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Crystal Structure and Magnetic Properties of a New Form of NH_4MnFeF_6

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The hydrothermal synthesis at 380°C, 200 MPa of NH_4MnFeF_6, NH_4MnCrF_6, and $RbMnFeF_6$ leads to a new $AM^{II}M^{III}F_6$ structural type of orthorhombic symmetry with $Z = 8$. Lattice constants are found to be, respectively, $a = 7.844$ (4), $b = 12.819$ (8), $c = 10.582$ (6); $a = 7.808$ (5), $b = 12.755$ (9), $c = 10.501$ (7); and $a = 7.913$ (5), $b = 12.858$ (9), $c = 10.619$ (5). The structure was solved for NH_4MnFeF_6 from 755 X-Ray reflections and refined to $R_\omega = 0.029$ in the space group $Pb2n$–C_{2v}^6. The network is built from edge-sharing $MnFeF_{10}$ bioctahedra connected to each other by their vertices. $RbMnFeF_6$ upon heating transforms irreversibly to the modified pyrochlore structure at 881 K. From magnetic and Mössbauer experiments, NH_4MnFeF_6 and NH_4MnCrF_6 are established to be antiferromagnetic with $T_N = 117.7 \pm 0.5$ K and <6 K, respectively.

Introduction

Transition metal fluorides $AM^{II}M^{III}F_6$ crystallize in various structural forms: trirutile, modified pyrochlore, tetragonal bronze, or trigonal Na_2SiF_6 types. To obtain new structural species for this composition, hydrothermal synthesis—which frequently favors the growth of metastable or low temperature forms—was applied to the crystallization of NH_4MnFeF_6, NH_4MnCrF_6, and $RbMnFeF_6$.

Experimental

Prismatic single crystals of NH_4MnFeF_6, NH_4MnCrF_6, and $RbMnFeF_6$ were grown by hydrothermal synthesis. The method was previously described (*1*): binary transition metal fluorides MnF_2 and FeF_3 or CrF_3 are mixed with 5 *M* RbF or NH_4F solutions ($AF/M'F_2/M''F_3 = 1/1/1$) in a platinum tube. After heating at 360°C, 200 MPa, for 3 days, and cooling of the autoclave, the crystals were isolated and characterized. Fluorine was analysed with a specific electrode, and metals by atomic absorption spectrometry (Table I).

Laue and Buerger precession photographs of the crystals show that reflections are consistent with space group $Pbcn$–D_{2h}^{14} Refined lattice parameters (Å) are given in Table II, powder diffraction data for NH_4MnCrF_6 are presented in Table III.

NH_4MnFeF_6 was used for the X-ray structure determination. Intensity data were collected on a CAD 4 Nonius diffractometer[1] with Mo$K\alpha$ radiation in the range

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TABLE I

CHEMICAL ANALYSIS AND SPECIFIC GRAVITY OF NH_4MnFeF_6

	Exp.	Calc.
Mn	20.9(1.7)[a]	22.6
Fe	23.9(1.9)	23.0
F	47.9(2.4)	47.0
ρ	3.04(5)	3.03

[a] Chemical analysis in wt% (specific gravity in g/cm³).

$-9 \leq h \leq +9$, $-15 \leq k \leq +15$, $0 \leq 1 \leq 12$ with no restrictive conditions. Operating features were graphite monochromator, $3° \leq \theta \leq 25°$; scan mode, ω-2θ; scan range, $s = (1.80 + 0.45 \tan 2\theta)°$; scintillation counter aperture, 3.00 mm; scanning speed, $v = (20.1166/NV)°$ min^{-1} with NV integers.

Intensities treatment and structure determination were carried out with SHELX program (*2*). A total of 2807 reflections were corrected for absorption, using the numerical Gauss method; the transmission factor varied from 0.594 to 0.432. Averaging, in the Laue group *mmm*, leads to 755 independent reflections with $|F|/\sigma(|F|) \geq 6$. The atomic scattering factors were taken from "International Tables for X-ray Crystallography" (1968) for N°, F^-, Fe^{3+}, Mn^{2+} (*3*).

Structure Determination

Direct methods, using triple phase relations between F_{hkl}, were tested in the centrosymmetric Pbcn space-group. After F_{hkl} ($l = 2n + 1$) renormalisation they yielded a solution with a good figure of merit. Metallic atoms were located from the corresponding E map. The Fourier map, built from the set of refined metallic coordinates ($R = 0.315$) provided information on the location of fluorine and nitrogen atoms. Refinement of positional and isotropic thermal parameters for all nonhydrogen atoms, of secondary extinction and weighting, did not yield a satisfactory R value ($R = 0.210$). This fact, in spite of the lack of a piezoelectric signal, lead us to consider the noncentric space groups derived from *Pbcn*: non-

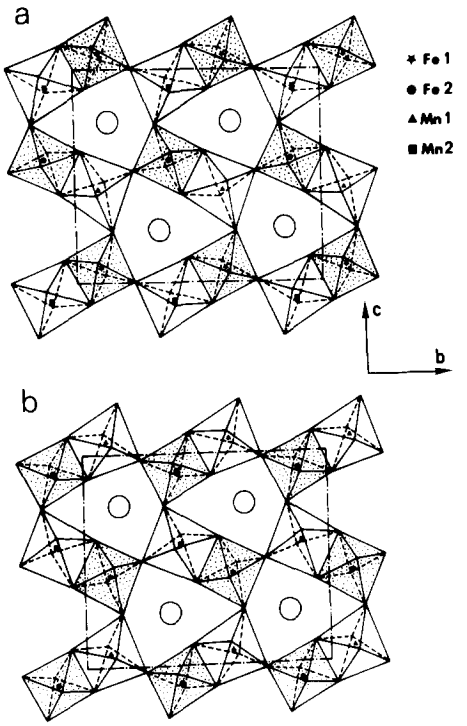

FIG. 1. Projections of NH_4MnFeF_6 along [100] at $x = \frac{1}{4}$ (a) and $x = \frac{3}{4}$ (b); MnF_6 octahedra are dotted.

TABLE II

		a	*b*	*c*
Symmetry: orthorombic	NH_4MnFeF_6	7.844(4)	12.819(8)	10.582(6)
Space group: *Pb2n* – C_{2v}^6 (*n*°30)	NH_4MnCrF_6	7.808(5)	12.755(9)	10.501(7)
$Z = 8$	$RbMnFeF_6$	7.913(5)	12.858(9)	10.619(5)

TABLE III

LATTICE SPACINGS AND OBSERVED X-RAY INTENSITIES FOR NH_4MnCrF_6

$h\ k\ l$	I_{obs}	d_{obs}	d_{calc}
0 2 0	15	6.382	6.378
0 2 1	60	5.446	5.451
0 0 2	65	5.246	5.250
1 2 1	4	4.461	4.470
1 0 2	4	4.342	4.357
0 2 2	6	4.049	4.054
2 0 0	100	3.894	3.904
2 2 0	10	3.325	3.330
0 4 0	95	3.188	3.189
2 2 1	5	3.171	3.174
2 0 2	35	3.130	3.133
0 2 3	90	3.068	3.069
0 4 2	10	2.725	2.726
0 0 4	4	2.627	2.625
1 4 2	4	2.572	2.573
2 1 3	2	2.546	2.553
3 1 1 / 2 4 0	15	2.470	2.478 / 2.470
1 1 4	5	2.441	2.442
0 2 4 / 1 5 0	25	2.428	2.428 / 2.425
2 4 1	8	2.403	2.404
1 5 1 / 0 4 3	5	2.359	2.363 / 2.357
3 1 2	10	2.291	2.294
2 0 4	5	2.178	2.178
1 3 4 / 2 1 4	5	2.148	2.148 / 2.147
0 6 0	8	2.126	2.126
0 6 1	15	2.084	2.084
2 2 4 / 3 1 3	10	2.061	2.062 / 2.061
2 4 3	4	2.017	2.018
0 2 5 / 1 5 3	20	1.995	1.995 / 1.993
0 6 2	15	1.970	1.971
4 0 0	40	1.950	1.952
1 6 2	4	1.911	1.911

standard $P2_1cn$–C_{2v}^9, $Pb2n$–C_{2v}^6, $Pbc2_1$–C_{2v}^5. Refinement of the structure with anisotropic thermal parameters for metallic atoms permitted selection of the $Pb2n$ space group. Refinement in the two other space groups lead to nondefinite thermal vibration ellipsoids. Manganese and iron atom locations were deduced from metal–fluorine distances; this technique was used recently by Banks *et al.* (*4*) in the crystal structure determination of the tetragonal bronze–like phase $KMnFeF_6$. The residual fell to $R = 0.021$ ($R_\omega = 0.029$) with refinement of anisotropic thermal parameters for all nonhydrogen atoms.[2] Attempts to solve the true structure were unsuccessful.

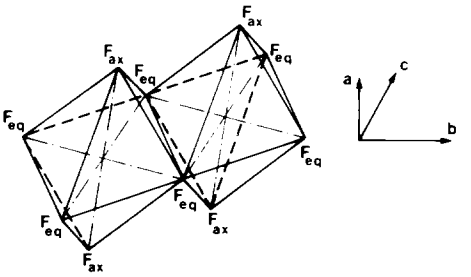

FIG. 2. $MnFeF_{10}$ unit in NH_4MnFeF_6

Table IV presents the final results for the 20 independent positions. Characteristic interatomic distances are given in Table V.

Discussion of the Structure

Figure 1 presents the (100) projection of the structure at $x = \frac{1}{4}$ and $x = \frac{3}{4}$. The three-dimensional network may be described in terms of binuclear $MnFeF_{10}$ groups formed by edge-sharing iron and manganese octahedra. Figure 2 shows this unit, its location with respect to the axes, and the so-called equatorial and axial fluorine atoms. These

[2] See NAPS document No. 04026 for 5 pages of supplementary material. Order from ASIS/NAPS. Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $30 for each additional page. All orders must be prepaid. Institutions and Organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material. $1.50 for postage of any microfiche orders.

TABLE IV

FINAL ATOMIC COORDINATES AND EQUIVALENT TEMPERATURE FACTORS IN NH_4MnFeF_6[a,b]

Atom	Site	x	y	z	Beq. (Å²)
Fe1	4c	0.2489(1)	0.1	0.0737(1)	0.71(9)
Fe2	4c	0.2502(1)	0.3775(1)	0.5745(1)	0.50(8)
Mn1	4c	0.7509(1)	0.0956(2)	0.0719(1)	0.79(9)
Mn2	4c	0.7504(1)	0.3817(2)	0.5718(1)	0.59(8)
F1	4c	0.2069(4)	0.1492(4)	0.2439(4)	1.43(15)
F2	4c	0.2781(3)	0.4533(2)	0.1131(2)	1.04(13)
F3	4c	0.2219(4)	0.5247(4)	0.6162(4)	1.33(15)
F4	4c	0.2894(5)	0.2397(3)	0.5188(3)	1.52(15)
F5	4c	0.0121(5)	0.1156(4)	0.0360(5)	1.95(15)
F6	4c	0.0103(4)	0.3634(4)	0.5397(4)	1.20(13)
F7	4c	0.2223(4)	0.3249(3)	0.7432(4)	1.00(14)
F8	4c	0.7178(4)	0.4317(3)	0.0982(4)	1.12(15)
F9	4c	0.7739(4)	0.5478(3)	0.6000(4)	1.03(14)
F10	4c	0.7063(4)	0.2393(2)	0.4897(2)	1.74(14)
F11	4c	0.4900(4)	0.0837(3)	0.1049(5)	1.52(16)
F12	4c	0.4877(4)	0.3887(3)	0.6091(4)	1.48(15)
*AM*1	2a	0	0.3423(5)	$\frac{1}{4}$	1.23(12)
*AM*2	2a	0	−0.1838(5)	$\frac{1}{4}$	0.87(20)
*AM*3	2b	0	0.1201(6)	$\frac{3}{4}$	1.98(12)
*AM*4	2b	0	−0.3288(6)	$\frac{3}{4}$	1.95(23)

[a] Estimated standard deviations are given in parenthesis.
[b] Wyckoff notation, symmetry, and coordinates of general and special equivalent positions for *Pb2n* space group

4c	1	$x\ y\ z$	$\frac{1}{2}-x\ \frac{1}{2}+y\ z$
		$\bar{x}\ y\ \frac{1}{2}-z$	$\frac{1}{2}+x\ \frac{1}{2}+y\ \frac{1}{2}-z$
2b	2	$0\ y\ \frac{3}{4}$	$\frac{1}{2}\ \frac{1}{2}+y\ \frac{3}{4}$
2a	2	$0\ y\ \frac{1}{4}$	$\frac{1}{2}\ \frac{1}{2}+y\ \frac{1}{4}$

TABLE V

CHARACTERISTIC INTERATOMIC DISTANCES (Å) IN NH_4MnFeF_6

Octahedron of Fe(1)		Octahedron of Fe(2)	
Fe1–F1	1.936(4)	Fe2–F3	1.949(4)
Fe1–F2	1.939(3)	Fe2–F4	1.891(4)
Fe1–F5	1.916(4)	Fe2–F6	1.919(3)
Fe1–F9	1.962(4)	Fe2–F7	1.922(3)
Fe1–F10	1.937(4)	Fe2–F8	1.978(3)
Fe1–F11	1.927(3)	Fe2–F12	1.909(3)
$\bar{d}_{Fe1-F}$ = 1.936		$\bar{d}_{Fe2-F}$ = 1.928	
d_{F2-F9} = 2.568(6)		d_{F3-F8} = 2.629(6)	
$\bar{d}_{F-F}$ = 2.734		$\bar{d}_{F-F}$ = 2.726	
Octahedron of Mn(1)		**Octahedron of Mn(2)**	
Mn1–F1	2.096(4)	Mn2–F2	2.175(3)
Mn1–F3	2.199(4)	Mn2–F6	2.084(3)
Mn1–F4	2.099(4)	Mn2–F7	2.095(3)
Mn1–F5	2.095(4)	Mn2–F9	2.125(4)
Mn1–F8	2.157(3)	Mn2–F10	2.059(4)
Mn1–F11	2.083(3)	Mn2–F12	2.094(3)
$\bar{d}_{Mn1-F}$ = 2.121		$\bar{d}_{Mn2-F}$ = 2.105	
$\bar{d}_{F-F}$ = 2.996		$\bar{d}_{F-F}$ = 2.974	

bioctahedra, slightly tilted from the a axis (approximately 13°), are linked to six similar groups by opposite equatorial vertices along b and c, and by axial vertices along a. At $x = \frac{1}{4}$ and $x = \frac{3}{4}$, they build infinite layers connected by axial F_{ax}, with alternating tiltings along three axes and alternating (Mn, Fe) disposition along a and c. Thus, each metallic octahedron is surrounded by five octahedra of the other metallic species. Ammonium ions adopt 12 coordination, existing in hexagonal close packing.

The large difference between ionic radii

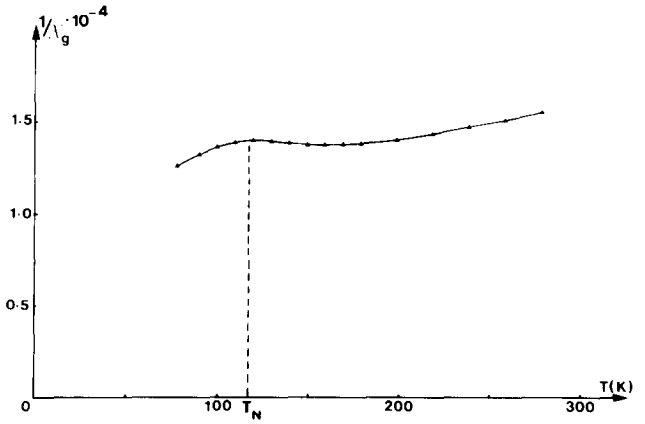

FIG. 3. Thermal variation of the inverse magnetic susceptibility (1/emu g^{-1}) of NH_4MnFeF_6.

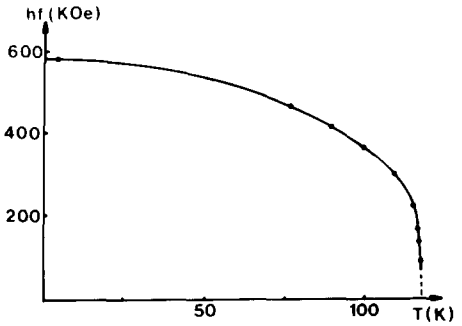

FIG. 4. Thermal variation of the magnetic hyperfine field for NH_4MnFeF_6.

of Mn^{2+} (0.83 Å) and Fe^{3+} (0.64 Å) (*5*) implies a strong distorsion of both metallic octahedra (Table V).

Further distance considerations show that the fluorine atoms which form the edge between manganese and iron octahedra present the shortest fluorine–fluorine distances, but correspond to the longest metal–fluorine distances (Table V).

Very few fluorides with M_2F_{10} units are known. In $Ba_2Ni_3F_{10}$ (*6*) these groups connect planes containing rutile chains. In $BaMnFeF_7$ (*7*), FeF_6 octahedra ensure bridging between Mn_2F_{10} entities. By contrast, numerous oxides, particularly niobates or tantalates, adopt a wide range of structures containing M_2O_{10} units. These groups, tied together by vertices or edges, build up *cis* or *trans* infinite files, or rings. Orthorhombic $CaTa_2O_6$ (*8*), and the high temperature form (HT) of $BaNb_2O_6$ (*9*) furnish, respectively, examples of *cis* and *trans* files connected by vertices. Double *trans* files connected by edges are encountered in $BaTi_4O_9$ and in related compounds (*10–13*). Three membered rings form parts of the hexagonal $BaTa_2O_6$ structure (*14*).

Therefore, NH_4MnFeF_6 appears to be the first fluoride with trans chains of M_2F_{10} units. Its structure is closely related to that of HT-$BaNb_2O_6$, as roughly determined from X-ray powder diffraction. The structural difference relative to HT-$BaNb_2O_6$ derives from the cationic order between Mn^{2+} and Fe^{3+}.

Structural Transformation

At 881 K, DTA experiments on RbMn FeF_6 show an irreversible endothermic phase transition from niobate to a modified pyrochlore type structure. When a solid state reaction is carried out between 823 and 1023 K and is followed by slow cooling, the distorted modified pyrochlore RbMn FeF_6 (a = 7.153(7) Å, b = 7.434(5) Å, c = 12.34(1) Å, β = 125°64(2)) is the only form obtained (*15*); by contrast, hydrothermal synthesis under our experimental conditions, always leads to the structure presently described.

NH_4MnFeF_6 and NH_4MnCrF_6 undergo decomposition before the structural transformation temperature is reached.

TABLE VI

MÖSSBAUER DATA OF NH_4MnFeF_6

T (K)	δ^a (mm sec^{-1})	ΔEQ (mm sec^{-1})	$4\varepsilon^b$ (mm sec^{-1})	H (kOe)	Γ (mm sec^{-1})
295	0.460(2)	0.346(4)	—	—	0.30(1)
118	0.562(2)	0.391(4)	—	—	0.31(1)
77	0.56(1)	—	−0.42(4)	463(2)	0.32(1)
4.2	0.56(1)	—	−0.42(4)	581(2)	0.50(1)

[a] δ = isomer shift relative to Fe metal (T = 300 K).
[b] ε = quadrupolar shift of the outer Zeeman lines.

Magnetic and Mössbauer Studies

A plot of inverse susceptibility χ^{-1} versus T for NH_4MnFeF_6 is shown in Fig. 3. It exhibits a flat minimum around 170 K and, even at 293 K, the Curie–Weiss law is not obeyed; thus, the molar Curie constant and θ_p value can not be obtained. Magnetization, measured by a vibrating sample magnetometer, indicates a superimposed parasitic ferromagnetism below T_N, with $\sigma_{4.2\,K} = 0.005(2)\ \mu_B\ mole^{-1}$. $RbMnFeF_6$ displays an inverse susceptibility curve similar to that of NH_4MnFeF_6. NH_4MnCrF_6 is antiferromagnetic with $T_N < 6$ K, $\theta_p = -8$ K and $C_{exp} = 6.45 \pm 0.10$ ($C_{th} = 6.25$).

Mössbauer experiments on NH_4MnFeF_6 provided an accurate determination of $T_N = 117.7 \pm 0.5$ K and confirmed the three-dimensional magnetic ordering (*16*) with $\beta = 0.34$ and $D = 1.33$. As deduced from bond lengths and the consideration of angles the two types of iron III sites are very similar. They cannot be distinguished by Mössbauer spectroscopy, due to the relative insensitiveness of iron III spectrum towards the surrounding (*17*). The thermal variation of their common hyperfine magnetic field is shown in Fig. 4; characteristic Mössbauer data are provided in Table VI. From the ε values, the angle between the magnetic hyperfine field direction and the main electric field gradient axis is probably 90°.

Conclusion

In this structure, magnetic interactions proceed from superexchange coupling. Fe–F–Mn angles are close to 157, 136 and 102°. So, ~180°, ~90°, and intermediate couplings exist. The magnetic structure determination, scheduled at the ILL Grenoble, should specify the spin directions, particularly inside the bioctahedron, and correlate the Mössbauer resonance and magnetization results.

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