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Structure and Magnetic Behavior of the Na_2NiInF_7 Weberite

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The indium weberite Na_2NiInF_7 has been synthesized in the form of single crystals. The symmetry of the unit cell is orthorhombic: $a = 7.356(1)$ Å, $b = 10.334(2)$ Å, and $c = 7.5231(1)$ Å, with space group *Pmnb*, $Z = 4$. The structure has been determined using 831 independent reflections ($R = 0.026$, $R_w = 0.017$). It is isostructural with Na_2CuCrF_7 and Na_2CuInF_7. Parallel $[NiF_5]_n^{3n-}$ octahedra chains run along the [100] axis separated by In atoms with octahedral coordination (In–F = 2.083 Å) with a seventh further atom at 2.730 Å. The sodium atoms are 7- and 8-coordinated. The expected one-dimensional magnetic behavior has been confirmed, with a 3D-ordering temperature $T_N = 9$ K. Below this temperature, a weak ferromagnetic component is observed. © 1992 Academic Press, Inc.

Introduction

Following the structural determination of the mineral weberite Na_2MgAlF_7 carried out a long time ago *(1)*, a lot of investigations have been devoted to homologous quaternary fluorides $Na_2M^{II}M^{III}F_7$ *(1–7)*. In those compounds the M^{2+} cations are arranged in chains of $[M^{II}F_6]$ octahedra sharing *trans*-vertices; these chains are interconnected by $[M^{III}F_6]$ units to form a three-dimensional network. Most of these fluorides exhibit an orthorhombic cell. However, a trigonal symmetry has been encountered in the $Na_2MnM^{III}F_7$ series, probably favored by the presence of larger Mn^{2+} ions *(8, 9)*, whereas other structural arrangements are observed for copper compounds *(10–12)*.

Some ambiguities remain concerning the space group of the orthorhombic weberites, but they have been removed for some phases such as the frustrated magnetic compounds Na_2NiFeF_7 *(13)*. But since slightly different structures had been observed in the Mn^{2+}-based series, it seemed possible therefore that new modifications could result also from the presence of bigger trivalent cations in the octahedral sites.

Such an assumption encouraged us to achieve the structural investigation of Na_2NiInF_7. Another interest arising from the presence of large diamagnetic In^{3+} ion was in modifying the dimensionality of the magnetic sublattice and producing quasi-isolated magnetic nickel (II) chains. This paper is thus devoted to the structural determi-

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TABLE I

CRYSTALLOGRAPHIC CHARACTERISTICS AND CONDITIONS OF DATA COLLECTION

Crystal data	
Formula, M	Na_2NiInF_7, 352.5
Space group	$Pmnb$, $Z = 4$
Lattice constants ($\rho_c = 4.09$ g · cm^{-3})	$a = 7.356(1)$ Å
	$b = 10.334(2)$ Å
	$c = 7.523(1)$ Å
	$V = 571.9$ Å
Data collection	
Radiation	Mo$K\alpha$
2θ range (°)	4–60
Scanning mode	ω-scan
Scan angle (°)	$0.9 + 0.35 \tan \theta$
Measurement range	$-10 < h < 10$
	$-10 < k < 10$
	$0 < l < 10$
Reflections	
Measured	3206
Symmetry independent	877
Used in refinement $[F_0 > 3\sigma(F_0)]$	831
Absorption coefficient	$\mu = 71.2$ cm^{-1}
Extinction coefficient	$\varepsilon = 7.5 \times 10^{-8}$

TABLE III

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) IN Na_2NiInF_7

Ni–F1	2× 1.951(1)	In–F4	2.047(3)
Ni–F5	2× 1.992(2)	In–F3	2.075(3)
Ni–F6	2× 2.004(2)	In–F6	2× 2.085(2)
		In–F5	2× 2.103(2)
Ni–F average : 1.983		In–F average: 2.083	
		In–F1	2.730(3)
Na1–F3	2× 2.349(2)	Na2–F4	2.211(3)
Na1–F4	2× 2.461(2)	Na2–F3	2.277(3)
Na1–F6	2× 2.673(2)	Na2–F6	2× 2.388(2)
Na1–F5	2× 2.734(2)	Na2–F1	2.412(2)
		Na2–F5	2× 2.524(2)
Na1–F average: 2.554		Na2–F average: 2.389	
F1–Ni–F6	82.5/97.5(1)	F1–In–F3	109.8(1)
F1–Ni–F5	83.8/96.2(1)	F1–In–F4	74.9(1)
F5–Ni–F6	86.3/93.7(1)	F1–In–F5	131.2(1)
		F1–In–F6	63.8(1)
		F3–In–F4	175.4(1)
		F3–In–F5	93.8(1)
		F3–In–F6	83.5(1)
Ni–F1–Ni	141.1(2)	F4–In–F5	82.8(1)
Ni–F6–In	117.8(1)	F4–In–F6	98.9(1)
Ni–F5–In	142.4(1)	F5–In–F5	86.7(1)
		F5–In–F6	78.1/164.2(1)
		F6–In–F6	116.9(1)

Note. Standard deviations are given in parentheses.

nation and magnetic study of this new indium weberite.

Experimental

Polycrystalline samples of Na_2NiInF_7 were prepared by solid state interaction of a stoichiometric mixture of the elementary fluorides. After mixing in a glove box, the starting materials were introduced into a platinum tube which was sealed under dry argon. The reaction was carried out at 600°C for 15 hr. After grinding in a dry atmosphere

TABLE II

FINAL ATOMIC COORDINATES AND ANISOTROPIC TEMPERATURE FACTORS IN Na_2NiInF_7[a]

Atom	Position	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Na1	4b	0	0	0.5	0.022(1)	0.026(1)	0.044(1)	0.002(1)	0.003(1)	−0.004(1)
Na2	4c	0.25	0.2323(2)	0.2475(2)	0.0215(8)	0.0243(8)	0.018(1)	0.0022(8)	0	0
Ni	4a	0	0	0	0.0074(2)	0.0100(2)	0.0110(3)	−0.0003(2)	−0.0009(2)	−0.0011(2)
In	4c	0.25	0.23484(3)	0.76607(4)	0.0097(1)	0.0147(1)	0.0145(2)	−0.0026(1)	0	0
F1	4c	0.25	0.0575(3)	0.0350(4)	0.007(1)	0.040(2)	0.056(2)	−0.027(2)	0	0
F3	4c	0.25	0.3415(2)	−0.0050(3)	0.028(1)	0.019(1)	0.013(1)	−0.001(1)	0	0
F4	4c	0.25	0.1404(2)	0.5227(3)	0.023(1)	0.023(1)	0.017(1)	−0.004(1)	0	0
F5	8d	−0.0556(2)	0.1299(2)	0.1880(3)	0.019(1)	0.022(1)	0.027(1)	−0.0114(8)	−0.0036(8)	0.0015(7)
F6	8d	0.0063(2)	0.1323(2)	0.8053(3)	0.021(1)	0.021(1)	0.023(1)	0.0090(8)	−0.0016(8)	−0.0038(7)

[a] *Note.* Estimated standard deviations are given in parentheses.

A list of the calculated and observed structure factors may be obtained on request from one of the authors (W.M.).

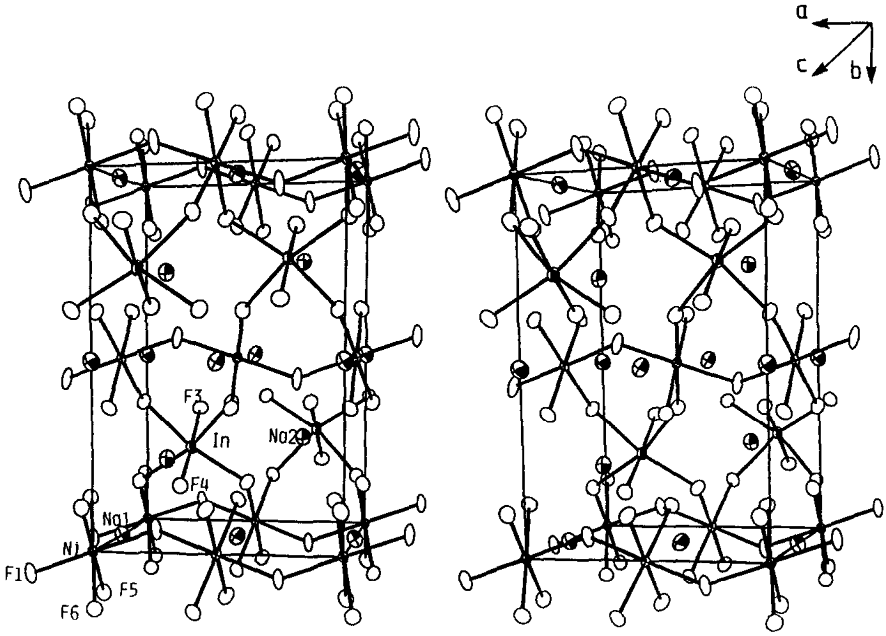

FIG. 1. Stereoview of the structure of Na_2NiInF_7 showing the ordering of the coordination polyhedra in the unit cell [ORTEP drawing (*16*)].

the mixture was annealed for 24 hr in the same conditions in order to eliminate possible traces of Na_3InF_6 and NiF_2. The thermal process was ended by a temperature quenching.

In a second step single crystals were obtained by melting the sample at 810°C and by cooling down to room temperature at a 3°C/hr rate. A spherical crystal of about 0.1 mm diameter was selected for the structure determination. Preliminary Weissenberg and precession photographs using Cu$K\alpha$ and Mo$K\alpha$ radiations, respectively, showed the symmetry to be orthorhombic; the systematic extinctions were consistent with the *Pmnb* space group.

The unit-cell parameters were refined from 55 reflections on the powder diffraction pattern by a least-squares method. The intensities, collected on an automatic four-circle Enraf Nonius CAD4 diffractometer, were corrected for Lorentz and polarization effects, followed by an absorption correction. Table I reports the crystallographic characteristics of the crystal and the experimental conditions of data collection.

Structural Determination and Refinement

All calculations were performed using SHELX programs (*14*). Atomic scattering factors and anomalous dispersion corrections were taken from the "International Tables for X-Ray Crystallography" (*15*).

Starting from the atomic positions given by Kummer *et al.* for Na_2CuCrF_7 (*10*), the refinement rapidly converged down to a residual $R = 0.026$ ($R_w = 0.017$) for 831 reflections, with anisotropic thermal parameters. Table II presents the final results for the nine independent positions. Characteristic distances and angles are given in Table III.

Description of the Structure

Figure 1 represents a stereoview of the Na_2NiInF_7 structure, showing the way the

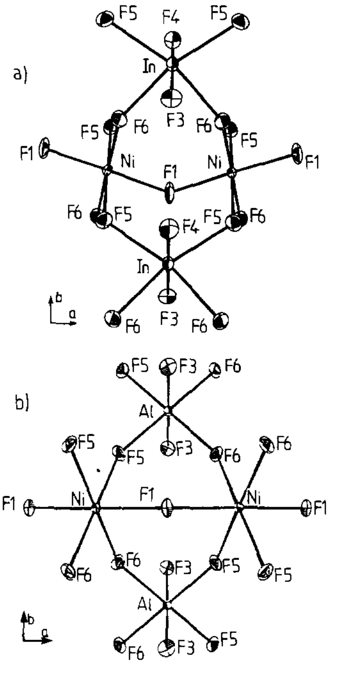

FIG. 2. Comparison of the linking of $(NiF_6)^{2-}$ and $(M^{III}F_6)^{3-}$ octahedra in Na_2NiInF_7 (a) and in Na_2NiAlF_7 (b).

polyhedra are linked in the network. As listed in Table III, the average Ni–F bond length is of the same order of magnitude as those found for Na_2NiCrF_7 (*7*) and Na_2NiFeF_7 (*5*, *13*).

The new peculiarity of this indium compound is the symmetry lowering, which is unusual in the absence of a Jahn–Teller-type ion. Such a result may be related to the value of the $r(M^{2+})/r(M^{3+})$ ratio of the M^{2+} and M^{3+} ionic radii; whereas in the previously investigated orthorhombic weberites this ratio is larger than unity, it is significantly lower in the present case: $r(Ni^{2+})/r(In^{3+}) \approx 0.86$ (*17*). As a consequence, the intrachain Ni–Ni distance reaches 3.678 Å in Na_2NiInF_7, whereas it is equal for example to 3.617 Å in Na_2NiFeF_7 (*13*).

The large size of trivalent indium disturbs the octahedral environment of nickel due to bridging by the F5 and F6 atoms (Fig. 1). As a consequence the F1 fluorine atom linking two neighboring nickel octahedra becomes closer to the indium polyhedron. Indium adopts therefore an octahedral coordination (In–F = 2.083 Å) with a seventh further fluorine atom at 2.730 Å. The In–F1 distance, although still relatively large (2.73 Å), is indeed much shorter than the corresponding M^{III}–F1 length usually encountered in other weberites (M^{III}–F1 > 3 Å). Such a peculiarity results from a different tilting of the chains in $z = 0$ and $z = \frac{1}{2}$. Figure 2 compares the way in which the octahedra are connected in Na_2NiInF_7 and Na_2NiAlF_7 (*18*).

The Na1 atom exhibits a eightfold coordination as previously mentioned in orthorhombic and trigonal weberites. Two distances (Na1–F3 = 2.349 Å) are shorter than the sum of Shannon's radii (for Na^+ with C.N. = 8) (*17*) which corresponds to 2.51 Å. Such values are, however, larger than some of those observed in distorted hexagonal bipyramid environments: for example apical Na–F distances of 2.111 and 2.124 Å are found in the trigonal Na_2MnCrF_7 (*9*) and Na_2MnFeF_7 (*8*), respectively, whereas 2.215 Å is observed for the shortest Na1–F2 axes in the orthorhombic Na_2NiFeF_7 (*13*). But the distance deviation is smaller for Na_2NiInF_7 and the polyhedron around the Na1 atom can be considered as a distorted prism.

In contrast, the Na2–F average distance is considerably smaller than the former one, with the two shortest distances Na2–F3 = 2.277 Å and Na2–F4 = 2.211 Å. The polyhedron surrounding the Na2 atom can, therefore, be ascribed to a pentagonal bipyramid, as shown in Fig. 3. Such a NaF_7 coordination thus differentiates Na_2NiInF_7 from the previously studied weberites.

In comparison with the "normal" weberite Na_2NiFeF_7, Na_2NiInF_7 has lost the I-centering, but the general arrangement of the orthorhombic network is maintained: $[M^{II}F_5]_n^{3n-}$ chains are formed, constituted of

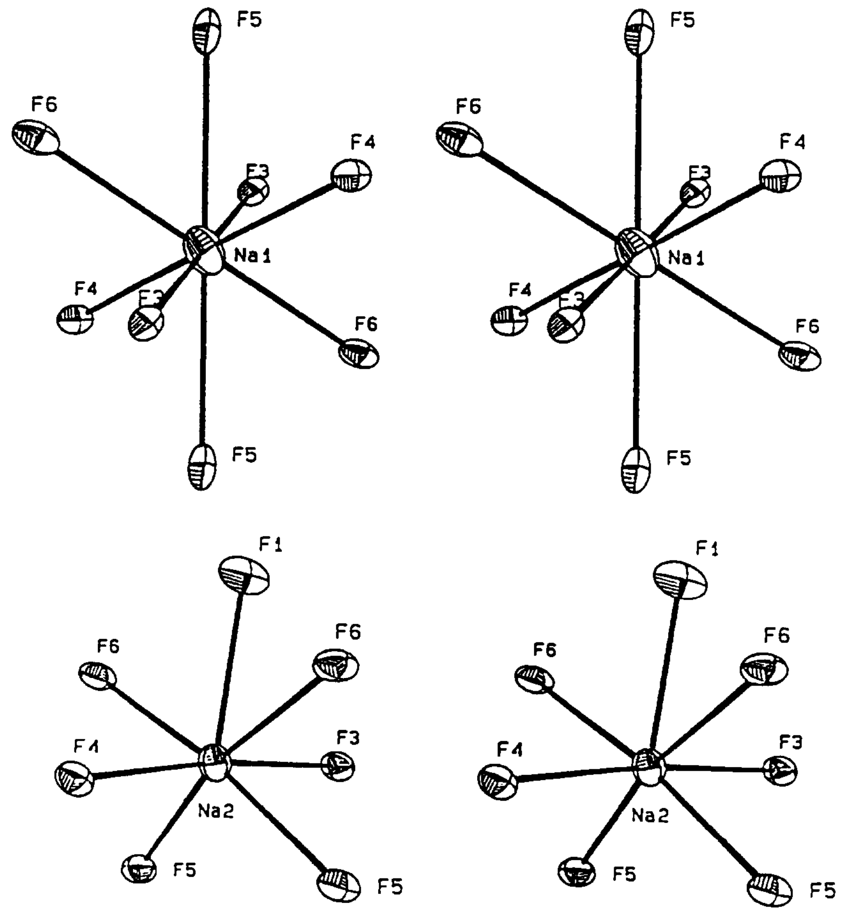

FIG. 3. Stereoview of the distorted polyhedra surrounding Na1 and Na2 atoms in Na_2NiInF_7.

$[M^{II}F_6]$ octahedra sharing *trans*-vertices, parallel to the [100] direction (Fig. 4).

Magnetic Investigation

The magnetic measurements were carried out on a powder sample using a Faraday-type balance in the 4 to 300 K temperature range and a SQUID magnetometer down to 2 K.

A linear dependence of the reciprocal susceptibility is obtained for temperatures higher than about 100 K (Fig. 5). The molar Curie constant $C_M = 1.20$ is quite similar to those obtained for Ag_2NiInF_7 ($C_M = 1.19$) (*20*) and is very close to the calculated spin-only value ($C_M = 1$). The extrapolated paramagnetic Curie temperature is $\theta_p = -35 \pm 2$ K. For temperatures lower than 100 K the departure from the Curie–Weiss straight line illustrates clearly a low-dimensional magnetic behavior. Since highly isotropic ions (Ni^{2+}) are involved, the intrachain exchange constant has been calculated from a Heisenberg isotropic Hamiltonian with the usual convention of a negative J value corresponding to antiferromagnetic interactions. Initially determined for $S = \frac{1}{2}$, the susceptibility calculations have been further extended to higher spin values. For antiferromagnetic Heisenberg chains of finite lengths, Fisher and Weng have proposed a more general equation (*21, 22*). In these conditions, for a chain with spins $S = 1$, the estimated value is $J/k = -24 \pm 2$ K. It may be compared to that found for Na_2NiAlF_7 ($J/k = -11 \pm 2$ K) (Fig. 5).

At low temperature a three-dimensional ordering appears which is characterized by the occurrence of a weak spontaneous magnetization σ_0. The ordering temperature has been determined for vanishing values of σ_0. The antiferromagnetic ordering temperature of Na_2NiInF_7 is $T_N = 9$ K; this value, lower than those observed for Na_2NiAlF_7 ($T_N = 12 \pm 2$ K as shown is Fig. 5) or Na_2FeAlF_7 ($T_N = 19 \pm 1$ K) (*3*), results probably from the presence of the bigger In^{3+} cation which increases the distance between two chains, reducing consequently the interchain magnetic interactions.

In Fig. 5 the temperature dependence of the zero-field magnetization is also represented; the values of σ_0 have been obtained by extrapolating down to $H = 0$ the $\sigma = f(H)$ curves. The weak ferromagnetic component reaches 0.027 μ_B at 2 K for Na_2NiInF_7 and 0.15 μ_B for Na_2NiAlF_7; such a behavior can be correlated with a slightly canted antiferromagnetism.

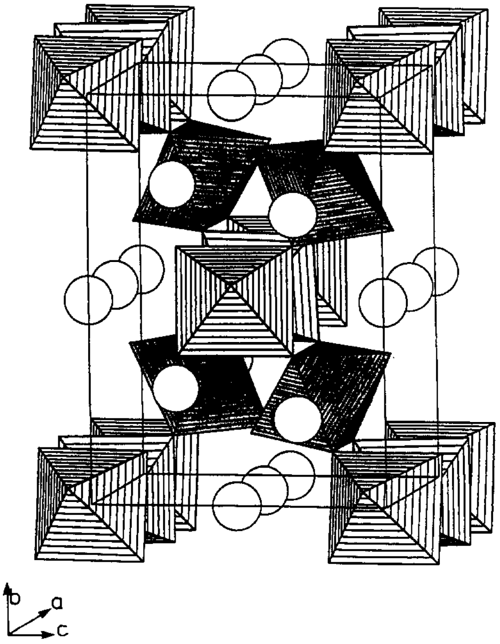

FIG. 4. Perspective view of Na_2NiInF_7 showing the $[NiF_5]_n^{3n-}$ chains. $(InF_6)^{3-}$ octahedra are shaded and $(NiF_6)^{4-}$ octahedra are not [STRUPLO program (*19*)].

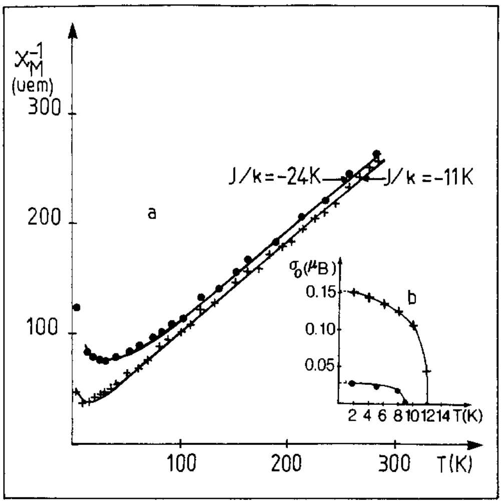

FIG. 5. Temperature dependence of the reciprocal susceptibility (a) and zero-field magnetization (b) for Na_2NiInF_7 and Na_2NiAlF_7. (●) Experimental for Na_2NiInF_7; (+) experimental for Na_2NiAlF_7; (—) calculated curves with $J/k = -24$ K for Na_2NiInF_7 and $J/k = -11$ K for Na_2NiAlF_7.

Table IV summarizes selected structural and magnetic data of Ni^{II}-based weberites. It can be noted that for the two antiferromagnetic compounds, namely Na_2NiAlF_7 and Na_2NiInF_7, in which a high temperature susceptibility fitting can be achieved, the J/k intrachain constant seems to be dependent on the bonding Ni–F1–Ni angle, whereas the 3D T_N depends of course on the distance between $[NiF_5]_n^{3n-}$ chains.

Conclusions

Na_2NiInF_7 is a new example of a compound whose structure derives from the "normal" weberite, with parallel Ni(II) chains. In this structure the I-centering disappears because of a tilting difference between the chains on $z = 0$ and $z = \frac{1}{2}$ levels.

TABLE IV

SELECTED STRUCTURAL AND MAGNETIC DATA OF SOME Ni^{II}-BASED WEBERITES

	Ni–Ni intrachain distance (Å)	Ni–Ni interchain distance (Å)	Intrachain Ni–F1–Ni bond angle (°)	T_N (K)	Intrachain J/k (K)	Reference
Na_2NiAlF_7	3.66	6.15	135	11	—	23
				12	−11	[a]
Na_2NiFeF_7	3.617	6.36	133.9	Ferrim. ordering, T_C = 88 K		5, 13
Na_2NiInF_7	3.678	6.39	141.1	9	−24	[a]

[a] This work.

Such a feature can be correlated with the presence of a large trivalent cation in the octahedra connecting the chains. As a result a peculiar octahedral coordination (In–F = 2.083 Å) with a seventh further fluorine atom at 2.730 Å has been found for the indium atoms.

The structure determination of Na_2NiInF_7, therefore, provides a new example of the large variety of space groups in which weberite compounds may crystallize. Investigations on new copper weberites, Na_2CuGaF_7 and Na_2CuInF_7, containing diamagnetic trivalent cations are also in progress (*24*).

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