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Crystal Structure and Magnetic Characterization of $(NH_4)_2FeF_5 \cdot H_2O$

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The compound $(NH_4)_2FeF_5 \cdot H_2O$ is prepared by hydrothermal synthesis in HF solutions. The material is orthorhombic, space group *Pbcn*, $a = 10.491(4)$ Å, $b = 8.090(3)$ Å, $c = 7.997(3)$ Å, $Z = 4$. The crystal structure—isotypic with that of $(NH_4)_2AlF_5 \cdot H_2O$—is determined from single-crystal diffraction intensity data and refined to the conventional values of the indexes $R = 0.0272$ and $R_w = 0.0262$. The structure is characterized by isolated $[FeF_5(H_2O)]^{2-}$ octahedra linked together by O–H . . . F strong hydrogen bonds and forming zigzag chains running along 001. NH_4^+ ions connect these chains by N–H . . . F hydrogen bonds. As expected, the compound exhibits a paramagnetic behavior in the range 80–300 K and is not magnetically ordered at 4.2 K as shown by Mössbauer spectroscopy.

Introduction

During the study of the system GuF–FeF_3–HF_{aq}—where Gu^+ stands for the guanidinium cation $[C(NH_2)_3]^+$—we accidently encountered the phase $(NH_4)_2FeF_5 \cdot H_2O$, formed by a noncontrolled decomposition process of the Gu^+ cation. The synthesis of single crystals incited us to solve the crystal structure and to investigate its magnetic properties.

Preparation

Single crystals of $(NH_4)_2FeF_5 \cdot H_2O$ can be grown in closed Teflon vessels in HF aqueous solutions. Typically 15 mmole of $FeF_3 \cdot 3H_2O$ mixed with 37.5 mmole of NH_4F in 10 cm^3 of 5 *M* HF solutions are heated at 150°C for 22 hr, then the bomb is allowed to cool naturally. The crystals are washed rapidly with a dilute HF solution and air-dried.

Crystallographic Characterization and Data Collection

The X-ray powder diffraction spectrum of crushed crystals is readily indexed on the basis of an orthorhombic cell, $a = 10.49$ Å, $b = 8.08$ Å, and $c = 7.99$ Å. These values and the observed limiting conditions for the possible reflections—$0kl$ with $k = 2n$ and $hk0$ with $h + k = 2n$ leading to the space group *Pbcn*—allow us to propose for $(NH_4)_2FeF_5 \cdot H_2O$ the structural model described for $(NH_4)_2AlF_5 \cdot H_2O$ by Knop *et al.* (*1*).

A small crystal of approximate size $(3 \times 6 \times 7) \times 10^{-6}$ mm^3 is chosen for the structure determination. Table I gathers the conditions of the diffraction experiment.

The cell parameters are refined from the position of 15 reflections well distributed in the reciprocal space. Owing to the small value of the absorption factor and to the good agreement within the equivalent in-

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TABLE I

CONDITIONS OF THE DATA COLLECTION (SIEMENS AED2)

$(NH_4)_2FeF_5 \cdot H_2O$ Molecular weight: 204.91 g
Space group: *Pbcn*
a = 10.491(5) Å
b = 8.090(3) Å
c = 7.997(3) Å
V = 678.78 Å^3, Z = 4 $\rho_{calc} = 2.00$ g · cm^{-3}
$\rho_{obs} = 2.02(1)$ g · cm^{-3} (flotation method)
$\mu(MoK\alpha) = 22.41$ cm^{-1}
Radiation: Mo$K\alpha$ (graphite monochromatized)
T = 20°C
Scanning: $\omega/2\theta$
Angular range $4° \leq 2\theta \leq 40°$
Reciprocal space explored $-10 \leq h \leq 10$
$-7 \leq k \leq 7$
$-7 \leq l \leq 7$
Total number of reflections measured: 1624
Number of independent reflections after average operation: 313 (R_{int} = 0.0368)
Number of independent reflections with $\sigma(I)/I <$ 0.33 used for the refinement: 261

tensities, we did not judge it necessary to apply an absorption correction.

Structure Resolution

All the calculations are made with SHELX 76 (*2*) in the *Pbcn* space group. Atomic scattering factors and $\Delta f'$ and $\Delta f''$ values are from "International Tables for X-Ray Crystallography" (*3*).

All nonhydrogen atoms were located by analogy with the $(NH_4)_2AlF_5 \cdot H_2O$ model. With these positions and isotropic thermal motion for all atoms, the factors R and R_w were 0.0428 and 0.0489, respectively. At this stage of the refinement, calculation of a Fourier difference series did not reveal the positions of the hydrogen atoms. They were, however, introduced near the positions described for the aluminium compound with appropriate bond-length constraints. The R and R_w values stabilize then to 0.0272 and 0.0262, respectively, with the weighting scheme $w = 4.9645/[\sigma^2(F) + 27 \times 10^{-6} \times F^2]$.[1]

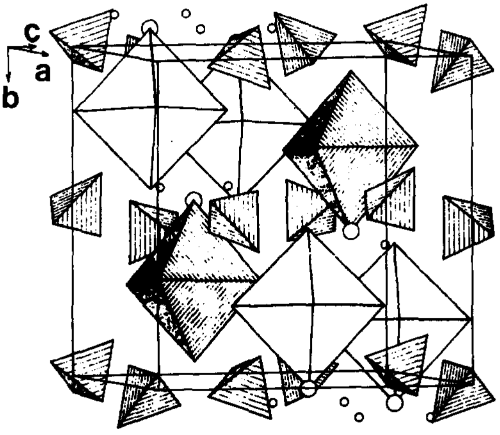

FIG. 1. View of the structure drawn by means of the STRUPLO 84 program (*10*). Unshaded octahedra are those centered at $x = 0$; shaded ones are centered at $x = \frac{1}{2}$.

Table 2 shows the best set of the atomic coordinates and the thermal motion parameters.

Structure Description

Isolated $[FeF_5(H_2O)]^{2-}$ octahedra and NH_4^+ tetrahedra form a distorted antifluorite network as mentioned by Knop *et al.* (*1*) for $(NH_4)_2AlF_5 \cdot H_2O$. Figure 1 presents the structure and Fig. 2 shows the projection on the (100) plane. Table 3 gathers selected distances and angles.

The $[FeF_5(H_2O)]^{2-}$ octahedra exhibit three independent Fe–F distances—mean Fe–F, 1.901 Å—and a longer Fe–O distance; this kind of isolated octahedra is also encountered in $Cs_2FeF_5 \cdot H_2O$ (*4*) and $K_2FeF_5 \cdot H_2O$ (*5*) where the F–O and the mean Fe–F distances are, respectively, 2.12 and 1.917 Å and 2.07 and 1.916 Å.

The octahedra centered at the same level (x = 0 or $\frac{1}{2}$) are, respectively, bound to-

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[1] F_o and F_c values may be obtained on request to J. L. Fourquet.

TABLE II

STRUCTURAL PARAMETERS OF $(NH_4)_2FeF_5 \cdot H_2O$

Atom	x	y	z	U_{11} (a)	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	B_{eq} (Å^2)
N	3013(5)	306(6)	347(7)	372(31)	372(38)	335(35)	93(32)	35(27)	54(30)	2.89
Fe	0(0)	2005(1)	2500(0)	313(7)	266(7)	259(7)	0(0)	−30(5)	0(0)	2.20
F1	0(0)	4360(4)	2500(0)	417(26)	313(31)	377(27)	0(0)	62(23)	0(0)	2.91
F2	509(3)	2012(4)	216(4)	606(21)	441(21)	341(21)	−62(19)	29(16)	−31(15)	3.65
F3	1761(3)	1970(4)	3151(4)	374(19)	552(21)	539(24)	−111(19)	−116(15)	132(17)	3.85
O	0(0)	−504(7)	2500(0)	1531(68)	275(39)	287(43)	0(0)	303(46)	0(0)	5.50
H1	2609(60)	−646(56)	−234(77)	1048(282)						8.27
H2	2490(58)	575(85)	1360(57)	1191(281)						9.40
H3	3196(62)	1239(56)	−419(68)	983(261)						7.76
H4	3683(42)	−308(69)	957(71)	902(241)						7.12
H_w(b)	−110(61)	−930(72)	3606(37)	901(242)						7.11

[a] All values are ×10^4. Estimated deviations are between parentheses. The vibrational coefficients are relative to the expression $T = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$.

[b] H_w stands for the hydrogen atoms of the water molecules.

gether by symmetric hydrogen bonds with the characteristic distances F2–O 2.547 Å and F2–H_w 1.69(3) Å. Figure 3 shows the bonding between the octahedra. The F2–O distance is at the lower limit of the O . . . F range in the classification of Simonov and Bukvetsky (*6*); this value is to be compared to those encountered in $K_2FeF_5 \cdot H_2O$ and $Cs_2FeF_5 \cdot H_2O$: 2.54 and 2.61 Å, respectively.

This strong association forms pseudochains of octahedra that zigzag along the *c* axis direction; the type of chaining is the same in $K_2FeF_5 \cdot H_2O$, $Cs_2FeF_5 \cdot H_2O$, and $(NH_4)_2AlF_5 \cdot H_2O$. The Fe–Fe distances are 5.15 and 6.60 Å within and between the chains, respectively.

Furthermore, NH_4^+ ions ensure the cohesion between these chains with N–H . . . F bonds: each ammonium ion is surrounded

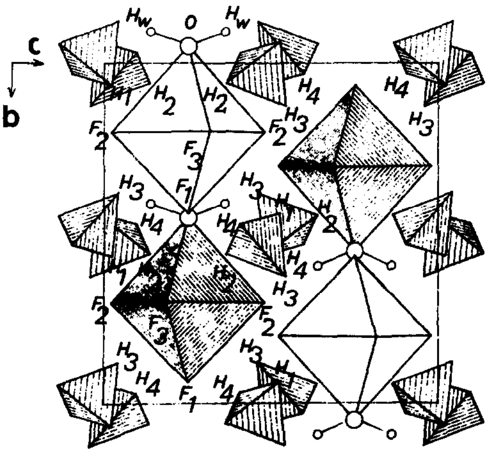

FIG. 2. Projection of the structure on the (100) plane.

TABLE III

SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°)

$[FeF_5(H_2O)]^{2-}$ octahedra		$(NH_4)^+$ tetrahedra	
Fe–F1	1.905(4)	N–H1	0.99(2)
Fe–F2	1.903(3)	N–H2	1.00(2)
Fe–F3	1.920(3)	N–H3	0.99(2)
Fe–O	2.03(4)	N–H_4	0.99(2)
O–H_w	0.96(6)		
H_w–O–H_w	137(5)	H_4–N–H3	123.3(5.2)
F1–Fe–F2	89.8(1)	H4–N–H2	95.7(5.0)
F1–Fe–F3	90.8(1)	H4–N–H1	98.3(49)
F2–Fe–F3	89.5(1)	H3–N–H1	112.6(5.2)
O–Fe–F3	89.2(1)	H3–N–H2	116.1(5.4)
O–Fe–F2	90.2(1)	H2–N–H1	108.3(5.5)

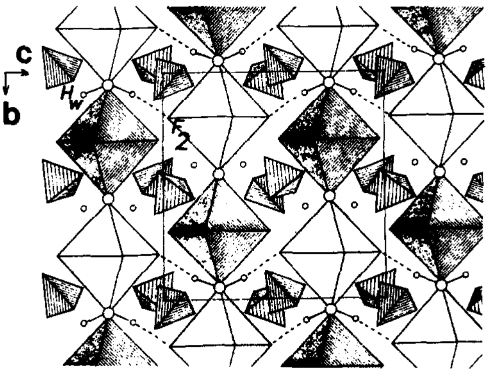

FIG. 3. Part of the hydrogen bond network between the octahedra. Here, O–H . . . F bonds are drawn only for the octahedra centered at $x = 0$. The zigzag chains are clearly visible.

by four octahedra (two centered at $x = 0$ and two at $x = \frac{1}{2}$) and is bound to four fluorine atoms, each belonging to a different octahedra. Figure 4 shows the hydrogen-bonding system around NH_4^+. Thus two H4 are symmetrically bound to F1 (F1–H4, 1.872 Å) and F3 atoms are linked to H1, H2, and H3 (F3–H1, 1.900 Å; F3–H2, 1.978 Å; and F3–H3, 1.846 Å). The mean F–H distance is 1.899 Å and can be compared to that observed in $(NH_4)_2AlF_5 \cdot H_2O$ (1.84 Å) and in NH_4AlF_4 (7) (1.898 Å).

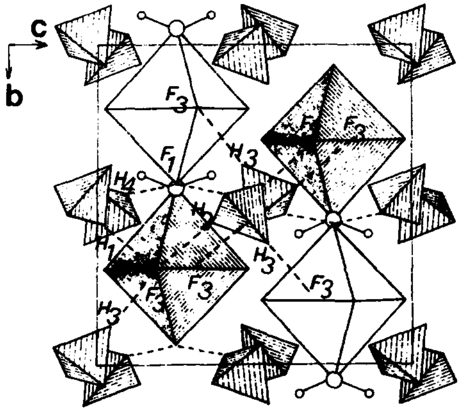

FIG. 4. Part of the hydrogen-bonding system around the ammonium cations.

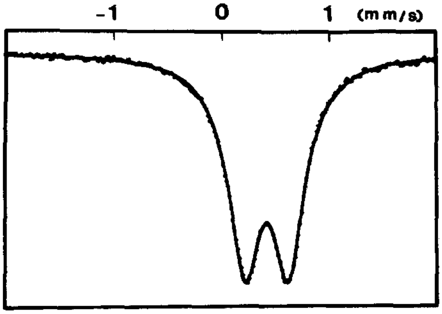

FIG. 5. Mössbauer spectrum of $(NH_4)_2FeF_5 \cdot H_2O$ at 4.2 K.

Magnetic Characterization

The magnetic susceptibility was measured on crushed single crystals by the Faraday method in the temperature range 80–300 K. The data were corrected from diamagnetism and then fitted by least-squares to a classical Curie–Weiss law, leading to $\mu_{exp} = 5.78\ \mu_B$ and $\theta_p = -8.5$ K.

This behavior, down to 4.2 K, is confirmed by a Mössbauer resonance study performed on a spectrometer with the constant acceleration mode, with a ^{57}Co source diffused into a rhodium matrix. All Mössbauer spectra between 4.2 and 300 K consist of well-resolved doublets. The spectrum at 4.2 K is shown in Fig. 5 and the fitted data are given in Table 4. The δ values, relative to Fe metal, are characteristic for Fe^{3+} and the observed paramagnetic state at 4.2 K is in agreement with the structure which presents isolated octahedra as

TABLE IV

MÖSSBAUER DATA OF $(NH_4)_2FeF_5 \cdot H_2O$

T (K)	δ^a (mm/sec)	ΔE_Q (mm/sec)	Γ (mm/sec)
300	0.417(4)	0.355(4)	0.33(1)
77	0.526(4)	0.420(4)	0.38(1)
4.2	0.536(4)	0.410(4)	0.40(1)

[a] Isomer shift relative to Fe metal (T = 300 K).

we observed recently in Gu_3FeF_6 (*8*). But contrary to this compound, which exhibits a single broad absorption line indicating a very small electric field gradient, we observe for $(NH_4)_2FeF_5 \cdot H_2O$ a noticeable quadrupole splitting value, 0.353 mm/sec at 300 K. It is caused by the presence of a water molecule in the coordination sphere of Fe^{3+} which increases the EFG.

However, as for $K_2FeF_5 \cdot H_2O$ (*9*), the structure gives clear evidence for quasi-one-dimensional superexchange paths along the zigzag chains, and the magnetic ordering for such an antiferromagnet with very low exchange constant is expected to occur under 4.2 K as observed in $K_2FeF_5 \cdot H_2O$ where $J/k = -0.4$ K. Zero-field magnetic susceptibility measurements and further Mössbauer spectroscopy measurements on single crystals are needed to confirm this hypothesis.

Acknowledgments

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