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# The Crystal Structure of the Low-Temperature Phase of Methylammonium Alum

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At 170 °K methylammonium alum undergoes a phase change from the room-temperature structure, which is cubic with unit-cell edge of length 12·50 Å, to a low-temperature structure which is orthorhombic with unit-cell edges of length $a=12{\cdot}57$, $b=12{\cdot}33$ and $c=12{\cdot}38$ Å. The change from the symmetry of the non-polar class $m3$, space group $Pa3$, to that of the polar class $mm2$, space group $Pca2_1$ is consistent with the onset of ferroelectricity which is known to occur at a temperature in the region of 170 °K; in conformity also with the conditions associated with a ferroelectric transition are the absence of interchange of atoms between different sites and, with the exception of the methylammonium group, the absence, too, of large displacements of atoms from the positions occupied in the structure of higher symmetry. In the low-temperature phase the methylammonium group is shown to be fixed and not to simulate, either by statistical or by rotational means, the possession of the centre of symmetry required of the room-temperature structure.

## Introduction

A marked increase in the value of the dielectric loss in methylammonium alum has been observed at low temperature both by Griffiths & Powell (1952) and by Pepinsky, Jona & Shirane (1956), the respective quoted values of the transition temperature being 170 °K and 176 °K. Pepinsky and his co-workers also observed that the anomaly coincided with the onset of ferroelectricity in the crystal and they were able to obtain saturated ferroelectric loops at temperatures which ranged from 177 °K to 154 °K. The dielectric anomaly is clearly associated with the abrupt transition at 170 °K in the crystal structure of methylammonium alum reported by Fletcher & Steeple (1961), and it is possibly significant that the temperature range over which the ferroelectric phenomena were observed is similar to that of 170 °K to 150 °K over which Fletcher & Steeple noted gradual changes in the colours of the optical interference pattern obtained with a single crystal of the alum. The present investigation was undertaken to determine the structure of the low-temperature phase of the crystal and hence to ascertain the nature of the structural changes which accompany both the abrupt transition in the value of the dielectric constant and the initiation of ferroelectric behaviour.

## Experimental

Fletcher & Steeple (1961) have established that methylammonium alum exists as a single phase between room temperature and 170 °K and from 150 °K to 90 °K, the latter temperature being the lowest that could be obtained with cold-gas streaming; the conclusion concerning the structure between 170 °K and 150 °K was that in this range two different phases were present simultaneously. From X-ray diffraction data collected for the present investigation it was confirmed that above and below the temperature range 170 °K to 150 °K the crystal exists as single but different phases. Within the range, however, it was now apparent that what were originally thought to be two different phases are, in fact, two orientations of the structure of the same single phase which exists below 150 °K in one orientation only. There was thus only one crystal structure to be determined and, since the intensity data obtained from a single diffraction pattern were more reliable than the data which could be obtained from two almost overlapping patterns, zero-layer Weissenberg photographs were taken with the crystal maintained at some constant temperature below 150 °K. A convenient temperature was 113 °K and Cu $K\alpha$ radiation was used.

The single crystal of methylammonium alum was oscillated about the original [100] direction of the room-temperature cubic phase, and it was fortunate that the principal axes of the low-temperature structure coincided in direction with those of the cubic phase. It was, however, a matter of chance as to which of the $\langle 100 \rangle$ directions of the new structure coincided with that of the rotation axis, but eventually Weissenberg data were collected for oscillations about each of the new $\langle 100 \rangle$ directions and from these the space group and unit-cell dimensions of the low-temperature structure were determined. The structure is orthorhombic with space group $Pca2_1$, and there are four asymmetric units in the unit cell whose edges, measured to an accuracy of $\pm\frac{1}{2}\%$, are

$$a=12{\cdot}57,\ b=12{\cdot}33,\ c=12{\cdot}38\ \text{Å}.$$

Estimations of the intensities of the recorded reflexions from the $\{hk0\}$ and the $\{h0l\}$ planes were made by eye; no absorption corrections were made as these

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were not considered to be sufficiently significant, but the Lorentz and polarization factors were applied, as also were the temperature and scaling factors (Wilson, 1942).

Collection of three-dimensional data was started but not completed because the time required was prohibitive owing to the uncertainty as to which of the three possible orientations the crystal would adopt at low temperature.

## Determination of the structure

The fact that the crystal remained single during the phase change indicated that the atomic shifts would be small and that the coordinates published by Lipson (1935) for the room-temperature structure of methylammonium alum would give a reasonable trial structure for the low-temperature phase. Before the coordinates could be utilized, however, transformation of axes from those of space group $Pa3$ to those of space group $Pca2_1$ had to be effected and this involved transformation of fractional coordinates from $(x, y, z)$ to $(y, x, -z)$ with the origin of coordinates transferred to $(0, \frac{1}{4}, \frac{1}{4})$. Initially the values of the agreement residuals for the projections along the [001] and the [010] directions were 0·50 and 0·40 respectively, and from these stages the refinement of the two projections proceeded independently by means of two-dimensional Fourier syntheses until the value of the residual for the former, centrosymmetrical, projection reached 0·23 and that for the latter, non-centrosymmetrical, projection reached 0·17. Two further independent attempts were made to refine the centrosymmetrical projection by $(F_o - F_c)$ syntheses, but each one failed to improve the residual beyond the value 0·23; three cycles of the Minimum Residual refinement program of Bhuiya & Stanley (1963) were, however, sufficient to reduce the agreement residual to 0·15. Substitution of the new $x$ coordinates in the structure-factor and residual calculations of the non-centrosymmetrical projection resulted in an immediate decrease in the value of that residual from 0·17 to 0·13, and after continuation of the refinement of both projections by difference syntheses the final values of the residuals, when the two projections had common $x$ coordinates, were 0·116 for the centrosymmetrical [001] projection and 0·099 for the non-centrosymmetrical [010] projection. Excluded from the calculations of the agreement residuals were those reflexions for which the calculated value of the intensity was less than the minimum observed value in the appropriate region of $\sin\theta$ values.

Of the thirty hydrogen atoms in the asymmetric unit, the coordinates of the twenty-four which, with oxygen atoms, formed water molecules were obtained by inspection of a model of the structure and were included in the structure-factor calculations during the later stages of refinement; in almost every instance these coordinates coincided with those of suitable election-density peaks on the difference maps for the two projections. Finally, the coordinates of the six hydrogen atoms of the methylammonium ion were determined from the relevant difference maps.

The values of the overall isotropic thermal parameter $B$ utilized in calculating the structure factors which are shown, along with the observed structure factors, in Table 1 were 0·02 Å$^2$ for the [001] projection and −0·40 Å$^2$ for the [010] projection; both were sensitive to changes in coordinate values and although they were sometimes positive and sometimes

Table 1. *Comparison of observed and calculated structure factors*

| h k 0 | $\|F_o\|$ | $F_c$ |
|---|---|---|
| 0 1 0 | Not recorded | |
| 0 2 0 | 16 | -15 |
| 0 3 0 | <7 | 7 |
| 0 4 0 | 171 | 176 |
| 0 5 0 | 32 | -20 |
| 0 6 0 | 216 | -202 |
| 0 7 0 | 25 | 24 |
| 0 8 0 | 34 | 38 |
| 0 9 0 | 18 | 12 |
| 0,10,0 | 48 | 52 |
| 0,11,0 | 28 | 33 |
| 0,12,0 | 91 | 105 |
| 0,13,0 | 26 | -28 |
| 0,14,0 | 48 | -56 |
| 0,15,0 | <10 | 0 |
| 1 1 0 | 17 | -18 |
| 1 2 0 | 117 | -131 |
| 1 3 0 | 17 | -11 |
| 1 4 0 | 125 | -127 |
| 1 5 0 | 53 | -56 |
| 1 6 0 | <11 | -5 |
| 1 7 0 | 21 | 12 |
| 1 8 0 | 36 | 29 |
| 1 9 0 | <14 | +1 |
| 1,10,0 | 45 | 37 |
| 1,11,0 | 16 | -14 |
| 1,12,0 | 53 | -54 |
| 1,13,0 | <14 | 14 |
| 1,14,0 | 54 | -56 |
| 1,15,0 | <10 | 5 |
| 2 0 0 | <5 | -4 |
| 2 1 0 | <5 | 8 |
| 2 2 0 | 112 | -109 |
| 2 3 0 | <8 | +2 |
| 2 4 0 | 45 | -58 |
| 2 5 0 | 18 | +11 |
| 2 6 0 | 169 | -184 |
| 2 7 0 | 15 | 9 |
| 2 8 0 | 75 | 92 |
| 2 9 0 | 23 | -22 |
| 2,10,0 | 59 | -61 |
| 2,11,0 | 21 | 18 |
| 2,12,0 | 55 | 55 |
| 2,13,0 | <14 | -9 |
| 2,14,0 | <2 | -58 |
| 2,15,0 | <9 | 10 |
| 3 1 0 | 24 | -28 |
| 3 2 0 | 21 | +21 |
| 3 3 0 | 22 | -25 |

| h k 0 | $\|F_o\|$ | $F_c$ |
|---|---|---|
| 3 4 0 | 48 | -48 |
| 3 5 0 | 10 | +8 |
| 3 6 0 | 55 | 58 |
| 3 7 0 | <12 | +5 |
| 3 8 0 | 56 | 51 |
| 3 9 0 | 17 | 14 |
| 3,10,0 | 36 | 36 |
| 3,11,0 | <15 | 12 |
| 3,12,0 | 19 | -19 |
| 3,13,0 | 25 | -25 |
| 3,14,0 | <12 | 17 |
| 3,15,0 | <9 | 5 |
| 4 0 0 | 141 | 155 |
| 4 1 0 | 12 | -16 |
| 4 2 0 | 121 | -114 |
| 4 3 0 | 20 | 15 |
| 4 4 0 | 46 | 48 |
| 4 5 0 | <11 | -6 |
| 4 6 0 | <12 | 8 |
| 4 7 0 | 14 | 15 |
| 4 8 0 | 37 | 42 |
| 4 9 0 | 14 | -14 |
| 4,10,0 | 19 | 30 |
| 4,11,0 | 18 | -16 |
| 4,12,0 | 22 | 16 |
| 4,13,0 | 25 | -20 |
| 4,14,0 | 37 | -25 |
| 4,15,0 | 10 | 7 |
| 5 1 0 | 9 | 7 |
| 5 2 0 | 14 | -8 |
| 5 3 0 | 22 | 16 |
| 5 4 0 | 29 | -28 |
| 5 5 0 | 20 | +19 |
| 5 6 0 | 30 | 31 |
| 5 7 0 | 31 | 27 |
| 5 8 0 | 33 | -37 |
| 5 9 0 | 18 | +17 |
| 5,10,0 | 31 | -21 |
| 5,11,0 | <15 | 1 |
| 5,12,0 | 31 | -27 |
| 5,13,0 | 17 | -18 |
| 5,14,0 | 14 | 15 |
| 6 0 0 | 161 | 158 |
| 6 1 0 | 24 | -21 |
| 6 2 0 | <11 | +10 |
| 6 5 0 | 25 | -24 |
| 6 4 0 | 61 | 66 |
| 6 5 0 | <12 | 4 |
| 6 6 0 | 154 | -145 |
| 6 7 0 | 33 | 34 |
| 6 8 0 | 35 | 35 |
| 6 9 0 | <15 | 13 |
| 6,10,0 | 44 | -45 |
| 6,11,0 | 31 | 32 |

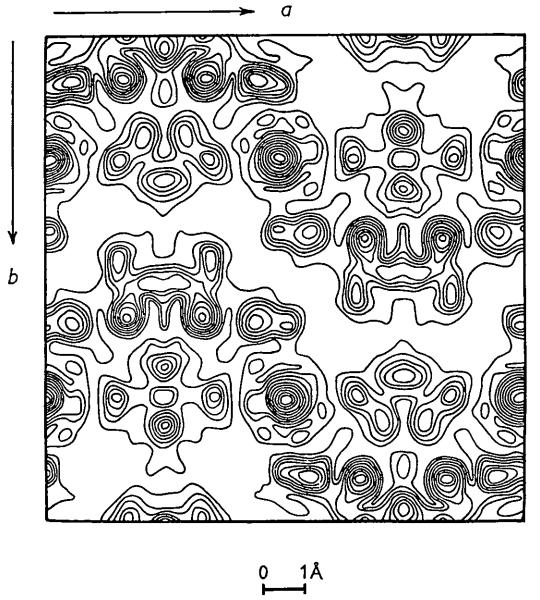
| h k 0 | $\|F_o\|$ | $F_c$ |
|---|---|---|
| 6,12,0 | 78 | 78 |
| 6,13,0 | 22 | -22 |
| 6,14,0 | 22 | -26 |
| 7 1 0 | 45 | -44 |
| 7 2 0 | 75 | -80 |
| 7 3 0 | 41 | 45 |
| 7 4 0 | 51 | -49 |
| 7 5 0 | 15 | 17 |
| 7 6 0 | 25 | 23 |
| 7 7 0 | 35 | 33 |
| 7 8 0 | 78 | 80 |
| 7 9 0 | 18 | 22 |
| 7,10,0 | 61 | 73 |
| 7,11,0 | <15 | 7 |
| 7,12,0 | 24 | -23 |
| 7,13,0 | 15 | -9 |
| 7,14,0 | 17 | -8 |
| 8 0 0 | 21 | 19 |
| 8 1 0 | 22 | 17 |
| 8 2 0 | 71 | -68 |
| 8 3 0 | 28 | -30 |
| 8 4 0 | 71 | 84 |
| 8 5 0 | 22 | -20 |
| 8 6 0 | 24 | 16 |
| 8 7 0 | <13 | 14 |
| 8 8 0 | 49 | 48 |
| 8 9 0 | 23 | -28 |
| 8,10,0 | 30 | -38 |
| 8,11,0 | <14 | -15 |
| 8,12,0 | 15 | -7 |
| 8,13,0 | 16 | -22 |
| 9 1 0 | 15 | -10 |
| 9 2 0 | 19 | 13 |
| 9 3 0 | 36 | -36 |
| 9 4 0 | 34 | -30 |
| 9 5 0 | 44 | 45 |
| 9 6 0 | 16 | 12 |
| 9 7 0 | 16 | 18 |
| 9 8 0 | 57 | -56 |
| 9 9 0 | 31 | -33 |
| 9,10,0 | 15 | -5 |
| 9,11,0 | <12 | 9 |
| 9,12,0 | 16 | -16 |
| 9,13,0 | 18 | -19 |
| 10,0,0 | 66 | -73 |
| 10,1,0 | 15 | -12 |
| 10,2,0 | 61 | -65 |
| 10,3,0 | <15 | -9 |
| 10,4,0 | 18 | 18 |
| 10,5,0 | 18 | 17 |
| 10,6,0 | 20 | 21 |
| 10,7,0 | <15 | 5 |
| 10,8,0 | 34 | -34 |
| 10,9,0 | 14 | -14 |
| 10,10,0 | 25 | -15 |
| 10,11,0 | 16 | -20 |
| 10,12,0 | 9 | -11 |

| h k 0 | $\|F_o\|$ | $F_c$ |
|---|---|---|
| 11,1,0 | 30 | -27 |
| 11,2,0 | 55 | 57 |
| 11,3,0 | 34 | 30 |
| 11,4,0 | 69 | 69 |
| 11,5,0 | <15 | 1 |
| 11,6,0 | 20 | -21 |
| 11,7,0 | <15 | 1 |
| 11,8,0 | 48 | -47 |
| 11,9,0 | <12 | -5 |
| 11,10,0 | 35 | -36 |
| 11,11,0 | 46 | -5 |
| 12,0,0 | 85 | 108 |
| 12,1,0 | <15 | -5 |
| 12,2,0 | 24 | 20 |
| 12,3,0 | <15 | 4 |
| 12,4,0 | 16 | 8 |
| 12,5,0 | <14 | -6 |
| 12,6,0 | 69 | -67 |
| 12,7,0 | 20 | 27 |
| 12,8,0 | 18 | 21 |
| 12,9,0 | 13 | 14 |
| 12,10,0 | 8 | 9 |
| 13,1,0 | 15 | -11 |
| 13,2,0 | 16 | -10 |
| 13,3,0 | 20 | 23 |
| 13,4,0 | 15 | -16 |
| 13,5,0 | 15 | 5 |
| 13,6,0 | <12 | -1 |
| 13,7,0 | 42 | 43 |
| 13,8,0 | 16 | 17 |
| 13,9,0 | 23 | -22 |
| 14,0,0 | 38 | 40 |
| 14,1,0 | <15 | 1 |
| 14,2,0 | 50 | -47 |
| 14,3,0 | <12 | -1 |
| 14,4,0 | 51 | 25 |
| 14,5,0 | 27 | -32 |
| 14,6,0 | 35 | -38 |
| 14,7,0 | 18 | -18 |
| 15,1,0 | 37 | -37 |
| 15,2,0 | 12 | 15 |
| 15,3,0 | 18 | -19 |
| 15,4,0 | 25 | 23 |
| 15,5,0 | 24 | -30 |
| 16,0,0 | 18 | 22 |
| 16,1,0 | 9 | 12 |

| h 0 1 | $\|F_o\|$ | $F_c$ |
|---|---|---|
| 0 0 2 | 22 | 10 |
| 0 0 4 | 148 | 164 |
| 0 0 6 | 194 | 186 |
| 0 0 8 | 34 | 22 |
| 0,0,10 | 90 | 86 |

| h 0 1 | $\|F_o\|$ | $F_c$ |
|---|---|---|
| 0,0,12 | 120 | 122 |
| 0,0,14 | 60 | 68 |
| 2 0 0 | <6 | 4 |
| 2 0 1 | 112 | 140 |
| 2 0 2 | 100 | 112 |
| 2 0 3 | 84 | 88 |
| 2 0 4 | 156 | 152 |
| 2 0 5 | 16 | 6 |
| 2 0 6 | 30 | 26 |
| 2 0 7 | 92 | 92 |
| 2 0 8 | 98 | 96 |
| 2 0 9 | <18 | 14 |
| 2,0,10 | 100 | 98 |
| 2,0,11 | 86 | 76 |
| 2,0,12 | 54 | 46 |
| 2,0,13 | 26 | 18 |
| 2,0,14 | 56 | 62 |
| 2,0,15 | 20 | 22 |
| 4 0 0 | 150 | 156 |
| 4 0 1 | 120 | 140 |
| 4 0 2 | 80 | 78 |
| 4 0 3 | 62 | 72 |
| 4 0 4 | 46 | 48 |
| 4 0 5 | 58 | 58 |
| 4 0 6 | 86 | 84 |
| 4 0 7 | 88 | 82 |
| 4 0 8 | 92 | 100 |
| 4 0 9 | 60 | 54 |
| 4,0,10 | 34 | 32 |
| 4,0,11 | 76 | 78 |
| 4,0,12 | 42 | 46 |
| 4,0,13 | 34 | 36 |
| 4,0,14 | 42 | 40 |
| 4,0,15 | 10 | 26 |
| 6 0 0 | 166 | 162 |
| 6 0 1 | 60 | 58 |
| 6 0 2 | 152 | 178 |
| 6 0 3 | 50 | 46 |
| 6 0 4 | 24 | 18 |
| 6 0 5 | 52 | 50 |
| 6 0 6 | 150 | 140 |
| 6 0 7 | 48 | 48 |
| 6 0 8 | 38 | 40 |
| 6 0 9 | 24 | 18 |
| 6,0,10 | 22 | 24 |
| 6,0,11 | 28 | 30 |
| 6,0,12 | 108 | 120 |
| 6,0,13 | 20 | 12 |
| 6,0,14 | 46 | 42 |
| 8 0 0 | 22 | 20 |
| 8 0 1 | 42 | 34 |
| 8 0 2 | 84 | 84 |
| 8 0 3 | 62 | 62 |
| 8 0 4 | 40 | 44 |
| 8 0 5 | 44 | 42 |
| 8 0 6 | 82 | 80 |
| 8 0 7 | 84 | 84 |
| 8 0 8 | 76 | 76 |

| h 0 1 | $\|F_o\|$ | $F_c$ |
|---|---|---|
| 8 0 9 | 46 | 40 |
| 8,0,10 | 54 | 58 |
| 8,0,11 | 64 | 58 |
| 8,0,12 | 50 | 46 |
| 8,0,13 | 54 | 56 |
| 10,0,0 | 86 | 82 |
| 10,0,1 | 74 | 66 |
| 10,0,2 | 62 | 68 |
| 10,0,3 | 56 | 56 |
| 10,0,4 | 56 | 54 |
| 10,0,5 | 56 | 56 |
| 10,0,6 | 42 | 40 |
| 10,0,7 | 92 | 94 |
| 10,0,8 | 68 | 62 |
| 10,0,9 | 44 | 42 |
| 10,0,10 | 44 | 38 |
| 10,0,11 | 52 | 42 |
| 10,0,12 | 26 | 34 |
| 12,0,0 | 112 | 118 |
| 12,0,1 | 52 | 50 |
| 12,0,2 | 26 | 22 |
| 12,0,3 | 22 | 28 |
| 12,0,4 | 28 | 22 |
| 12,0,5 | 56 | 58 |
| 12,0,6 | 100 | 98 |
| 12,0,7 | <20 | 8 |
| 12,0,8 | <18 | 6 |
| 12,0,9 | 28 | 22 |
| 12,0,10 | 22 | 20 |
| 14,0,0 | 48 | 46 |
| 14,0,1 | 52 | 44 |
| 14,0,2 | 56 | 44 |
| 14,0,3 | 50 | 22 |
| 14,0,4 | 68 | 62 |
| 14,0,5 | 20 | 26 |
| 14,0,6 | 32 | 32 |
| 14,0,7 | 40 | 34 |
| 16,0,0 | 24 | 26 |
| 16,0,1 | 32 | 36 |



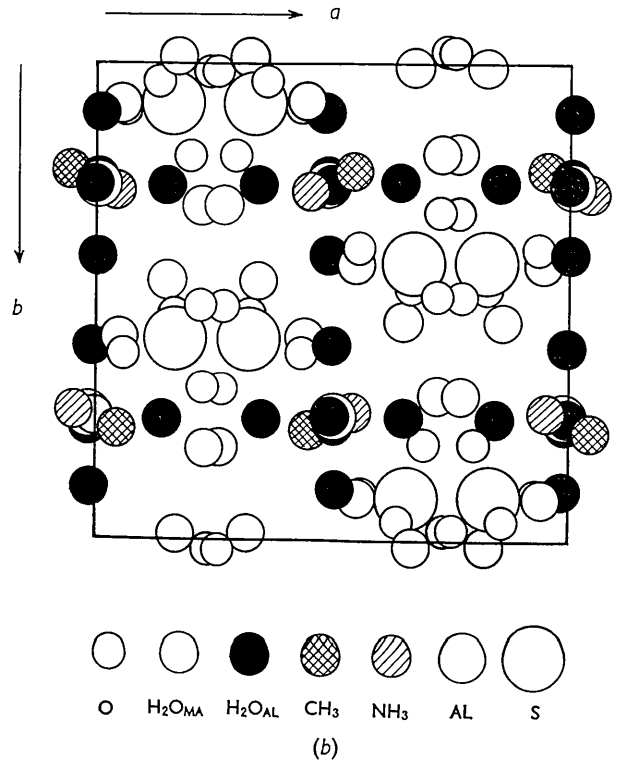
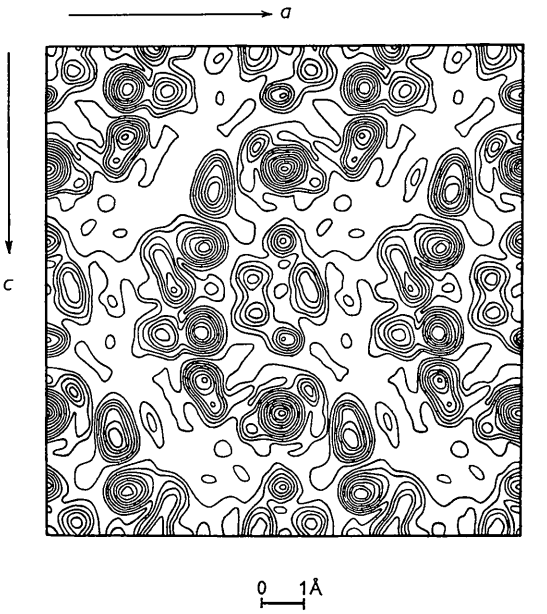




Fig. 1. (*a*) Projection of the electron-density distribution along [001]; contours are drawn at 3, 6, 9, 12, 15, 20, 25, 35, 45 and 55 e.Å$^{-2}$. (*b*) Corresponding projection of the atomic arrangement.



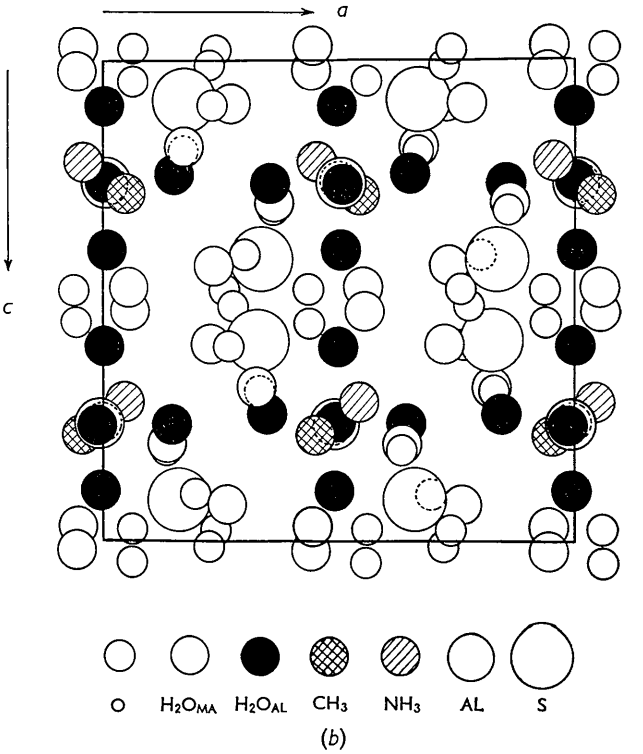




Fig. 2. (*a*) Projection of the electron-density distribution along [010]; contours are drawn at 3, 6, 9, 12, 15, 20, 25, 35, 45, 55 and 65 e.Å$^{-2}$. (*b*) Corresponding projection of the atomic arrangement.

negative they were tending towards the value zero with the increasing accuracy of the structure determination. The electron-density distributions and the corresponding atomic positions are shown in projection in Fig. 1(*a*) and (*b*), plane group *pmg*, and Fig. 2(*a*) and (*b*), plane group *pg*, respectively.

Table 2. *The fractional coordinates of non-equivalent atoms*

| Atom | $x$ | $y$ | $z$ | Atom | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|---|---|
| Al | 0·006 | 0·259 | 0·256 | $H(H_2O_{Al})$ | 0·193 | 0·774 | 0·825 |
| C | 0·047 | 0·770 | 0·280 | $H(H_2O_{Al})$ | 0·076 | 0·057 | 0·235 |
| N | 0·045 | 0·268 | 0·711 | $H(H_2O_{Al})$ | 0·048 | 0·953 | 0·781 |
| S | 0·163 | 0·088 | 0·915 | $H(H_2O_{Al})$ | 0·070 | 0·455 | 0·220 |
| S | 0·171 | 0·581 | 0·085 | $H(H_2O_{Al})$ | 0·059 | 0·542 | 0·768 |
| O | 0·136 | 0·040 | 0·811 | $H(H_2O_{Al})$ | 0·026 | 0·180 | 0·450 |
| O | 0·240 | 0·022 | 0·978 | $H(H_2O_{Al})$ | 0·024 | 0·698 | 0·960 |
| O | 0·064 | 0·096 | 0·976 | $H(H_2O_{Al})$ | 0·025 | 0·192 | 0·048 |
| O | 0·199 | 0·202 | 0·904 | $H(H_2O_{Al})$ | 0·021 | 0·680 | 0·547 |
| O | 0·169 | 0·528 | 0·190 | $H(H_2O_{MA})$ | 0·006 | 0·012 | 0·502 |
| O | 0·225 | 0·510 | 0·011 | $H(H_2O_{MA})$ | 0·136 | 0·060 | 0·507 |
| O | 0·061 | 0·610 | 0·046 | $H(H_2O_{MA})$ | 0·247 | 0·385 | 0·557 |
| O | 0·231 | 0·684 | 0·097 | $H(H_2O_{MA})$ | 0·243 | 0·264 | 0·012 |
| $H_2O_{Al}$ | 0·153 | 0·257 | 0·236 | $H(H_2O_{MA})$ | 0·225 | 0·488 | 0·752 |
| $H_2O_{Al}$ | 0·145 | 0·748 | 0·759 | $H(H_2O_{MA})$ | 0·183 | 0·480 | 0·885 |
| $H_2O_{Al}$ | 0·012 | 0·105 | 0·258 | $H(H_2O_{MA})$ | 0·004 | 0·503 | 0·502 |
| $H_2O_{Al}$ | 0·003 | 0·405 | 0·247 | $H(H_2O_{MA})$ | 0·139 | 0·552 | 0·490 |
| $H_2O_{Al}$ | 0·007 | 0·242 | 0·397 | $H(H_2O_{MA})$ | 0·249 | 0·757 | 0·490 |
| $H_2O_{Al}$ | 0·000 | 0·256 | 0·098 | $H(H_2O_{MA})$ | 0·244 | 0·893 | 0·445 |
| $H_2O_{MA}$ | 0·228 | 0·302 | 0·591 | $H(H_2O_{MA})$ | 0·249 | 0·010 | 0·743 |
| $H_2O_{MA}$ | 0·154 | 0·456 | 0·801 | $H(H_2O_{MA})$ | 0·202 | 0·002 | 0·108 |
| $H_2O_{MA}$ | 0·235 | 0·808 | 0·425 | $H(CH_3)$ | 0·120 | 0·784 | 0·340 |
| $H_2O_{MA}$ | 0·174 | 0·988 | 0·182 | $H(CH_3)$ | 0·033 | 0·840 | 0·245 |
| $H_2O_{MA}$ | 0·057 | 0·086 | 0·521 | $H(CH_3)$ | 0·083 | 0·710 | 0·225 |
| $H_2O_{MA}$ | 0·053 | 0·577 | 0·472 | $H(NH_3)$ | 0·119 | 0·275 | 0·665 |
| $H(H_2O_{Al})$ | 0·210 | 0·237 | 0·305 | $H(NH_3)$ | 0·017 | 0·330 | 0·755 |
| $H(H_2O_{Al})$ | 0·199 | 0·277 | 0·175 | $H(NH_3)$ | 0·080 | 0·205 | 0·775 |
| $H(H_2O_{Al})$ | 0·196 | 0·722 | 0·693 | | | | |

All arithmetical operations were performed by the Mercury computer and for the structure-factor calculations the scattering-factor data were in the form published by Forsyth & Wells (1959).

## Discussion

Of the fractional coordinates of all non-equivalent atoms shown in Table 2 those designated $H_2O_{Al}$ refer to the water molecules associated with the aluminum ion and those referred to as $H_2O_{MA}$ are the coordinates of the methylammonium water molecules. Because of the severe overlap encountered in projection it was not possible to calculate the standard deviations of the fractional coordinates, but from the order of magnitude of the changes in the values of the coordinates during the later stages of refinement and from the differences in the values of the common $x$ coordinates derived from the two projections it is estimated that the sulphur parameters are not in error by more than $\pm 0{\cdot}001$ and that the errors in the parameters of the other atoms are not greater than $\pm 0{\cdot}003$; this means that interatomic distances are not in error by more than $\pm 0{\cdot}05$ Å.

The onset of the ferroelectric behaviour at 177 °K reported by Pepinsky, Jona & Shirane (1956) must be accompanied by symmetry changes in methylammonium alum which place the crystal in a polar class and give rise to a pseudosymmetric structure. The proposed low-temperature structure satisfies these conditions in that it belongs to the polar class *mm*2 and is derived from the room-temperature structure by small displacements of atoms, some of which have been released from special positions by the disappearance of the triad axes and one of the sets of glide planes; apart from those of the atoms of the methylammonium group the maximum change in the value of any one fractional coordinate is 0·03, corresponding to 0·36 Å. Further, there is neither creation nor destruction of linkages between atoms so that the general details of the low temperature phase are substantially the same as those of the room-temperature structure described by Lipson (1935). However, the symmetry of the structure at low temperature does not require that the methylammonium ion should appear to possess a centre of symmetry, and from the electron-density projections shown in Figs. 1(*a*) and 2(*a*) it is evident that the ion, in fact, no longer does so; in the low-temperature phase it straddles the point $(0, \frac{1}{4}, \frac{1}{4})$ with the C–N bond of length $1{\cdot}51 \pm 0{\cdot}05$ Å and with the mean values of the H–C–H angles of the methyl group and the H–N–H angles of the $NH_3^+$ ion respectively equal to 106 and 107°. When viewed along the C–N bond the hydrogen atoms are at the corners of a more or less regular hexagon indicating that the relative orientation of the methyl group and the $NH_3^+$ ion about this bond is such as to make a minimum contribution to the potential energy of the system.

Although in the new phase the arrangement is not regular, there are still six water molecules grouped octahedrally round the aluminum ion; the average $Al–H_2O_{Al}$ distance is 1·86 Å, compared with 1·87 Å at room temperature, but individual values of the twelve distances involved range from 1·76 to 1·96 Å. The $H_2O_{Al}–H_2O_{Al}$ distances vary in length from 2·42 to 2·75 Å and have a mean value of 2·62 Å compared with 2·65 Å at room temperature. As a result of the

low-temperature orientation of the methylammonium ion, the other six water molecules of the asymmetric unit no longer form six of the nearest neighbours of the ion, with a mean contact distance of 3·55 Å (Lipson, 1935), but instead form two groups of three which are at respective average distances of 2·98 and 4·21 Å from the $NH_3^+$ ion and 4·19 and 3·24 Å from the $CH_3$ group.

Again, consequent upon the disappearance of the apparent centre of symmetry from the methylammonium ion, the six sulphate oxygen atoms, which along with the set of six water molecules form at room temperature the nearest neighbours of the spherically symmetric ion, form at low temperature six contacts with each of the separate complexes of the group. The six oxygen atoms are in two of the sulphate groups and are those which are in general positions at room temperature and for which, at room temperature, the $CH_3NH_3^+ \cdots O$ contact distance is 3·58 Å (Lipson, 1935); at low temperature the average contact distances between the ammonium ion and the two sets of three oxygen atoms are 3·46 and 3·42 Å and those between the methyl group and the same two sets are 3·33 and 3·48 Å respectively. It is evident from these distances and from the two $NH_3^+ \cdots S$ contact lengths of 3·68 and 3·62 Å and the two $CH_3 \cdots S$ contacts of 3·56 and 3·71 Å that in the low-temperature phase each one of the two groups of the methylammonium ion is approximately equidistant from the two sulphate ions and that each sulphate ion is approximately equidistant from the two groups. The distances of the contacts of the nearest neighbours either with the methyl group or with the ammonium ion need not be, and in the event are not, influenced by the tetrahedral configuration of the groups themselves and consequently none of the contacts concerned, whether with oxygen atoms or with water molecules, is a hydrogen bond. In Fig. 3 are compared the disposition of the contacts in the respective phases between the methylammonium ion and the two sulphate ions.

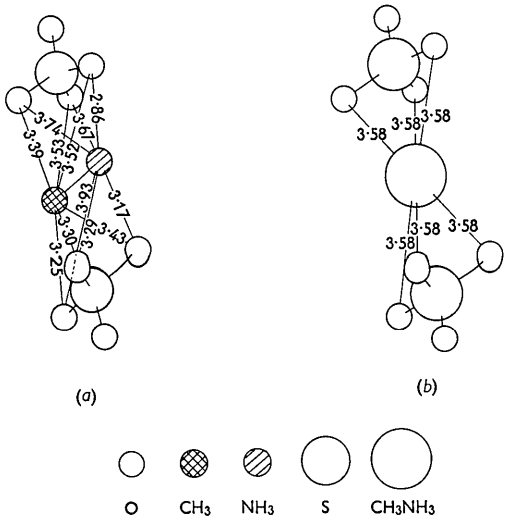



Fig. 3. The nature of the contacts between the methylammonium ion and the sulphate ions (*a*) at low temperature, (*b*) at room temperature. Distances in Å.

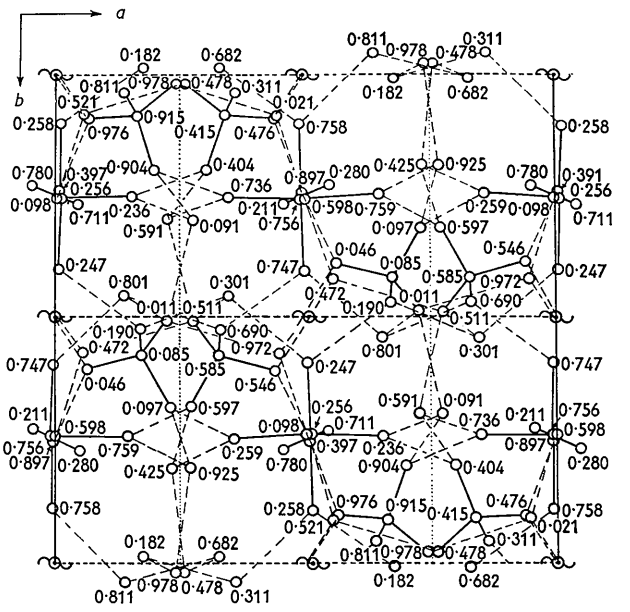



Fig. 4. The disposition of the hydrogen bonds (broken lines) in methylammonium alum; the *z* coordinates of the atoms are also shown.

Within the two sulphate groups of the asymmetric unit the eight S–O bonds vary in length from 1·44 ± 0·04 Å to 1·51 ± 0·04 Å with a mean value of 1·47 Å compared with a mean at room temperature of 1·50 Å, and the average value of the sulphate tetrahedral angle is 109°; when the limits of accuracy are considered it may be concluded that the sulphate groups are regular.

The change in phase does not alter the mechanics of the bonding between the two different sets of water molecules nor between the water molecules and the oxygen atoms of the sulphate groups. There are, in all, twenty-four different hydrogen bonds of these types (Fig. 4) and they range in length from one very short one of 2·40 Å to two very long ones of 2·91 Å. Each $H_2O_{A1}$ is in contact with an $H_2O_{MA}$ and with an oxygen atom, the average values of the hydrogen bonds being 2·60 and 2·70 Å respectively. In addition to its contact with an $H_2O_{A1}$, each $H_2O_{MA}$ has hydrogen bonds of average length 2·78 Å to two oxygen atoms.

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