a Cu^{2+} ion in the C plane cannot be determined by the direction of the long axes of those four Cu^{2+} 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 $K_2[CuF_4]$.

From these results one can state that in this kind of structure type the Jahn–Teller interaction between two Cu^{2+} 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 $Rb_3[Mn_2Cl_7]$ structure only do not result in an elongated octahedron with approximate D_{4h} 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 $a\sqrt{2}/b$ and c/a values, respectively for $Rb_3[Cu_2Cl_7]$: 4·88 and $Rb_3[Mn_2Cl_7]$: 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 **c** 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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Disordered Structure of Ferroelectric Ammonium Lithium Sulphate in the High-Temperature Phase

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Abstract. NH_4LiSO_4, $T = 478$ K, orthorhombic, *Pmcn*, $a = 5·299$ (2), $b = 9·199$ (2), $c = 8·741$ (3) Å, $V = 426·1$ Å^3, $Z = 4$, $D_c = 1·933$ Mg m^{-3}. Residual maps displayed double-peaked contours for O atoms. The structure was refined to $R = 0·055$ for 1060 observed reflexions on the basis of the split-atom method. SO_4 and LiO_4 tetrahedra lie, respectively, with equal probability in two equilibrium arrangements which have mirror symmetry with respect to each other.

Introduction. NH_4LiSO_4 undergoes two phase transitions at about 283 K (Pepinsky, Vedam, Okaya & Hoshino, 1958) and 459·7 K (Mitsui, Oka, Shiroishi,

Takashige, Iio & Sawada, 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 $(NH_4)_2SO_4$ and $Li_2SO_4.H_2O$ 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 $478 \pm 1\cdot0$ K with a heated air flow. The measurements were made in the θ–2θ scanning mode with a scan speed of $8°$ min^{-1} in 2θ and corrected for background and Lp factors but not for absorption ($\mu r = 0\cdot26$). Reflexions with $2\theta \leq 80°$ were measured with Mo $K\alpha$ 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 $|F_o|$ greater than $\sigma(|F_o|)$ were used for least-squares calculations. The space group is either $P2_1cn$ 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 $x = \frac{1}{4}$ and $\frac{3}{4}$ 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 $R = \sum ||F_o| - |F_c||/\sum |F_o| = 0\cdot093$, but large thermal parameters were obtained for O

Table 1. *Positional parameters and thermal parameters [U_{eq} (×10^2) for S, NH$_4$ and O; U_{iso} (×10^2) for Li] with e.s.d.'s in parentheses*

The equivalent isotropic thermal parameters have been calculated from $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

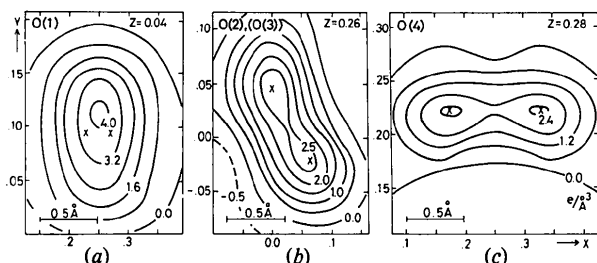|	x	y	z	U_{eq} or U_{iso} (Å^2)
S	0·25	0·08639 (6)	0·20494 (6)	3·37 (1)
NH$_4$	0·75	0·2058 (3)	0·5004 (3)	5·39 (7)
O(1)'	0·2706 (36)	0·0959 (6)	0·0429 (3)	12·6 (3)
O(2)'	0·0661 (7)	−0·0225 (4)	0·2546 (5)	7·6 (1)
O(3)'	0·4972 (6)	0·0479 (4)	0·2588 (5)	6·7 (1)
O(4)'	0·1741 (8)	0·2214 (3)	0·2712 (6)	11·1 (2)
Li	0·25	0·4168 (5)	0·3273 (5)	4·4 (1)

Fig. 1. Difference Fourier maps of the constituent O atoms. O(3) is in the mirror-image position of O(2) with respect to $x = 0\cdot25$. The crosses are the atomic positions determined by the split-atom refinement.
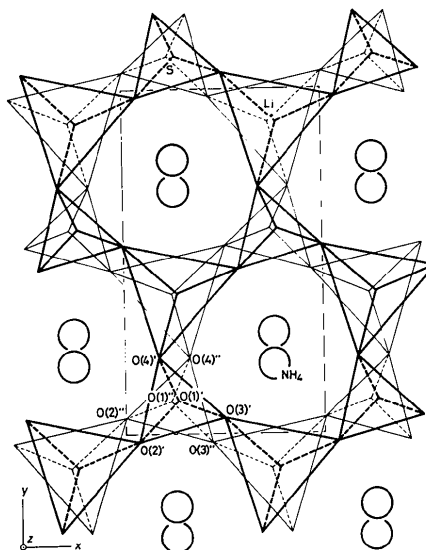

Fig. 2. A c-axis view of one tetrahedral layer. The structures drawn by thick and thin lines are two equilibrium atomic arrangements. In nearest-neighbour layers, an SO$_4$ tetrahedron pointing up is replaced by an LiO$_4$ tetrahedron pointing down, *etc.*

Table 2. *Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses*

S—O(1)'	1·423 (3)	NH$_4$—O(1^{iv+a})'	3·328 (16)
—O(2)'	1·463 (4)	—O(2^{+a})'	3·440 (4)
—O(3)'	1·436 (3)	—O(2^{ii+c})'	2·895 (5)
—O(4)'	1·428 (4)	—O(2^{iii})'	3·487 (4)
Li—O(1^{iv})'	1·892 (5)	—O(3)'	2·892 (4)
—O(2^{iii})'	1·905 (4)	—O(3^{ii+c})'	3·404 (5)
—O(3^{iii-a})'	1·953 (5)	—O(3^{iv})'	3·469 (4)
—O(4)'	1·906 (4)	—O(4^{+a})'	3·014 (5)
NH$_4$—O(1^{iv})'	3·150 (16)	—O(4^{iv+a})'	3·332 (5)

O(1)'—S—O(2)'	112·8 (6)	O(1^{iv})'—Li—O(2^{iii})'	110·0 (6)
O(1)'—S—O(3)'	105·8 (8)	O(1^{iv})'—Li—O(3^{iii-a})'	117·5 (5)
O(1)'—S—O(4)'	111·8 (4)	O(1^{iv})'—Li—O(4)'	102·2 (3)
O(2)'—S—O(3)'	109·9 (2)	O(2^{iii})'—Li—O(3^{iii-a})'	106·1 (3)
O(2)'—S—O(4)'	106·7 (2)	O(2^{iii})'—Li—O(4)'	111·4 (2)
O(3)'—S—O(4)'	109·8 (2)	O(3^{iii-a})'—Li—O(4)'	109·8 (2)

Symmetry code: $(+a)$ $1 + x, y, z$; (ii) $\frac{1}{2} + x, \bar{y}, z$; (ii $+ c$) $\frac{1}{2} + x, \bar{y}, 1 + \bar{z}$; (iii) $\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii $- a$) $-\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (iv $+ a$) $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$.

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

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 $0.4 \sim 0.6$ e Å^{-3} were located near O(1) and O(4). According to the significance test (Hamilton, 1965), the dis-ordered 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

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35791 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

obtained are depicted in Fig. 2. The shapes of the SO_4 and LiO_4 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 SO_4 tetrahedron ($\sim5°$) 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 SO_4 tetrahedron with tem-perature. Ferroelectric structures are now being investi-gated at several temperatures.

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Hydrazinium(2+) Hexafluorogermanate(IV) Monohydrate

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Abstract. $N_2H_6^{2+}[GeF_6]^{2-}.H_2O$, $M_r = 238.66$, ortho-rhombic, *Pnma*, $a = 8.869$ (1), $b = 9.292$ (1), $c = 7.400$ (1) Å, $V = 609.8$ Å^3, $D_x = 2.599$ Mg m^{-3}, $Z = 4$, $\mu(\text{Mo } K\alpha) = 5.395$ mm^{-1}, $T = 293$ (1) K. R and R_w were 0.018 and 0.024 for 794 contributing reflexions [$I > 4\sigma(I)$]. The structure consists of $N_2H_6^{2+}$ ions [staggered conformation, N—N $= 1.428$ (2) Å], GeF_6^{2-} octahedra [mean Ge—F $= 1.786$ (2) Å] and H_2O units interconnected by a network of three-dimensional N—H$\cdots$O and N—H$\cdots$F hydrogen bonds.

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Introduction. This investigation is part of a structural study of hydrazinium(2+) fluorometallates(IV) syn-thesized at the J. Stefan Institute, Ljubljana. The crystal structures of $N_2H_6[TiF_6]$, $N_2H_6[ZrF_6]$, $N_2H_6F_2[TiF_6]$ and $N_2H_6[SiF_6]$ have already been determined (Kojić-Prodić, Matković & Ščavničar, 1971; Kojić-Prodić, Ščavničar & Matković, 1971; Golič, Kaučič & Kojić-Prodić, 1980; Frlec, Gantar, Golič & Leban, 1980). Colourless single crystals were obtained by dissolving $N_2H_6F_2$ and GeO_2 in HF (40 wt %) and slowly evaporating the solution at room temperature. The systematically absent reflexions (0*kl*: $k + l = 2n + 1$ and *hk*0: $h = 2n$) on Weissenberg films