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# Giant Oxygen isotope effect on the metal-insulator transition of $RNiO_3$ perovskites

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# Giant Oxygen isotope effect on the metal-insulator transition of $RNiO_3$ perovskites

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The metal to insulator transition displayed by all the members of the perovskite family $RNiO_3$ (R = 4f rare earth different from La) has attracted a lot of interest since it constitutes one of the few examples of this phenomenon in perfectly stoichiometric compounds. In spite of the great deal of work performed during the last six years, the mechanism responsible for the electronic localization is still a matter of controversy. The observation of unusually large O isotope shifts on the metal-insulator temperature $T_{MI}$ reported in this study represents an important advance since it clearly proves the dominant role of the electron lattice interaction as driving force for the transition. Moreover, the good agreement between this observation and a simple model based on the existence of Jahn-Teller polarons in the metallic state gives further qualitative and quantitative support to the polaronic picture recently suggested to account for O isotope effects in other 3d transition metal oxides containing Jahn-Teller ions.

KEY WORDS: Oxygen isotope effect; metal-insulator transition; Jahn-Teller polarons.

## 1. INTRODUCTION

Since its discovery in 1991 [1], several mechanisms have been proposed to explain the occurrence of a metal-insulator transition in Ni perovskites [2]. Together with a magnetic origin (disregarded after recent studies on $SmNiO_3$ and $EuNiO_3$ [3]), a rather appealing possibility was a gap opening due to a Jahn-Teller induced distortion. However, though $Ni^{3+}$ displays in these compounds the low spin, potentially Jahn-Teller active $t_{2g}^6\, e_g^1$ configuration, the $NiO_6$ octahedra appeared to be nearly perfect in previous high resolution neutron diffraction studies. In a first stage it was then believed that the Jahn-Teller effect was either drastically reduced, dynamic in character or simply non existent in Ni perovskites. However, the unusual magnetic structure reported for these compounds (they display a propagation vector **k** = (1/2 0 1/2) which is unprecedented in an oxide with perovskite structure [2]) strongly suggested the existence of an ordering of the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals.

## 2. EXPERIMENTAL

Since in the neutron diffraction studies reported up to now no evidence of superstructure peaks related to the orbital ordering could be observed [3], we decided to try an alternative way to investigate the role of the Jahn-Teller effect as possible motor for the transition. For this purpose we synthesized two series of nickelates,

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one prepared using natural oxygen (99.76% $^{16}O$) and the other using the heavier isotope $^{18}O$. The influence of the O mass on the metal-insulator temperature was explored using both differential scanning calorimetry (DSC) and neutron powder diffraction. The neutron diffraction experiments were performed at the ILL on the diffractometers D1A and D1B.

## 3. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the unit cell volume and the ordered $Ni^{3+}$ magnetic moment for the two $PrNiO_3$ samples. The metal-insulator temperature is indicated by the volume anomaly at $T_{MI}$, as well as by the sudden suppression of the magnetic ordering above this temperature. To be noted is the huge displacement of the transition by increasing the mass of the O isotope (≈ +8.2K).

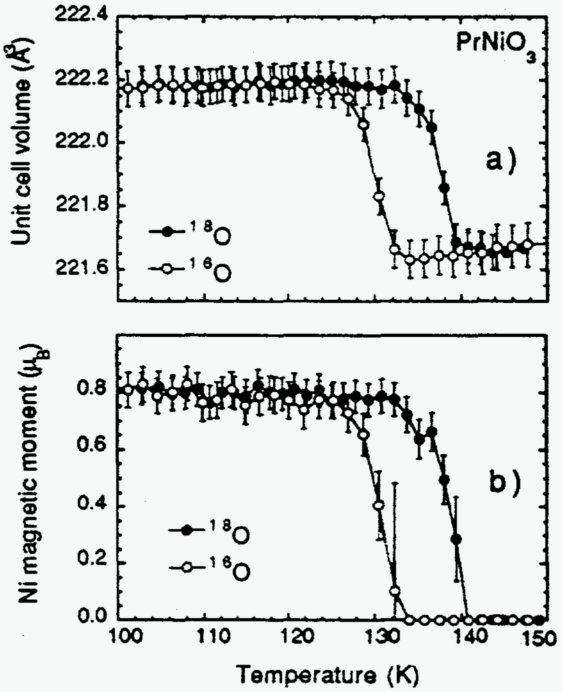

**Fig. 1.** Temperature dependence of a) the unit cell volume and b) the $Ni^{3+}$ magnetic moment across $T_{MI}$ for $PrNi^{16}O_3$ and $PrNi^{18}O_3$.

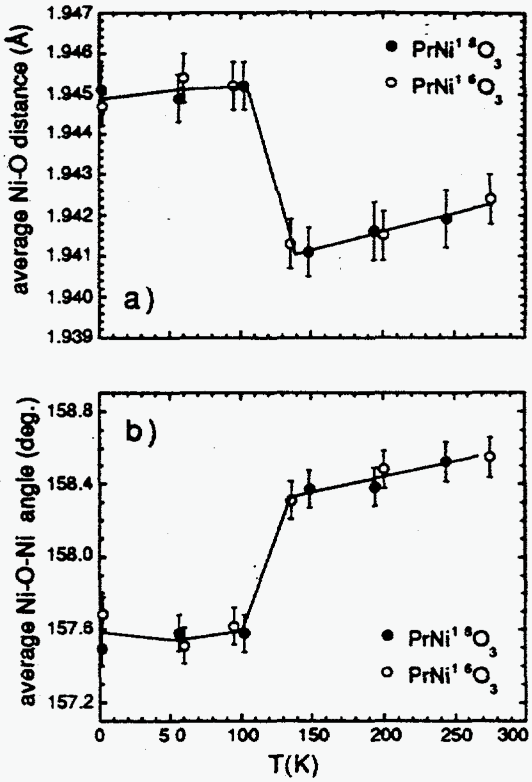

**Fig. 2.** Temperature dependence of a) the average Ni-O distance and b) the Ni-O-Ni superexchange angle across $T_{MI}$ for $PrNi^{16}O_3$ and $PrNi^{18}O_3$.

The effect has been confirmed by DSC measurements and by O back exchange. Furthermore, the values of the Ni-O distances (Fig. 2a), the Ni-O-Ni superexchange angles (Fig. 2b) and the O content (3+δ with δ=0.00(2))obtained from the high resolution D1A data indicate that, within the experimental accuracy, no structural changes are induced by exchanging the O isotope.

Shifts on $T_{MI}$ ranging between +1.7 K (for $EuNiO_3$) and +10.3 K (for $La_{0.1}Pr_{0.9}NiO_3$) have been measured for the remaining members of the series [4], [5], the last being the largest *positive* O isotope shift ever reported for any kind of transition temperature. Larger absolute values have been recently reported for the

Curie temperature of hole-doped. magnetoresistive manganites, but both the sign of $\Delta T_C$ an its evolution with the radius of the rare earth ion were opposite [6].

The origin of the O isotope effect in cuprates and manganites is actually a matter of discussion. However, several recent studies [6], [7] strongly suggest an interpretation based on the existence of Jahn-Teller polarons (electrons dressed by their associated Jahn-Teller distortion [8]). The present work gives strong support to this picture since this concept is also able to give a qualitative explanation of the isotope effect in Ni perovskites [4], [5]. Moreover, it constitutes an important advance since, for the first time, a quantitative explanation which perfectly reproduces the experimental observations is proposed. The model, based on Jahn-Teller polarons in a charge-transfer system (see refs. [4] and [5] for details), implies the following evolution of the metal-insulator transition temperature $T_{MI}$:

$$k_B T_{MI} = \Delta - \alpha \exp(-\gamma E_{JT}/h\omega) \cos\phi$$

Here $\Delta$ is the charge-transfer energy, $E_{JT}$ the Jahn-Teller energy, $\phi$ the tilt angle of the $NiO_6$ octahedra and $\omega$ the phonon frequency dependent of the O isotope mass. Figure 3 shows the evolution of $T_{MI}$ and $\Delta T_{MI}$ along the nickelate series together with the fit obtained with this mode by using $E_{JT}$ = 400 meV and $\omega$ = 80 meV. To be noted is the excellent agreement between the experiment and the calculation, as well as the fact that the values of the parameters involved in the model (the charge transfer energy $\Delta \approx 3$eV and the bare band width $W_b = \alpha \cos\phi \approx 8$ eV ) are of the same order of magnitude than previously published estimates from spectroscopic techniques [9].

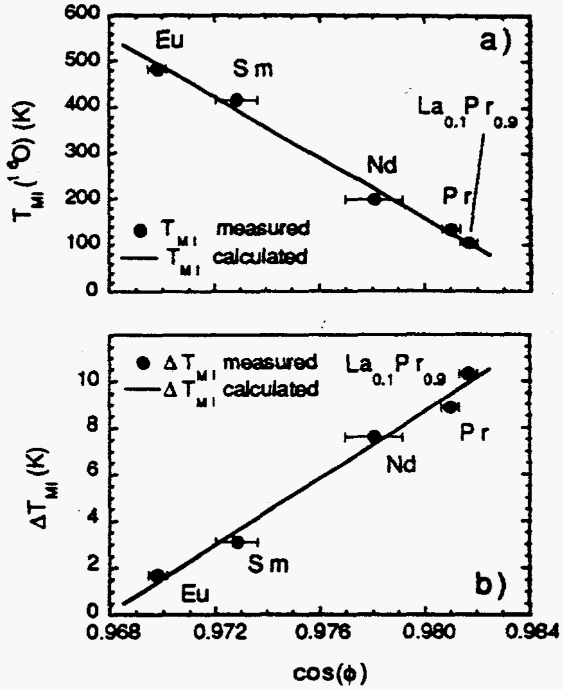

**Fig. 3** Evolution of the isotope shift $\Delta T_{MI}$ along the nickelate series from DSC and neutron diffraction data. cosinus of the tilting angle of the $NiO_6$ octahedra $\phi$ represented in the abcissa axis is a measure of the distortion of the perovskite structure. The straight lines are the fits mentioned in the text.

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