Charge disproportionation in RNiO$_3$ perovskites

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Abstract

RNiO$_3$ perovskites are one of the few families of undoped oxides showing a metal–insulator transition as a function of temperature. The origin of first-order transition has been one of the long-standing questions associated with these compounds. Neutron and synchrotron diffraction data of small rare-earth members of the series provide the first observation of changes in the crystal symmetry at the metal–insulator (MI) transition in RNiO$_3$ perovskites. At high temperatures, RNiO$_3$ are orthorhombic and metallic and below $T_{MI}$ they change to a monoclinic insulator. The structural reorganization at $T_{MI}$ gives rise to two crystallographically independent Ni positions and the insulating phase consist of alternating expanded (Ni$_1$O$_6$) and contracted (Ni$_2$O$_6$) octahedra along the three directions of the crystal cell. The magnetic structure shows unequal magnetic moments for the two Ni sites. These findings indicate a Ni charge disproportionation.

Transition–metal oxides with perovskite structure show an interesting ensemble of physical properties due to the tight relationship between lattice degrees of freedom, charge ordering, magnetism and carriers density. Such a strong interaction between charge carriers and lattice phonons becomes evident in two extensively studied systems. In manganese perovskites colossal magnetoresistance effect appears in the vicinity of metal–insulator (MI) transition. When doped with determinate quantities of holes, these compounds present a transition to a charge ordered state as a function of temperature [1,2]. Another perovskite-related family, the cuprates, when doped with carriers present the high-temperature superconductivity transition, but this superconducting transition temperature is sharply reduced in La$_{2-x}$Ba$_x$CuO$_4$ when $x = \frac{1}{4}$. Tranquada et al. [3], indicate that this suppression results from the real-space-ordered phase consisting of antiferromagnetic “stripes” separated by antiphase, hole-rich domain walls. The same kind of ordering has been observed in the hole-doped isostructural nickelates [4]. These examples led us to point out two conspicuous phenomena, the metal-to-insulator transition and the real-space charge-ordering transition. Even if in recent years they have attracted much attention their mechanism is far from being fully understood.

In most of these cases, the MI transition or electronic processes are achieved by doping holes or electrons into the insulating parent compound, which are thought to be Mott charge-transfer-type insulators. This is the main reason why the perovskite family RNiO$_3$ has been the object of our investigations. Nickel perovskites present two important particularities that make from these oxides an almost ideal system for the study of the interplay between structural and physical properties. In contrast to the other families mentioned before, they are perfectly stoichiometric which prevents the possibility of local disorder, and their physical properties depend in a continuous way upon the size of the rare earth [5]. The most

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appealing feature is the existence of a MI transition for the compounds with R different from La, whose critical temperature increase with decreasing size of the rare-earth ion. The origin of the first-order temperature-driven metal-to-insulator transition and the nature of their insulating state has been one of the major questions associated with RNiO₃ perovskites. For several years this entropy-driven change was thought to take place accompanied just by small quantitative changes of the structure as the expansion of the unit cell volume (about 0.2%) [6]. But in the insulating state, their magnetic structure is characterized by an unexpected propagation vector \( k = (\frac{1}{3} \ 0 \ \frac{1}{3}) \). This magnetic symmetry is not compatible with nearest-neighbor (NN) exchange coupling of the same sign and requires alternating ferromagnetic (FM) and AFM Ni–O–Ni couplings along the three pseudocubic axis. This fact together with the possible Jahn–Teller character of the Ni\(^{2+}\) ion has induced to think about a particular \( d_{2\pi} = 2/d_{2\pi} \)-orbital ordering that breaks down the inversion center at the Ni site in the orthorhombic symmetry. Nevertheless, the structural distortion from such orbital ordering has so far not been verified [7]. A recent relevant result has been the observation of very large positive and rare earth dependent \(^{16}\)O–\(^{18}\)O isotope shifts in the metal–insulator transition temperatures of RNiO₃ [8]. These results state the importance of the electron–lattice coupling for the MI transition and suggest the presence of Jahn–Teller polaron. A possible way to enhance the electron–lattice coupling is to investigate the small rare-earth compounds of the series. The increase in the relative strength of the electron–lattice interaction is mainly due to the electronegativity increase along the 4f series that induces more ionic Ni–O bonds.

In spite of the difficulties found in the synthesis, inherent to the stabilization of Ni\(^{2+}\) cations and which are more severe for smaller rare earths, we have been able to prepare polycrystalline YNiO₃ with high-pressure methods, and to perform synchrotron and neutron experiments [9]. Synchrotron X-ray diffraction (SXRD) patterns were collected at the BM16 high-resolution powder diffractometer of the ESRF using a short wavelength of \( \lambda = 0.518056(3) \) Å. Several patterns were collected across the MI transition, previously characterized by differential scanning calorimetric measurements. A room temperature (RT) neutron powder diffraction (NPD) pattern was collected at the D2B high-resolution diffractometer of the ILL, using a wavelength of 1.594 Å. The magnetic intensities were obtained from the low-temperature NPD patterns collected with \( \lambda = 2.52 \) Å at the D1B diffractometer. The data were analyzed by the Rietveld method, using the GSAS [10] and FULLPROF [11] programs.

The most important result that came out from the close examination of SXRD profiles from YNiO₃ in the insulating phase is the splitting of some reflections, characteristic of a monoclinic structural distortion. This finding represent the first observation of a modification of the crystallographic symmetry concomitant with the electronic localization in Ni perovskites. The resulting structural symmetry obtained for YNiO₃ below \( T_{\text{MI}} \) corresponds to the monoclinic \( P_{2_1}/n \) space group. Fig. 1 shows the temperature variation of unit-cell parameters of YNiO₃ across the transition. The main feature arising from the \( P_{2_1}/n \) symmetry is that there are two crystallographically independent Ni positions (Ni1 and Ni2), as well as three nonequivalent oxygen atoms (O1, O2, and O3). A simultaneous refinement of the SXRD and NPD data taken at RT allowed us to obtain very accurate oxygen positions for the monoclinic phase. In Fig. 2 we have represented the octahedral oxygen coordination around Ni1 and Ni2 atoms, which alternate along the three directions of the crystal. The most relevant finding is that the monoclinic symmetry gives rise to alternating expanded (\( d_{\text{Ni1–O}} = 1.994(3) \) Å) and contracted (\( d_{\text{Ni2–O}} = 1.923(3) \) Å) NiO₆ octahedra along the three directions of the crystal cell. Using the phenomenological Brown’s bond-valence model which relates the bond length and the valence of a bond [12,13], the calculated valences in the ionic limit are 2.62(1) and 3.17(1) for Ni1 and Ni2 cations, respectively. Consequently, the appearance of two alternating Ni states with \( 3 - \delta \) and \( 3 + \delta \) valences constitutes the first observation of a mutual self-doping process or charge disproportionation phenomenon associated with the insulating phase of pure RNiO₃ perovskites. We are thus led to conclude that the occurrence of a commensurate charge -modulation with the same periodicity of the structural cell is the driving force for the orthorhombic-to-monoclinic transition concurrent with the charge localization at \( T_{\text{MI}} \).

![Fig. 1. Temperature dependence of YNiO₃ lattice parameters through the metal–insulator transition.](image-url)
We shall now focus on the magnetic structure. Neutron diffraction data in YNiO$_3$ reveal the appearance of magnetic reflections below $T_N = 145$ K. The magnetic peaks can be indexed with a propagation vector $k = (\frac{1}{2}, 0, \frac{1}{2})$, the same found for the previously studied members of the family [7,14]. A satisfactory fit of the magnetic intensities was obtained for the collinear magnetic structure shown in Fig. 3. All magnetic moments lie in the $a$–$c$ plane, deviated around 45° from the $z$-axis. The main difference with the previously published magnetic structures is that using the monoclinic model the fit clearly converges to unequal moment values for the two Ni sites. The best magnetic fit corresponds to the moment values 1.4(1) and 0.7(1)$\mu_B$ at, respectively, Ni1 and Ni2 sites. This finding corroborates the partial charge disproportionation arising from structural considerations. This unusual magnetic structure continues to be somehow intriguing, but several consideration could help to explain the existence of ferromagnetic (FM) and AFM Ni–O–Ni couplings. The fact that the Ni2 positions tend to a diamagnetic state, could imply that the Ni1–Ni1 magnetic interactions between second-nearest neighbors become very significant compared with those between the nearest-neighbors Ni1–Ni2 atoms. Moreover, the possible localization of $e_g$ electrons in wave packets large enough to extend over nearest-neighbor sites could give rise to the observed ferromagnetic interactions.

The orthorhombic-to-monoclinic structural transition concurrent with the MI transition has been found for the rest of the smaller rare-earth compounds up to the LuNiO$_3$. The remaining question is whether this transformation is inherent to the electronic localization or there exist a critical value of the rare-earth radius above which the itinerant electrons localize at the Ni sites. To illustrate that, the variation of the Ni valence as a function of R$^{+3}$ ionic radius has been plotted in Fig. 4. In any case, the monoclinic distortion should be extremely small for the light rare-earth elements of the series, and preliminary high-resolution NPD data seems to indicate that the lowering of symmetry takes place at $T_{MI}$ already for the first element PrNiO$_3$ [15].

As a final comment we would like to come back to the charge ordering in manganites. The existence of a real-space ordering of charges is a well-established feature which takes place at determinate Mn$^{3+}$/Mn$^{4+}$ proportions, but important discrepancies remain in the determination of the ordered pattern. Two examples are the interpretation of the charge ordering in La$_{1.3}$Ca$_{2.7}$MnO$_3$ [16–18] and in La$_{0.875}$Sr$_{0.125}$MnO$_3$ [19,20]. We think that it would be possible that a similar scenario than the one presented here for the RNiO$_3$ could be present in the manganese perovskites at least for some cases. It could be that the localization of carriers does not necessarily imply that they reside on the structural lattice sites, but that the nodes of the electronic lattice could be formed elsewhere.

In summary, we have reported the first observation of changes in the crystallographic symmetry at the metal–insulator transition in RNiO$_3$ perovskites. The single Ni site in the metallic phase of YNiO$_3$ breaks up into two sublattices at the gap opening. The insulating phase of this nickelate with enhanced electron-lattice
coupling consists of expanded (Ni\textsubscript{1}O\textsubscript{6}) and contracted (Ni\textsubscript{2}O\textsubscript{6}) octahedra that alternate along the three directions of the crystal. The results show evidence for the stabilization of an uncompleted charge disproportionation, associated with the MI transition. Below $T_N$ the magnetic propagation vector $\mathbf{k} = (1/2, 0, 1/2)$ is the same to the previously reported for less-distorted RNiO\textsubscript{3} compounds. Corroborating the charge disproportionation, unequal moments are found at Ni\textsubscript{1} and Ni\textsubscript{2} sites in the low-temperature monoclinic phase. These findings represent an important advance for the understanding of the charge localization in transition metal oxides with orbitally degenerated electrons.

References