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Phase Transition Orthorhombic $\longleftrightarrow$ Rutile in the Oxyfluoride Phases $A_xFe_xNi_{1-x}O_{4x}F_{2(1-x)}$ (A = Nb^{5+}, Ta^{5+}, and $x > 0.3$). Influence on the Magnetic Properties

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Solid solutions between $AFeO_4$ ($A = Nb^{5+}, Ta^{5+}$) and NiF_2 are studied by means of X-ray diffraction, susceptibility, and magnetization measurements. The solid solution $A_xFe_xNi_{1-x}O_{4x}F_{2(1-x)}$ exists for $x > 0.3$, and presents either the rutile structure or the α-PbO_2-type structure. Nb^{5+} and low annealing temperatures favor the latter. Predominant antiferromagnetic interactions characterize all the studied phases except the ordered phase $Nb_{0.9}Fe_{0.9}Ni_{0.1}O_{3.6}F_{0.2}$. This latter phase exhibits a ferromagnetic component below 200 K, and magnetization measurements within the field magnetic range 0–2000 Oe show a metamagnetic transition at about 900 Oe. This peculiar behavior is explained on the basis of the magnetic structure of wolframite $NbFeO_4$. © 1992 Academic Press, Inc.

Introduction

The compounds $NbFeO_4$ and $TaFeO_4$ have been known for several decades. $NbFeO_4$ is reported to have three types of structure: rutile (quadratic; space group $P4_2/mnm$) above 1380°C, of α-PbO_2 type(orthorhombic; space group *Pbcn*) between 1085 and 1380°C, and wolframite (monoclinic; space group *P*2/*c*) below 1085°C (*1*, *2*). $TaFeO_4$ generally crystallizes in the rutile structure under normal conditions of pressure (*3*), while the wolframite form has been pointed out under pressure (*4*). The three structures are characterized by strings of octahedra sharing an edge, straight in the *c* axis in the rutile, staggered along the *c* axis in the two other arrangements (Fig. 1). The wolframite form is an ordered and slightly distorted variant of the α-PbO_2 structure in which every zig-zag chain contains either Fe or Nb atoms.

$NbFeO_4$ and $TaFeO_4$ have been recently synthesized at low temperature using a coprecipitation method (*6*). By annealing the precipitate at temperatures between 700 and 1200°C, different arrangements between the cations have been obtained: either a disordered structure, of rutile type for $TaFeO_4$ and of α-PbO_2 type for $NbFeO_4$, or an ordered arrangement of wolframite structure for $NbFeO_4$. Such transitions between rutile and α-PbO_2-type structures have been also encountered in the solid solutions $xAMO_4 - (1-x)M'F_2$ with $A = Nb^{5+}, Ta^{5+}$, $M = V^{3+}$, Fe^{3+}, and $M' = Zn^{2+}$, Mn^{2+} (*7*, *8*). The rutile structure is preferentially obtained with tantalum and vanadium and the α-PbO_2 arrangement with niobium and iron. In both structures, the phases are antiferro-

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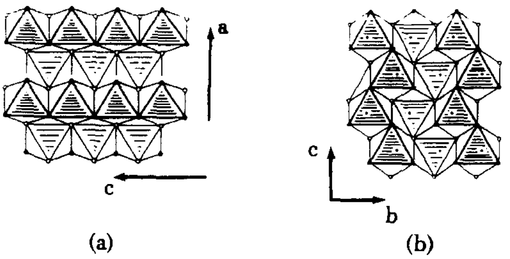

FIG. 1. Schematic representation of rutile (a) and α-PbO_2 (b) structures (after Hyde and Andersson (*5*)).

magnetic. When a cationic order appears in the α-PbO_2 structure, the phase becomes ferromagnetic. We present here the structural and magnetic properties of the phases $xAFeO_4 - (1 - x)NiF_2$ with $A = Nb^{5+}$, Ta^{5+}.

Experimental

Solid solutions between $AFeO_4$ ($A = Nb^{5+}, Ta^{5+}$) and NiF_2 are prepared by using the starting oxides Nb_2O_5, Ta_2O_5, and Fe_2O_3 (*8*). NiF_2 is synthesized as described elsewhere (*9*). A_2O_5 ($A = Nb^{5+}, Ta^{5+}$), Fe_2O_3, and NiF_2, taken in a stoichiometric ratio, are ground together and introduced into a gold crucible. The whole is put into an inconel tube and heated under dried argon. The different thermal treatments are listed in Table I. The temperatures given first are the temperatures for which a total reaction has been observed. Then, the powders are heated at lower or higher temperature in order to modify the crystallographic structure. The phases corresponding to $x = 1$, $TaFeO_4$ and $NbFeO_4$, are prepared as described elsewhere (*6*).

The samples are studied by means of X-ray diffraction and magnetic measurements. X-ray powder diffraction patterns have been taken at room temperature by using a Kristalloflex Siemens diffractometer and cobalt radiation ($\lambda = 1.79026$ Å). Parameters are calculated by using Al_2O_3 as the internal standard. Magnetic measurements are performed with a pendulum-type magnetometer, an ac susceptometer, and a SQUID magnetometer in the temperature range 4.2–300 K. The raw susceptibility data are corrected from diamagnetism values given by Bernier and Poix according to the Slater and Angus method (*10*).

Results

General Characteristics—Limit of Solid Solutions

The solid solutions $xAFeO_4 - (1 - x)NiF_2$ with $A = Ta^{5+}, Nb^{5+}$ are studied for several x values, 0.1, 0.3, 0.5, 0.75, and 0.9. While the mixtures A_2O_5–Fe_2O_3 ($A = Ta^{5+}, Nb^{5+}$) react above 1000°C (*1, 11*), the oxyfluorides reported here are characterized by lower reaction temperatures, all the more low because NiF_2 concentration is great. X-ray diffraction measurements show

TABLE I

THERMAL TREATMENTS AND PHASES DETECTED (R = RUTILE STRUCTURE; O = α-PbO_2 STRUCTURE) FOR DIFFERENT SOLID SOLUTIONS $A_xFe_xNi_{1-x}O_{4x}F_{2(1-x)}$ ($A = Nb^{5+}, Ta^{5+}$). THE MOST IMPORTANT PHASE IS GIVEN FIRST.

x	0.3		0.5		0.75		0.9	
$Ta_xFe_xNi_{1-x}O_{4x}F_{2(1-x)}$	600°C-2d R		650°C-3d R	550°C-3d R + O	700°C-3d R	600°C-2d R + O	700°C-2d R + O	800°C-2d R
$Nb_xFe_xNi_{1-x}O_{4x}F_{2(1-x)}$	650°C-2d R + O	800°C-2d R	700°C-2d R + O	850°C-2d R	700°C-2d O	900°C-2d O + R $+ NiFe_2O_4$	700°C-2d O	

that A_2O_5 and Fe_2O_3 ($A = Ta^{5+}$, Nb^{5+}) always disappear, whatever x may be, while NiF_2 is detected when $x < 0.3$. The phases $A_xFe_x Ni_{1-x}O_{4x}F_{2(1-x)}$ ($x > 0.3$) are isomorphous with the oxyfluoride phases previously synthesized, i.e., they crystallize in the orthorhombic structure of α-PbO_2-type or in the rutile structure (*7*, *8*). Owing to the cation involved, the annealing temperature, and the concentration of NiF_2, either of them or both of them are encountered. When tantalum is involved, pure rutile phases are obtained at high temperatures and a partial transition to the orthorhombic structure is observed for $x = 0.5$, 0.75, and 0.9 at 550, 600, and 700°C, respectively, and not for $x = 0.3$. The transition temperatures are higher in the niobium case: pure orthorhombic samples are obtained at 700°C for $x = 0.75$ and 0.9. Let us note that a cationic order occurs and diffraction lines 100, 011, and 120 show. Nevertheless, pure rutile phases have not been observed for these niobium phases, because the transition temperature is too high and the compounds decompose giving thus a spinel phase which can only be $NiFe_2O_4$, and probably NbF_5 which evolves.

Crystallographic Study of Rutile Phases $Ta_xFe_xNi_{1-x}O_{4x}F_{2(1-x)}$ *($x = 0.3, 0.5, 0.75, 0.9$) and* $Nb_xFe_xNi_{1-x}O_{4x}F_{2(1-x)}$ *($x = 0.3, 0.5$)*

The cell parameters of rutile phases $A_x Fe_xNi_{1-x}O_{4x}F_{2(1-x)}$ ($A = Ta^{5+}$, Nb^{5+} with $x \geq 0.3$) are listed in Table II in addition to those of $TaFeO_4$ and $NbFeO_4$ (1). They present a slight variation in the solid solution domain, are close to the oxide ones, and very different from NiF_2 parameters. Intensities of 21 diffraction lines were measured (among them 17 reflections are independent) for the samples $Ta_{0.9}Fe_{0.9}Ni_{0.1}O_{3.6}F_{0.2}$ and $Nb_{0.5}Fe_{0.5}Ni_{0.5}O_2F$. Their lattice spacings and their corresponding intensities are reported in Tables III and IV, respectively. The intensities have been computed assuming a statistical occupation of the metallic sites (2*a*) and a mean positional parameter u for the anions in site 4*f*. A distinction between the anionic sites has not been taken into account since it does not modify the intensities to a great extent. The very weak 120 diffraction line has been eliminated from the calculation. The best agreement between the experimental and calculated in-

TABLE II

LATTICE PARAMETERS OF PURE OXYFLUORIDE PHASES $A_xFe_xNi_{1-x}O_{4x}F_{2(1-x)}$ ($A = Ta^{5+}$, Nb^{5+}) (R = Rutile Structure; O = α-PbO_2 STRUCTURE; W = WOLFRAMITE SURSTRUCTURE)

Compound	x	Structure	a(nm) (±0.0005)	b(nm) (±0.0005)	c(nm) (±0.0005)	β	V (nm³ · 10³/mol)
$Ta_xFe_xNi_{1-x}O_{4x}F_{2(1-x)}$	1.0(4)	R	0.468_2		0.304_8		33.4
	0.9	R	0.468_3		0.305_3		33.5
	0.75	R	0.468_3		0.305_9		33.6
	0.5	R	0.468_2		0.305_8		33.4
	0.3	R	0.468_2		0.306_0		33.6
$Nb_xFe_xNi_{1-x}O_{4x}F_{2(1-x)}$	1.0 (1)	W	0.465_3	0.562_0	0.500_1	89,84°	32.7
	0.9	O	0.464_6	0.562_3	0.500_8		32.7
	0.75	O	0.464_7	0.562_3	0.501_7		32.8
	1.0 (1)	R	0.469_4		0.304_3		33.5
	0.5	R	0.469_2		0.305_5		33.6
	0.3	R	0.469_0		0.305_6		33.6
NiF_2	0.0 (9)	R	0.464_6		0.308_5		33.3

TABLE III

EXPERIMENTAL AND CALCULATED LATTICE SPACINGS AND DIFFRACTION LINE INTENSITIES OF THE RUTILE PHASE $Ta_{0.9}Fe_{0.9}Ni_{0.1}O_{3.6}F_{0.2}$ (SPACE GROUP $P4_2/mnm$)

hkl	d_{obs}	I_{obs}	d_{calc}	I_{calc}
110	3.308	100	3.311	100
011	2.553	72	2.558	71
200	2.340	19	2.342	21
111	2.242	4	2.245	4
120	2.093	2	2.094	2
121	1.726	63	1.727	60
220	1.655	15	1.656	14
002	1.522	6	1.527	6
130	1.479	14	1.481	13
301	1.388	31	1.389	13
112	1.383		1.386	16
202	1.278	8	1.280	7
231	1.194	13	1.195	13
400	1.170	5	1.171	4
222	1.122	10	1.122	8
330	1.103	5	1.104	4
141	1.063	30	1.064	14
132	1.063		1.063	13
240	1.046	6	1.047	7
103	0.992	8	0.994	7
402	0.929	10	0.929	11

tensities of diffraction lines is given by the smallest reliability factor,

$$R = \sum \mid I_{calc} - I_{obs} \mid / \sum I_{obs}.$$

The smallest values $R = 5\%$ and $R = 4\%$ have been obtained with $u = 0.300 \pm 0.005$ and $u = 0.298 \pm 0.005$ for the tantalum and niobium phases, respectively.

Crystallographic Study of Orthorhombic Phases $Nb_xFe_xNi_{1-x}O_{4x}F_{2(1-x)}$ ($x = 0.75$ and 0.9)

The orthorhombic phases $Nb_{0.9}Fe_{0.9}Ni_{0.1}O_{3.6}F_{0.2}$ and $Nb_{0.75}Fe_{0.75}Ni_{0.25}O_3F_{0.5}$ are isomorphous of $NbFeO_4$, respectively. The cell parameters are reported in Table II and the lattice spacings and their corresponding intensities are reported in Table V for the phase $Nb_{0.9}Fe_{0.9}Ni_{0.1}O_{3.6}F_{0.2}$. This diffraction pattern is similar to the ordered $NbFeO_4$ one, i.e., the reflections 100 and 011 forbidden in the α-PbO_2 structure are not zero in our case. The latter disappear in the diffraction pattern of the niobium phase $x = 0.75$, isomorphous to α-PbO_2. As their intensities are very weak, these reflections have been eliminated from the computations. So, the intensities of 46 reflections have been calculated assuming a statistical distribution of the cations and the anions on sites $4c$ and $8d$, respectively. The smallest reliability factor $R = 7\%$ has been obtained for the positional parameters

Cations: $x = 0$, $y = .174$, $z = 0.250$
Anions: $x = 0.260$, $y = 0.390$, $z = 0.420$.

TABLE IV

EXPERIMENTAL AND CALCULATED LATTICE SPACINGS AND DIFFRACTION LINE INTENSITIES OF THE RUTILE PHASE $Nb_{0.5}Fe_{0.5}Ni_{0.5}O_2F$ (SPACE GROUP $P4_2/mnm$)

hkl	d_{obs}	I_{obs}	d_{calc}	I_{calc}
110	3.312	100	3.310	100
011	2.560	55	2.554	58
200	2.345	10	2.340	10
111	2.247	12	2.242	12
120	2.099	4	2.091	3
121	1.729	52	1.725	52
220	1.658	13	1.653	14
002	1.527	6	1.525	6
130	1.484	9	1.480	9
301	1.390	25	1.390	15
112	1.390		1.385	10
202	1.280	4	1.280	4
231	1.197	6	1.193	6
400	1.173	3	1.170	3
222	1.124	7	1.121	6
330	1.106	4	1.102	3
141	1.067	15	1.063	8
132	1.063		1.062	7
240	1.047	3	1.045	4
103	0.994	4	0.993	3
402	0.930	6	0.931	7

TABLE V

EXPERIMENTAL AND CALCULATED LATTICE SPACINGS AND DIFFRACTION LINE INTENSITIES OF THE ORTHORHOMBIC PHASE $Nb_{0.9}Fe_{0.9}Ni_{0.1}O_{3.6}F_{0.2}$ (SPACE GROUP *Pbcn*)

hkl	d_{obs}	I_{obs}	d_{calc}	I_{calc}
100	4.645	1	4.646	0
011	3.733	1	3.740	0
110	3.578	28	3.582	26
111	2.911	100	2.913	100
020	2.809	7	2.812	7
002	2.503	12	2.504	12
021	2.450	12	2.452	14
120	2.387	<1	2.405	0
200	2.322	53	2.323	51
102	2.203	15	2.204	4
121	2.167	0	2.168	8
112	2.052	9	2.052	9
211	1.972	<1	1.973	<1
022	1.870	7	1.870	7
220	1.790	6	1.791	6
130	1.738	13	1.738	14
202	1.703	42	1.703	18
221	1.686	0	1.686	24
113	1.514	12	1.513	14
310	1.493		1.493	1
222	1.457	4	1.457	4
023	1.440		1.435	9
311	1.429	34	1.431	12
132	1.429		1.428	14
040	1.405	1	1.406	1
041	1.353	5	1.353	6
302	1.319	1	1.319	1
321	1.310	<1	1.310	<1
312	1.283	3	1.282	2
141	1.283		1.299	<1
232	1.253	2	1.260	<1
004	1.253		1.252	2
223	1.221	2	1.221	2
042	1.221		1.226	<1
330	1.194		1.194	4
322	1.194		1.193	<1
114	1.184	20	1.182	2
241	1.170		1.170	7
400	1.162		1.162	4
331	1.161		1.161	<1
313	1.114		1.113	6
124	1.114		1.111	<1
411	1.103	13	1.109	<1
204	1.103		1.102	5
150	1.093		1.093	2
332	1.078	12	1.078	8
043	1.076		1.075	3
421	1.051	4	1.050	4

Magnetic Properties

In order to avoid the presence of little amounts of NiF_2, invisible in the X-ray diffraction pattern and which could distort the physical properties, the magnetic studies have been performed on the phases $x = 0.5$, 0.75, and 0.9. Two different magnetic behaviors have been pointed out in these phases owing to the crystallographic order. The disordered phases, the rutile $Ta_xFe_xNi_{1-x}O_{4x}F_{2(1-x)}$ ($x = 0.5$, 0.75, and 0.9), $Nb_{0.5}Fe_{0.5}Ni_{0.5}O_2F$, and the orthorhombic $Nb_{0.75}Fe_{0.75}Ni_{0.25}O_3F_{0.5}$ are characterized by an increasing susceptibility when T decreases and experimental Curie constants between 200 and 300 K far below the theoretical ones (Table VI). No susceptibility maximum is observed, but the negative Weiss temperatures suggest that antiferromagnetic interactions are dominant (Fig. 2). The ordered niobium phase $Nb_{0.9}Fe_{0.9}Ni_{0.1}O_{3.6}F_{0.2}$ is characterized by a field-dependent susceptibility. A ferromagnetic component appears below 150 K, in agreement with the maximum of χT product when the measurements are performed at an H value of 3000 Oe (Fig. 3). Ac susceptibility measured versus temperature is characterized by broad maxima at 40 and 15 K (Fig. 4). At 4.2 K, the first magnetization curve at low field exhibits a threshold field between 600 and 900 Oe (Fig. 5).

TABLE VI

THEORETICAL AND EXPERIMENTAL CURIE CONSTANTS FOR PURE $A_xFe_xNi_{1-x}O_{4x}F_{2(1-x)}$ PHASES WITH $A = Ta^{5+}$, Nb^{5+} WHOSE SUSCEPTIBILITY IS NOT FIELD DEPENDENT

$A_xFe_xNi_{1-x}O_{4x}F_{2(1-x)}$	x	Structure	C_{th}	C_{exp}	θ(K)
$Ta_xFe_xNi_{1-x}O_{4x}F_{2(1-x)}$	1.0	Rutile	4.375	3.1	354
	0.9	Rutile	4.038	3.30	335
	0.75	Rutile	3.531	3.03	246
	0.5	Rutile	2.688	2.35	250
$Nb_xFe_xNi_{1-x}O_{4x}F_{2(1-x)}$	1.0	Wolframite	4.375	4.27(1)	92(1)
	0.75	α-PbO_2	3.531	3.15	127
	0.5	Rutile	2.688	1.78	146

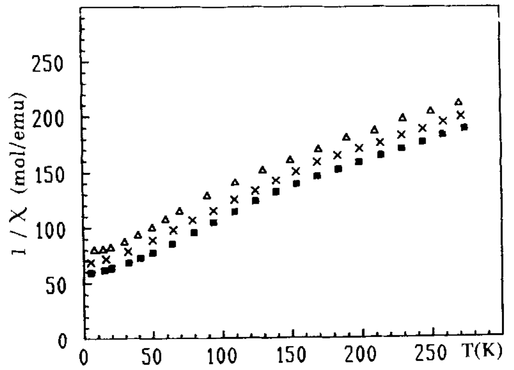

FIG. 2. Variation of inverse susceptibility versus temperature for the rutile phase $Ta_xFe_xNi_{1-x}O_{4x}F_{2(1-x)}$ (x = 0.9 (■), 0.75 (×), and 0.5 (△) measured with H = 14,000 Oe.

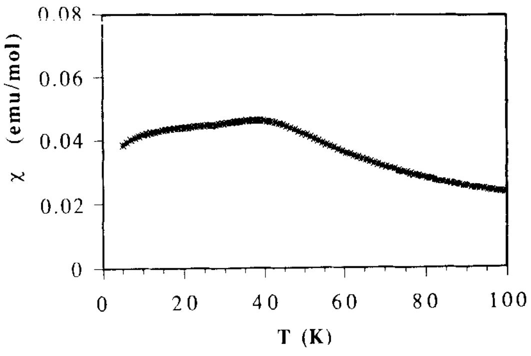

FIG. 4. Ac susceptibility measurements versus temperature for the phase $Nb_{0.9}Fe_{0.9}Ni_{0.1}O_{3.6}F_{0.2}$.

Discussion

The mixtures A_2O_5 (A = Ta^{5+}, Nb^{5+}), Fe_2O_3, and NiF_2 react below 900°C, giving pure phases of rutile, or α-PbO_2 structures. Comparing the reaction temperature between the oxides A_2O_5 and Fe_2O_3 which is more than 1000°C, it can be concluded that the fluoride NiF_2 decreases the reaction temperature. This can be assigned to the formation of an intermediate gaseous phase, TaF_5 or NbF_5, which is very reactive toward the solids. Furthermore, the formation of NbF_5 may explain the partial decomposition observed when the ordered and disordered orthorhombic phases, $Nb_{0.9}Fe_{0.9}Ni_{0.1}O_{3.6}F_{0.2}$ and $Nb_{0.75}Fe_{0.75}Ni_{0.25}O_3F_{0.5}$, respectively, are annealed above 900°C in order to observe their transformation into the rutile structure.

The phases $A_xFe_xNi_{1-x}O_{4x}F_{2(1-x)}$ (A = Ta^{5+}, Nb^{5+}) exist only when $x > 0.3$, showing that the oxides cannot be dissolved in the fluoride. In other words, the oxides $AFeO_4$(A = Ta^{5+}, Nb^{5+}) accept fluorine in their crystallographic lattice, while the reverse is impossible. This is in agreement with the variation of crystallographic pa-

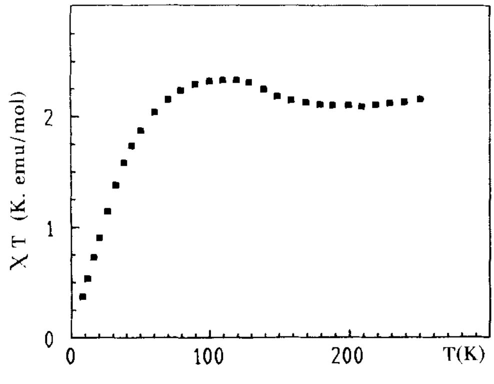

FIG. 3. Variations of χT product versus temperature for the phase $Nb_{0.9}Fe_{0.9}Ni_{0.1}O_{3.6}F_{0.2}$ for a magnetic field H = 3000 Oe.

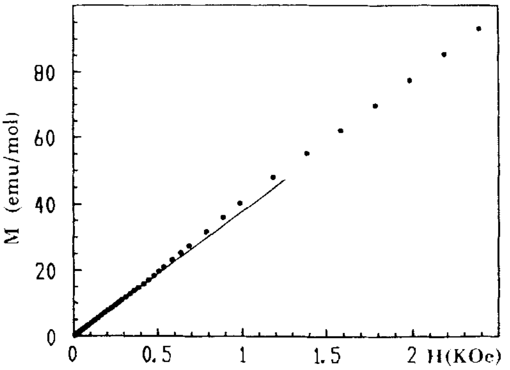

FIG. 5. First magnetization curve versus magnetic field for $Nb_{0.9}Fe_{0.9}Ni_{0.1}O_{3.6}F_{0.2}$ at 4.2 K.

rameters in the solid solution domain. Although the solid solution domain is extended, the cell parameters do not change a lot all along the domain of solid solution. They keep almost constant values, close to the oxides ones, until the limit of solubility is reached. The cell parameters of fluoride NiF_2 are very different from those of the oxides (the c/a ratios show that NiF_2 presents two short and four long distances and that the opposite is observed for the oxides) and a strong jump is observed between cell parameters of NiF_2 and the limit phase $x = 0.3$. Furthermore, the difference between the sizes of Ni^{2+} on one hand and Fe^{3+}, Ta^{5+}, Nb^{5+} on the other hand may prevent the existence of a total solid solution. While the three latter have equivalent characteristic distances in an octahedral environment, 2.016, 2.012, and 2.020 Å, respectively, Ni^{2+} is slightly bigger (2.088 Å) (*12*). It must be noted that when Mn^{2+} or Zn^{2+} (characteristic distances 2.220 and 2.141 Å) are substituted for Ni^{2+}, the solid solution domain gets narrower (*7, 8*).

The refinement of diffraction lines intensities confirms the rutile and orthorhombic structures. For the phase $Nb_{0.9}Fe_{0.9}Ni_{0.1}O_{3.6}F_{0.2}$, the computation has been performed, assuming a zero value for the lines 100, 011, and 120. The good agreement between the calculated and observed values shows that the structure is basically of α-PbO_2 type. The emergence of the lines 100, 011, and 120, characteristic of the wolframite surstructure, is related to a crystallographic order between the metallic ions. The order is of the same type as in $NbFeO_4$, i.e., due to the different electronic charges, the niobium ions and the magnetic cations do not belong to the same site. However, as niobium ions are less numerous than the magnetic cations, the site occupation is probably the following: one site contains Ni^{2+} and Fe^{3+} and the other Nb^{5+} and few Fe^{3+}.

Within the domain of the solid solutions, the oxyfluoride phases present two types of structure as it has been pointed out before, a rutile structure and an orthorhombic structure, which are the high and the low temperature structure, respectively (*7, 8*). Owing to the concentration of NiF_2 and the cations involved, niobium and tantalum, three cases are encountered: a pure rutile structure, a pure orthorhombic structure, or a mixture of both structures. However, the orthorhombic structures are obtained at lower temperatures in the niobium case than in the tantalum case; in other words, Nb^{5+} favors the orthorhombic arrangement. This is consistent with the previous results obtained in the similar oxyfluoride phases containing Zn^{2+} in place of Ni^{2+} (*8*). Such a difference between the crystallographic structures of niobium- and tantalum-containing phases is well known, and has been already encountered for $NiTa_2O_6$ of trirutile structure and $NiNb_2O_6$ of columbite structure, surstructure of the α-PbO_2 one (*13, 14*). Moreover, the stability domain of each structure with regard to the synthesis temperature changes when the concentration of NiF_2 increases, i.e., the temperatures for which the orthorhombic structure is stable decrease. That means that the rutile arrangement is stabilized either by Ni^{2+} or F^- (*15*).

Two different magnetic behaviors are encountered, either a field-dependent magnetic susceptibility or not. The cationic order seems to be the striking fact, much more than the type of structure. Indeed, the disordered phases, rutile or orthorhombic, are characterized by predominant antiferromagnetic interactions since the Weiss temperatures calculated in the range 200–300 K are negative. Furthermore, the highest values are found in the tantalum case, showing that the magnetic interactions are stronger when Ta^{5+} is involved. This difference can be explained by a greater covalency of tantalum with regard to that of niobium, allowing an easier exchange between magnetic ions. Despite these predominant antiferromagnetic interactions, the susceptibility does not exhibit a maximum in the temperature range 4.2–300 K. The maximum observed at 10 K for $TaFeO_4$ disappears for the oxyfluoride phases, probably because the nickel introduced causes a supplementary disorder (*6*). The behavior of the orthorhombic $Nb_{0.75}Fe_{0.75}Ni_{0.25}O_3F_{0.5}$ is in agreement with the recent study of $NbFeO_4$ of α-PbO_2 structure for which no magnetic structure has been observed above 4.2 K (*16*). The behavior of the ordered orthorhombic niobium phase $Nb_{0.9}Fe_{0.9}Ni_{0.1}O_{3.6}F_{0.2}$ is quite different, since the magnetic susceptibility is field-dependent below 200 K. At 4.2 K, the first magnetization curve exhibits a threshold field characteristic of a metamagnetic phase, and a ferromagnetic component appears when the applied field is greater than 1000 Oe. An attempt to explain this astonishing behavior can be done, considering the magnetic structure of $NbFeO_4$ of wolframite structure. The planes (100) are made up of ferromagnetic Fe^{3+} chains in which the iron ions are center of edge-sharing octahedra. These ferromagnetic chains are ferromagnetically coupled within the plane (100), the planes being antiferromagnetically coupled through niobium octahedra (*17*). In the oxyfluoride phase, the diamagnetic layers contain some magnetic ions, as they are in excess with regard to the niobium ions. Assuming different signs for intrachain (through an edge) and interchain (through an apex) exchange interactions, the presence of magnetic cations between two magnetic layers would disturb the antiferromagnetic coupling of these layers, being thus responsible of the emergence of a ferromagnetic component below 200 K. Moreover, because of these defects, the tridimensional transition is not so sharp as in $NbFeO_4$. If Ni^{2+} is not statistically distributed within the phase, the tridimensional order does not occur at the same temperature in every part of the material. The transition at 45 K may be related to the tridimensional order in $NbFeO_4$ (T = 50 K), thus to a phase containing few Ni^{2+}. The second broad maxima at about 15 K in the ac susceptibility may be the consequence of the presence of a more disordered phase, with more defaults, so more Ni^{2+}. This may also explain the extended magnetic field range of the metamagnetic transition.

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