Direct Observation of Charge Order in an Epitaxial $NdNiO_3$ Film

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The first direct observation of charge order of $Ni^{3+\delta'}$ and $Ni^{3-\delta}$ by resonant x-ray scattering experiments in an epitaxial film of $NdNiO_3$ is reported. A quantitative value of $\delta + \delta' = (0.45 \pm 0.04)e$ was obtained. The temperature dependence of the charge order deviates significantly from those of the magnetic moment and crystallographic structure. This might be an indication of a difference in their fluctuation time scales. These observations are discussed in terms of the temperature-driven metal-insulator transition in the $RNiO_3$ family.

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The $3d$ transition-metal oxides exhibit a fascinating variety of physical properties ranging from high-T_c superconductivity to colossal magnetoresistance. One of the long-standing issues associated with these strongly correlated electron systems is the microscopic origin of the metal-to-insulator transitions and the nature of their ground state.

A prototype bandwidth-controlled metal-insulator transition is $RNiO_3$, R being the trivalent rare-earth ions (La to Lu) or Y [1]. $RNiO_3$ crystallizes in the orthorhombically distorted perovskite structure *Pbnm* with unit cell $\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$, where a_p is the perovskite cell parameter. The nominal valence of Ni is 3+ with d-electron configuration $t_{2g}^6 e_g^1$ and spin $S = 1/2$. $RNiO_3$ has a small charge-transfer energy and can be regarded as a self-doped Mott insulator [2]. In the $RNiO_3$ series, $LaNiO_3$ has the largest one-electron bandwidth and is metallic down to the lowest temperatures. All other $RNiO_3$ compounds have an insulating ground state; i.e., they have a charge-transfer gap between the O-$2p$ and the Ni-$3d$ upper Hubbard band. $RNiO_3$ exhibits a thermally driven metal-insulator transition at T_{MI} and a further transition to long-range antiferromagnetic order at $T_N \leq T_{MI}$. Examples are $NdNiO_3$ with $T_{MI} = T_N = 200$ K, $SmNiO_3$ with $T_{MI} = 400$ K and $T_N = 225$ K [3], and $YNiO_3$ with $T_{MI} = 480$ K and $T_N = 205$ K [4]. Associated with T_{MI} is a slight but abrupt expansion of the crystallographic unit cell, which causes a narrowing of the bandwidth, eventually leading to the opening of a gap at the Fermi surface [3,5].

Below T_N, $RNiO_3$ shows an unusual magnetic ordering with propagation vector $(1/2, 0, 1/2)$, with respect to the orthorhombic unit cell [5–7]. This corresponds to an up-up-down-down stacking of ferromagnetic planes along the pseudocubic [111] direction. As the twofold degenerate orbital e_g is singly occupied, one may expect a significant Jahn-Teller distortion and associated orbital ordering (of $x^2 - y^2/3z^2 - r^2$ type) in the insulating state of the $RNiO_3$ compounds [6]. Such a formation of an orbital superlattice could indeed explain the unusual magnetic ordering. In addition, the observed large isotope effect on T_{MI} [8] is an indication of a strong interaction with the lattice, and points to the presence of Jahn-Teller polarons [9]. However, thus far, no evidence for a Jahn-Teller distortion has been found. Moreover, it was argued that the orbital ordered state has a relatively high energy, suggesting that it is not responsible for the magnetic structure [10,11].

Recently, indirect evidence was found from high-resolution synchrotron powder diffraction that the strongly distorted members of the $RNiO_3$ series, for example $YNiO_3$, have a charge-ordered ground state (also called charge disproportionation) [4,12,13]. This interpretation is based on the observed symmetry lowering to monoclinic $P2_1/n$ crystal structure ($\beta = 90.08°$) at $T < T_{MI}$, which breaks up the single Ni site in the metallic phase into two individual crystallographic sites when the charge-transfer gap opens (*Pbnm* at $T > T_{MI}$ to $P2_1/n$ at $T < T_{MI}$). Thus far, no indication of a monoclinic distortion as in $YNiO_3$ has been found [12] for the larger rare-earth atoms Pr, Nd, Sm, and Eu, based on high-resolution diffraction. Indications for symmetry breaking were recently reported in an electron diffraction and Raman study on $NdNiO_3$ [14], supporting the idea that charge order may occur for all R ions.

In this Letter, we present resonant x-ray scattering data on an epitaxial film of $NdNiO_3$. This technique is ideal to study charge and orbital ordering [15] because the structure factor strongly depends on the electronic structure in the vicinity of an absorption edge of an ion. The observed site-selective electronic information is put into the context of the discussion of magnetic order and the metal-insulator transition. Thus far, the lack of single crystals has precluded such experiments on the nickelate series.

High-quality epitaxial films of $NdNiO_3$ have been grown on (001)-oriented $NdGaO_3$ substrates (*Pbnm*) by pulsed laser deposition. The lattice constants of the film grown

along the c axis are in plane expended $a \approx b = 5.48$ Å and $c = 7.59$ Å compared to polycrystalline $NdNiO_3$ ($a = 5.38$ Å, $b = 5.39$ Å, $c = 7.61$ Å). As a target, we used polycrystalline $NdNiO_3$ synthesized as in Ref. [16]. The films are deposited in 0.3 mbar oxygen atmosphere at $T = 740$ °C. After deposition, the sample is cooled slowly in $PO_2 = 1$ bar. The energy of the KrF eximer laser was 800 mJ at 5 Hz. The resistivity of the film was measured with the conventional four-probe technique. No impurity phases have been detected with Cu K_α radiation. The rocking curve full width at half maximum of the film is 0.14° (inset of Fig. 1). Synchrotron x-ray scattering experiments have been performed at ID20 of the ESRF. A Cu (222) crystal was used for polarization analysis. The energy resolution was approximately 1 eV. The x-ray absorption data were collected at Gilda CRG (BM08) of the ESRF in fluorescence mode at ambient temperature.

Figure 1 shows the resistivity of the 500-Å-thick $NdNiO_3$ film. A first-order metal-insulator transition is observed at approximately 170 and 150 K on the heating and cooling runs, respectively. T_{MI} is lower than in polycrystalline $NdNiO_3$, probably because of epitaxial strain. The resonant x-ray scattering experiments focused on reflections of type $(0hl)$ and $(h0l)$, with h and l odd. In *Pbnm* symmetry, these reflections have no contribution from the Ni site. Figure 2 shows the energy dependence of the (105) and (015) reflections with σ-σ polarization in the insulating state at 20 K. The spectrum of the (105) shows a strong maximum [minimum for (015)] at 8344 eV, approximately 10 eV above the Ni K-edge (8333 eV). This shows that these reflections contain a significant contribution from the electronic states of the Ni ions. Therefore, the resonant x-ray scattering data clearly indicate that, for $T < T_{MI}$, the *Pbnm* symmetry is lowered ($P2_1/n$). This symmetry breaking has not been observed with high-resolution powder diffraction for $NdNiO_3$ [12]. No indication of orbital order was found from the measurements with σ-π polarization. Figure 3 shows the resonant scattering of the (105) reflection for different temperatures. The nonresonant x-ray intensities as well as the energy dependence decrease for increasing

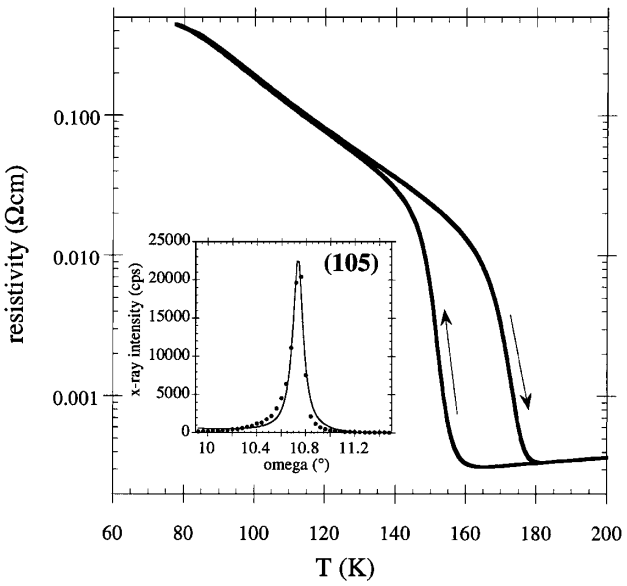

FIG. 1. The resistivity of epitaxial films of $NdNiO_3$ on $NdGaO_3$. Inset: Rocking curve of the (105) reflection taken at 190 K.

temperatures. Above T_{MI}, the scattering is independent of the energy, and there no longer is a resonant contribution from Ni. This confirms that there is a single electronic configuration of the Ni ions in the metallic phase ($T > T_{MI}$).

The energy dependence of the x-ray intensity is $I \propto |F(\mathbf{Q},E)F^*(\mathbf{Q},E)|$. $F(\mathbf{Q},E)$ is the structure factor given by $F(\mathbf{Q},E) = \sum_i f_i(Q,E)e^{i\mathbf{QR}_i}\delta(\mathbf{Q} - \tau)$, neglecting the Debye-Waller term. Here, $\mathbf{Q}$ and E are the x-ray momentum transfer and the x-ray energy, $f_i(\mathbf{Q},E)$ is the x-ray scattering factor of the ith ion at position R_i within the unit cell, and τ is a reciprocal lattice vector. $f_i(\mathbf{Q},E)$ is given by $f_i(\mathbf{Q},E) = f_i^0(Q) + f_i'(E) + if_i''(E)$, where $f_i^0(Q)$ corresponds to the Thompson scattering and $f_i'(E)$ and $if_i''(E)$ to the real and imaginary energy-dispersive correction factors, respectively. In monoclinic symmetry $P2_1/n$, there are two inequivalent Ni sites labeled Ni_I and Ni_{II}. The structure factor $F(\mathbf{Q},E)$ of the (015) and (105) reflections is then given by

$$\begin{aligned} F_{015}(\mathbf{Q},E) &= A_{O,Nd}(\mathbf{Q}) + 2\Delta f_{Ni}^0(Q) + 2\Delta f_{Ni}'(E) + 2i\Delta f_{Ni}''(E), \\ F_{105}(\mathbf{Q},E) &= B_{O,Nd}(\mathbf{Q}) - 2\Delta f_{Ni}^0(Q) - 2\Delta f_{Ni}'(E) - 2i\Delta f_{Ni}''(E), \end{aligned} \tag{1}$$

where $\Delta f_{Ni}'(E) = f_{Ni_I}'(E) - f_{Ni_{II}}'(E)$, $\Delta f_{Ni}''(E) = f_{Ni_I}''(E) - f_{Ni_{II}}''(E)$, $\Delta f_{Ni}^0 = f_{Ni_I}^0 - f_{Ni_{II}}^0$, and $A_{O,Nd}$ and $B_{O,Nd}$ correspond to the O and Nd contributions to the structure factor. For a single electronic Ni configuration $f_{Ni_I} = f_{Ni_{II}}$, $F_{015} = A_{O,Nd} = 0$, and $F_{105} = B_{O,Nd}$. An energy dependence of the Bragg reflections occurs only when $f_{Ni_I} \neq f_{Ni_{II}}$. Therefore, our data directly prove that $NdNiO_3$ has a long-range charge-ordered ground state with the two distinct Ni sites, $Ni^{3+\delta'}$ and $Ni^{3-\delta}$.

To determine the size of this charge order and the site-selective electronic structure of the Ni ions, we will now discuss the Ni K-edge energy shift between Ni_I and Ni_{II}. The resonant x-ray scattering intensities for the (105) reflections [Eq. (1)] can be approximated by $I(E)_{(105)} \propto (B_{O,Nd}')^2 - 4B_{O,Nd}'\Delta f_{Ni}'(E)$ (using $B_{O,Nd}^{\prime(105)} \gg B_{O,Nd}^{\prime\prime(105)}$, with $'$ and $''$ indicating the real and imaginary part). This shows that the resonant scattering intensity depends linearly on the difference of the real part

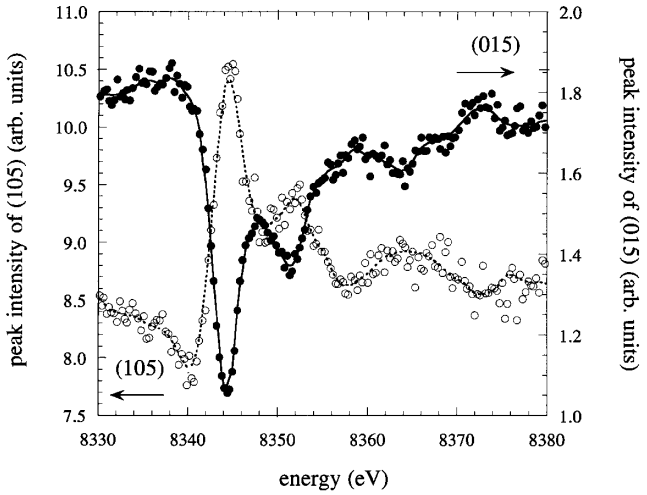

FIG. 2. Energy-dependent x-ray intensity of the (015) and (105) reflections taken at 20 K with σ-σ polarization. The lines are guides to the eye.

of the scattering factors $f'_{\mathrm{Ni_I}}(E) - f'_{\mathrm{Ni_{II}}}(E)$. On the other hand, the x-ray absorption spectrum is sensitive to the sum $f''_{\mathrm{Ni_I}}(E) + f''_{\mathrm{Ni_{II}}}(E)$. From the *sum* and *difference,* and the Kramers-Kronig relation, the site-selective real and imaginary parts of the scattering factors of the $\mathrm{Ni_I}$ and $\mathrm{Ni_{II}}$ sites are obtained (Fig. 4). The energy shift between the $\mathrm{Ni_I}$ and $\mathrm{Ni_{II}}$-site scattering factors at the Ni K-edge is found to be 0.90 ± 0.08 eV. The Ni K-edge shift for different electronic states of Ni has been studied for $LaNiO_{3-x}$, La_2NiO_4, and $LaNiO_2$ [17]. A linear dependence of the Ni valence as a function of K-edge shift for these oxides was found. Using these results, the 0.9-eV K-edge shift translates into $\delta + \delta' = 0.42 \pm 0.04e$ in the ground state. Alternatively, the 0.9-eV shift can be compared with the energy shift of 2 eV between the $3d^7$ and $3d^8\underline{L}$ ($\underline{L}$ denotes a ligand hole) configurations as obtained by multiple scattering calculations [18], which results in a similar value of $\delta + \delta' = 0.45 \pm 0.04e$. These values are smaller than those obtained by bond-valence sum calculations for the monoclinic distorted $R\mathrm{NiO_3}$ with smaller R ions [13] of $\delta \approx \delta' \approx 0.3e$ or $\delta + \delta' \approx 0.6e$.

X-ray absorption spectroscopy and Hartree-Fock calculations [19] found that the Ni average electronic state is not 3+. They propose a mixture of approximately 70% $3d^7$ and 30% $3d^8\underline{L}$, corresponding to a Ni average valence of 2.7 and implying that $\delta' \neq \delta$. Taking this into account, we find that the $\mathrm{Ni_I}$ and $\mathrm{Ni_{II}}$ sites have valences of approximately 3+ and 2.5+, respectively ($\delta' \approx 0$ and $\delta \approx 0.5e$). As $3d^7$ and $3d^8\underline{L}$ correspond to $\mathrm{Ni^{3+} - O^{2-}}$ and $\mathrm{Ni^{2+} - O^{-}}$ configurations, respectively, this result indicates charge order on Ni as well as O sites. This is in contrast to the prediction of the Hartree-Fock calculations [2] that yielded charge order on Ni for the smaller R ions (e.g., Ho, Y) and on O for the larger R ions (e.g., Nd).

The charge-order order parameter can be extracted from the temperature dependence of the integrated x-ray intensity of the (105) reflection. Because $B'^{(105)}_{\mathrm{O,Nd}} \gg B''^{(105)}_{\mathrm{O,Nd}}$, the charge-order order parameter is, in good approximation, proportional to $\sqrt{I(E_{\mathrm{res}})} - \sqrt{I(E_{\mathrm{offres}})}$, where

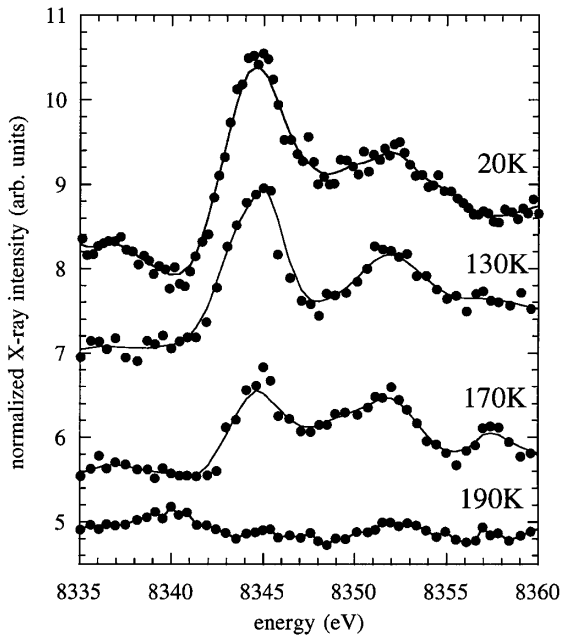

FIG. 3. Energy-dependent x-ray intensity of the (105) reflection for selected temperatures. The lines are guides to the eye.

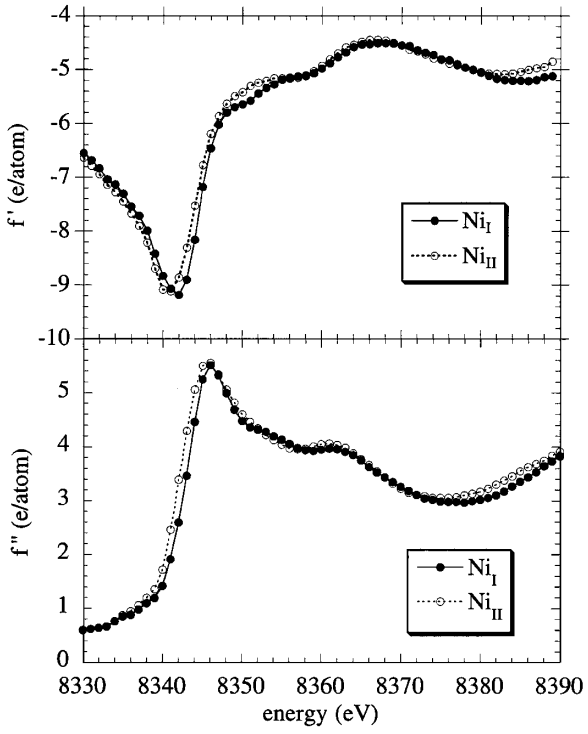

FIG. 4. Site-selective real (upper panel) and imaginary (lower panel) parts of the energy-dependent correction to the scattering factors of Ni.

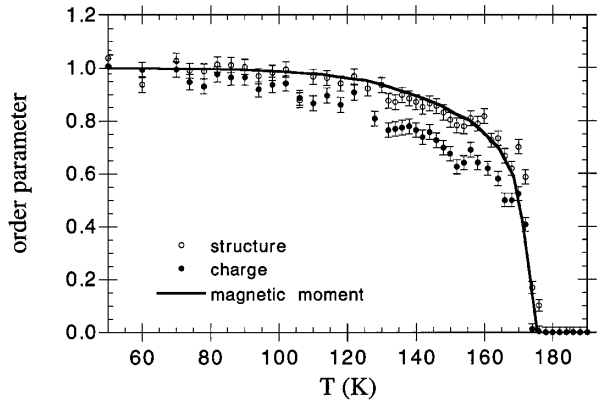

FIG. 5. The temperature dependence (heating) of the charge-order order parameter, structural order parameter, and magnetic moment (rescaled from Ref. [21]).

$E_{\mathrm{res}} = 8344.5$ eV and $E_{\mathrm{offres}} = 8330$ eV. The temperature dependence of the change in intensity off resonance is dominated by $(B_{\mathrm{O,Nd}}^{\prime(105)})^2$, i.e., the square of the "crystallographic" structural order parameter. Note that the direct contribution of the charge order to the structure factor off resonance is negligible [the difference in the Thomson scattering being $<0.13e$ [20] at the (105) and (015) reflections]. Figure 5 shows the temperature dependence (on heating) of the charge-order order parameter and the structural order parameter extracted from the integrated intensities of the (105) reflection. These curves are compared with the ordered magnetic moment of the Ni ions in polycrystalline $NdNiO_3$ taken from neutron scattering [21] (rescaled to unity and with the same T_N for the magnetic moment). The structural and magnetic order parameters are identical within experimental accuracy. The charge-order order parameter, however, behaves differently. This may indicate a difference in the fluctuation time scales of the magnetic moment and structure as compared to the charge. $NdNiO_3$ is highly conducting; i.e., the charge fluctuations above T_{MI} are very fast and inhibit magnetic order. This is in contrast to, for example, the $R\mathrm{BaCo_2O_5}$-type cobaltites, for which $T_N > T_{\mathrm{MI}}$ ($T_N \approx 340$ K and $T_{\mathrm{MI}} \approx 210$ K [22]). For these cobaltites, the conductivity is smaller than in $R\mathrm{NiO_3}$ [22] at $T > T_{\mathrm{MI}}$. This means that the charge fluctuations are much slower, and magnetic order can occur already at temperatures above T_{MI}. If $NdNiO_3$ had a comparably low conductivity, one would expect the magnetic order to occur at a higher temperature [23]. In $NdNiO_3$, the magnetic moments can already saturate while the charge fluctuations are slowing down. The structure, for which the fluctuations are slow (massive particles involved), can relax only when the charge fluctuations are slow enough, which could explain their different observed order parameters. These results were obtained on a strained epitaxial film, and care has to be taken when compared with bulk properties (e.g., magnetic order parameter).

In conclusion, we directly observe charge order ($Ni^{3+\delta'}$ and $Ni^{3-\delta}$) at the metal-insulator transition in $NdNiO_3$, using resonant x-ray scattering. This finding shows that the metal-insulator transition in $NdNiO_3$ can be understood on the basis of charge order. This charge order can also account for the unusual magnetic propagation vector, rendering models with orbital order obsolete. The size of the charge order was determined to be $\delta + \delta' = 0.45 \pm 0.04e$. The site-selective electronic states of Ni_{I} and Ni_{II} are determined to be approximately $3d^7$ and a 50% mixture of $3d^7$ and $3d^8\underline{L}$, respectively. Finally, the order parameters of the magnetic moment and the structural deviation differ significantly from the charge-order order parameter, providing insight into the differences of the time scales in the fluctuations.

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