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^{57}Fe Mössbauer Investigation on Doped Nickelates $ANiO_3$ (A = Y, Lu, Tl)

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$ANi(III)O_3$ perovskites (A = rare earth with A ≠ La), have been prepared under high oxygen pressure.[1] Their electronic properties are correlated with the structural distortion, in particular the Ni−O−Ni angle, decreasing from Pr^{3+} to Lu^{3+}. Metal−insulator (MI) transition has been revealed in these $ANiO_3$ perovskites,[2] and the corresponding transition temperature T_{MI} rises systematically as the rare-earth size becomes smaller. Recent spectroscopic measurements indicate that the degree of hybridization between Ni 3d and O 2p orbitals is extremely high, the ground-state being described as a mixing between two formal states $3d^7\ 2p^6$ and $3d^8L$ (L corresponding to an electron hole on oxygen ($2p^5$) [$\varphi = \alpha(3d^7\ 2p^6) + \beta\ (3d^8L)$]).[3] The magnetic properties were first analyzed as an antiferromagnetic ordering for $YNiO_3$ and $LuNiO_3$.[1] According to recent neutron diffraction studies, the large A members (A = Pr−Eu) have an orthorhombic structure at 300 K, which is stable across T_{MI}, and they show an unusual antiferromagnetic order with a complex magnetic structure below T_N.[4] On the other hand, for the small A members (A = Y, Ho−Lu), a small monoclinic distortion has been pointed out at $T < T_{MI}$ with two hexacoordinated Ni^{3+} sites in the perovskite lattice leading to the $P2_1/n$ space group. Such a structural distortion, implying two different Ni−O bonds: Ni(1)−O and Ni(2)−O, has been correlated with a charge disproportionation $2Ni^{3+} \rightarrow Ni^{(3+\alpha)+} + Ni^{(3-\alpha)+}$ phenomenon.[5]

Very recently, the $TlNiO_3$ oxide has been prepared to evaluate the role of the A cations (in particular the A−O bond) on the structural distortion of the $ANiO_3$ perovskite lattice.[6]

The unit-cell volume of $TlNiO_3$, larger than that expected from the V versus $r(A^{3+})$ plot for other $ANiO_3$ (A = rare earth and yttrium), is induced by different coordination environments around Tl^{3+}. $TlNiO_3$ has the lowest T_N (104 K) among all the perovskites, although the superexchange Ni−O−Ni angle (147.6°) is very similar with that observed in $YNiO_3$ (Ni−O−Ni angle = 147.3° and T_N = 153 K). Such structural and magnetic behaviors have been attributed to the strongly covalent Tl^{3+}−O bond leading to a weaker Ni−O orbital hybridization. To examine the local structure of Ni in the $ANiO_3$ perovskites for the smallest A^{3+} cations, a Mössbauer study has been conducted for $ANi_{1-\epsilon}{}^{57}Fe_{\epsilon}O_3$ with A = Y, Lu, and Tl ($\epsilon = 0.02$).[7]

The participation of ^{57}Fe to the $ANiO_3$ lattice was evaluated by magnetic measurement, showing that T_N values and magnetic susceptibilities χ_M were slightly modified by iron doping.[8] The Mössbauer spectra of three nickelates, $ANi_{0.98}{}^{57}Fe_{0.02}O_3$ (A = Lu, Y, and Tl) at 300 K can be described as a superposition of two quadrupole doublets (Figure 1) which underlines that Fe is simultaneously stabilized in two nonequivalent crystallographic positions. These Fe sites are characterized by different values for the isomer shift δ and the quadrupole splitting Δ (Table 1). The large difference in two δ values for the same ^{57}Fe-doped nickelate denotes two different degrees of covalent mixing in Fe−O bonds suggesting two sites, $Ni(1)O_6$ and $Ni(2)O_6$. This result confirms the neutron diffraction analysis of small rare-earth nickelates (Ho−Lu and Y) which indicates the reduction in lattice symmetry from orthorhombic (*Pbnm*) to monoclinic ($P2_1/n$) driven by two independent crystallographic positions: $Ni(1)O_6$ and $Ni(2)O_6$.[5]

The very distinct δ values suggest the possibility of a charge disproportionation phenomenon: $2Ni^{3+} \rightarrow Ni^{(3-\alpha)} + Ni^{(3+\alpha)}$ in such a largely distorted perovskite lattice. Considering that an increase of the formal oxidation state of Fe^{n+} cations leads to isomer shift reduction, the δ_2 value would correspond to nickel site characterized by higher oxidation state ($Ni^{(3+\alpha)+}$) and the δ_1 value to nickel site with lower oxidation state ($Ni^{(3-\alpha)+}$). The difference of the quadrupole splittings for the two types of irons, $\Delta_2(Fe^{(3+\alpha)+}) < \Delta_1(Fe^{(3-\alpha)+})$ is also in agreement with neutron diffraction results which claim that $Ni^{(3-\alpha)+}O_6$ octahedra should be more distorted than $Ni^{(3+\alpha)+}O_6$ ones.[5] For $YNi_{0.98}Fe_{0.02}O_3$ at T = 100 K [$T < T_N$(147 K)], the quadrupole doublets split into diffuse sextets as a result of the nuclear Zeeman effect below magnetic ordering temperature (Figure 2a). This result confirms the participation of iron ions to the nickelates lattices as mentioned before through the observed modifications of the magnetic data (T_N, χ_M) between ^{57}Fe-doped and nondoped nickelates. The diffuse magnetic structure in the spectrum for $YNiO_3$:^{57}Fe is probably due to relaxation processes occurring near T_N. Similar results have been obtained through other research works for various iron compounds upon measuring near T_N.[9] This phenomenon was interpreted as a result of slowing down of electron-spin fluctua-

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[7] The polycrystalline samples were prepared under high oxygen pressure. A_2O_3 (A = Y, Lu, and Tl) and $Ni_{0.98}Fe_{0.02}O$ were used as starting materials. $Ni_{0.98}Fe_{0.02}O$ was preprared by dissolving an appropriate amounts of $Ni(NO_3)_2$-$6H_2O$ and ^{57}Fe in 1 M nitric acid and then by precipitating in aqueous KOH (3 M) solution, washing with distilled water, and drying at 300 °C. The mixtures of the starting materials and $KClO_3$ were put into gold capsules before heating for 5 min at 700 °C under 7.5 GPa for Tl $Ni_{0.98}Fe_{0.02}O_3$ and at 900 °C under 6GPa for $YNi_{0.98}Fe_{0.02}O_3$ and $LuNi_{0.98}Fe_{0.02}O_3$. For synthesis of $SmNi_{0.98}Fe_{0.02}O_3$, Sm_2O_3, $Ni_{0.98}Fe_{0.02}O$, and excess of citric acid were dissolved in dilute nitric acid. The solution was evaporated with controlling pH to 5−6, until blue gel appeared. The gel was then decomposed at 750 °C for in air. $SmNi_{0.98}Fe_{0.02}O_3$ was prepared by heating the precursor at 850 °C for 4 days under 100 MPa of oxygen pressure.

[8] T_N: $YNiO_3$ 153 K, $YNi_{0.98}Fe_{0.02}O_3$ 147 K, $LuNiO_3$ 127 K, $LuNi_{0.98}Fe_{0.02}O_3$ 122 K, $TlNiO_3$ 104 K, $TlNi_{0.98}Fe_{0.02}O_3$ 94 K.

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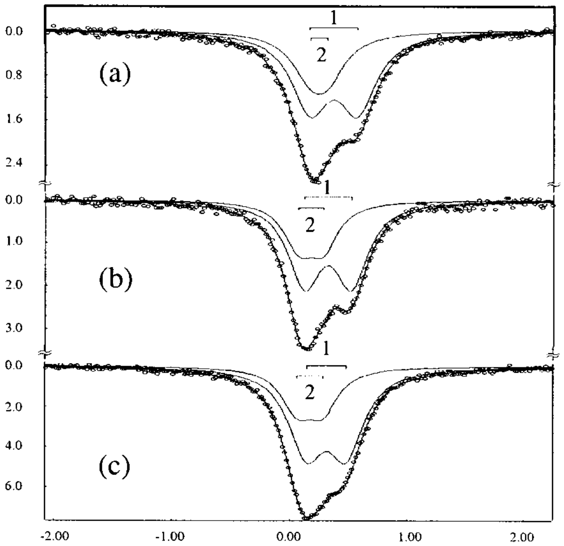

Figure 1. Mössbauer spectra at 300 K for (a) $TlNi_{0.98}Fe_{0.02}O_3$ (b) $LuNi_{0.98}Fe_{0.02}O_3$, and (c) $YNi_{0.98}Fe_{0.02}O_3$. (**1** = Fe(1), **2** = Fe(2))

Table 1. Mössbauer Parameters for $ANi_{0.98}Fe_{0.02}O_3$ (A= Y, Lu, and Tl)

compound	*T*(K)	Fe site	*δ* mm/s	Δ mm/s	Γ mm/s	A %
$YNi_{0.98}Fe_{0.02}O_3$	300	Fe(1)	0.32(1)	0.34(1)	0.31(1)	70(2)
		Fe(2)	0.18(1)	0.23(1)	0.31(1)	30(2)
$LuNi_{0.98}Fe_{0.02}O_3$	300	Fe(1)	0.31(1)	0.38(1)	0.30(1)	67(2)
		Fe(2)	0.16(1)	0.21(1)	0.30(1)	33(2)
$TlNi_{0.98}Fe_{0.02}O_3$	300	Fe(1)	0.36(1)	0.40(1)	0.31(1)	67(2)
		Fe(2)	0.23(1)	0.18(1)	0.30(1)	33(2)
	100	Fe(1)	0.49(1)	0.44(2)	0.32(1)	67(3)
		Fe(2)	0.24(1)	0.34(1)	0.31(1)	33(3)

tions in the critical domain. However, the Mössbauer spectrum of $TlNi_{0.98}Fe_{0.02}O_3$ remains paramagnetic [$T > T_N$(94 K)] (Figure 2b).

In the case of $TlNi_{0.98}{}^{57}Fe_{0.02}O_3$, some differences can be mentioned: (i) The δ values observed at 300 K for Fe(1) and Fe(2) are slightly higher than the corresponding ones for $ANi_{0.98}Fe_{0.02}O_3$ (A = Y, Lu), (ii) As temperature decreases from 300 K to 100 K, the δ_1 value increases, while the δ_2 one remains constant so that the difference between the δ_1 and δ_2 values increases. ($\Delta\delta_{300K} = 0.13$ mm/s and $\Delta\delta_{100K} = 0.25$ mm/s)

The percentages of Fe(1) and Fe(2) are approximately constant whatever the lattice [66% for site (1) and 33% for site (2)]. Such a distribution may be induced by the fact that the iron prefers to Ni(1) site rather than Ni(2) site since $Fe^{3+}-O$ bond distance (2.03 Å) is closer to the average bond distance of Ni(1)−O (2.00 Å) than that of Ni(2)−O distance (1.92 Å).[5]

To evaluate the role of the size of the A^{3+} cation on the $ANiO_3$ structure, a preliminary Mössbauer study of $SmNi_{0.98}{}^{57}Fe_{0.02}O_3$ has been done. At 300 K the ^{57}Fe Mössbauer spectrum consists of a poorly resolved single quadrupole doublet (Figure 3) with the following Mössbauer parameters ($\delta = 0.26 \pm 0.01$ mm/s, $\Delta = 0.11 \pm 0.01$ mm/s), which is consistent with the orthorhombic structure for $SmNiO_3$ with only one Ni site.[4]

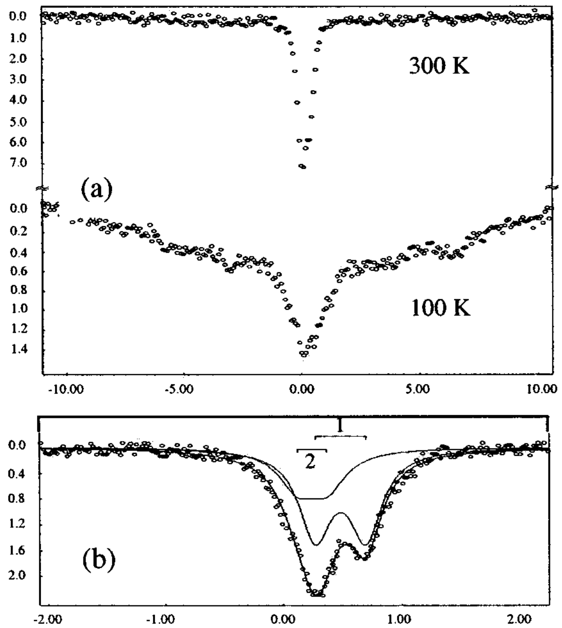

Figure 2. Mössbauer spectra for (a) $YNi_{0.98}Fe_{0.02}O_3$ (300 and 100 K) and (b) $TlNi_{0.98}Fe_{0.02}O_3$. (100 K) (**1** = Fe(1), **2** = Fe(2))

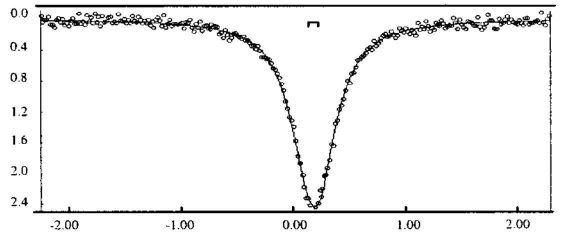

Figure 3. Mössbauer spectrum at 300 K for $SmNi_{0.98}Fe_{0.02}O_3$.

Consequently the structural change from orthorhombic (*Pbnm*) to monoclinic ($P2_1/n$) associated to the charge disproportionation seems correlated to the A^{3+} size. This preliminary Mössbauer study involving nickelates perovskites, $ANiO_3$ with A = Y, Lu, and Tl confirms the existence of two different crystallographic sites (NiO_6) in the strongly distorted perovskite lattice, which supports the recent neutron diffraction studies[5] suggesting a nickel disproportionation. In $TlNiO_3$ being the first perovskite nickelate with A ≠ rare earth, the role of the A−O bonds on the structural distortion is underlined, as well as the importance of the $Ni_{e_g}-O_{2p}$ overlap governing the T_N value. Such a study will be improved using in particular a diamagnetic probe as Mössbauer doping element in order to investigate the electronic phenomena for $T < T_N$ and also the MI transition.

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Supporting Information Available: Figure showing temperature dependence of molar magnetic susceptibility for $ANiO_3$ and $ANi_{0.98}Fe_{0.02}O_3$ (A = Sm, Y, Lu, and Tl) (PDF). This material is available free of charge via the Internet at http://pub.acs.org.

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