Giant ^{16}O-^{18}O Isotope Effect on the Metal-Insulator Transition of RNiO$_3$ Perovskites (R = Rare Earth)

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(Received 24 September 1997)

The observation of unusually large, positive and rare-earth dependent ^{16}O-^{18}O isotope shifts in the metal-insulator transition temperature T_{MI} of RNIO$_3$ perovskites is reported ($\Delta T_{\mathrm{MI}} \leq +10.3$ K). The results clearly indicate that the mechanism of the transition involves a strong electron-lattice interaction. A simple model based on the existence of Jahn-Teller polarons in a stoichiometric, metallic, charge-transfer system is used to account for the evolution of ΔT_{MI} along the series. [S0031-9007(98)05540-9]

PACS numbers: 71.30.+h, 71.38.+i

Rare earth nickelates with the perovskite structure have several common characteristics with the homologue RMnO$_3$ series. From the technological point of view, both systems display extremely unusual electronic and magnetic properties which can be monotonously tuned by changing the composition or by applying either high pressures or magnetic fields. From a more fundamental point of view, nickelates and manganites contain $3d$ transition metal Jahn-Teller (JT) ions with a single electron in an orbitally degenerate ground state ($t_{2g}^3 e_g^1$ and $t_{2g}^6 e_g^1$ for Mn^{3+} and Ni^{3+}, respectively). A direct consequence of this fact is that neither Ni^{3+} nor Mn^{3+} display the conventional antiferromagnetic ordering expected for $3d$ ions in the perovskite structure. At least for manganites [1] (and probably also for nickelates [2]), the observed magnetic structure is due to the ordering of the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ e_g orbitals which, below a given temperature T_{JT}, are no longer degenerate due to spontaneous JT-induced distortions. Concerning transport properties, both series display important differences; Stoichiometric (RMnO$_{3.00}$) manganites are very good insulators, whereas Ni perovskites display a temperature-driven transition from a "bad" insulator to a "bad" metal [3]. In the classification proposed by Zaanen, Sawatzky, and Allen [4], manganites are believed to be Mott-Hubbard insulators, whereas nickelates are placed at the boundary separating low-Δ metals (Δ is the charge-transfer energy) and charge-transfer insulators.

Since temperature-driven metal-to-insulator transitions are extremely rare in oxides, a great deal of work has been done in order to understand the origin of this phenomenon in Ni perovskites [5]. The coincidence of T_{MI} and T_{N} for PrNiO$_3$ and NdNiO$_3$ (T$_{\mathrm{N}}$ is the Néel temperature) first suggested a magnetic origin for the transition. However, this possibility has been disregarded after recent studies on the magnetic behavior of the nickelates with $T_{\mathrm{MI}} \neq T_{\mathrm{N}}$ [6]. An alternative, rather appealing possibility was a gap opening done to a JT-induced distortion of the same kind of that observed in stoichiometric LaMnO$_{3.00}$ below $T_{\mathrm{JT}} \approx 600$ K [7]. However, no anisotropy could be detected in the NiO$_6$ octahedra neither above or below T_{MI} (the six Ni-O distances differ only in a few thousands of Å). This seems to indicate that Jahn-Teller effect is either drastically reduced (maybe due to the more covalent character of Ni oxides), dynamic in character, or simply nonexistent in Ni perovskites. However, as we pointed out before, the unusual magnetic structure reported for these compounds (they display a propagation vector $\mathbf{k} = (\frac{1}{2}\,0\,\frac{1}{2})$ which is unprecedented in an oxide with perovskite structure [2]) strongly suggests the existence of an ordering of the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals. If this orbital ordering actually exists, it should produce a small but significant distortion of the NiO$_6$ octahedra, which will manifest by the appearance of superstructure peaks with $\mathbf{k} = (\frac{1}{2}\,0\,\frac{1}{2})$ periodicity in the diffraction patterns. To be noted is that the unit cell associated with this propagation vector is 4 times larger than that observed in the metallic region. Thus, the metal-to-insulator transition will proceed through a gap opening in the quarter-filled Ni e_g-O $2p$ σ^* band which will displace the filled and empty states with respect to each other in a similar way as in a Peierls transition.

Since up to now we could not find any evidence of purely nuclear superstructure peaks in the insulating region [6], we decided to try an alternative way to investigate the role of the electron-lattice interaction as a possible motor for the transition. For this purpose we synthesized two series of nickelates (R = La$_{0.1}$Pr$_{0.9}$, Pr, Nd, Sm, and Eu), one prepared using natural oxygen (99.76% ^{16}O) and the other using the heavier isotope ^{18}O. The influence of the O mass in the metal-insulator temperature was explored using both differential scanning calorimetry (DSC) and neutron powder diffraction.

The powder samples used in this work were prepared following the high pressure synthesis procedure described in Ref. [3]. All compounds showed excellent crystallinity (reflected by the narrow diffraction peaks observed in the x-ray and neutron diffraction experiments) and were free of impurities. The good sample quality was confirmed by the small hysteresis observed on T_{MI} (less than 5°, see Fig. 1). The $R\mathrm{Ni}^{16}\mathrm{O}_3$ and $R\mathrm{Ni}^{18}\mathrm{O}_3$ series were prepared from the same batch of the starting material containing natural O. They were subjected to the same thermal treatment in closed ampoules, one containing $^{16}\mathrm{O}_2$ and the other $^{18}\mathrm{O}_2$ gas. The exchange was carried out at 725 °C in an oxygen pressure of ≈ 1.2 bar, the $^{16}\mathrm{O}_2$ and $^{18}\mathrm{O}_2$ partial pressures differing by less than 2%. After exchange, no evidence of decomposition was detected by x-ray and neutron diffraction (at this pressure, nickelates start to lose oxygen above 1000 °C). The $^{18}\mathrm{O}$ concentration was determined from weight measurements of the different isotope-enriched samples and in all cases was larger than 92(2)%. The total O content was in all cases $3 + \delta$, where $\delta = 0.00(2)$.

Several neutron powder diffraction experiments were performed at the Institut Laue Langevin (Grenoble). The diffractometers used in this work were D1B (PG, $\lambda \approx 2.52$ Å) and the Swiss CRG instrument D1A [Ge(115), $\lambda \approx 1.91$ Å]. Several powder diffraction patterns were recorded on D1B between 100 and 150 K ($\mathrm{PrNi}^{16}\mathrm{O}_3$ and $\mathrm{PrNi}^{18}\mathrm{O}_3$) in order to determine the temperature dependence of both the unit cell volume and the Ni magnetic moment. The measurements were performed by heating at a constant rate of 0.1 K/min. Additional high resolution patterns were recorded on D1A to investigate the eventual structural changes associated with the isotopic substitution. The data were analyzed with the Rietveld program FULLPROF [8]. DSC measurements were performed for the two sets of $^{16}\mathrm{O}/^{18}\mathrm{O}$ samples with a Perkin-Elmer DSC-4/TADS system. The heating/cooling ratio was 10 K/min.

Figure 1 shows the DSC curves measured by heating and by cooling for the two series of nickelates ($^{16}\mathrm{O}$ and $^{18}\mathrm{O}$). A sharp maximum/minimum indicating the occurrence of the metal-insulator transition is observed in all cases (the difference between the endothermic and exothermic curves just reflects the first order character of the transition). For the $^{16}\mathrm{O}$-enriched samples, T_{MI} coincides with that previously reported for the same compounds containing natural O. For the $^{18}\mathrm{O}$ samples, a *positive* isotope shift $\Delta T_{\mathrm{MI}} = T_{\mathrm{MI}}^{18} - T_{\mathrm{MI}}^{16} \approx +10.3$, +8.5, +7.6, +3.1, and +1.7 K for $R = \mathrm{La}_{0.1}\mathrm{Pr}_{0.9}$, Pr, Nd, Sm, and Eu is observed. A similar shift ($\approx +8.2$ K) has also been measured in the case of PrNiO_3 by means of neutron powder diffraction (see Fig. 2). To be noted is that the orthorhombic to rhombohedral structural transition displayed by the nickelates at higher temperatures is not affected at all by the mass of the oxygen isotope ($T_{\mathrm{OR}} = 787$ K for both $\mathrm{PrNi}^{16}\mathrm{O}_3$ and $\mathrm{PrNi}^{18}\mathrm{O}_3$), thus indicating that the observed isotope shift is a specific feature of the metal-insulator transition. A final proof that the change in T_{MI} is due to the substitution of $^{16}\mathrm{O}$ by $^{18}\mathrm{O}$ was obtained through oxygen back-exchange $^{18}\mathrm{O} \to {}^{16}\mathrm{O}$ and $^{16}\mathrm{O} \to {}^{18}\mathrm{O}$. Furthermore, the values of the Ni-O distances $d_{\mathrm{Ni\text{-}O}}$, the Ni-O-Ni superexchange angles θ, and the O content $3 + \delta$ obtained from high resolution neutron diffraction indicate that, within the experimental accuracy (± 0.0007 Å, $\pm 0.1°$, and ± 0.02 for $d_{\mathrm{Ni\text{-}O}}$, θ, and δ, respectively), no structural changes are induced by exchanging the O isotope [9].

The relative change of the metal-insulator temperature is better described by the oxygen isotope exponent, defined as $\alpha_{\mathrm{O}} = -d \ln T_{\mathrm{MI}} / d \ln M_{\mathrm{O}}$ (M_{O} is the O isotope mass). Its value for the five nickelates is displayed in Fig. 3 together with the values recently reported for the Curie temperature T_C of hole-doped manganites [10]. To be noted is that, although T_C is also an insulator to metal transition, the mechanism of the electronic localization has, in this case, a magnetic origin (the double exchange mechanism is believed to favor the stabilization of a ferromagnetic metallic state below T_C). This is a strong difference with respect to Ni perovskites, where the magnetic and the electronic transitions are completely decoupled [6]. It is then not surprising to find completely opposite behaviors in both series of compounds: For nickel perovskites, α_{O} is negative and increases in absolute value with the average radius of the rare earth ion r_{Re}. For manganites, it is positive, and it decreases with r_{Re}. It is also worth stressing that α_{O} of $\mathrm{La}_{0.1}\mathrm{Pr}_{0.9}\mathrm{NiO}_3$ (≈ -0.79) is the largest *negative* oxygen isotope exponent ever measured for any kind of transition temperature.

The sign and the evolution of the isotope shift along the nickelate series can be both qualitatively and quantitatively understood using a simple model based on the concept of the Jahn-Teller polaron. JT polarons were first introduced

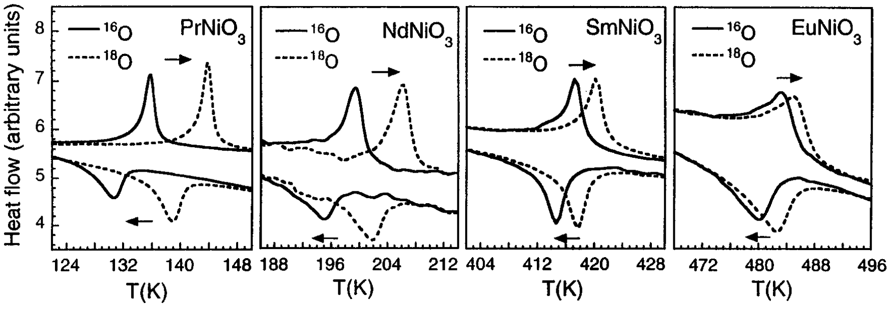

FIG. 1. DSC curves across the metal-insulator transition recorded by heating and by cooling (see arrows) for the two series of nickelates ($^{16}\mathrm{O}$ and $^{18}\mathrm{O}$).

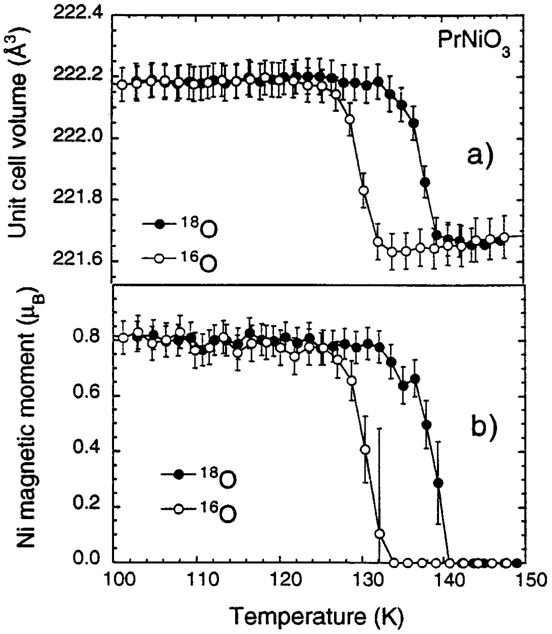

FIG. 2. Temperature dependence of (a) the unit cell volume and (b) the Ni^{3+} magnetic moment across T_{MI} for $PrNi^{16}O_3$ and $PrNi^{18}O_3$.

by Höck in 1983 [11], which defined them as the entities formed by the electron plus its induced JT distortion around it. In hole-doped manganites, where the charge fluctuations correspond to electron transfers of the type $Mn^{3+}Mn^{4+} \leftrightarrow Mn^{4+}Mn^{3+}$, JT polarons are believed to exist in the high temperature insulating phase [12] as a consequence of the motion of the JT distortion when an e_g electron is transferred from a Mn^{3+} to a Mn^{4+}. The extension of this concept to stoichiometric nickelates depends basically on the two following points: first, on the adequacy of using the polaron concept in the metallic state [in the insulating region ($T < T_{MI}$) we will assume the existence of the static $\mathbf{k} = (\frac{1}{2}\,0\,\frac{1}{2})$ orbital ordering], and second, on the possibility of defining JT polarons for an undoped system.

Although polaronic effects are expected to be much more pronounced in insulators than in metals, nickelates constitute a special case since they are intrinsically close to the boundary separating the two regimes. Moreover, the metallic state in these compounds is characterized by a large value of the resistivity (≈0.4 and 1.3 mΩ cm at room temperature for $PrNiO_3$ and $NdNiO_3$, respectively, see the works of Xu *et al.* and Cheong *et al.* cited in Ref. [5]), an extremely low density of carriers (0.25 e^-/Ni atom [13]), a large effective carrier mass ($11m_e$ [14]), and a small diffusivity (3×10^{-2} cm$^2/s$ [14]). The screening of the polaronic effects usually provided by conduction electrons is then expected to be significantly smaller than in normal metals. Concerning the definition of JT polarons, it is worth remembering that Ni perovskites are believed to be charge-transfer insulators. Thus, the charge fluctuations in the metallic regime (above T_{MI}) are expected to correspond to electron transfers between Ni and O sites ($Ni^{3+}O^{2-} \leftrightarrow Ni^{2+}O^{1-}$). Since Ni^{2+} is not a JT ion, JT polarons will appear as a consequence of the suppression of the JT distortion when an e^- moves from an O^{-2} to a Ni^{3+}. Conduction electrons will move through the lattice destroying the JT distortion at the Ni sites in a similar way as e_g electrons in Mn hole doped perovskites do.

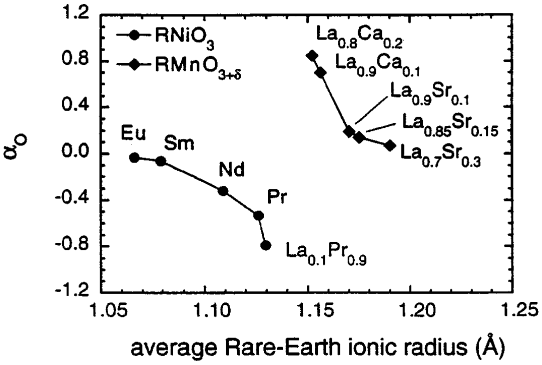

FIG. 3. ^{16}O-^{18}O isotope coefficient α_0 as a function of the average radius of the rare earth ion for nickelates and manganites.

The main effect of JT polarons in the transport properties is to reduce the bandwidth by means of an exponential renormalization factor of the type $W = W_b \exp(-\gamma E_{JT}/\hbar\omega)$ [15]. Here W_b is the bare bandwidth, E_{JT} the Jahn-Teller energy [16], ω is the frequency of the active Jahn-Teller mode(s), and γ is an increasing function of E_{JT}/W whose value ranges between 0 and 1. Since ω is inversely proportional to the square root of the oxygen isotope mass M_O, the polaron-induced band narrowing can be modified by substituting ^{16}O by ^{18}O. The sign of the expected shift of the metal-to-insulator temperature can be deduced from the following expression:

$$k_B T_{MI} = \Delta - \frac{W_b}{2} \exp(-\gamma E_{JT}/\hbar\omega)\,, \qquad (1)$$

which just reflects the fact that, for a change-transfer insulator, the gap energy E_g ($\approx k_B T_{MI}$) can be expressed in a first approximation as the difference between the charge-transfer energy Δ and half of the bandwidth. Equation (1) predicts a reduction of W by increasing the O isotope mass and consequently, a raise of T_{MI}. This is exactly what we observe in the nickelates studied in this work. In hole-doped manganites, the Curie temperature T_C is proportional to $W_b \exp(-\gamma E_{JT}/\hbar\omega)$, and, in consequence, the opposite behavior holds [10].

The evolution of α_O along the series can be easily explained by using the dependence of W_b with the structural parameters. For values of the Ni-O-Ni superexchange angle θ close to 180° (as is the case in Ni perovskites), W_b is proportional to $\cos\phi/d_{\text{Ni-O}}^{3.5}$, where $\phi = (180° - \theta)/2$ is the tilting angle of the NiO_6 octahedra [17]. Since $d_{\text{Ni-O}}$ is the same for all nickelates (≈1.94 Å), the relevant parameter in tuning the bare bandwidth is ϕ. Its value for the nickelates studied in this work ranges between

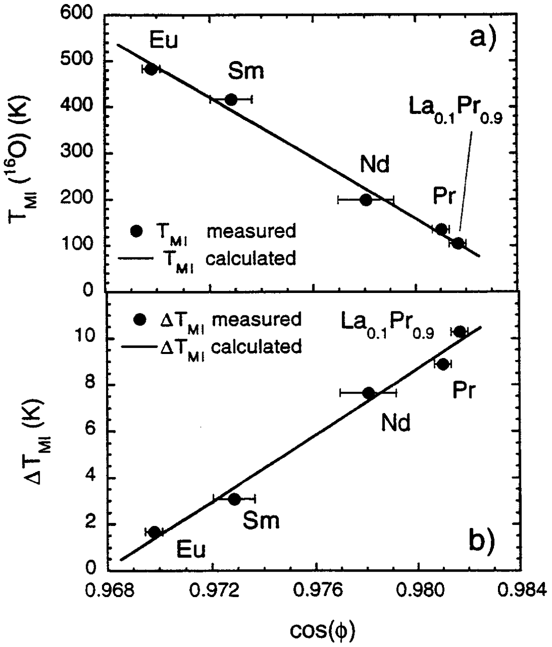

FIG. 4. Dependence of (a) T_{MI} (^{16}O) and (b) ΔT_{MI} with $\cos\phi$. The straight lines correspond to the fits described in the text.

10.98°(5) ($La_{0.1}Pr_{0.9}$) and 14.08°(5) (Eu), W_b decreasing in consequence along the series. One should note that this approach is not strictly valid when other parameters (as, for example, hole doping or compositional disorder) contribute to change W_b. In this sense, RNiO$_3$ perovskites constitute an ideal system since, due to their perfect O stoichiometry, the variation of W_b is controlled only by the distortion of the structure. By combining the expression of α_{O} and Eq. (1) it is straightforward to obtain

$$\alpha_{\mathrm{O}} = -\frac{W_b \gamma E_{\mathrm{JT}}}{4\hbar\omega\Delta\exp(\gamma E_{JT}/\hbar\omega) - 2\hbar\omega W_b}\,. \tag{2}$$

Since all variables in (2) are positive and W_b increases for larger rare earth ions, α_{O} is negative and increases in absolute value with the size of the rare earth ion. Expression (2) is therefore able to explain the qualitative behavior of α_{O} in nickel perovskites. An interesting point is that such a simple model also gives reasonable estimates of the different parameters involved in Eq. (1). In order to show this, we have substituted W_b by A $\cos\phi/d^{3.5}_{\text{Ni-O}}$ in (1) (A is just a proportionality constant), and we have fitted the observed dependence of T_{MI} with $\cos\phi$ for the two sets of ^{16}O and ^{18}O samples. By taking $\hbar\omega_{16} = 80$ meV (a typical energy for O modes in perovskites [18]) and $E_{\mathrm{JT}} = 400$ meV [16], we obtain a reasonable set of parameters ($\Delta_{16} = 2.89$ eV, $\Delta_{18} = 2.83$ eV, $W_b/\cos\phi = 8.53$ eV, $\gamma = 0.075$) as well as the fits shown in Fig. 4. To be noted is the excellent agreement between the experiment and the calculation, as well as the fact that the values of Δ_{16}, Δ_{18}, and W_b are of the same order of magnitude as previously published estimates from spectroscopic techniques [19].

In summary, we would like to stress that the results presented in this work constitute the first observation of large ($\Delta T_{\mathrm{MI}} \leq 10.3$ K) ^{16}O-^{18}O isotope effects (a) in a pure (nonmagnetic) metal-insulator transition, (b) in a Ni-based oxide family, and (c) in perfectly stoichiometric (no mixed-valence) compounds. Moreover, they represent an important advance in the understanding of the MI transition in Ni perovskites since they clearly prove the dominant role of the electron-lattice interaction as a driving force for the transition. Also, the excellent agreement between the measured isotope shifts and a simple model based on the existence of Jahn-Teller polarons in a stoichiometric, metallic, charge-transfer system gives strong qualitative and quantitative support to the polaronic picture suggested for other perovskite oxides containing Jahn-Teller transition metal ions [10,12,20,21].

The authors would like to thank the JLL for the allocation of beam time, R. Retoux for having refurbished the low temperature DSC apparatus, and H.-B. Braun, J. Mesot, and K. A. Müller for helpful discussions.

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