a Cu²⁺ ion in the C plane cannot be determined by the direction of the long axes of those four Cu²⁺ ions in the B plane, because in the two possible cases this results in the same interaction mechanism (antiferrodistortive twice and ferrodistortive twice). But the interaction between layers C and D is apparently antiferrodistortive, which is similar to what has been found in K₂[CuF₄].

From these results one can state that in this kind of structure type the Jahn–Teller interaction between two Cu²⁺ ions favours antiferrodistortive interactions. This implies that the long axes of the closest Jahn–Teller centres are perpendicular.

Because the shifts of the Cl⁻ ions in the bc plane with respect to the Rb₂[Mn₂Cl₇]₁ structure only do not result in an elongated octahedron with approximate D₄h symmetry, a strain should be noticed along the a axis, so that the a axis is compressed with respect to the b and c axes. Compare, therefore, the a/√2/b and c/a values, respectively for Rb₂[Cu₂Cl₇]: 4.88 and Rb₂[Mn₂Cl₇]: 5.13.

All crystals examined have the same space group and are very well crystallized. If stacking disorder is present, one should notice a seemingly large thermal movement of the Cl(3) ion along the b and e directions. No evidence of disorder was found in the anisotropic temperature factors of the Cl(3) ion. So it seems that the most stable configuration in this kind of compound is an antiferrodistortive ordering between nearest layers [within the double layer (A and B)] and next-nearest layers [between the double layers (C and D)].

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References


Disordered Structure of Ferroelectric Ammonium Lithium Sulphate in the High-Temperature Phase

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Abstract. NH₄LiSO₄, T = 478 K, orthorhombic, Pmcn, a = 5.299 (2), b = 9.199 (2), c = 8.741 (3) Å, V = 426.1 Å³, Z = 4, Dc = 1.933 Mg m⁻³. Residual maps displayed double-peaked contours for O atoms. The structure was refined to R = 0.055 for 1060 observed reflections on the basis of the split-atom method. SO₄ and LiO₄ tetrahedra lie, respectively, with equal probability in two equilibrium arrangements which have mirror symmetry with respect to each other.

Introduction. NH₄LiSO₄ undergoes two phase transitions at about 283 K (Pepinsky, Vedam, Okaya & Hoshino, 1958) and 459.7 K (Mitsui et al., 1975). The intermediate phase is ferroelectric with spontaneous polarization along the a axis (Mitsui et al., 1975). The room-temperature structure was determined by Dollase (1969). We now report the crystal structure of the high-temperature phase, as part of a continuing study of the mechanism of successive phase transitions from the structural point of view.

Colourless single crystals were grown by evaporation of an aqueous solution containing equimolar amounts of (NH₄)₂SO₄ and Li₂SO₄, H₂O at room temperature. An untwinned spherical specimen, 0.8 mm in diameter, was mounted on a Rigaku AFC-5
automatic four-circle diffractometer. The temperature was regulated at 478 ± 1.0 K with a heated air flow. The measurements were made in the 0-20 scanning mode with a scan speed of 8° min⁻¹ in 20 and corrected for background and Lp factors but not for absorption (μr = 0.26). Reflexions with 2θ ≤ 80° were measured with Mo Kα radiation monochromatized by a graphite plate. Three standard reflexions were monitored every 200 measurements and no significant variation was observed. 1154 independent reflexions were obtained; of these, 32 were rejected because of the appreciable extinction effect. Finally, 1060 reflexions with values of |Fo| greater than σ(Fo) were used for least-squares calculations. The space group is either P2₁cn or Pmcn from the systematic extinctions but it has been uniquely determined to be Pmcn because spontaneous polarization vanishes in the high-temperature phase.

The structure was refined by the use of the averaged positions of Dollase and their mirror-image ones with respect to x = ½ and ½ as initial parameters. In the calculations equal weights were used throughout, the quantity minimized being \( \sum (|F_o| - |F_c|)^2 / \sum |F_o|^2 \). Refinement using neutral scattering factors (International Tables for X-ray Crystallography, 1968) converged with R = \( \sum |F_o| - |F_c| / \sum |F_o| = 0.093 \), but large thermal parameters were obtained for O atoms. Examining difference Fourier maps excluding each O atom, we found that O atoms exhibited unusually extended or double-peaked contours, as shown in Fig. 1. Two equilibrium positions of each O atom were estimated from the contours. Least-squares refinement was carried out on the basis of the split-atom method with an occupancy of 0.5 which was required from the mirror symmetry for O(1) and O(4) and from the contours obtained for O(2) and O(3). The H atoms were not located, as in the case of the room-temperature structure. In the final cycle all parameter shifts were less than one tenth of their e.s.d.'s and the R factor reached 0.055. Positional and

![Fig. 1. Difference Fourier maps of the constituent O atoms. O(3) is in the mirror-image position of O(2) with respect to x = 0.25. The crosses are the atomic positions determined by the split-atom refinement.](image)

Table 1. Positional parameters and thermal parameters [Ueq × 10²] for S, NH₄ and O; Uiso × 10²) for Li with e.s.d.'s in parentheses

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Uiso or Ueq (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>0.25</td>
<td>0.08639 (6)</td>
<td>0.20494 (6)</td>
<td>3.37 (1)</td>
</tr>
<tr>
<td>NH₄</td>
<td>0.75</td>
<td>0.2058 (3)</td>
<td>0.5004 (3)</td>
<td>5.39 (7)</td>
</tr>
<tr>
<td>O(1)'</td>
<td>0.2706 (36)</td>
<td>0.0959 (6)</td>
<td>0.429 (3)</td>
<td>12.6 (3)</td>
</tr>
<tr>
<td>O(2)'</td>
<td>0.0661 (7)</td>
<td>0.0225 (4)</td>
<td>0.2546 (5)</td>
<td>7.6 (1)</td>
</tr>
<tr>
<td>O(3)'</td>
<td>0.4972 (6)</td>
<td>0.0479 (4)</td>
<td>0.2588 (5)</td>
<td>6.7 (1)</td>
</tr>
<tr>
<td>O(4)'</td>
<td>0.1741 (8)</td>
<td>0.2214 (3)</td>
<td>0.2712 (6)</td>
<td>11.1 (2)</td>
</tr>
<tr>
<td>Li</td>
<td>0.25</td>
<td>0.4168 (5)</td>
<td>0.3273 (5)</td>
<td>4.4 (1)</td>
</tr>
</tbody>
</table>

![Fig. 2. A c-axis view of one tetrahedral layer. The structures drawn by thick and thin lines are two equilibrium atomic arrangements. In nearest-neighbour layers, an SO₄ tetrahedron pointing up is replaced by an LiO₄ tetrahedron pointing down, etc.](image)
AMMONIUM LITHIUM SULPHATE

thermal parameters are given in Table 1* and bond lengths and angles in Table 2. The structure is shown in Fig. 2. Primed and double-primed symbols represent two split atoms for each O atom.

Discussion. A residual map of the electron density computed after the final refinement showed maximum anomalies of 0.2 e Å⁻³. Irregular maxima of 0.4 ~ 0.6 e Å⁻³ were located near O(1) and O(4). According to the significance test (Hamilton, 1965), the disordered model is rejected below the 0.005 level at every stage of the proposal that there are two disordered positions for an O atom, i.e. we are quite sure that the structure has disordered O atoms. It should be noted that a harmonic model for the vibrations describes well the contours of the S, N and Li atoms, but the values of the thermal parameters of these atoms are about twice those estimated from the room-temperature structure.

The sharing of the split atoms for the tetrahedral arrangements is determined from the condition that the centre of mass of the unit cell must be unchanged for polarization reversal. The two arrangements thus obtained are depicted in Fig. 2. The shapes of the SO₄ and LiO₄ tetrahedra are quite reasonable and one of the polar structures (drawn with thick lines in Fig. 2) can be superimposed on Dollase's structure, apart from the difference of about 0.1 Å found in the atomic positions in the ab plane. Atomic shifts associated with polarization reversal are 0.22 (3) Å for O(1), 0.730 (5) Å for O(2), O(3) and 0.804 (6) Å for O(4).

It should be noted that the rotation of the SO₄ tetrahedron (~5°) about the c axis nearly carries Dollase's structure into one of the polar structures at 478 K. This suggests that the order parameter in the ferroelectric phase is not simply determined by the split ratio of the O atoms but is also connected with a gradual rotation of the SO₄ tetrahedra with temperature. Ferroelectric structures are now being investigated at several temperatures.

References


Hydrazinium(2+) Hexafluorogermanate(IV) Monohydrate

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Abstract. N₂H₄⁺[GeF₆]²⁻·H₂O, Mᵣ = 238.66, orthorhombic, Pnma, a = 8.869 (1), b = 9.292 (1), c = 7.400 (1) Å, V = 609.8 Å³, Dₓ = 2.599 Mg m⁻³, Z = 4, µ(Mo Kα) = 5.395 mm⁻¹, T = 293 (1) K. R and R_w were 0.018 and 0.024 for 794 contributing reflexions [I > 4σ(I)]. The structure consists of N₂H₄⁺ ions [staggered conformation, N–N = 1.428 (2) Å], GeF₆⁻ octahedra [mean Ge–F = 1.786 (2) Å] and H₂O units interconnected by a network of three-dimensional N–H···O and N–H···F hydrogen bonds.

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