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Ammonium Trifluoroberyllate(II), $(NH_4)[BeF_3]$, at Room Temperature

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Abstract. $M_r = 84$, monoclinic, Pn, $a = 5·770$ (2), $b = 4·619$ (3), $c = 12·819$ (1) Å, $\beta = 90·12$ (2)°, $V = 341·6$ (4) Å^3, $Z = 4$, $D_m = 1·63$ (2), $D_x = 1·632$ (3) Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1·54051$ Å, $\mu = 2·04$ mm^{-1}, $F(000) = 168$. Final $R = 0·049$ for 536 observed reflections. At room temperature the crystal is ferroelastic. Hydrogen-bonded chains of BeF_4 tetrahedra run along the b axis and undergo a pronounced thermal motion around this axis. Diffuse streaks observed at room temperature on Weissenberg photographs are probably connected with the phase transition to the orthorhombic phase at 334·3 K.

Introduction. NH_4BeF_3 crystals undergo successive phase transitions at 252·2, 334·3 and 347·3 K. Below 334·3 K the crystal is ferroelastic and at room temperature exhibits spontaneous polarization along the a axis and spontaneous strain (Makita & Suzuki, 1980; Czapla, Czupiński & Waśkowska, 1982). Weissenberg photographs taken at temperatures corresponding to the particular phases revealed the symmetry of each phase (Łukaszewicz, Waśkowska & Tomaszewski, 1983). On heating, the sequence of the phases is as follows:

$$\mathrm{IV}\ (P1) \xrightarrow{252·2\ \mathrm{K}} \mathrm{III}\ (Pn) \xrightarrow{334·3\ \mathrm{K}} \mathrm{II}\ (P2_12_12_1) \xrightarrow{347·3\ \mathrm{K}} \mathrm{I}\ (Pmnb).$$

Observations at room temperature under a polarizing microscope indicated that the crystal was twinned with the (105) plane as a twin plane. The earlier paper of Milkova & Porai-Koshits (1962) described the twinning of NH_4BeF_3, as well as giving a preliminary model of the structure. A full crystal-structure determination of the room-temperature phase is now presented as a part of X-ray studies on the phase-transition mechanism in this crystal.

Experimental. D_m measured by flotation in gradient column. Plates elongated in **b** (from water solution) ground to sphere ($2r = 0·35$ mm). Syntex $P2_1$ diffractometer, monochromated Cu $K\alpha$. 15 reflections in least-squares determination of lattice parameters. Three standard reflections showed only statistical fluctuations during data collection. 736 independent reflections (h 7, k 5, $l \pm 16$) with $\theta < 70°$, 536 with $|F| > \sigma(|F_o|)$. $R_{\mathrm{int}} = 6·3\%$. Lp and isotropic extinction ($g = 3·326$) corrections applied, absorption ignored. Space-group choice Pn based on physical properties [piezoelectric signal observed at room temperature by Makita & Suzuki (1980)]. Direct methods (*MULTAN*78, Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Anisotropic full-matrix least-squares refinement on F (XRAY76, Stewart, 1976). Three H atoms around each NH_4^+ ion fixed at positions found from ΔF synthesis with refined B_{iso}, fourth H calculated from geometry. $R = 0·049$, $R_w = 0·054$; $w = 1/\sigma^2(F_o)$. Ratio of max. LS shift to error $\frac{1}{3}\sigma$. Max. and min. height in final ΔF map 0·3 and 0·5 e Å^{-3}. Scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974).

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Table 1. *Atomic coordinates and isotropic thermal parameters with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$. For H atoms B_{iso} is given.

	x	y	z	U_{eq}(Å^2 × 10^2) or B_{iso}(Å^2)
N(1)	0·7265†	0·7227 (25)	0·1010†	4·0 (5)
N(2)	0·7769 (10)	0·2317 (24)	0·3997 (5)	4·2 (5)
Be(1)	0·2309 (27)	0·1774 (26)	0·1797 (11)	2·8 (3)
Be(2)	0·2854 (27)	0·6774 (35)	0·3153 (13)	3·7 (3)
F(11)	0·2483 (21)	−0·1502 (15)	0·2122 (9)	4·9 (3)
F(12)	0·4215 (21)	0·2457 (19)	0·1044 (9)	5·3 (6)
F(13)	−0·0069 (26)	0·2374 (20)	0·1359 (12)	7·0 (6)
F(21)	0·2648 (21)	0·3456 (12)	0·2864 (9)	4·8 (5)
F(22)	0·1035 (23)	0·7521 (22)	0·3922 (9)	5·8 (6)
F(23)	0·5269 (24)	0·7240 (21)	0·3520 (11)	7·5 (8)
H(11)	0·563	0·734	0·139	8·5 (3·5)
H(12)	0·806	0·541	0·119	5·7 (2·1)
H(13)	0·819	0·896	0·120	8·4 (3·5)
H(14)	0·694	0·731	0·023	6·1 (2·0)
H(21)	0·925	0·241	0·358	8·6 (3·5)
H(22)	0·687	0·413	0·383	8·5 (3·5)
H(23)	0·685	0·056	0·381	6·8 (3·2)
H(24)	0·813	0·235	0·477	8·1 (4·0)

† Fixed to define the origin of the coordinate system.

Table 2. *Bond lengths* (Å) *in* BeF_4^{2-} *ions with their e.s.d.'s in parentheses*

The average corrections (Å) for the effect of rigid-body libration (R.b.) are given.

	Uncorrected	R.b.		Uncorrected	R.b.
Be(1)—F(11)	1·57 (1)	0·003	Be(2)—F(21)	1·58 (2)	0·025
F(12)	1·50 (2)	0·024	F(22)	1·48 (2)	0·031
F(13)	1·51 (2)	0·025	F(23)	1·48 (2)	0·026
F(21)	1·58 (2)	0·025	F(11^i)	1·56 (2)	0·007

Symmetry code: (i) $x,1+y,z$.

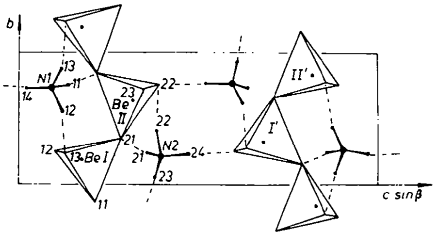

Fig. 1. Projection of the structure down the *a* axis.

Discussion. Atomic parameters are given in Table 1.*

The structure consists of BeF_3^- ions which share corners forming long chains of $(BeF_4)_n$ tetrahedra almost parallel to the *b* axis (Fig. 1). As the periodicity of the chain equals two tetrahedra and a doubled edge of a tetrahedron is longer than the *b* axis, the edges sharing common corners deviate by about 15° from the chain axis. In one of the chains the apices of the tetrahedra point up, while in the other symmetrically equivalent chain the bases point up. The BeF_4^{2-} ions are significantly distorted tetrahedra. In each of the BeF_4 groups there are two shorter and two longer distances than the mean Be—F distance equal to 1·53 (2) Å (Table 2). Bond angles vary from 103·6 (9) to 112·9 (1·2)° in the first tetrahedron and from 106·6 (1·1) to 114·9 (1·3)° in the second one. Such a configuration of BeF_4 tetrahedra might be the result of stretching forces acting along the *b* axis. The average bond lengths are shorter by 0·01–0·02 Å than those of other crystals containing BeF_4^{2-} ions, *e.g.* γ-Na_2BeF_4 (Deganello, 1972) and $(NH_2CH_2COOH)_3.H_2BeF_4$ (Waśkowska, Olejnik, Łukaszewicz & Ciechanowicz-Rutkowska, 1979), where the average Be—F bonds are 1·557 (3) and 1·546 (6) Å respectively. The thermal parameters of the F atoms are highly anisotropic. Especially large are the U_{33} components for F(13) and F(23). These facts indicate the need to correct Be—F distances for the rigid-body thermal motion. The coordinate corrections were carried out by the method of Cruickshank (1956). The calculations were performed using the program *XANADU* from the *SHELX*78 program system (Sheldrick, 1978). The average magnitudes of these corrections range from 0·003 to 0·31 Å and are mostly within the limits of standard deviations (Table 2). No significant changes are found for the bond angles. The largest translational tensor (**T**) components are: $T_x = 0·030\ (2)$ Å and $T_z = 0·045\ (3)$ Å, the largest librational vibration tensor (**L**) component $L_y = 0·027\ (4)$ rad^2. All components of the screw translational tensor (**S**) were smaller by one order of magnitude.

The two independent ammonium ions form quite good tetrahedra; however, a discussion concerning H atoms on the base of the present data is of little significance. The environments of the two ammonium ions are shown in Fig. 2. N(1) and N(2) are surrounded by eight F atoms with average interatomic distances of 3·01 (1) and 3·04 (1) Å for N(1) and N(2) respectively. For each of the N atoms, among N—F distances, there are several shorter than 2·87 Å but only three of them may be regarded as hydrogen bonds of N—H···F type. Dimensions of the proposed hydrogen bonds are given in Table 5.* N(1)—H(14)···F(22^v) and N(2)—H(24)···F(12^{vii}) are interchain hydrogen bonds while the remaining ones are intrachain hydrogen bonds. These hydrogen bonds fasten the structure and it is natural to consider that the reorientation of ammonium ions is closely connected with the thermal motions of BeF_4 tetrahedra.

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* Lists of structure factors, anisotropic thermal parameters, bond angles in BeF_4^{2-} ions (Table 3), bond lengths and angles in NH_4^+ ions (Table 4), dimensions of the proposed hydrogen bonds (Table 5) and N—F distances (Table 6) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38583 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* See previous footnote.

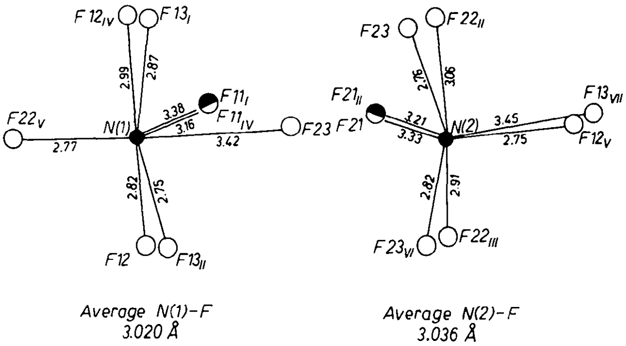

Fig. 2. Environments of the ammonium ions viewed along the *a* axis. The interatomic distances between N and F atoms are given in Å. E.s.d. = 0·001 Å for all these distances. [Symmetry code: none x,y,z; (i) $x+1, y+1, z$; (ii) $x+1, y, z$; (iii) $x+1, y-1, z$; (iv) $x, 1+y, z$; (v) $\frac{1}{2}+x, \frac{3}{2}-y, z-\frac{1}{2}$; (vi) $x, y-1, z$; (vii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.]

In spite of satisfactory R values the standard deviations of the atomic positions are high which suggests some disorder in the structure. At room temperature strong diffuse streaks parallel to the $\mathbf{b}^*$ axis were observed on Weissenberg photographs. This diffuse scattering may be connected with the partial disorder in the structure and is probably related to the mechanism of the phase transition. At 334·4 K the crystal passes into the orthorhombic phase and in place of the diffuse streaks there appear quite new and sharp Bragg reflections which are consistent with the space group $P2_12_12_1$. The crystal structure of this phase and measurements of the lattice parameters as a function of temperature will be the subject of a subsequent paper.

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Structure of Orthopyroxene-Type and Clinopyroxene-Type Magnesium Germanium Oxide MgGeO$_3$

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Abstract. (i) Orthopyroxene-type: $M_r = 144{\cdot}92$, orthorhombic, *Pbca*, $a = 18{\cdot}8099\ (12)$, $b = 8{\cdot}9484\ (8)$, $c = 5{\cdot}3451\ (4)$ Å, $V = 899{\cdot}69\ (12)$ Å^3, $Z = 16$, $D_x = 4{\cdot}28$ gcm^{-3}, $\lambda(\text{Ag } K\alpha) = 0{\cdot}56087$ Å, $\mu(\text{Ag } K\alpha) = 75{\cdot}64$ cm^{-1}, $T = 300$ K, $F(000) = 1088$, $R = 0{\cdot}025$ for 975 independent reflections. (ii) Clinopyroxene-type: $M_r = 144{\cdot}92$, monoclinic, $C2/c$, $a = 9{\cdot}6010\ (8)$, $b = 8{\cdot}9323\ (6)$, $c = 5{\cdot}1592\ (5)$ Å, $\beta = 101{\cdot}034\ (9)°$, $V = 434{\cdot}27\ (6)$ Å^3, $Z = 8$, $D_x = 4{\cdot}43$ gcm^{-3}, $\lambda(\text{Ag } K\alpha) = 0{\cdot}56087$ Å, $\mu(\text{Ag } K\alpha) = 78{\cdot}35$ cm^{-1}, $T = 300$ K, $F(000) = 544$, $R = 0{\cdot}021$ for 1025 independent reflections. Orthorhombic MgGeO$_3$ (the high-temperature and low-pressure phase) is isostructural with orthoenstatite, MgSiO$_3$. The structure of monoclinic MgGeO$_3$ (the low-temperature and high-pressure phase) is different from that of clinoenstatite which crystallizes in $P2_1/c$. The orthorhombic (*Pbca*) to monoclinic ($C2/c$) transformation in MgGeO$_3$ is accompanied by a fairly large volume decrease (3·5%). A smaller distortion of the Mg(2) octahedron in the structure of monoclinic MgGeO$_3$ causes the higher density.

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