them yielded a solution. It was found later that parameter correlation in the refinement of the 'average structure' had resulted in atom separations that were incorrect both in magnitude and in direction. Nevertheless, Bhuiya & Stanley's method rapidly yielded a solution. Starting positions corresponding to different allocations of the 'average structure' coordinates were tried. All refined to essentially the same structure, with the $R$ index dropping from $\sim 120\%$ to $\sim 30\%$ in three cycles in each case. The largest movement in these refinements was 0·4 Å. The two symmetrically inequivalent molecules of the AHS structure were now correctly distinguished in the (010) projection. From this point the deduction of a good trial structure in three dimensions was moderately straightforward.

The structure was refined using a full-matrix least-squares program written by Dr G. S. Pawley of this Department. The scattering factors ($f$ curves) used for the sulphur and oxygen atoms were the neutral atom $f$ curves published by Doyle & Turner (1968) amended by the real part of the dispersion correction (Templeton, 1962). No attempt was made to allow for 'ionization' of atoms involved in the sulphate ion. So long as spherical atom $f$ curves are used such practice is of doubtful validity, especially where strong valence bonds are involved. For the ammonium ion an $f$ curve for a freely rotating ion was used (Davis & Whitaker, 1966). The adequacy of this $f$ curve is discussed later. The remaining hydrogen atoms were not included. In this first stage of refinement DAT1 was used to refine 111 parameters. Each observation was given the weight $w = 1/\sigma^2(|F_o|)$. The overall $R$ index fell to 9·0% (7·0% excluding accidentally absent reflexions).

Before embarking upon a final refinement an attempt was made to locate the hydrogen atoms of the $HSO_4^-$ ions. Consideration was given to the treatment of accidentally absent reflexions and those affected by extinction, and also to the validity of the weighting scheme.

From the dimensions of the S–O bonds of the sulphate ions the S–O(H) bonds were identified (Cruickshank, 1961); it appeared that the ions were linked by O–H$\cdots$O bonds approximately along **b**. Approximate coordinates for the hydrogen atoms were calculated from the observed O$\cdots$O separations (see Hamilton, 1962). These positions, together with the refined parameters of the other atoms, were used as starting values for the neutron diffraction analysis.

Scattering lengths for the oxygen, nitrogen and hydrogen nuclei were taken from Table 2 of Bacon (1962). For sulphur the value used was that found by Elcombe & Taylor (1968).

The parameters of the two hydrogen atoms, H(9) and H(10), located as above linking the sulphate ions, refined satisfactorily and appeared clearly in Fourier syntheses. No satisfactory model was found for the protons of the $NH_4^+$ group: the results suggested that the group was executing pronounced thermal motion. The final $R$ index was 20% (13% on 'strong' reflexions alone). By combining the refined $x$ and $z$ coordinates for H(9) and H(10) derived from the neutron data with the O$\cdots$O separations found in the X-ray results, estimates for the $y$ coordinates of H(9) and H(10) were also obtained (see Hamilton, 1962). Three-dimensional difference syntheses were calculated, using the X-ray data out to $\sin\theta/\lambda = 0.5$ Å$^{-1}$, to look for evidence of hydrogen atoms at these coordinates; significant peaks containing 0·25 electron appeared at the expected positions. (In the regions containing the two symmetrically inequivalent $NH_4^+$ ions there were a few positive and negative peaks containing $\sim 0.05$ electron. Otherwise these regions were featureless. This gave further support to the adequacy of the $NH_4^+$ scattering curve in use).

The final least-squares refinement of the X-ray data was performed with H(9) and H(10) included, with the hydrogen atom scattering factor published by Stewart, Davidson & Simpson (1965). DAT2 was used with weights, $w$, as above. The values of $\sigma(|F_o|)$ included the counting statistical error, the stability error estimated from the variation in the 'standard' intensity, and the uncertainty in the counting loss correction.

38 strong reflexions showed a discrepancy between $|F_o|$ and $|F_c|$ attributable to extinction effects, and of a magnitude greater than or comparable with $\sigma(|F_o|)$. These were removed from DAT2.

Dunning & Vand (1969) have recently pointed out that implicit in the commonly employed method of dealing with accidentally absent reflexions (Cruickshank & Pilling, 1961, p. 46) is the false premise that the 'true' values of their structure amplitudes are normally distributed about a mean of $\frac{1}{2}F_{\lim}$. $F_{\lim}$ is the minimum $|F_o|$ which could have been detected in the relevant part of the spectrum – under the given experimental conditions. There is an objection in principle to the alternative procedure that they suggest: the weights for these reflexions are made dependent on $|F_c|_a$ (the calculated structure amplitudes for acci-
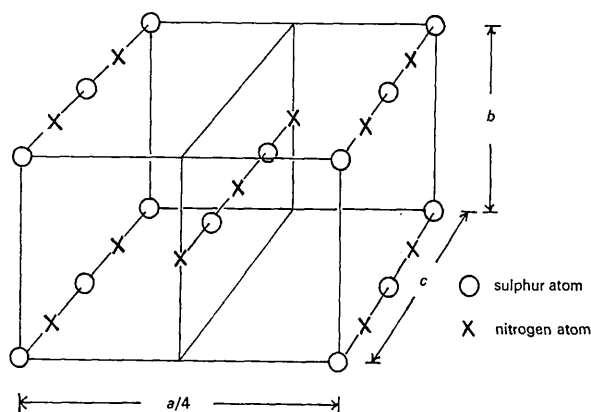
Fig. 2. Schematic representation of the approximate disposition of the sulphur and nitrogen atoms. The origin has been moved to a sulphur atom.

dentally absent reflexions). The procedure adopted for the AHS refinement was to give a very low weight to those reflexions with $|F_c|_a < F_{lim}$ and a constant weight of the order of $F_{lim}^{-2}$ to those with $|F_c|_a > F_{lim}$. Otherwise the suggestions of Dunning & Vand were implemented:

(i) that as many as possible of the $|F_c|_a$ should be less than $F_{lim}$;

(ii) that the accidentally absent reflexions should be excluded from the calculation of the standard deviation of parameters; and

(iii) that the usual $R$ index should be quoted for the measurable $|F_o|$ alone, with the proportion of $|F_c|_a < F_{lim}$ given separately.

The dependence of $w\Delta^2$ on $\sin\theta/\lambda$ and on $|F_o|$ was determined for the measurably observed reflexions (see Cruickshank, 1965, p. 113). The dependence on $|F_o|$ was not marked except for a decrease in $\overline{w\Delta^2}$ at low $|F_o|$. The dependence on $\sin\theta/\lambda$ was less satisfactory; $\overline{w\Delta^2}$ showed a pronounced decrease for $\sin\theta/\lambda > 0.35$ Å$^{-1}$. However, the weighting scheme was not altered. The estimated standard deviations, $\sigma(|F_o|)$, included all known sources of random error; and, when the random errors are known, obscuring systematic errors in an empirical weighting scheme is of doubtful validity. A dependence of the weighting on $\sin\theta/\lambda$ will affect mainly the scale factor and atomic thermal parameters.

To obtain reasonable thermal parameters for H(9) and H(10) it was found that, as suggested by the difference syntheses (see above), the charge associated with these atoms had to be less than one electron. The final values obtained are given in Table 1.

Table 1. *The charge and the thermal parameters for the hydrogen atoms of the* HSO$_4^-$ *groups*

|      | Charge        | $B$                 |
|------|---------------|---------------------|
| H(9) | 0·6 ± 0·1 e   | 3·5 ± 1·0 Å$^2$     |
| H(10)| 0·7 ± 0·1     | 3·0 ± 1·0           |

Table 2. *Final values of the structural parameters and their standard deviations as given by the least-squares refinement*

Temperature factor $= \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{23}kl + 2\beta_{31}lh)]$.

The fractional coordinates, $x$, $y$ and $z$, and thermal parameters, $\beta_{ij}$, are referred to the full cell. Standard deviations ($\times 10^5$) are given in brackets.

|       | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{23}$ | $\beta_{31}$ | $\beta_{12}$ |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| S(1)  | 0·06208 (2) | 0·71422 (9) | 0·11079 (3) | 0·00107 (1) | 0·02160 (19) | 0·00355 (2) | −0·00098 (5) | 0·00031 (1) | −0·00054 (3) |
| S(2)  | 0·31343 (1) | 0·76186 (9) | 0·10707 (2) | 0·00084 (1) | 0·02100 (16) | 0·00237 (1) | −0·00048 (5) | −0·00008 (1) | −0·00051 (3) |
| O(1)  | 0·01521 (5) | 0·61791 (36) | 0·15926 (9) | 0·00134 (2) | 0·05505 (94) | 0·00445 (7) | −0·00231 (23) | −0·00079 (3) | −0·00255 (12) |
| O(2)  | 0·10986 (6) | 0·70472 (51) | 0·16386 (11) | 0·00137 (3) | 0·1112 (170) | 0·00582 (9) | −0·00586 (34) | −0·00049 (4) | −0·00134 (17) |
| O(3)  | 0·05250 (9) | 0·98660 (39) | 0·06552 (15) | 0·00411 (6) | 0·03212 (87) | 0·00981 (14) | 0·00605 (30) | −0·00238 (7) | 0·00353 (17) |
| O(4)  | 0·07093 (8) | 0·51118 (40) | 0·02896 (11) | 0·00300 (4) | 0·03886 (87) | 0·00350 (7) | −0·00233 (22) | 0·00124 (4) | −0·00190 (16) |
| O(5)  | 0·26636 (5) | 0·68751 (34) | 0·15988 (9) | 0·00116 (2) | 0·05329 (91) | 0·00372 (6) | −0·00044 (20) | −0·00057 (3) | −0·00204 (11) |
| O(6)  | 0·29432 (6) | 0·88429 (30) | 0·15996 (8) | 0·00121 (2) | 0·03728 (69) | 0·00316 (6) | 0·00064 (17) | −0·00062 (3) | −0·00190 (10) |
| O(7)  | 0·33160 (5) | 0·99568 (32) | 0·03814 (10) | 0·00162 (3) | 0·02373 (60) | 0·00403 (7) | 0·00185 (18) | −0·00089 (3) | −0·00061 (10) |
| O(8)  | 0·52234 (27) | 0·52234 (27) | 0·05042 (9) | 0·00144 (2) | 0·02413 (59) | 0·00385 (6) | −0·00102 (16) | −0·00009 (3) | 0·00061 (9) |
| N(1)  | 0·06223 (5) | 0·63909 (38) | 0·35245 (10) | 0·00097 (2) | 0·03649 (77) | 0·00347 (7) | −0·00007 (20) | −0·00005 (3) | −0·00024 (11) |
| N(2)  | 0·31258 (5) | 0·79758 (38) | 0·34988 (10) | 0·00118 (2) | 0·04439 (96) | 0·00282 (6) | 0·00007 (21) | −0·00007 (3) | −0·00065 (13) |
| H(9)  | 0·0691 (140) | 0·3614 (890) | 0·0502 (240) | * | | | | | |
| H(10) | 0·3057 (100) | 0·1299 (650) | 0·0449 (190) | * | | | | | |

\* The thermal parameters of these atoms are given in Table 1.

At the end of refinement the $R$ index, excluding the accidentally absent reflexions, was 6·9%; 72% of the $|F_c|_a$ were less than $F_{lim}$. The final values of the structural parameters are given in Table 2 for the atoms in the asymmetric unit (see Figs. 1 and 3). A complete list of $|F_o|$, and of $F_c$ at the end of refinement, is available from the author.

The matrix of correlation coefficients between the 117 structural parameters was extracted at the end of refinement. Of the ~7000 non-self-correlation coefficients only 83 were greater than 0·2. Of these none was greater than 0·5 and all but 12 were 0·3 or less. These coefficients are not large enough to suggest that the structure of AHS is in any way indeterminate (Geller, 1961).

Difference syntheses, computed with the final structural parameters and all the X-ray data, showed that a small scale-factor error remained – probably caused by the inclusion of reflexions slightly affected by extinction, that even with the higher angle data included the regions of the ammonium ions showed no significant features, and that there was slight misplacing of the oxygen atoms, O(3) and O(4). These atoms were the only ones to show a significant correlation between their $x$ and $z$ coordinates, being the two which most nearly overlap in the (010) projection.

## 4. The structure

The structure that has emerged from this study is composed of distorted sulphate tetrahedral ions linked into chains along **b** by short hydrogen bonds in which the protons are in ordered acentric positions, these chains alternating in both the **a** and **c** directions with rows, along **b**, of ammonium ions (Figs. 1 and 2). The relative disposition of the sulphur and nitrogen atoms is shown schematically in Fig. 2.

The errors on the parameters in Table 2 are 'correct' standard deviations in the sense that they were calculated by a complete solution of the least-squares equations. However, because of uncorrected systematic errors the parameters are likely to be less well determined than these figures suggest. This is particularly true of the thermal motion parameters. Though it is difficult to estimate their errors it is probable that the relative magnitude of the thermal parameters will be correct for each atom. Nevertheless, no analysis of atomic or ionic thermal motion was made in this study. Hamilton (1969) recently reviewed the problem of random and systematic errors in currently obtainable values of $|F_o|$ and $F_c$. It is inferred from his conclusions that the estimated errors given in Table 2 may need to be increased by a factor of four or five to be realistic.

It is emphasized again that the *known* sources of systematic error in the data are expected to have affected the thermal parameters, whose actual values are to be regarded with suspicion, but to have had little effect on the positional parameters. It is worthy of note that no pairs of positional and thermal parameters were significantly correlated.

All pertinent bond lengths and bond angles are given in Table 3. They were calculated from the refined positional parameters (Table 2) and the measured cell dimensions. The increments in parameter errors suggested above are not included in the quoted errors. No

## Table 3. *Bond lengths and angles*

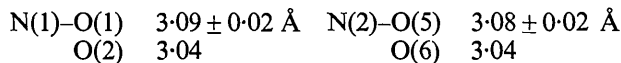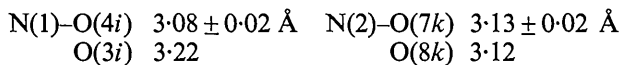Errors are given in brackets: distances ($\times 10^3$), angles ($\times 10$).

(a) Bond lengths

| | | | | | |
|---|---|---|---|---|---|
| S(1) —O(1) | 1·430 (2) Å | | S(2) —O(5) | 1·440 (2) Å |
| O(2) | 1·419 (2) | | O(6) | 1·441 (2) |
| O(3) | 1·441 (3) | | O(7) | 1·557 (2) |
| O(4) | 1·546 (3) | | O(8) | 1·455 (2) |
| N(1)—O(6b) | 3·134 (5) | | N(2)—O(5b) | 2·965 (4) |
| O(6b″) | 2·972 (4) | | Ô(5b″) | 3·070 (5) |
| O(1h′) | 3·070 (5) | | O(2d) | 3·006 (5) |
| [O(1h′)]″ | 2·921 (4) | | O(2d″) | 2·990 (5) |
| O(4i) | 3·079 (4) | | O(7k) | 3·131 (4) |
| O(3i) | 3·219 (5) | | O(8k) | 3·122 (4) |
| O(1) | 3·093 (4) | | O(5) | 3·082 (4) |
| O(2) | 3·044 (4) | | O(6) | 3·042 (4) |
| O(8b) | 3·081 (3) | | O(7b″) | 3·254 (3) |
| O(3h′) | 3·156 (3) | | | |
| O(3)—H(9″) | 1·790 (40) | | O(7)—H(10″) | 0·690 (30) |
| H(9″)-O(4″) | 0·760 (40) | | H(10″)-O(8″) | 1·920 (30) |
| O(3)—O(4″) | 2·514 (6) | | O(7)—O(8″) | 2·598 (5) |

(b) Bond angles

| | | | | |
|---|---|---|---|---|
| O(1)–S(1)–O(2) | 112·5 (1)° | | O(5)–S(2)–O(6) | 113·3 (1)° |
| O(1)–S(1)–O(3) | 111·7 (1) | | O(5)–S(2)–O(7) | 106·0 (1) |
| O(1)–S(1)–O(4) | 108·6 (1) | | O(5)–S(2)–O(8) | 112·4 (1) |
| O(2)–S(1)–O(3) | 115·0 (1) | | O(6)–S(2)–O(7) | 108·2 (1) |
| O(2)–S(1)–O(4) | 107·5 (1) | | O(6)–S(2)–O(8) | 112·5 (1) |
| O(3)–S(1)–O(4) | 100·5 (1) | | O(7)–S(2)–O(8) | 103·8 (1) |
| O(3)···H(9″)–O(4″) | 160±4° | | O(7)–H(10″)...O(8″) | 172±6° |

correction was applied to bond lengths for thermal motion. The correction is small (Lipson & Cochran, 1966, p. 354): the thermal parameters are subject to uncertain systematic errors.

The method of labelling atoms is illustrated in Fig. 3. The disposition of the atoms involved in the listed bond lengths and angles is illustrated diagrammatically in a (010) projection in Fig. 4.

Even if the bond length 'standard deviations' are increased by a factor of four or five, it is clear that both sulphate tetrahedra are distorted, and that they differ in dimensions and distortion. Taking a random error of $\pm 0.01$ Å on the S–O bond lengths, the average length of the S(1)–O bonds is $1.460 \pm 0.005$ Å and that of the S(2)–O bonds $1.473 \pm 0.005$ Å – it is assumed that any systematic errors will affect the two ions similarly. The lengthening of the S–O(H) bond is clearly significant in both ions. The bond lengths agree quite closely with expected values, in particular with those found in $KHSO_4$ (Cruickshank, 1961). With regard to bond angles, the S(1) ion shows a greater distortion than the S(2) ion.

Tables 4.1.1 and 4.1.12 of *International Tables for X-ray Crystallography* (1962) give the range of $NH_4^+$–O distances as $2.8$–$3.4$ Å and the range of N$\cdots$O separations in hydrogen bonds as $2.7$–$3.2$ Å. Table 3 lists all N–O separations in AHS less than $3.5$ Å. The environments of the two ammonium ions are very similar. Both are almost at the centre of a square array of oxygen atom neighbours. With a conservative error of $\pm 0.02$ Å on each of N(1)–O(6b), O(6b''), O(1h') and [O(1h')]'', their mean length is $3.02 \pm 0.01$ Å. N(2)–O(5b), O(5b''), O(2d) and O(2d'') have a mean length of $3.02 \pm 0.01$ Å. The effects of systematic error are expected to be the same for both means. Each ammonium ion has neighbouring oxygen atoms displaced from it approximately along $\pm c$, and the N–O distances are again quite similar:

N(1)–O(4i)  $3.08 \pm 0.02$ Å    N(2)–O(7k)  $3.13 \pm 0.02$ Å
    O(3i)  $3.22$                 O(8k)  $3.12$

N(1)–O(1)  $3.09 \pm 0.02$ Å    N(2)–O(5)  $3.08 \pm 0.02$ Å
    O(2)  $3.04$                  O(6)  $3.04$

However, N(1) has two other near neighbours, O(3h') and O(8b), at distances of $3.16$ and $3.08$ Å respectively, while N(2) has only O(7b'') at a distance of $3.25$ Å (see Fig. 4).

The two hydrogen bonds are illustrated in Fig. 5. The 'expected' O–H nuclear separations, $r$(O–H), for the values of $r$(O$\cdots$O), the oxygen separations, are (Hamilton, 1962):

$r$[O(4'')–H(9'')]          $r$[O(7)–H(10'')]
$0.99 \pm 0.03$ Å           $0.98 \pm 0.03$ Å

From the studies of Hamilton (1962) and Chidambaram & Sikka (1968) of the dimensions and angles of O–H$\cdots$O bonds occurring in many different compounds, the 'expected' values of $\theta$ and ranges of $\delta$ (see
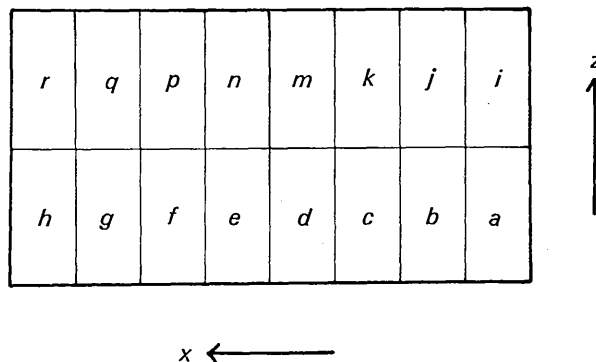


Fig. 3. The method of labelling symmetry related atoms. The full cell $a \times b \times c$ is divided into sixteen 'subcells', $a/8 \times b \times c/2$, each containing one formula unit. These cells are labelled $a$ to $r$.
S(1), O(1), O(2), O(3), O(4), N(1) and H(9) are in $a$;
S(2), O(5), O(6), O(7), O(8), N(2) and H(10) are in $c$.
These atoms constitute the asymmetric unit.
Symmetrically equivalent atoms in $b$ are designated S(2b), O(5b), etc. Atoms in the adjacent unit cell along $\pm x$, $\pm y$, or $\pm z$ are shown by single, double and triple primes respectively, e.g. [O(1h')]'' is the atom symmetrically equivalent to] O(1) in the $h$ subcell of the unit-cell next to the principal one along $\pm x$ and next to this second cell along $\pm y$.

Fig. 5) are:

(a)                                    $\theta$          $\delta$
  O(3)$\cdots\cdots$H(9'')—O(4'')    $177 \pm 6°$      $0$–$7°$
  O(7)—H(10'')$\cdots\cdots$O(8'')    $174 \pm 6$       $0$–$9$

Combining the $x$ and $z$ coordinates for H(9) and H(10) found in the neutron study with the known O$\cdots$O separations and estimated O–H distances (see above) the following values are obtained:

(b)                                    $\theta$          $\delta$
  O(3)$\cdots\cdots$H(9'')—O(4'')    $164 \pm 5°$      $10 \pm 3°$
  O(7)—H(10'')$\cdots\cdots$O(8'')    $168 \pm 4$       $7.5 \pm 2$

The values found from the least-squares refinement of the X-ray data were:

(c)                                    $\theta$          $\delta$
  O(3)$\cdots\cdots$H(9'')—O(4'')    $160 \pm 4°$      $14 \pm 3°$
  O(7)—H(10'')$\cdots\cdots$O(8'')    $172 \pm 6$       $6 \pm 4$

which are in agreement with (b). If it is assumed that the X-ray refinement displaces the hydrogen atoms along a line joining the proton position to the relevant oxygen nucleus, and the O–H distances are increased along these lines to their 'expected' values of $\sim 0.98$ Å (see above), the $\delta$ values remain the same, of course, but the $\theta$ values become:

(d)                                    $\theta$
  O(3)$\cdots\cdots$H(9'')—O(4'')    $158 \pm 4°$
  O(7)—H(10'')$\cdots\cdots$O(8'')    $171 \pm 6$

Comparing (a), (b), (c) and (d) it seems clear that while the O(7)–H(10'')$\cdots$O(8'') bond is bent by an 'expected'

amount for the given O(7)$\cdots$O(8″) separation, the O(3)$\cdots$H(9″)–O(4″) bond is abnormally strongly bent. There is no reason to suppose that the O(3)$\cdots$O(4″) separation is incorrect to a degree that would vitiate this conclusion; and the strong bending is apparent in both the neutron and the X-ray results.

## 5. Conclusion

The following conclusions have been reached regarding the room-temperature structure of AHS:

(i) the two symmetrically inequivalent sulphate ions show significant differences in distortion and dimensions – though the difference in the latter is small;

(ii) both sulphate ions show one very significantly lengthened S–O bond while the three other bonds are, within error, of equal length;

(iii) the length of this longer S–O bond is, within error, the same as that found for S–O(H) bonds in other structures containing $HSO_4^-$ ions;

(iv) both of the symmetrically inequivalent ammonium ions are in very similar asymmetric environments: with one exception there is no significant difference to be found in the two sets of N–O separations;

(v) although the evidence is not conclusive it all suggests that the ammonium ions are executing pronounced motion: this is probably not simply a thermal motion of high amplitude in a single potential well but a motion between several possible configurations of the ions;

(vi) the two symmetrically inequivalent O–H$\cdots$O hydrogen bonds are significantly different: both are short and the shorter of the two is abnormally strongly bent;
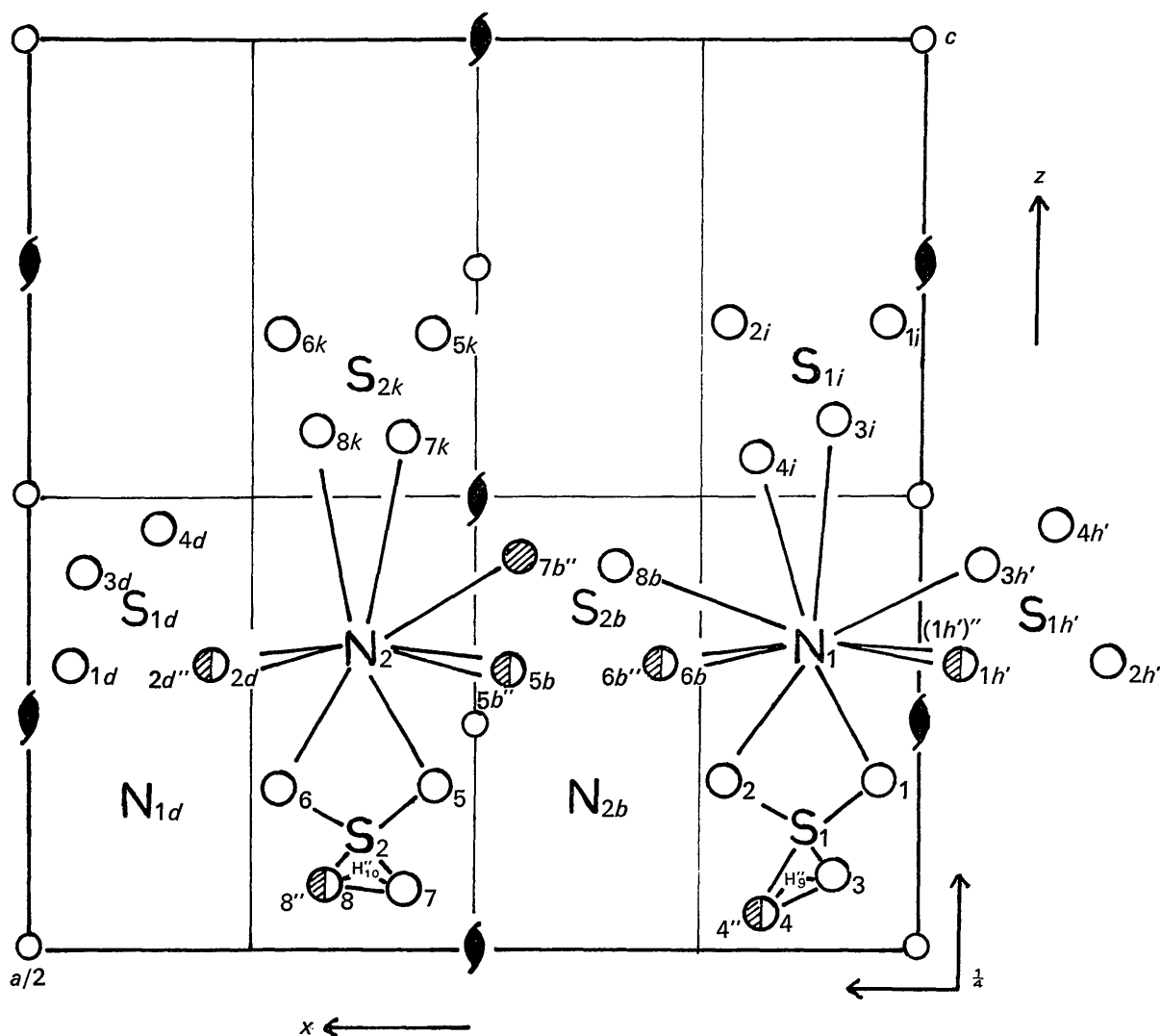


Fig. 4. The disposition of atoms involved in the bond lengths and angles listed in Table 3 is shown in (010) projection. Oxygen atoms (shown as large circles) displaced by one lattice repeat along b are shaded (and double primed). All bonds whose lengths are listed in Table 3 are marked by solid lines joining the atoms. $B2_1/a$ space group symmetry elements are shown. (cf. Fig. 1).
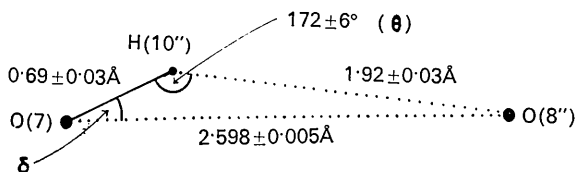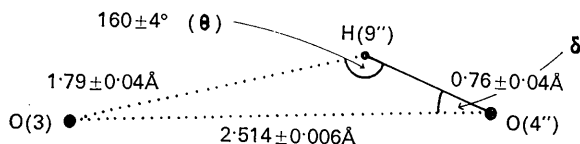
Fig. 5. The two symmetrically inequivalent O–H···O bonds connecting sulphate tetrahedra along b. The dimensions given for each bond are as found from the X-ray refinement.

(vii) the hydrogen atoms in these bonds are in ordered acentric positions.

With the exception of (v) no conclusions are reached regarding the thermal motion of atoms or ions in the structure. The thermal parameters are subject to too many sources of error – though their relative magnitudes are expected to be meaningful. No firm conclusion has been reached as to the character of the bonding between the ammonium ions and the sulphate groups.

This, the non-ferroelectric structure of AHS, displays two unusual features: first it is pseudo-symmetric, and secondly the protons are already ordered in acentric positions in the hydrogen bonds which are expected to play some rôle in the transition. It is more usual for a ferroelectric to become pseudo-symmetric in its ferroelectric phase, and for protons to be disordered in such bonds in the non-ferroelectric phase (see Jona & Shirane, 1962).

The pseudo-symmetry of the structure suggests the existence of a higher symmetry phase at a higher temperature. However, this phase would be orthorhombic, and it is reported that single crystals of (monoclinic) AHS can be grown from the melt (Pepinsky et al., 1958). Hence no such phase can exist below the melting point at atmospheric pressure.

Regarding the transition to the ferroelectric phase, the most salient feature of this structure is that, unlike the non-ferroelectric phases of many related ferroelectrics, it is ordered – except for the ammonium ions, which all present information shows to play no part in the transition. Hence it is possible that the transition will prove to be associated with the 'freezing-in' of a well defined transverse optical mode (Cochran, 1960), rather than with a very over-damped oscillation as, for example, in KDP (see Kaminow & Damen, 1968; Buyers, Cowley, Paul & Cochran, 1968). Neutron inelastic scattering and Raman scattering techniques will

be applied to investigating this aspect of the transition, together with the d.m.r. experiments already mentioned (§1). Meanwhile work has started on the determination of the structure of AHS in its ferroelectric phase.

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# Anisotropy of the Sodium Atom in Low Albite

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Measurements of diffraction intensities at elevated temperatures have been used to study the anisotropy of the sodium atom in low albite. The new observations provide strong support for the interpretation of the observed anisotropy in terms of anisotropic thermal vibration of the atom.

## 1. Introduction

In both low albite and high albite the electron density distribution around the sodium atom is markedly anisotropic, the atom appearing to be elongated (Ferguson, Traill & Taylor, 1958; Ribbe, Ferguson & Taylor, 1962; Ribbe, Ferguson, Traill & Taylor, 1963). In high albite the anisotropy is very large and probably corresponds to the space-average of a multipartite structure with faulted domains. In low albite the much smaller anisotropy is probably to be interpreted as the time-average of the anisotropic thermal vibration of the sodium atom, though the evidence is not sufficiently conclusive to rule out the possibility of a space average of the kind proposed for high albite (Ribbe, Megaw & Taylor, 1969).

The most direct way of deciding whether the anisotropy of the sodium atom in low albite represents true anisotropic thermal vibration or a space average is to study the anisotropy over a wide range of temperature. For on any physically reasonable model of the variation of thermal vibration with temperature the amplitude of vibration must be reduced at lower temperatures, increased at higher temperatures. An earlier inconclusive study at −180°C (Williams, 1961; Williams & Megaw,

1964) was taken into account by Ribbe, Megaw & Taylor (1969) in their discussion of the anisotropy in low albite. The experiments now reported have given information about the anisotropy at 300 and 600°C, and when combined with a re-examination of the measurements of Williams (1961) leave little doubt that in low albite the observed anisotropy of the sodium atom represents true anisotropic thermal vibration.

## 2. Experimental measurements

A sample of low albite from the Schmirntal, Tyrol, was obtained from the Gasser collection in the Mineralogical Museum of the University of Padua.

Axial lengths and interaxial angles of the conventional base-centred unit cell (space group $C\bar{1}$) were determined at 20, 300 and 600°C, using a precession camera calibrated with quartz and sodium chloride. They are listed in Table 1, together with the average expansion coefficient over the range 20–600°C for each of the axes $a$, $b$, $c$.

The major axis of the elongated sodium atom lies very nearly in the plane (100), so that a two-dimensional projection on this plane offers the simplest method of studying the variation of anisotropy with temperature.