JOURNAL OF SOLID STATE CHEMISTRY **109**, 64–69 (1994)

Crystallographic and Magnetic Studies of $Nb_{0.947}Fe_{0.947}M_{0.106}O_{3.79}F_{0.21}$ (M = Ni, Co)

F. Bayi, G. Pourroy,[1] P. Rabu, and P. Poix

Groupe des matériaux Inorganiques, I.P.C.M.S., E.H.I.C.S., 1 rue Blaise Pascal BP296, 67008 Strasbourg Cedex, France

Received November 6, 1992; in revised form April 12, 1993; accepted June 18, 1993

The crystallographic structures of the oxyfluoride phases $Nb_{0.947}Fe_{0.947}M_{0.106}O_{3.79}F_{0.21}$ (M = Ni, Co) are refined from their X-ray powder diffraction pattern by means of a Rietveld method in the wolframite structural type. Both compounds exhibit a partial cationic disorder, i.e., between Nb^{V} on one hand and the magnetic cations (Fe^{III} and Ni^{II} or Co^{II}) on the other hand. The cobalt-containing phase is more ordered than the nickel-containing phase. The consequence of incomplete order is a field-dependent magnetic susceptibility at low temperatures. Alternative susceptibility measurements versus temperature exhibit a maximum around 35 K. © 1994 Academic Press, Inc.

INTRODUCTION

$NbFeO_4$ is reported to have three types of structure varying with the temperature (1, 2). The rutile type (quadratic, space group $P4_2/mnm$) occurs above 1380°C, the α-PbO_2 type (orthorhombic, space group *Pbcn*) in the range 1085–1380°C, and the wolframite type (monoclinic, space group $P2/c$) below 1085°C. The three structures may be described as different ways of filling half the octahedral sites in an *hcp* array of oxygen atoms by niobium or iron. In the rutile case, alternate rows of interstices are occupied by cations in each layer, which gives rise to characteristic strings of edge-sharing octahedra parallel to the fourth order axis *c*. The α-PbO_2 type consists of a planar arrangement (perpendicular to the *a* axis) of octahedra sharing edges to form zigzag chains. The stacking is completed by joining the strings at two levels through common octahedral corners. When idealizing the structure to an *hcp* array of oxygen, half the octahedral sites in each edge-sharing row are then occupied (3). The wolframite form is an ordered and slightly distorted variant of the α-PbO_2 structure in which every zigzag chain contains either Fe or Nb atoms (Fig. 1). A low temperature synthesis route has been recently developed. Owing to thermal treatments, intermediate structures between the α-PbO_2 and the wolframite types can be obtained, allowing the study of phases characterized by different order degrees between niobium and iron (4). In these cases, the cationic distribution may be revealed from X-ray powder patterns. (For example, existence of the 100, 011, and 120 diffraction lines are characteristic of the wolframite structure.) It may also constitute a determining factor for the magnetic properties. Indeed, totally disordered sample (α-PbO_2 structure) exhibits no magnetic order down to 4.2K, while low temperature susceptibility of the wholly ordered sample (wolframite structure) exhibits a sharp peak at 50 K (4, 5). This antiferromagnetic behavior results from ferromagnetic (100) planes of iron, antiferromagnetically coupled together (6). However, an intermediate compound exhibits predominant ferromagnetic interactions. An out-of phase signal at the susceptibility maximum temperature indicates the presence of a net magnetic moment in the ordered state (7). Such peculiar magnetic properties have also been encountered in the oxyfluorides $Ta_{0.947}Fe_{0.947}M_{0.106}O_{3.79}F_{0.21}$ (M = Zn^{2+}, Mn^{2+}) and $Nb_{0.947}Fe_{0.947}Ni_{0.106}O_{3.79}F_{0.21}$, for which an intermediate structure between the wolframite and α-PbO_2 types has been suggested (8–11). However, the observed X-ray diffraction lines characteristic of the wolframite distortion (with regard to the α-PbO_2 structural type) were not taken into account for structural analysis. Thus it seems interesting to study the structure of this family of material on the basis of the wolframite type arrangement, which should allow an appropriate description of its structural features. Moreover, this new investigation could be useful in order to determine precise magneto-structural correlations. We present here a structural study of the $Nb_{0.947}Fe_{0.947}M_{0.106}O_{3.79}F_{0.21}$ (M = Ni, Co) phases using a Rietveld analysis of X-ray powder diffraction data. Then their magnetic properties are described and discussed according to the structural results.

EXPERIMENTAL

$Nb_{0.947}Fe_{0.947}M_{0.106}O_{3.79}F_{0.21}$ (M = Ni, Co) samples have been synthesized by using the starting oxides Nb_2O_5 and Fe_2O_3, and MF_2. The oxides and NiF_2 have been pre-

---

[1] To whom correspondence should be addressed.

0022-4596/94 $6.00

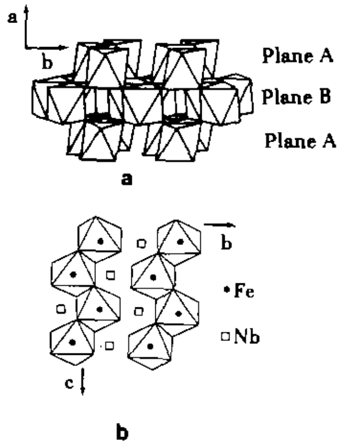

FIG. 1. (a) Schematic representation of the α-PbO_2 structure. (b) The wolframite type arrangement in $NbFeO_4$.

TABLE 1
Details of Rietveld Refinement for $Nb_{0.947}Fe_{0.947}M_{0.1}O_{3.79}F_{0.21}$ (M = Co, Ni)

Formula unit	$Nb_{0.947}Fe_{0.947}M_{0.106}O_{3.79}F_{0.21}$	
M	Co	Ni
a (Å)	4.6519 (1)	4.6474 (1)
b (Å)	5.6273 (1)	5.6212 (1)
c (Å)	5.0129 (1)	5.0073 (1)
β (°)	90.081 (3)	90.050 (4)
V (Å^3)	131.227 (8)	130.811 (8)
Z	2	2
Space group	$P2/c$	$P2/c$
2Θ range	15–130	15–130
Step scan increment (°2Θ)	0.04	0.04
Range of calc. prof. (HW units)	4.5	4.5
No. of reflections	146	146
No. of profile parameters	13	13
No. of atoms	6	6
$R_F = \Sigma \mid I_0^{\frac{1}{2}} - I_C^{\frac{1}{2}} \mid / \Sigma I_0^{\frac{1}{2}}$	0.0291	0.0318
$R_B = \Sigma \mid I_0 - I_c \mid / \Sigma I_0$	0.0323	0.0273
$R_p = \Sigma \mid y_i - y_{ic} \mid / \Sigma y_i$	0.130	0.105
$R_{wp} = [\Sigma w_i (y_{i0} - y_{ic})^2 / \Sigma w_i y_{i0}]^{\frac{1}{2}}$	0.162	0.132
"*Expected*" R_{wp}	0.0893	0.0849

pared as described elsewhere (*8–11*). CoF_2 has been obtained by fluoration of $CoCl_2$.

Nb_2O_5, Fe_2O_3, and MF_2, taken in a stoichiometric ratio, were ground together and introduced into a closed gold crucible. This tube was covered with a mixture (Nb_2O_5, NiF_2), put into an inconel tube, and heated under dried argon at 850°C for 2 days.

X-ray powder diffraction data have been collected at room temperature using a D500 Siemens diffractometer equipped with a primary beam quartz monochromator ($CoK\alpha_1$ = 1.78897 Å). Magnetic measurements were performed in the temperature range 4.2–300 K with a pendulum-type magnetometer and an a.c. susceptometer at 333 Hz (Lakeshore). The raw susceptibility data are corrected from diamagnetism values given by Bernier and Poix according to the Slater–Angus method (12).

STRUCTURAL REFINEMENTS

The indexing of the two powder patterns (M = Co, Ni) indicates that the crystal structure of both compounds is isomorphous with the wolframite type $NbFeO_4$ (a = 4.637 Å, b = 5.607 Å, c = 4.992 Å, β = 90.06°, $P2/c$ (2)). Therefore, the latter has been taken as the starting model for the refinement of the structures of the phases $Nb_{0.947}Fe_{0.947}M_{0.106}O_{3.79}F_{0.21}$ (M = Ni, Co). The structure refinements were carried out following the Rietveld profile refinement method, by means of the program FULLPROF (13). A pseudo-Voigt function was chosen for the representation of the individual reflection profiles. The scattering factors for ions were used, taking into account the anomalous dispersion. The cationic distribution on both sites (2e) and (2f) has been refined. In order to limit the number of parameters, only Fe^{3+}, Nb^{5+}, and O^{2-} have been considered. The contributions of Ni^{2+} or Co^{2+} (in view of their scattering factor values and their concentration) have not been distinguished from those of Fe^{3+}. Consequently, the refined iron occupancy corresponds indeed to that of iron and nickel (or cobalt). The same approximation was introduced for oxygen and fluor atoms. Then considering the formulation of the title compounds, an Fe^{3+}/Nb^{5+} occupancy ratio of 1.0/0.9 was fixed for the refinements. Let us note that the anion sites 4g are fully occupied. Thus, the formulation of the "refined compounds" may be expressed as $Nb_{0.947}Fe_{1.053}O_4$, with Z =2. Because of partial cationic disorder, the thermal parameters of all cations have been assumed to be identical. The details of the Rietveld profile refinement for $Nb_{0.947}Fe_{0.947}Co_{0.106}O_{3.79}F_{0.21}$ and $Nb_{0.947}Fe_{0.947}Ni_{0.106}O_{3.79}F_{0.21}$ are given in Table 1. Because of the background aspect, the angular range 15–18° (2Θ) has been omitted for the calculation. The final atomic parameters are displayed in Tables 2 and 3, and bond lengths in Table 4. The experimental and calculated X-ray diffraction patterns of $Nb_{0.947}Fe_{0.947}Co_{0.106}O_{3.79}F_{0.21}$ are plotted in Fig. 2.

MAGNETIC PROPERTIES

The temperature dependence of the magnetic susceptibility χ_M of both phases is displayed in Figs. 3 and 4, for different external fields. Below 150 or 100 K (for the nickel or cobalt variety, respectively) the susceptibility depends on the applied field, indicating the presence of

TABLE 2
Cristallographic Positions, Isotropic Thermal Coefficients, and Cation Concentrations for $Nb_{0.947}Fe_{0.947}Co_{0.106}O_{3.79}F_{0.21}$ (esd in Parentheses)

Atoms (site)	x	y	z	B (Å^2)	Multiplicity
Fe, Co (2*f*)	0.5	0.67180 (50)	0.25	1.04 (4)	1.752 (11)
Nb (2*f*)	0.5	0.67180 (50)	0.25	1.04 (4)	0.248 (11)
Nb (2*e*)	0	0.17947 (34)	0.25	1.04 (4)	1.652 (11)
Fe, Co (2*e*)	0	0.17947 (34)	0.25	1.04 (4)	0.348 (11)
O_I (4*g*)	0.7739 (13)	0.1140 (14)	0.9237 (14)	0.42 (23)	4.0
O_{II} (4*g*)	0.7312 (13)	0.3830 (14)	0.4154 (16)	1.18 (24)	4.0

TABLE 3
Cristallographic Positions, Isotropic Thermal Coefficients, and Cation Concentrations for $Nb_{0.947}Fe_{0.947}Ni_{0.106}O_{3.79}F_{0.21}$ (esd in Parentheses)

Atoms (site)	x	y	z	B (Å^2)	Multiplicity
Fe, Ni (2*f*)	0.5	0.6730 (6)	0.25	1.009 (28)	1.504 (11)
Nb (2*f*)	0.5	0.6730 (6)	0.25	1.009 (28)	0.496 (11)
Nb (2*e*)	0	0.1775 (4)	0.25	1.009 (28)	1.404 (11)
Fe, Ni (2*e*)	0	0.1775 (4)	0.25	1.009 (28)	0.596 (11)
O_I (4*g*)	0.7699 (12)	0.1170 (20)	0.9212 (16)	0.31 (25)	4.0
O_{II} (4*g*)	0.7274 (12)	0.3871 (20)	0.4171 (17)	0.75 (26)	4.0

TABLE 4
Cation–Anion Distances in Å for $Nb_{0.947}Fe_{0.947}M_{0.106}O_{3.79}F_{0.21}$ (M = Co, Ni) Compared with Those of $NbFeO_4$ (esd in Parentheses)

	$Nb_{0.947}Fe_{0.947}M_{0.106}O_{3.79}F_{0.21}$		
	M = Co	M = Ni	$NbFeO_4$(2)
	(2*f*)		
d(Cation–anion$_I$)	1.957 (8)	1.923 (9)	1.927
d(Cation–anion$_{II}$)	2.117 (8)	2.097 (10)	2.115
d(Cation–anion$_{II}$)	2.017 (8)	2.003 (8)	2.014
	(2*e*)		
d(Cation–anion$_I$)	1.978 (7)	1.991 (8)	2.008
d(Cation–anion$_I$)	2.143 (8)	2.149 (10)	2.161
d(Cation–anion$_{II}$)	1.888 (8)	1.922 (9)	1.858

large fluctuations of the resulting magnetic moment. In the cobalt case, $\chi_M(T)$ exhibits a maximum in the temperature range 20–30 K. Between 200 and 300 K, the magnetic susceptibilities follow a Curie–Weiss law, with $\chi_M = 2.11/(T + 20)$ and $\chi_M = 3.91/(T + 38)$ for the nickel and cobalt phases, respectively. The negative Weiss temperatures indicate that antiferromagnetic interactions predominate. With respect to the common values found in the literature (14), the Curie constants are lower than those theoretically expected, especially for nickel compounds, i.e., $C = 4.04$ K·emu/mol and $C = 4.12$ K·emu/mol for nickel and cobalt derivatives, respectively. This indicates that the paramagnetic domain is not reached below 300 K. Magnetization versus magnetic field measurements are shown in Figs. 5 and 6 at characteristic temperatures. A ferromagnetic component appears below 100 K. At 6 K, the linear part of magnetization $M = f(H)$ fits with $M = 0.0320H + 33.46$ and $M = 0.0350H +$

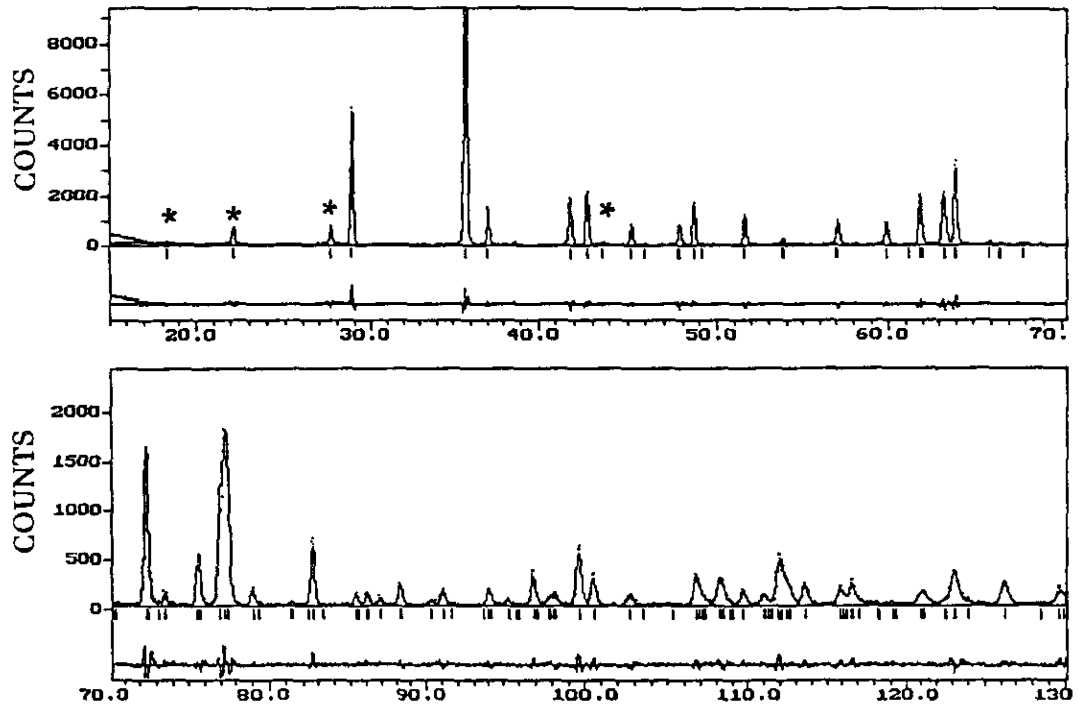

FIG. 2. Observed (...) and calculated (-) X-ray powder diffraction profile of $Nb_{0.947}Fe_{0.947}Co_{0.106}O_{3.79}F_{0.21}$. The difference profile appears below at the same scale. Characteristic lines of wolframite structure are indicated by (*).

34.00 for nickel and cobalt oxyfluoride, respectively. The coefficients found for the field variation of M hint at similar ferromagnetic exchange interactions in both compounds. Alternative susceptibility measurements performed in the temperature range 4.2–100 K reveal one maximum for both phases, at 35 K, sharper for the cobalt containing oxyfluoride (Fig. 7). A second anomaly, very reduced, is observed at 10–20 K. No out-of-phase signals are detected in the temperature range 4.2–150 K, whatever the frequency may be.

DISCUSSION

While the formation of $NbFeO_4$ from the stoichiometric mixture Nb_2O_5–Fe_2O_3 occurs above 1000°C, the oxyfluoride phases are obtained below 900°C. Thus, the fluoride NiF_2 or CoF_2 added to Nb_2O_5 and Fe_2O_3 strongly decreases the reaction temperature. This property has been recently assigned to the formation of an intermediate gaseous phase NbF_5, which is very reactive toward the solid (15). Note, however, that a possible decomposi-

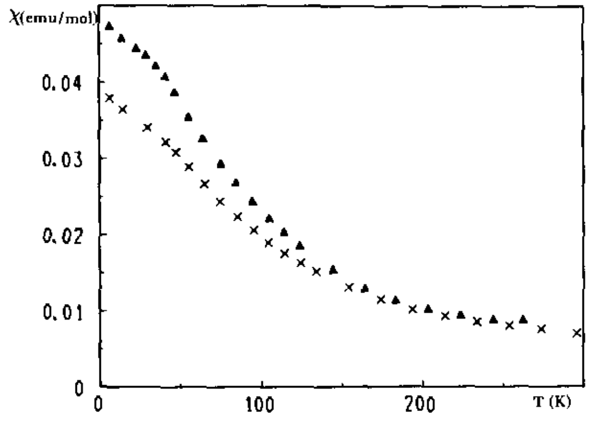

FIG. 3. Thermal variation of magnetic susceptibilities for $Nb_{0.947}Fe_{0.947}Ni_{0.106}O_{3.79}F_{0.21}$ (H = 14 kOe(×), H = 6 kOe(▲)).

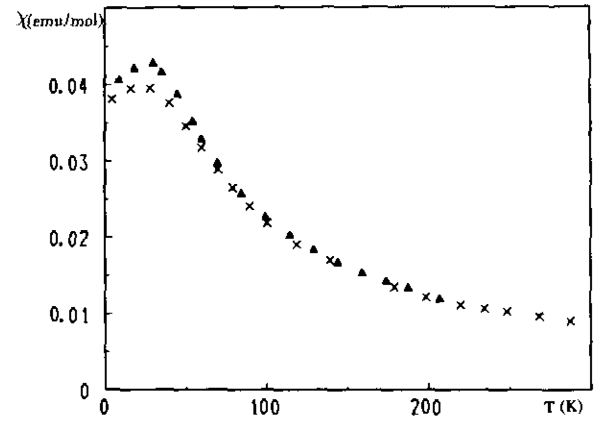

FIG. 4. Thermal variation of magnetic susceptibilities for $Nb_{0.947}Fe_{0.947}Co_{0.106}O_{3.79}F_{0.21}$ (H = 14 kOe(×), H = 6 kOe (▲)).

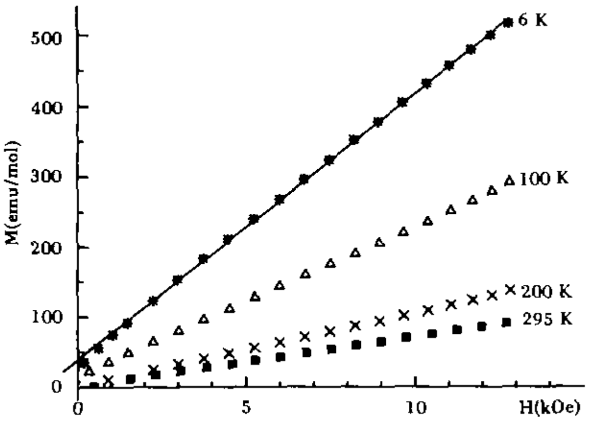

FIG. 5. Magnetization versus magnetic field at different temperatures for $Nb_{0.947}Fe_{0.947}Ni_{0.106}O_{3.79}F_{0.21}$. The full line represents the linear fit of the magnetization (see text).

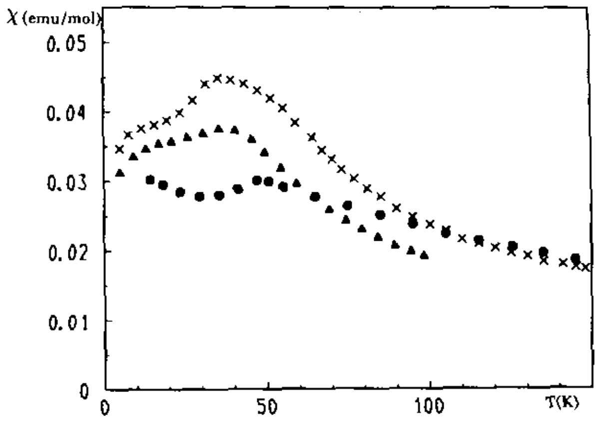

FIG. 7. Thermal variation of alternative magnetic susceptibility for $Nb_{0.947}Fe_{0.947}Ni_{0.106}O_{3.79}F_{0.21}$ (▲), $Nb_{0.947}Fe_{0.947}Co_{0.106}O_{3.79}F_{0.21}$ (×) and $NbFeO_4$ (●).

tion of the phase, which could result from this intermediate reaction, is avoided by the presence of (Nb_2O_5, NiF_2) which creates an atmosphere of NbF_5. Furthermore, since the magnetic susceptibility is not field dependent at room temperature, an NbF_5 evolution from the compound is definitively ruled out. Indeed, it has been previously shown that a slight decomposition would result in the formation of ferrimagnetic impurities such as $NiFe_2O_4$ or Fe_3O_4 (15).

X-ray diffraction patterns have been successfully refined in the *P*2/*c* space group. The oxyfluoride phases have the wolframite structure of $NbFeO_4$. However, while in $NbFeO_4$ the sites 2*e* and 2*f* are occupied by niobium and iron, respectively, a partial disorder occurs in the oxyfluoride phases. The site 2*e* contains mainly niobium (87 or 74% of total niobium for cobalt or nickel phases, respectively), but also a small quantity of iron and cobalt (or nickel). The reverse is observed for the site 2*f*. Let us note that, as the whole niobium concentration is smaller than that of iron and cobalt (or nickel), the complete order would correspond to 1.8948 niobium atoms on site 2*e* and the complete disorder to 0.9474 niobium atoms. Thus, if we define an order rate such that complete order corresponds to 1 and complete disorder to 0, the order ratio is then 0.73 for the cobalt phase and 0.44 for the nickel phase. These values correspond to a macroscopic order degree in the compound.

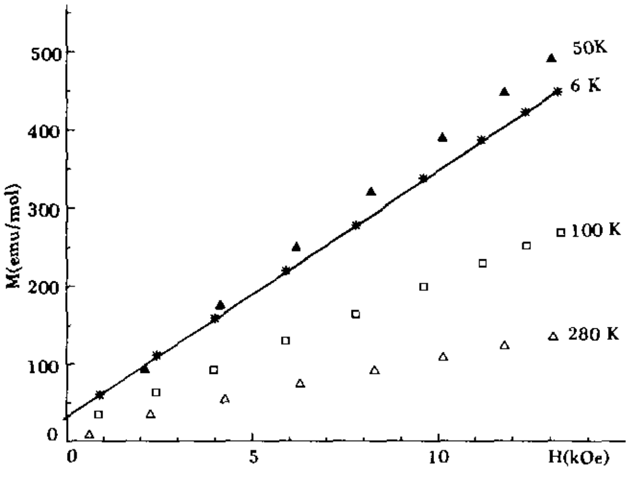

FIG. 6. Magnetization versus magnetic field at different temperatures for $Nb_{0.947}Fe_{0.947}Co_{0.106}O_{3.79}F_{0.21}$. The full line represents the linear fit of the magnetization (see text).

The cationic order has a leading effect on the magnetic properties, since the susceptibility of $Nb_{0.947}Fe_{0.947}Ni_{0.106}O_{3.79}F_{0.21}$ or $Nb_{0.947}Fe_{0.947}Co_{0.106}O_{3.79}F_{0.21}$ is field dependent at low temperatures, contrary to that of ordered $NbFeO_4$ (7). Because of the high value of the order ratio, mainly for the cobalt-containing derivative, the discussion can be based on the magnetic structure of $NbFeO_4$. In $NbFeO_4$, the (100) planes containing iron (plane *A*) alternate with planes containing niobium (plane *B*) (Fig. 1). The magnetic cations are ferromagnetically coupled through octahedra edges in the *A* planes, and antiferromagnetic exchange coupling takes place between these planes. Let us note that no low-dimensional magnetic behavior is observed, although the compound may be described from chain or plane units. In the present oxyfluorides, the magnetic ions which lie in the *B* planes interact with magnetic ions of planes *A* through an apex. Whatever the sign of interaction through the apex may be, the resulting magnetic moment in the ordered state is nonzero. The ferromagnetic components observed at 6 K are of the same order for both phases, although both compounds do not present the same order ratio. It seems difficult to draw conclusions about these values, since magnetization is not saturated at 6 K in the range of the measurements.

The maximum in the alternative susceptibility ($T_c = 35$ K) takes place at lower temperatures than in $NbFeO_4$ ($T_c = 50$ K) (4). The decrease of T_c is assigned to the higher disorder in the oxyfluoride phases with regard to $NbFeO_4$. The reduced maximum observed at 10–20 K is similar to that encountered in disordered $NbFeO_4$ (7). It can be assigned to a local disorder gradient in the compound, the magnetic properties being very sensitive to short-range cationic order. The effect of short-range cationic order is also observable on the Curie constants measured in the temperature range 150–300 K. Indeed, their values are lower than those generally expected, the deviation being more pronounced for the less ordered nickel phase. It can be assigned to the order degree since this phenomenon has already been encountered for $NbFeO_4$, whose Curie constant between 150 and 300 K is 3.61 K·emu/mol for the disordered phase and 4.27 K·emu/mol for the ordered phase.

ACKNOWLEDGMENTS

We thank D. Bizot (Laboratoire de Cristallochimie du Solide Université Paris 6 France) for supplying CoF_2 powder and F. Sapina (Departamento Quimica Inorganica Facultad de Quimicas Burjasot Valencia Spain) for performing alternative susceptibility measurements. This work was partly supported by "Programme d'Action Intégrée Franco–Espagnole 92/230."

REFERENCES

1. R. S. Roth and J. L. Waring, *Am. Mineral.* **49,** 242 (1964).
2. M. Harder and Hk. Muller-Buschbaum, *Z. Anorg. Allg. Chem.* **456,** 99 (1979).
3. A. F. Wells, *in* "Structural Inorganic Chemistry," 5th ed. Clarendon, Oxford, 1984. B. G. Hyde and S. Anderson, *in* "Inorganic Crystal Structures." Wiley–Interscience, New York, 1989.
4. G. Pourroy, A. Malats i Riera, P. Poix, and R. Poinsot, *J. Solid State Chem.* **88,** 476 (1990).
5. W. T. A. Harrison and A. K. Cheetham, *Mater. Res. Bull.* **24,** 523 (1989).
6. H. Weitzel, *Solid State Commun.* **8,** 2071 (1970).
7. G. Pourroy, E. Coronado, and F. Sapina, *J. Alloys Compounds* **188,** 234 (1992).
8. G. Pourroy, P. Poix, and S. Marin, *J. Solid State Chem.* **81,** 112 (1989).
9. G. Pourroy, E. Lutanie, and P. Poix, *J. Solid State Chem.* **86,** 41 (1990).
10. F. Bayi, G. Pourroy, P. Poix, and A. Derory, *J. Solid State Chem.* **100,** 16 (1992).
11. F. Bayi, G. Pourroy, and P. Poix, *Eur. J. Solid State Chem. Inorg. Chem.* **30,** 325 (1993).
12. J. C. Bernier and P. Poix, *Actual. Chim.* **2,** 7 (1978).
13. J. Rodriguez-Carvajal, (ILL) FULLPROF Program FEB90-ILLJRC Original code: D. B. Wiles, R. A. Young, and A. Saktivel. Adaptation for PC software. Data limited to 3100 values.
14. A. K. Cheetham and P. Day, *in* "Solid State Chemistry: Techniques," Clarendon, Oxford, 1988.
15. G. Pourroy, P. Poix, and J. P. Sanchez, *J. Solid State Chem.* **74,** 27 (1988).