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Orbital ordering in $NdNiO_3$ and $SmNiO_3$ investigated by Mössbauer spectroscopy

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A Mössbauer study of ^{57}Fe doped Ni^{III} perovskites, $NdNi_{0.98}Fe_{0.02}O_3$ and $SmNi_{0.98}Fe_{0.02}O_3$, in the magnetic ordering domain ($T \ll T_N$) has revealed that the Fe probes occupy two types of sites, i.e., Fe(1) and Fe(2), showing very different values of the magnetic hyperfine fields ($H_1 \approx 430-450$ kOe, $H_2 \approx 15-22$ kOe). The close values of the isomer shift (δ) and the second-order quadrupole perturbation parameter (ε) in the subspectra, for both Fe sites, have underlined that all the Fe sites are crystallographically equivalent. In the light of orbital ordering model suggested by the neutron diffraction studies, the partial substitution of Ni^{III} ($t_{2g}^6 e_g^1$) by Fe^{3+} ($t_{2g}^3 e_g^2$) may induce significant topological frustration of Fe^{3+} spins in surroundings of Ni^{III} orbitals, leading to two different magnetic environments around Fe below T_N. Additionally, the Mössbauer spectra at 300 K ($>T_N$) indicate that all the available sites for probe atoms are crystallographically equivalent in the insulating $SmNi_{0.98}Fe_{0.02}O_3$ as well as in the metallic $NdNi_{0.98}Fe_{0.02}O_3$. The present result may be an evidence of the important role of the orbital ordering in determining the electronic properties of the Ni^{III} perovskites containing large rare earth.

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The rare-earth nickel pervoskites ANiO$_3$ (A, rare earth), which were synthesized for the first time in 1971,[1] are being investigated with renewed interest in recent years due to their unusual electronic/magnetic properties. This family undergo two transitions, an insulator-metal transition at T_{IM} and an antiferromagnetic ordering at T_N ($T_N = T_{\mathrm{IM}}$ for $A=\mathrm{Pr}$ and Nd, whereas $T_N \leqslant T_{\mathrm{IM}}$ for $A = \mathrm{Sm} \rightarrow \mathrm{Lu}$).[2] T_{IM} and T_N are systematically related with a variation of the Ni-O-Ni bond angle driven by the size of rare earth. For the large rare-earth compounds (A=Pr, Nd, Sm, and Eu), no reduction in the crystal symmetry across T_{MI} was detected by neutron diffraction.[3,4] Only slight expansion of the unit-cell volume takes place as a result of a small increase in Ni-O distance on reducing the temperature through T_{MI}. Below T_N, their magnetic ordering was characterized by the propagation vector $\mathbf{k} = (1/2, 0.1/2)$. In this magnetic structure, each Ni^{III} ion is coupled ferromagnetically to three nearest neighboring Ni^{III} ions and antiferromagnetically to three remaining neighbors through the oxygen ions of the NiO_6 octahedron. Based on these findings, an orbital ordering was proposed for ANiO$_3$ (A=Pr, Nd, Sm, and Eu), which might result from the breakdown of the degeneracy of the e_g^1 state in low spin Ni^{III} due to electronic correlation.[4] This model (Fig. 1) assumed a nonuniform distribution of the half occupied $d_{x2\text{-}y2}$ or d_{z2} orbitals and the magnetic structure was interpreted as a result of the Kanamori-Goodenough (KG) rules: the neighboring Ni^{III} ions with electrons in the same orbital are antiferromagnetically coupled and those occupying different orbitals prefer to align their spin parallel. However, the expected $\mathbf{2a} \times \mathbf{b} \times \mathbf{2c}$ superstructure reflections due to the orbital ordering are too weak to be revealed by neutron diffraction. Other possible explanation is that the magnetic structure results from the alternating arrangement of more strongly covalent Ni-O-Ni layers and more ionic Ni-O-Ni layers.[5] The ferromagnetic coupling might be a consequence of the covalent exchange due to strong Ni-O hybridization in the covalent layers, in contrast to the superexchange coupling responsible for the antiferromagnetic interaction in the ionic layers.

On the other hand, recent neutron diffraction studies[6] for small rare-earth nickelates, ANiO$_3$ (A=Ho, Y, Er, Tm, Yb, and Lu), have pointed out a subtle monoclinic distortion (space group $P2_1/n$) of the perovskite lattice at $T < T_{\mathrm{IM}}$, which allows two kinds of Ni positions in the lattice leading to two distinct mean Ni-O bond distances for Ni(1) and Ni(2). From these observations, partial charge disproportionation $2\mathrm{Ni}^{3+} \rightarrow \mathrm{Ni}^{(3+\varepsilon)+} + \mathrm{Ni}^{(3-\varepsilon)+}$ has been suggested for insulating regime. The magnetic structure for these compounds, which has the same propagation vector $\mathbf{k} = (1/2, 0.1/2)$ as observed in the large rare-earth nickelates, has been described by the ordering of two kinds of nickel ions with different charges.

Very recently, we had attempted to examine such controversial problems in the electronic, magnetic, and crystallographic structures of ANiO$_3$ perovskites by means of Mössbauer spectroscopy after doping with small amount of ^{57}Fe probe atoms in nickel site. For the small rare-earth nickelates, the partial charge disproportionation phenomenon could be confirmed by detecting two kinds of Mössbauer absorption peaks with distinct values of isomer shift for the small rare-earth nickelates (A=Y,Lu,Tl).[7] This work is to extend the ANiO$_3$ perovskites containing a large rare earth. We report here the hyperfine interactions parameters of ^{57}Fe

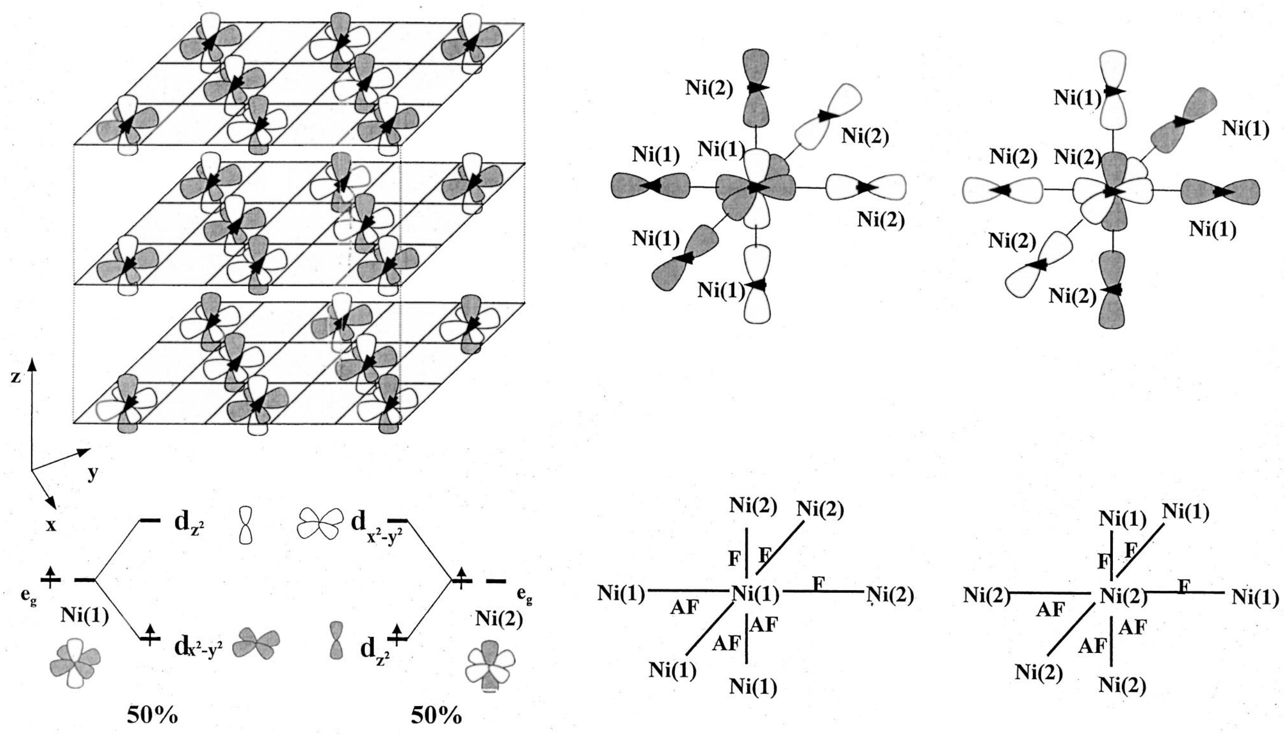

FIG. 1. Magnetic arrangements of the Ni moments in the ANiO$_3$ (A=Nd,Sm) at $T<T_N$. The different shading of the octahedra corresponds to the occupation of either d_{z2}- or $d_{x2\text{-}y2}$-type orbitals and local magnetic surrounding of Ni(1) and Ni(2) cations.

atoms introduced as Mössbauer probes into NdNiO$_3$ and SmNiO$_3$ and discuss the magnetic structures in the light of the orbital ordering[4] proposed by the previous neutron diffraction studies.

The polycrystalline ^{57}Fe doped samples, NdNi$_{0.98}$Fe$_{0.02}$O$_3$ and SmNi$_{0.98}$Fe$_{0.02}$O$_3$, were prepared by the high oxygen pressure treatment of precursors obtained from sol-gel method. The appropriate amount of A_2O$_3$ (A=Nd,Sm), Ni(NO$_3$)$_2$ 6H$_2$O, ^{57}Fe metal, and citric acid were dissolved in dilute nitric acid. The solution was evaporated keeping its pH 5–6 until a blue gel was obtained. The gel was decomposed at 750 °C for 6 h in air. The resulting powder was heated at 850 °C for 4 days under an oxygen pressure of 100 MPa. The Fe-doped samples show lower values of T_N than those for undoped compounds [T_N (NdNi$_{0.98}$Fe$_{0.02}$O$_3$) $=150$ K and T_N (SmNi$_{0.98}$Fe$_{0.02}$O$_3$)$=210$ K].[8] T_{IM} coincides T_N for NdNi$_{0.98}$Fe$_{0.02}$O$_3$, whereas T_{IM} (>370 K) for SmNi$_{0.98}$Fe$_{0.02}$O$_3$ is much higher than its T_N. The ^{57}Fe Mössbauer spectra were recorded at various temperatures using a conventional constant acceleration Mössbauer spectrometer. The radiation source ^{57}Co(Rh) was kept at room temperature. All isomer shifts refer to the α-Fe absorber at 300 K.

The Mössbauer spectra recorded in the paramagnetic domain ($T>T_N$) (Fig. 2) are characterized by a single unresolved quadrupole doublet with the isomer shift values ($\delta=0.23$ mm/s for NdNi$_{0.98}$Fe$_{0.02}$O$_3$ and $\delta=0.26$ mm/s for SmNi$_{0.98}$Fe$_{0.02}$O$_3$) corresponding to Fe^{3+} cations in oxygen octahedral coordination.[9] The small values of the quadrupole splitting ($\Delta=0.11$ mm/s for SmNi$_{0.98}$Fe$_{0.02}$O$_3$ and $\Delta=0.08$ mm/s for NdNi$_{0.98}$Fe$_{0.02}$O$_3$) are consistent with the nearly regular NiO$_6$ octahedra observed in the first members of the ANiO$_3$ family. The full linewidth at half height for each component of doublets ($\Gamma\approx0.28$ mm/s) was found to be close to the corresponding value for the calibration spectra ($\Gamma=0.26$ mm/s), which is evidence of equivalence of the crystallographic positions occupied by the dopant Fe^{3+} cations in the insulating SmNi$_{0.98}$Fe$_{0.02}$O$_3$ as well as in the metallic NdNi$_{0.98}$Fe$_{0.02}$O$_3$. This result contrasts with the case of ANiO$_{0.98}$Fe$_{0.02}$O$_3$ (A=Y,Lu,TI) (Ref. 7) in which the Mössbauer spectra show two kinds of doublets with different isomer shift values originated from the charge disproportionation of Ni$^{\mathrm{III}}$ (Table I).

The spectrum of SmNi$_{0.98}$Fe$_{0.02}$O$_3$ recorded in the metallic domain $T=500$ K ($>T_{\mathrm{IM}}$) is very similar to that in Fig. 2(b) and can be described as one doublet with the parameters $\delta=0.16$ mm/s and $\Delta=0.10$ mm/s. The isomer shift exhibits the decrease -0.10 mm/s, with respect to the room-temperature value. This decrease of the δ value is in agreement with the second-order Doppler shift[9] and suggests that the electronic configuration of the dopant Fe^{3+}($3d^n4s^m$) cations, in terms of effective n, m numbers of d and s electrons, is not temperature dependent.

Below the magnetic ordering temperatures ($T<T_N$) the Mössbauer spectra (Fig. 3) are resolved into two magnetic Zeeman sextets. Magnetic hyperfine fields values, H_1 and H_2 for the subspectra are considerably different. The ratio of the areas for two subspectra is close to unity. The isomer shift values (δ) for two subspectra are approximately the same (Table II). These features underline that a statistically equal amount of the probe atoms occupy two kinds of sites, i.e., Fe(1) and Fe(2), whose environments are chemically equiva-

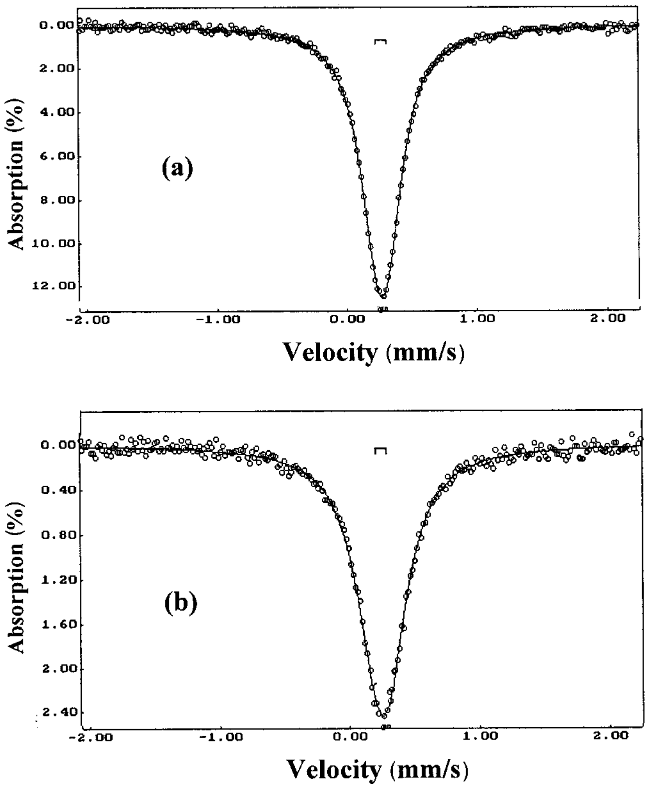

FIG. 2. ^{57}Fe Mössbauer spectra of (a) $NdNi_{0.98}Fe_{0.02}O_3$ and (b) $SmNi_{0.98}Fe_{0.02}O_8$ at room temperature.

lent but magnetically different. The second-order quadrupole perturbation parameters (ε) for two subspectra are of the same sign and similar magnitude, which implies the local structures for Fe(1) and Fe(2) are also approximately same. The ε values observed at $T<T_N$ cannot be easily correlated with the Δ values ($T>T_N$). From the equation for the quadrupole perturbation parameter in magnetic ordering domain,

$$\varepsilon=\Delta(3\cos^2\theta-1)/4,$$

where θ is the angle between the directions of electric field gradient and the hyperfine field (H) at the iron site, it can be shown that $0\leqslant|2\varepsilon/\Delta|\leqslant 1$. From the ε values for both nickelates it follows that $\Delta\geqslant 0.02$ mm/s at $T<T_N$. However, no magnetic data exist for $ANi_{0.98}Fe_{0.02}O_3$ concerning the spin direction of the Fe probes, which makes difficult the detailed analysis on the distortion of $Fe(1)O_6$ and $Fe(2)O_6$ octahedra below T_N.

TABLE I. Mössbauer parameters for $ANi_{0.98}Fe_{0.02}O_3$(A = Y,Lu).

Compound	T (K)	Site	δ (mm/s)	Δ (mm/s)	Γ (mm/s)	A (%)
$YNi_{0.98}Fe_{0.2}O_3$	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)

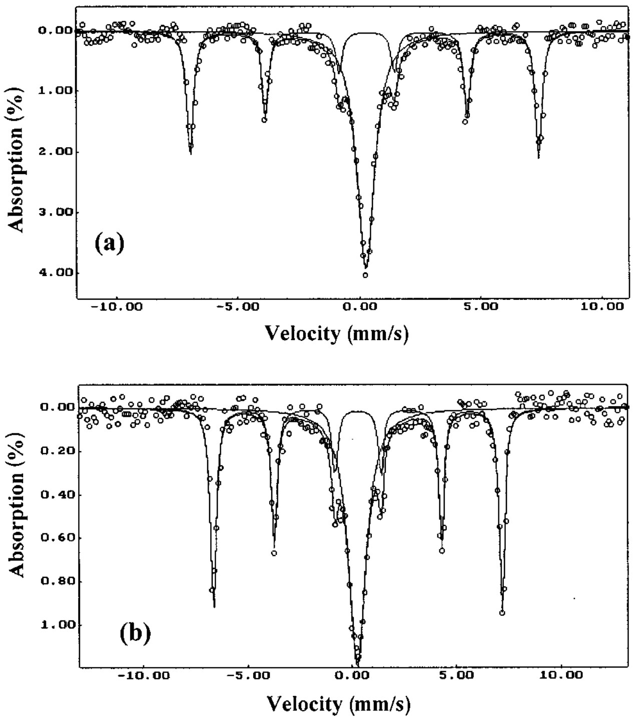

FIG. 3. ^{57}Fe Mössbauer spectra of (a) $NdNi_{0.98}Fe_{0.02}O_3$ at 60 K and (b) $SmNi_{0.98}Fe_{0.02}O_8$ at 80 K.

To explain the unusual aspect in the Mössbauer spectra for $SmNi_{0.98}Fe_{0.02}O_3$ and $NdNi_{0.98}Fe_{0.02}O_3$ the orbital ordering model previously proposed by Rodrigues-Carjaval *et al.*[4] could be used. Considering that a part of Ni^{III} cations is substituted by Fe^{3+} ones, the possible arrangements of the orbitals in the lattice are illustrated schematically in Fig. 4. Ni^{III} ions are in the electronic configuration ($t_{2g}^3e_g^1$) making the lattice break up into two orbital sublattices, each with predominantly one of the d_{z2} or $d_{x2\text{-}y2}$ orbitals half occupied, whereas Fe^{3+} ones have the ($t_{2g}^3e_g^2$) configuration with two half-filled e_g orbitals. In this scheme, the σ-superexchange interactions (e_g-p_σ-e_g) between Fe^{3+} and Ni^{III} are divided into two types: (i) the interactions that are in agreement with KG rules and (ii) the interactions in disagreement. According to Fig. 4, each Fe(1) cation in *x*-*y* planes is coupled ferromagnetically with two nearest neighboring Ni($t_{2g}^6d_{z2}^1$) ions through the overlap of a half-filled $d_{x2\text{-}y2}$ (Fe) and empty $d_{x2\text{-}y2}$ (Ni) orbitals and is coupled antiferromagnetically to the remaining two Ni ($t_{2g}^6d_{x2\text{-}y2}^1$) neighbors having the $d_{x2\text{-}y2}$ orbitals half occupied. These four Fe(1)-O-Ni magnetic in-

TABLE II. Mössbauer parameters for $NdNi_{0.98}\,^{57}Fe_{0.02}O_3$ (60 K) and $SmNi_{0.98}\,^{57}Fe_{0.02}O_3$ (85 K).

Compound	Sites	δ (mm/s)	ε (mm/s)	H (kOe)	A (%)
$NdNi_{0.98}Fe_{0.02}O_3$	Fe(1)	0.28(2)	0.03(1)	446(1)	47(2)
	Fe(2)	0.27(2)	0.03(1)	14(3)	53(2)
$SmNi_{0.98}Fe_{0.02}O_3$	Fe(1)	0.36(2)	0.02(2)	430(1)	52(2)
	Fe(2)	0.34(2)	0.02(2)	20(3)	48(2)

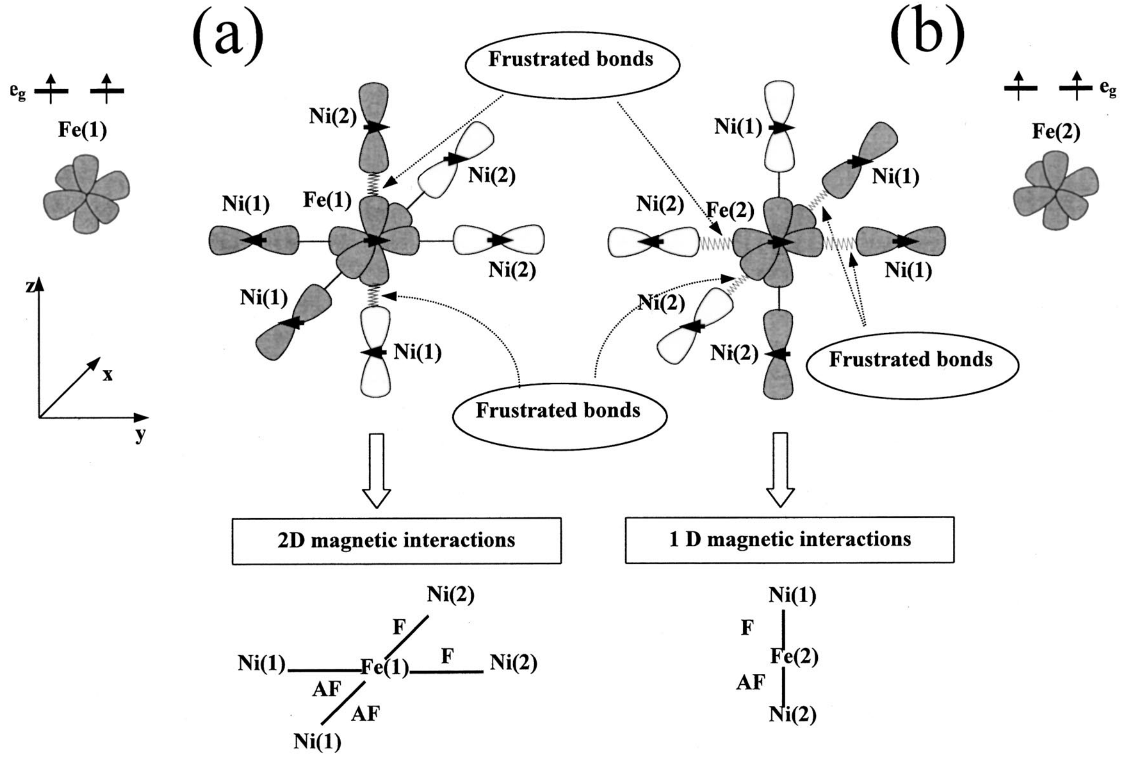

FIG. 4. A schematic representation of the orbital arrangement of Fe(1) and Fe(2) probe atoms in the ANiO$_3$ structure and expected magnetic interactions.

teractions in x-y planes satisfy the KG rules, whereas two magnetic interactions along z axis between Ni and Fe(1) will be in conflict with KG rules [Fig. 4(a)]. The conflicting interactions lead to topological frustration of Fe(1) spins along z axes (these are called "frustrated interactions"). Taking into account that the frustration makes magnetic interactions between the spins very weak, it is possible to neglect the magnetic interactions along z axes and to regard the magnetic environment around Fe(1) as a two-dimensional Ising magnet [Fig. 4(a)]. As a result of the weakening of total magnetic interactions through such process, the rapid relaxation of the Fe^{3+} spins is expected, allowing to explain the lower value of hyperfine field (H_1) (446–430 kOe) for Fe(1) in comparison to those observed for Fe^{3+} ions in other three-dimensional (3D) antiferromagnetic pervoskites, such as the rare-earth orthoferrites AFeO$_3$ ($H=540$–560 kOe).[10]

The similar analysis for Fe(2) ions reveals that two Fe(2)-O-Ni interactions along z axes are of predominant strength and four Fe(2)-O-Ni interactions in x-y plane appear to be very weak due to the frustration [Fig. 4(b)]. In this case, the local magnetic structure seems to have a quasimonodimensional character. This makes the spin relaxation time for Fe(2) ions become much shorter and the motional collapse of the magnetic spectrum commences so that the magnetic hyperfine field observed for Fe(2) is very weak ($H_2=14$–20 kOe). The magnetic behavior on the Mössbauer spectra is very similar to that observed for Sr$_{2.6}$La$_{0.4}$Fe$_2$O$_7$, Sr$_2$LaFe$_3$O$_{8.417}$, and SrFeO$_{2.71}$.[11] The magnetic properties of these compounds are presumably determined by the frustrated antiferromagnetic interactions between Fe^{3+} ($t_{2g}^3e_g^2$) and high-spin Fe$^{\mathrm{IV}}$($t_{2g}^3e_g^1$) as in case of Fe-doped Ni$^{\mathrm{III}}$ perovskites.

Very recently, a description including the charge ordering in oxygen $2p$ orbitals in ANiO$_3$ (A, large rare earth) has been proposed by Mizokawa *et al.*[5] Due to small charge-transfer energy (Δ) for the nickelates, the part of the oxygen $2p$ band can overlap with the Ni$^{3+/2+}$ redox couple so that the ground state is a mixture of d^7 and $d^8\underline{L}$, where $\underline{L}$ is a hole in the oxygen band. It was assumed that at $T<T_N$ half of the oxygen sites have more holes (O$^{1.33-}$) than the other half (O^{2-}). In this picture, the low-temperature phase of the ANiO$_3$ presents a coupled spin-density wave and charge-density wave propagating along a cubic [111] axis with the "ionic" antiferromagnetic Ni^{2+}-O^{2-}-Ni^{2+} and "covalent" ferromagnetic Ni^{2+}-O$^{1.33-}$-Ni^{2+} layers. It should be noted that in the approach of oxygen-site charge ordered, which suggests that all Ni^{2+} ($3d^8\underline{L}$) sites have the half-filled e_g orbitals, the substitution of Ni^{2+}($t_{2g}^6e_g^2$) with Fe^{3+}($t_{2g}^3e_g^2$) would not perturbate too much the local magnetic structure of ANiO$_3$. Moreover, the asymmetric distribution of negative charge (3O$^{2-}+3$O$^{1.33-}$) surrounding the Fe^{3+} cations in octahedral polyhedra FeO$_6$ must lead to a high quadrupole splitting. In our Mössbauer study, the small value of the quadrupole splitting seems to support the orbitals ordering model.

In conclusion, Mössbauer investigations of ANi$_{0.98}{}^{57}$Fe$_{0.02}$O$_3$ ($A=$Nd,Sm) underline that ^{57}Fe probes occupy the same crystallographic sites in the perovskite lattice. The two different hyperfine fields (H_i) observed in the antiferromagnetic domain ($T<T_N$) suggest two different magnetic surroundings for ^{57}Fe probes. On the basis of the model of ordering e_g orbitals for $\mathrm{Ni^{III}}$ in the $NdNiO_3$ and $SmNiO_3$ lattices, such different H_i values have been explained by frustrated magnetic interactions introduced by the substitution of $\mathrm{Ni^{III}}$ ($t_{2g}^6e_g^1$) by $\mathrm{Fe^{3+}}$ ($t_{2g}^3e_g^2$) leading to predominant 2D magnetic interactions for Fe(1) ($H_1 \approx 430-450$ kOe) and quasi-1D ones for Fe(2) ($H_2 \approx 14-20$ kOe). The close value for δ and $\varepsilon(\Delta)$ for each subspectra are consistent with only one nickel site into the $A\mathrm{NiO_3}$ lattices for the largest A^{3+} rare earth.

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[1] G. Demazeau, A. Marbeuf, M. Pouchard, and P. Hagenmuller, J. Solid State Chem. **3**, 582 (1971).

[2] P. Lacorre, J. B. Torrance, J. Pannetier, A. I. Nazzal, P. W. Wang, and T. C. Hwang, J. Solid State Chem. **91**, 225 (1991); J. B. Torrance, P. Lacorre, A. I. Nazzal, E. J. Ansaldo, and P. Niedermayer, Phys. Rev. B **45**, 8209 (1992); J. S. Zhou, J. B. Goodenough, B. Dabrowski, P. W. Klamut, and Z. Bukowski, *ibid.* **61**, 4401 (2000); M. Medarde, J. Phys.: Condens. Matter **9**, 1679 (1997).

[3] J. L. Garcia-Muñoz, J. Rodriguez-Carvajal, J. B. Torrance, and P. Lacorre, Phys. Rev. B **46**, 4414 (1992).

[4] J. L. García-Muñoz, J. Rodriguez-Carvajal, and P. Lacorre, Europhys. Lett. **20**, 241 (1992); J. L. Garcia-Muñoz, J. Rodriguez-Carvajal, and P. Lacorre, Phys. Rev. B **50**, 978 (1994); J. Rodriguez-Carvajal, S. Rosenkranz, M. Medarde, P. Lacorre, M. T. Fernandez-Diaz, F. Fauth, and V. Trounov, *ibid.* **57**, 456 (1998).

[5] J. B. Goodenough, J. Solid State Chem. **127**, 126 (1996); T. Mizokawa, D. I. Khomskii, and G. A. Sawatzky, Phys. Rev. B **61**, 11 263 (2000).

[6] J. A. Alonso, M. J. Martínez-Lope, M. T. Casais, M. A. G. Aranda, and M. T. Fernandez-Diaz, J. Am. Chem. Soc. **121**, 4754 (1999); J. A. Alonso, M. J. Martínez-Lope, M. T. Casais, J. L. García-Munoz, and M. T. Fernandez-Diaz, Phys. Rev. B **61**, 1756 (2000); J. A. Alonso, M. J. Martínez-Lope, M. T. Casais, J. L. Garcia-Munoz, M. T. Fernandez-Diaz, and M. A. G. Aranda, *ibid.* **64**, 094102 (2001).

[7] S. J. Kim, G. Demazeau, I. Presniakov, K. Pokholok, A. Sobolev, and N. Ovanesyan, J. Am. Chem. Soc. **123**, 8127 (2001).

[8] T_N (T_{IM}) = 200 K for $NdNiO_3$ and $T_N = 200$ K, $T_{\mathrm{IM}} = 400$ K for $SmNiO_3$. The difference of the transition temperature (-50 K) for $NdNiO_3$ after doping of 2% ^{57}Fe is larger than that for $SmNiO_3$, which may be attributed to different origins in IM transition for both phases. T_N(-10 K) after doping for $SmNiO_3$ is similar to those ($T_N = -10-20$ K) of $A\mathrm{NiO_3}$ (A = Y, Lu, Tl) (Ref. 7).

[9] A. J. Boyle and H. E. Hall, Rep. Prog. Phys. **25**, 441 (1962).

[10] M. Eibschütz, S. Shtrikman, and D. Treves, Phys. Rev. **156**, 562 (1967).

[11] P. Adler, J. Solid State Chem. **130**, 129 (1997); C. Gibb, J. Mater. Chem. **4**, 1445 (1994).