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Relation between Structural and Magnetic Properties of $Nb_{0.94}Fe_{1.06}O_{3.76}F_{0.24}$

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The oxyfluoride phases xNbFeO$_4$–$(1 - x)$FeF$_2$ have been synthesized. They exist in a limited range $0.8 < x < 1$. They are isomorphous with NbFeO$_4$, having the wolframite structure. The refinement of the crystallographic structure of the oxyfluoride phase $Nb_{0.94}Fe_{1.06}O_{3.76}F_{0.24}$ using a Rietveld method has pointed out a partial cationic disorder between niobium and iron. The consequence of incomplete order is a field-dependent magnetic susceptibility at low temperatures. Ac susceptibility measurements versus temperature exhibit a maximum at 35 K. Mössbauer measurements show that the valence is localized.

Introduction

Rutile structure, which is one of the most common structure of oxides and fluorides, is known to present a superstructure when two different metallic cations are involved. $CoTa_2O_6$, $NiTa_2O_6$, WV_2O_6, LiV_2F_6, and $LiFe_2F_6$ crystallize in the trirutile superstructure with a 1/2 order between the cations along the *c* axis (*1–4*). With regard to the magnetic properties, cobalt and nickel are isolated in the former, while the three latter are made up of magnetic dimers separated by diamagnetic ions. The fluorides have the interesting peculiarity of exhibiting dimers of the same cation with two different oxidation degrees: V^{II}–V^{III} and Fe^{II}–Fe^{III}. However, the extra electron is not delocalized between the metallic sites (*4*). Because of the different electronic charges on oxygen and fluorine, oxyfluoride compounds have a favorable configuration to stabilize the same cation at two different oxidation degrees. Due to their related structures, $NbFeO_4$ and FeF_2 can form solid solutions. Indeed, $NbFeO_4$ is reported to have three types of structure, rutile (quadratic, space group $P4_2/mnm$) above 1380°C, α-PbO_2 type (orthorhombic, space group *Pbcn*) between 1085 and 1380°C, and wolframite (monoclinic, space group $P2/c$) below 1085°C (*5, 6*); FeF_2 crystallizes in the rutile structure (*7*). The system $NbFeO_4$–FeF_2 may thus offer possibilities of obtaining mixed valence compounds. We report here the crystallographic structure and magnetic properties of the phase $Nb_{0.94}Fe_{1.06}O_{3.76}F_{0.24}$.

Experimental

The starting compounds Nb_2O_5, Fe_2O_3, and FeF_2 were prepared as described elsewhere (*8–12*). Stoichiometric mixtures of Nb_2O_5, Fe_2O_3, and FeF_2 were ground and introduced into a gold crucible. The whole was put into an inconel tube and heated under flowing dried argon at 700°C for 2 days.

The samples were studied by X-ray diffraction and magnetic measurements. X-ray diffraction data were collected at room temperature using a D500 Kristalloflex Siemens diffractometer equipped with a primary

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beam quartz monochromator ($CoK\alpha_1$ = 1.78897 Å). Magnetic measurements were performed with a pendulum type magnetometer and an ac susceptometer operating at 333 Hz with H = 10 Oe in the temperature range 4.2–300 K. The raw susceptibility data were corrected for diamagnetism values according to the Slater and Angus method (*13*). ^{57}Fe Mössbauer spectra were recorded at room temperature using conventional mechanical drives synchronized with multichannel analyzer operating in multiscaling mode.

Results

Several compositions between $NbFeO_4$ and FeF_2 have been studied. It appears that the solid solution $x$$NbFeO_4$–$(1 - x)$$FeF_2$ exists only for $0.8 < x < 1$; i.e., FeF_2 dissolves into $NbFeO_4$. The reverse has not been observed. All the phases with $0.8 < x < 1$ are isomorphous with $NbFeO_4$, having the wolframite structure, and present similar magnetic properties. The results are given for $Nb_{0.94}Fe_{1.06}O_{3.76}F_{0.24}$ corresponding to the composition $x = 0.9$.

Crystallographic Study

The wolframite structure has been taken as a starting model for the crystallographic study. This structure, whose space group is *P2/c*, is schematically represented in Fig. 1 for $NbFeO_4$. The octahedra sharing edges from zigzag chains in the c direction. The (a, b) planes are connected together through octahedra apices. In $NbFeO_4$, the successive (b, c) planes contain either iron or niobium, which gives rise to two different crystallographic sites, (2*f*) and (2*e*) respectively, in the space group *P2/c*. When a unique cation occupies both sites, the structure is of α-PbO_2 type (space group *Pbcn*).

The X-ray diffraction pattern has been refined by the Rietveld method, using the Fullprof program (*14*). A pseudo-Voigt function was chosen for the representation of the individual reflection profiles. The cationic distribution on both sites has been refined. The scattering factors for ions were used, taking into account the anomalous dispersion. The contributions of Fe^{2+}, its scattering factor and concentration, have not been distinguished from those of Fe^{3+}. A similar approximation was used for oxygen and fluorine. Thus, the formulation for the composition $x = 0.9$ may be expressed as $Nb_{0.94}Fe_{1.06}O_4$ with $Z = 2$. Because of partial cationic disorder, the thermal parameters of iron and niobium have been assumed to be identical. The details of the Rietveld profile refinement for $Nb_{0.94}Fe_{1.06}O_{3.76}F_{0.24}$ are given in Table I, final atomic parameters in Table II, and bond lengths in Table III. Figure 2 shows the experimental and calculated X-ray diffraction pattern of $Nb_{0.94}Fe_{1.06}O_{3.76}F_{0.24}$.

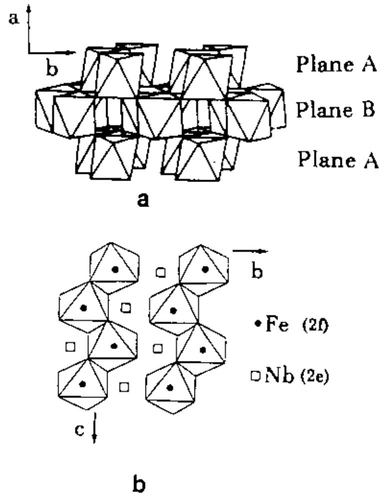

FIG. 1. Schematic representation of α-PbO_2 structure. (b) Cationic order in the $NbFeO_4$ wolframite arrangement.

Magnetic Properties

The thermal variation of susceptibility of phase $Nb_{0.94}Fe_{1.06}O_{3.76}F_{0.24}$ is displayed in Fig. 3 for two different magnetic fields, 6 and 14 kOe. Its magnetic susceptibility is field-dependent below 120 K. The susceptibility exhibits a maximum in the temperature range 20–50 K. Magnetization versus

TABLE I

DETAILS OF RIETVELD REFINEMENT FOR $Nb_{0.94}Fe_{1.06}O_{3.76}F_{0.24}$ IN THE SPACE GROUP $P2/c$

a	4.6504(2)
b	5.6219(2)
c	5.0079(2)
β	90.04(2)
V	130.926(8)
Z	2
Space group	$P2/c$
2θ range	15–105
Step scan increment (°2θ)	0.03
No. of reflections	95
No. of profile parameters	13
$R_F = \Sigma \lvert I_o^{1/2} - I_c^{1/2}\rvert / \Sigma I_o^{1/2}$	0.0339
$R_B = \Sigma \lvert I_o - I_c\rvert / \Sigma I_o$	0.0304
$R_p = \Sigma \lvert y_i - y_{ic}\rvert / \Sigma y_i$	0.138
$R_{wp} = [\Sigma w_i(y_{io} - y_{ic})^2 / \Sigma w_i y_{io}]^{1/2}$	0.164
R_{ewp}	0.0952

TABLE III

CATION–ANION DISTANCES IN Å FOR $Nb_{0.94}Fe_{1.06}O_{3.76}F_{0.24}$ COMPARED WITH THOSE OF $NbFeO_4$

Site	$Nb_{0.94}Fe_{1.06}O_{3.8}F_{0.24}$	$NbFeO_4$(6)
(2*f*)		
d(Cation–Anion$_I$):	1.914(17)	1.927
d(Cation–Anion$_{II}$):	2.143(18)	2.115
d(Cation–Anion$_{II}$):	2.000(12)	2.014
(2*e*)		
d(Cation–Anion$_I$):	2.006(13)	2.008
d(Cation–Anion$_I$):	2.122(20)	2.161
d(Cation–Anion$_{II}$):	1.906(15)	1.858

magnetic field measured at several temperatures is presented in Fig. 4. A ferromagnetic component is easily observable at 100 K. At 10 K, the linear part of magnetization, $\sigma = f(H)$, is written $\sigma = 0.0320\, H + 33.40$. Ac susceptibility measurements performed in the temperature range 4.2–150 K reveal one maximum at 35 K (Fig. 5).

Mössbauer Study

The ^{57}Fe Mössbauer spectrum of $Nb_{0.94}Fe_{1.06}O_{3.76}F_{0.24}$ recorded at 300 K is shown in Fig. 6. It presents two main slightly asymmetric Mössbauer lines plus a weak resonance at about 2.5 mm/sec. Assuming Lorentzian line shapes, the spectrum is satisfactorily analyzed as a superposition of two broadened quadrupole doublets indicating the presence of Fe^{3+} ions (88.4%) and Fe^{2+} ions (11.6%). The isomer shifts (δ_{IS}) and quadrupole splitting (ΔEQ) characterize ions in octahedral coordination ($Fe^{3+} : \delta_{IS} = 0.59$ mm/sec vs Fe and $\Delta EQ = 0.6$ mm/sec; $Fe^{2+} : \delta_{IS} = 1.25$ mm/sec vs Fe and $\Delta EQ = 2.5$ mm/sec).

Discussion and Conclusions

While the formation of $NbFeO_4$ from Nb_2O_5 and Fe_2O_3 requires temperatures higher than 1000°C, the oxyfluoride phase $Nb_{0.94}Fe_{1.06}O_{3.76}F_{0.24}$ is obtained at 700°C. Therefore, the presence of a small amount of FeF_2 strongly decreases the reaction temperature. This has been previously assigned to the formation of NbF_5 as intermediate

TABLE II

CRYSTALLOGRAPHIC POSITIONS, ISOTROPIC THERMAL FACTORS, AND OCCUPATION RATE IN THE WOLFRAMITE CELL OF $Nb_{0.94}Fe_{1.06}O_{3.76}F_{0.24}$ (SPACE GROUP $P2/c$)

Atoms		x	y	z	B(Å^2)	Site occupation
Fe	(2f)	0.5	0.6759(11)	0.215	1.032(48)	1.463(19)
Nb	(2f)	0.5	0.6759(11)	0.215	1.032(48)	0.537(19)
Nb	(2e)	0.	0.1741(9)	0.215	1.032(48)	1.363(19)
Fe	(2e)	0.	0.1741(9)	0.215	1.032(48)	0.637(19)
O_I	(4g)	0.7677(17)	0.113(3)	0.9176(22)	0.82(25)	4.0
O_{II}	(4g)	0.7286(18)	0.378(4)	0.41895(26)	0.90(25)	4.0

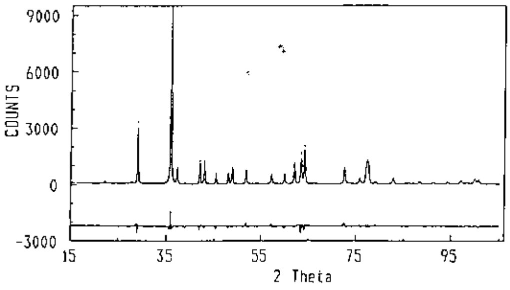

FIG. 2. Observed (· · ·) and calculated (—) X-ray powder diffraction profile of $Nb_{0.94}Fe_{1.06}O_{3.76}F_{0.24}$. The difference profile appears below at the same scale.

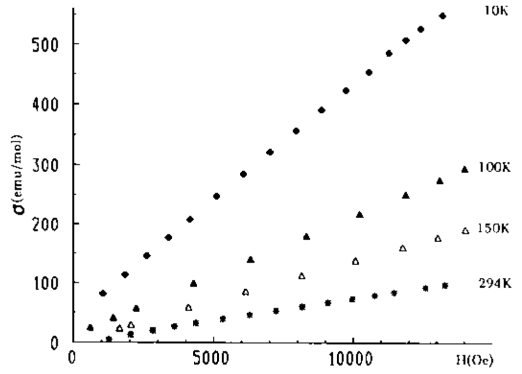

FIG. 4. Magnetization versus magnetic field at different temperatures for $Nb_{0.94}Fe_{1.06}O_{3.76}F_{0.24}$.

compound (*9–12*). This phase is gaseous and increases the reaction rate. However, the formation of NbF_5 could result in a decomposition of the oxyfluoride phase and the formation of ferrimagnetic impurities (*15*). Such a decomposition is ruled out, since susceptibility is not field-dependent at room temperature.

The solubility limit l of FeF_2 in $NbFeO_4$ can be assigned to the discrepancy between the sizes of Nb^{5+} and Fe^{3+} on one hand ($d(Nb^{5+}–O)_6$ = 2.020 Å and $d(Fe^{3+}–O)_6$ = 2.016 Å), and that of Fe^{2+} on the other hand ($d(Fe^{2+}–O)_6$ = 2.150 Å) (*16*). In previous work, it has been shown that the solubility domain is increased when Fe^{2+} is substituted for Ni^{2+} (l = 0.3) or Zn^{2+} (l = 0.75), and is decreased when Mn^{2+} is involved (l = 0.82). In other words, when M^{2+} size increases, the solubility domain decreases.

The X-ray diffraction pattern has been successfully refined in the $P2/c$ space group. However, while in $NbFeO_4$ the sites $2e$ and $2f$ are occupied by niobium and iron, respectively, a partial ordering occurs in $Nb_{0.94}Fe_{1.06}O_{3.76}F_{0.24}$. The site $2e$ contains mainly niobium (72% of total niobium), but also iron. The reverse is observed for the site $2f$. However, we must bear in mind that these values are mean values and that the phase can be made up of two phases, one very ordered and the other disordered.

Although the phase $Nb_{0.94}Fe_{1.06}O_{3.76}F_{0.24}$ contain Fe^{II} and Fe^{III} occupying identical crystallographic sites, an intermediate va-

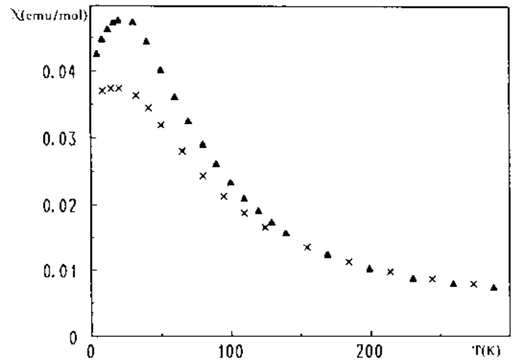

FIG. 3. Thermal variation of magnetic susceptibility for $Nb_{0.94}Fe_{1.06}O_{3.76}F_{0.24}$ (H = 14 kOe (×), H = 6 kOe (—).

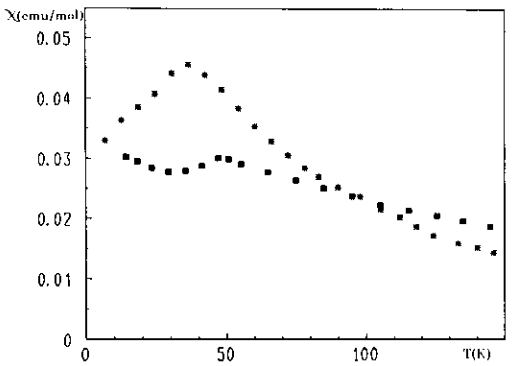

FIG. 5. Thermal variation of ac susceptibility for $NbFeO_4$ (■) and $Nb_{0.94}Fe_{1.06}O_{3.76}F_{0.24}$ (*).

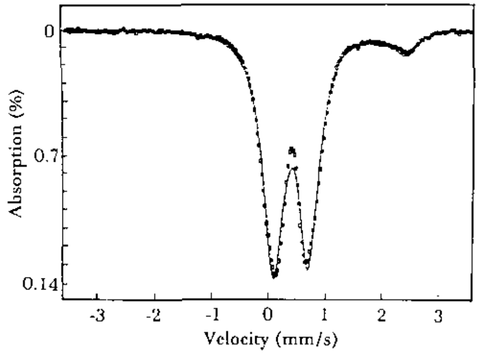

FIG. 6. ^{57}Fe Mössbauer spectra of $Nb_{0.94}Fe_{1.06}O_{3.76}F_{0.24}$ at 300 K.

lence has not been revealed by the Mössbauer spectroscopy. However, the concentration of Fe^{III} and Fe^{II} calculated from the spectra is in agreement with their respective concentration in the starting compound, confirming the purity of the compound.

The magnetic properties of $Nb_{0.94}Fe_{1.06}O_{3.8}F_{0.24}$ are field-dependent under 120 K, as are those of the other oxyfluoride phases of wolframite structure (*9–11*). This property can be explained on the basis of the structure of $NbFeO_4$. In $NbFeO_4$, the (100) planes containing iron (plane *A*) alternate with planes containing niobium (plane *B*) (Fig. 1). They are ferromagnetic and antiferromagnetically coupled (*17*). In $Nb_{0.94}Fe_{1.06}O_{3.76}F_{0.24}$, the magnetic ions which lie in the *B* planes interact with the magnetic ions of the *A* planes through an apex. Whatever the sign of interaction may be, the resulting magnetic moment in the ordered state is nonzero. The maximum of alternative susceptibility at 35 K has to be related to that encountered at 50 K in $NbFeO_4$ (*17*). The decrease of Néel temperature with regard to $NbFeO_4$ is assigned to the partial disorder. Nevertheless, only the determination of magnetic structure would allow to give definitive conclusions about the magnetic behavior.

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