Charge disproportionation in YNiO$_3$ : ESR and susceptibility study

M. T. Causa*, R. D. Sánchez, and M. Tovar
Centro Atómico Bariloche, CNEA, Av. Ezequiel Bustillo 9500, (8400)
San Carlos de Bariloche, Río Negro, Argentina.

J. A. Alonso and M. J. Martínez-Lope.
Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, E-28049
Madrid, Spain.

We present a study of the magnetic properties of YNiO$_3$ in the paramagnetic range, above and below the metal-insulator (MI) transition. The dc susceptibility, $\chi_{dc}$ (measured up to 1000 K) is a decreasing function of T for T > 150 K (the Néel temperature) and we observe two different Curie-Weiss regimes corresponding to the metallic and insulator phases. In the metallic phase, this behaviour seems to be associated with the small ionic radius of Y$^{3+}$. The value of the Curie constant for T < $T_{MI}$ allows us to discard the possibility of Ni$^{3+}$ localization. An electron spin resonance (ESR) spectrum is visible in the insulator phase and only a fraction of the Ni ions contributes to this resonance. We explain the ESR and $\chi_{dc}$ behaviour for T < $T_{MI}$ in terms of charge disproportionation of the type 2Ni$^{3+}$ $\rightarrow$ Ni$^{2+}$+$\delta$Ni$^{4+}$, that is compatible with the previously observed structural transition across $T_{MI}$.

PACS numbers: 71.30. +h, 71.45.Lr., 75.30.Cr, 76.30. -v

I. INTRODUCTION

The perovskite system RNiO$_3$ (with R trivalent rare-earth or Y) is a very attractive family of compounds around which an intense research activity was developed in the 90’s. The most studied property in these oxides was the metal-insulator (MI) transition from the high temperature metallic material to a charge transfer insulator, at a temperature $T_{MI}$. As is seen in the phase diagram of Fig. 1, this temperature increases when the ionic radius of R$^{3+}$ ($r_R$) diminishes. In the insulator phase the oxides show antiferromagnetic (AFM) order, with a complex structure, below a Néel temperature ($T_N$) also dependent on the $r_R$ size. The AFM structure was firstly explained in terms of localization of the Ni$^{3+}$-eg electrons and orbital ordering, Jahn-Teller driven. In spite of all the performed studies, the exact nature of the metal-insulator transition is not completely understood and a model including structural, magnetic and transport properties for all the RNiO$_3$ series is still lacking. The difficulties found in the synthesis of RNiO$_3$, partially related to the stabilization of the Ni$^{3+}$, are more severe for the smaller $r_R$ compounds and only recently, with new synthesis techniques, the samples with R = Dy, Y, Ho, Er, and Lu could be studied. Besides, improvements in the characterization of the structural changes accompanying the MI transition performed by synchrotron x-ray diffraction (SXRD) techniques allowed a more precise description of the different crystalline phases.

In this paper we present a study of the YNiO$_3$ oxide. Due to the non magnetic character of Y, the magnetic properties of the Ni lattice can be studied in YNiO$_3$ without interference with other magnetic species. Notice that the well known LaNiO$_3$, where R = La is also non magnetic, was found to be metallic for all T $\geq$ 1.4 K, without signatures of any magnetic ordering.

In a previous work, Alonso et al. determined the metal-insulating transition for YNiO$_3$, using differential scanning calorimetry, obtaining $T_{MI} = 582$ K. They observed a structural transition from the orthorhombic Pbnm phase (above $T_{MI}$) to a monoclinic $P2_1/n$ phase (below $T_{MI}$). This transition has been assumed to be driven by Ni charge disproportionation in the insulating phase, where 2Ni$^{3+}$ $\rightarrow$ Ni$^{2+}$+$\delta$Ni$^{4+}$ ($\delta \approx 0.3$). In this interpretation, the two Ni species coexist in the insulating phase, localized in two different crystalline sites characterized by expanded (Ni1 site) and contracted (Ni2 site), slightly distorted, NiO$_6$ octahedra. The AFM spin configuration at low temperature was also determined by neutron diffraction in the magnetically ordered phase, finding different magnetic moments that were associated with the two Ni sites. In this work we study the electron spin resonance (ESR) properties of YNiO$_3$. The aim of our work is to describe the changes in the magnetic properties associated to the MI transition. In the metallic phase all the Ni ions are expected to be in the low-spin (LS) Ni$^{3+}$ configuration ($3d^7, t^6_{2g} e^1$). The absence of an ESR spectrum that we found in the metallic phase is compatible with this Ni$^{3+}$ configuration where the eg electrons are itinerant and the localized $t_{2g}$ electrons have compensated spins. The same behavior (lack of ESR) has been observed for the metallic LaNiO$_3$ in the whole temperature range. The ESR spectrum present in the paramagnetic (PM) insulating phase of YNiO$_3$ is, as we discuss in this paper, a consequence of the Ni charge disproportionation and constitutes a direct experimental evidence of this effect.
II. EXPERIMENTAL DETAILS

Powder YNiO₃ samples were prepared under high-pressure and high-temperature conditions. Stoichiometric mixtures of Y₂O₃ and Ni(OH)₂ powders were ground with 30% of KClO₄. The mixture was packed into a 8 mm-diameter gold capsule, placed in a cylindrical graphite heater. The reaction was carried out in a pistoncylinder press, under a pressure of 20 kbar at 1173 K for 20 min. The reaction product, in the form of blackish dense polycrystalline pellets, was ground and the resulting powder washed with water to dissolve KCl. The sample was characterized by laboratory X-ray diffraction, with Cu Kα radiation. The temperature dependence of the dc-susceptibility, $\chi_{dc}(T)$, was measured with a SQUID magnetometer for T < 300K and with a Faraday balance magnetometer in the range 250 K - 1000 K. The ESR spectrum as a function of T was measured with a Bruker spectrometer operating at a frequency $\nu \approx 9.3$ GHz. We detected the derivative spectrum and obtained the T dependence of the three ESR parameters: resonance field $H_0(T)$, peak-to-peak linewidth $\Delta H_{pp}(T)$, and the double integrated intensity $I_{esr}(T)$. Notice that $I_{esr}$ can be approximated by $(\Delta H_{pp})^2 \times h_{pp}$, where $h_{pp}$ is the distance between peaks of the derivative spectrum. This method was preferred to the double integration for low signal-to-noise ratio spectra, in order to minimize possible spurious effects due to the cavity background. A standard Bruker X-band cavity was used for the T< 400 K measurements while a 4114HT cavity was employed in order to reach the high temperature range (up to 800 K in this case). The spectrum intensity was compared to that of other characterized samples (MnF₂ single crystal and Gd₂BaCuO₅ powder) in order to determine the ESR susceptibility, $\chi_{esr} \propto I_{esr}$, that should be equal to $\chi_{dc}$ if all the magnetic species contribute to the resonance. The detected lines were of relatively low intensity and 100 mg samples were used in order to obtain low noise spectra.

III. RESULTS AND DISCUSSION

In Fig. 2 we show $\chi_{dc}(T)$. Our results are in agreement with the pioneering experiment by Demazeau et al. in the range of their measurements (70 K / 480 K). At T = 150 K, $\chi_{dc}(T)$ shows a peak attributed to an AFM transition. As seen in Fig.2, at temperatures well below $T_N$, a Curie-like contribution to $\chi_{dc}$ is observed, as in other perovskites whose nature is unknown and could be originated in minority phases (0.5%). Measurement at 20 K of the magnetization as a function of H (up to 50 kG) showed a linear dependence, as is usual in AFM materials, although with a very small uncompensated magnetization, $M_0 \sim 10^{-4} \mu_B$/f.u.

In the inset of Fig.1 we show $\chi_{dc}^{-1}(T)$ vs. T. In the paramagnetic (PM) range ($T \geq T_N$) $\chi_{dc}(T)$ follows a Curie-Weiss (CW) law. For $T>T_{MI}$, a Curie constant $C = 0.79(2)$ emu-K/mol was obtained. Around $T_{MI}$ a change of slope was observed and $C = 0.90(2)$ emu-K/mol corresponds to $T<T_{MI}$. These values of C give, respectively, effective magnetic moments $\mu_{eff} = 2.5 \mu_B$ and 2.7 $\mu_B$. The simplest picture for the MI transition would be that of LS Ni³⁺ ions with itinerant $e_g$ electrons in the metallic phase becoming fully localized below $T_{MI}$. In metallic oxides we may describe $\chi_{dc}(T)$ in terms of a sum of a T-independent ($\chi_{0}$) and a CW-like ($\chi_{CW}$) susceptibilities corresponding to the itinerant and localized electrons, respectively. For RNiO₃ these should be the $e_g$ and $t_{2g}$ electrons of Ni³⁺. In this case only a temperature independent susceptibility $\chi_{0}$ is expected for $T>T_{MI}$ since the localized $t_{2g}$ electrons have fully compensated spins. This behavior was indeed observed in LaNiO₃. Instead, as was mentioned above, a CW susceptibility is measured in the metallic phase of YNiO₃. A similar situation occurs in SmNiO₃ and in La₁₋ₓEuₓNiO₃ (x > 0.6) after the subtraction of the Sm³⁺ and Eu³⁺ contribution to the susceptibility. It is interesting to notice that in the La₁₋ₓEuₓNiO₃ series, a transition from an independent to a CW behavior is observed as a function of x. Up to x ≈ 0.4, $\chi_{dc} = \chi_{0}$ and, for larger values of x, a CW component becomes increasingly important. These Eu concentrations correspond to the region of the phase diagram (see Fig. 1) characterized by the existence of an extended PM-insulator phase ($T_{MI} > T_N$). Then, it seems that the magnetic behavior in the metallic phase of RNiO₃ compounds is, as other magnetic and transport properties, strongly dependent on the size of the ionic radius $r_R$. This is shown in Fig. 1.

Below $T_{MI}$, the experimental results also fail to validate the simple model that suggest that in the PM insulating phase LS Ni³⁺ are fully localized. In this case a CW law with $C = 0.4$ emu-K/mol ($S = \frac{3}{2}$, $\mu_{eff} = 1.7 \mu_B$) is expected, value much smaller than the measured one. We will discuss this issue after the analysis of the ESR results.

In Fig. 3 we show the ESR spectrum taken at different temperatures. Between 150 K and 600 K, the spectrum consist of a single lorentzian line with a constant g-factor, $g = 2.16(2)$. At T ≈ 150 K this line suddenly broadens up, shifts to lower fields and is no longer visible for T < 145 K. This behavior is generally observed in powder samples below the AFM transition. This is due to the splitting, in several anisotropic branches, of the PM single-valued function $\nu = (g \mu_B/h)H$ and to the opening of a T dependent energy-gap $\nu = E_g(T)/h$. These effects combine in polycrystalline samples to give progressively broader and, consequently, lower amplitude spectra that are finally lost within the noise. Besides, when T diminishes, $E_g(T)$ increases and for temperatures where $E_g > \hbar \nu$ the spectrum is not detected even in single crystals. Our observation corroborate that the resonant Ni ions order AFM below $T_N = 150$ K in coincidence with the dc peak temperature. On the other hand, for temper-
atures approaching the MI transition, the line intensity also diminishes (see Fig. 3) but in this case both the linewidth and the resonance field remain approximately constant. Above 600 K the line extinguishes completely.

In Fig. 4 we plot the measured T dependence of $\Delta H_{pp}$. For the range $T_N < T < 450$ K the linewidth increases slowly showing a linear dependence $\Delta H_{pp}(T) = a + bT$ with $a \approx 1300$ G and $b \approx 1.5$ G/K. Above 450 K the linewidth stops to increase, a narrowing process installs, and $\Delta H_{pp}$ is reduced by 50% at 560 K. In Fig. 2 we show $\chi_{esr}(T)$ that is decreasing with T in all the range 150/600 K: between 150K and 450K we observe a behavior similar to that of $\chi_{dc}(T)$, for $T \approx 450$ K a change in the slope occurs, and above this temperature $\chi_{esr}$ goes rapidly to zero.

The ESR behavior can be explained taking into account the structural changes of the material. Above $T_{MI}$, in the orthorhombic phase, all the Ni ions are Ni$^{3+}$ and no resonance is visible. In the monoclinic phase, instead, it is very interesting to notice that, below $T_{MI}$, gradually more and more Ni ions contribute to the spectrum. In Fig. 2 we compare $\chi_{esr}$ with $\chi_{dc}$; finding that $\chi_{esr}$ is, for all temperatures, lower than $\chi_{dc}$ being $\chi_{esr} \approx 0.5 \chi_{dc}$ at $T \approx 150$K. This indicates that only part of the Ni ions contribute to the ESR. The g-factor values and the linear dependence found for $\Delta H_{pp}(T)$ suggest that the resonant species may be Ni$^{2+}$. These facts point to a charge disproportionation: $2Ni^{3+} \rightarrow Ni^{2+} + Ni^{4+}$ at the MI transition. If this were the case, the contracted octahedra would be occupied by low-spin Ni$^{4+}$ (3$d^6$ $e_g^2$) ions, having S = 0 ground state that would contribute to $\chi_{dc}$ through their excited levels, as in the case of the iso-electronic Co$^{3+}$. It is known that the pervoskite LaCoO$_3$ displays a T dependent magnetic susceptibility, in spite of the non magnetic character of the Co$^{3+}$ ground state. This magnetic behavior has been modeled including contributions from the Co$^{3+}$ high-spin and intermediate-spin excited levels. On the other hand, attempts to observe the LaCoO$_3$ ESR spectrum were unsuccessful. Therefore, our results suggest that (as in the case of Co$^{3+}$) excited levels of Ni$^{4+}$ contribute to $\chi_{dc}$ but are invisible to the ESR experiment. Supporting the strong interdependence of ESR, dc-susceptibility, and structural properties in YNiO$_3$, we have found that $\Delta H_{pp}(T)$ and $\beta(T)$ follow closely the behavior of the monoclinic angle $\beta(T)$ shown for comparison in the inset of Fig. 4. The correlation of $\Delta H_{pp}(T)$ and $\beta(T)$ is a consequence of the change of the site symmetry: an increase of the site symmetry is usually accompanied by a narrowing of the ESR line.

Our interpretation of the experiments is then consistent with the existence of two different Ni sites in the monoclinic structure. If Ni1 (expanded) sites were occupied by Ni$^{2+}$ and Ni2 (contracted) sites by Ni$^{4+}$ one would expect Ni-O distances of 2.06 Å and 1.88 Å, respectively. Alonso et al. have determined that across the structural transition at $T_{MI}$ the Ni-O distances pass from 1.958 Å to 1.994 Å and 1.923 Å for the two different sites. Based on the size of the octahedra they propose different effective valence states: +2.65 and +3.35 for the Ni ions, representing the stabilization of an incomplete charge disproportionation of Ni$^{3+}$ into Ni$^{2+}$ and Ni$^{4+}$. Their observation points in the same direction of our results.

In summary, we have studied the magnetic properties of the Ni lattice in YNiO$_3$. In the metallic phase, at variance with LaNiO$_3$, we observed a T-dependent susceptibility that we associate with the small Y$^{3+}$ ionic radius. In the insulator phase, the $\chi_{esr}$ behavior allow us to discard the possibility of Ni$^{3+}$ $e_g$-electron localization. In this phase, we have observed that Ni ions become resonant and the characteristics of the ESR spectrum correspond to Ni$^{2+}$. The integrated intensity indicates that only a portion of the Ni ions are resonant. Our results are then consistent with a charge disproportionation of the type 2Ni$^{3+} \rightarrow Ni^{2+} + Ni^{4+}$, accompanying the MI transition. In this description the Ni$^{4+}$ ions contribute to $\chi_{dc}$ but are not detected by ESR techniques.

IV. ACKNOWLEDGEMENT

We acknowledge J. Rodriguez-Carvajal and B. Alascio for helpful comments. This work was partially supported by ANPCyT (Argentina) through the PICT 03-05266, and by the Ministry of Science and Technology (Spain) under the project MAT2001-0539. R. D. S. is CONICET (Argentina) researcher.

1. J. B. Torrance, P. Lacorre, A. I. Nazzal, E. J. Ansaldio, and Ch. Niedermayer, Phys. Rev. B 45, R8209 (1992) and references therein.

2. J. Rodríguez-Carvajal, S. Rosenkranz, M. Medarde, P. Lacorre, M. T. Fernández-Díaz, F. Fauth, and V. Trounou, Phys. Rev. B 57, 456 (1998).

3. J. A. Alonso, J. L. García-Muñoz, M. T. Fernández-Díaz, M. A. G. Aranda, M. J. Martínez-Lope, and M. T. Casais, Phys. Rev. Letters 82, 3871 (1999).

4. G. Demazeau, A. Marbeuf, M. Pouchard, and P. Hagenmuller, J. Soli State Chem. 3, 582 (1971).

5. J. A. Alonso, J. Martínez-Lope, M. T. Casais, J. L. García-Muñoz, and M. T. Fernández-Díaz, Phys. Rev. B 61, 1756 (2000).

6. R.D. Sánchez, M.T. Causa, J.Sereni, M.J. Sayagués, M.Vallet-Regí, and J.M.González Calbet, J.Alloys and Compounds 191, 287(1993).

7. R. D. Sánchez, Thesis, Insituto Balseiro, San Carlos de Bariloche (Argentina), 1992.

8. G.F. Goya, R.C. Mercader, L.B. Steren, R.D. Sánchez, M.T. Causa, and M. Tovar, J. Physics: Cond. Matter 8, 4519 (1996).
C. Zobel, M. Kriener, D. Bruns, M. Grüniger, T. Lorenz, P. Reutler, and A. Revcolevschi, Phys. Rev. B 66, 020402 (2002). S. Yamaguchi, Y. Okimoto, H. Taniguchi, and Y. Tokura, Phys. Rev. B 53, R2926 (1996).

M. Darwin, M. McElfresh, P. M. Shand, J. Xu, B. C. Crooker, and J. Spalek, Phys. Rev. B 46, 6382 (1992).

M. Tovar, M. T. Causa, A. Butera, J. Navarro, B. Martínez, J. Fontcuberta and M. C. G. Passeggi, Phys. Rev. B 66, 024409 (2002).

J. Pérez, J. Blasco, J. García, M. Castro, J. Stankiewicz, M. C. Sánchez, and R. D. Sánchez. J. Mag. Mag. Materials 196-197, 541 (1999).

R. D. Sánchez, M. T. Causa, A. Seoane, J. Rivas, J. F. Rivadulla, M. A. López-Quintela, and J. J. Pérez Cacho, J. Solid State Chem. 151, 1 (2000).

J. H. Van Vleck, The theory of electric and magnetic susceptibilities, Oxford University Press 1932.

The g-factor for Ni$^{2+}$ is (see Ref. Bleaney) $g = 2.0023 - \frac{\lambda}{\Delta}$. The value $g = 2.16$ is obtained using $\lambda = -242$ cm$^{-1}$ for the spin-orbit constant and $\Delta = 12000$ cm$^{-1}$ for the energy gap to the first excited level (estimated from Ni$^{2+}$ in diamagnetic oxides).

M. T. Causa and M. C. G. Passeggi, Phys. Letters 98A, 291 (1983). D. L. Huber and M. S. Seehra, J. Phys. Chem. Solids 36, 801 (1982).

A. Abragam and B. Bleaney, Electron Paramagneti Resonance of Transition Ions, Clarendon Press, Oxford (U. K.) 1970.

R. D. Sánchez, R. Carbonio, and C. Rettori, private communication.

M. Tovar, G. Alejandro, A. Butera, A. Caneiro, M. T. Causa, F. Prado, and R. D. Sánchez, Phys. Rev. B 60, 10199 (1999).

J. Rodríguez Carvajal, private communication.

FIGURE CAPTIONS

FIG. 1: Temperatures $T_{MI}$ (open circles) and $T_N$ (open triangles) vs. ionic radius $r_R$ for RNiO$_3$ taken from the literature (Refs. 1, 5, and 20). With solid symbols we show the results for YNiO$_3$ (present work) and for the La$_{1-x}$Eu$_x$MnO$_3$ series (Ref. 13). Solid lines are eyes guide. The dashed line separates regions where T-dependent ($\chi_{CW}$) and T-independent ($\chi_0$) susceptibilities are observed, as explained in the text.

FIG. 2: (a) Temperature dependence of $\chi_{dc}(T)$ (solid lines) and $\chi_{esr}(T)$ (circles). The arrows indicate the AFM and MI transition temperatures. Dashed line is an eyes guide. In the inset $\chi_{dc}^{-1}(T)$ is shown.

FIG. 3: ESR spectra taken at different temperatures. Open circles for $T = 560$ K show the line obtained after subtracting spurious cavity spectra.

FIG. 4: Temperature dependence of the linewidth $\Delta H_{pp}(T)$. In the inset we show the monoclinic angle $\beta(T)$ vs. $T$ taken from Ref. 3.
