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Resonant x-ray scattering experiments on electronic orderings in $NdNiO_3$ single crystals

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We have carried out resonant x-ray scattering experiments on $NdNiO_3$ single crystals aiming at the observation of a predicted orbital ordering that may explain the presence of an antiferromagnetic ordering with unusual modulation wave vector, $q=(\frac{1}{2},0,\frac{1}{2})$. A first-order structural phase transition has been observed at $T_{MI}=200$ K although no new superlattice peaks are present at this q position. Our experiment thus rules out the presence of an orbital ordering with this modulation. It rather seems that the magnetic, as well as the electronic, properties of this compound should be explained by introducing models of charge localization, either at the metal sites or at the ligand oxygen. We further comment on the observability of this charge ordering by resonant x-ray scattering.

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I. INTRODUCTION

Rare-earth (R)/nickel perovskites have some common characteristics to their Mn homologue although they are placed at the boundary separating *low-Δ gap metals* (Δ is the charge transfer energy) and *charge transfer insulators*.[1] Qualitatively, many properties of these materials can be understood within the classical scheme of a hole-doped Mott–Hubbard insulator in which double exchange, Hund's rule coupling, and the Jahn–Teller (JT) effect play crucial roles. In $RNiO_3$ a metal-insulator (M-I) transition takes place as a function of temperature,[2] whereas the same transition is found on *doping* the manganites. $Ni^{3+}(t_{2g}^6e_g^1)$ as well as $Mn^{3+}(t_{2g}^3e_g^1)$ are JT ions with a single e_g electron with orbital degeneracy although the JT deformations are rather different between the two families. In stoichiometric $RMnO_3$, the JT deformations stabilized a layered antiferromagnetic structure,[3], whereas the NiO_6 octahedra are rather regular,[4] probably due to the higher covalency character of the Ni oxides.

$RNIO_3$ perovskites (excepting for $R=$La) display a first-order metal insulator phase transition from $Pbnm$ to $P2_1/n$, yielding two different crystallographic sites for Ni but with no change in the lattice coordinates. The lattice distortion occurring below T_{MI} has been detected for the smallest cations ($R=$Y,Ho,…,Lu),[5,6] whereas it has remained rather elusive for the largest cations ($R=$Pr, Nd, and Sm).[4,7] Recently, electron microscopy and Raman scattering experiments have evidenced a symmetry breaking at T_{MI} in $NdNiO_3$.[8] Interestingly, the M-I transition takes place between 550 and 600 K in the small rare-earth cation compounds, whereas it is strongly depleted for the largest cations (Sm, $T_{MI}\approx 400$ K; Nd, $T_{MI}\approx 200$ K; Pr, $T_{MI}\approx 135$ K).[9] Ni ions order antiferromagnetically at lower temperatures (through a continuous, second-order, phase transition) and the transition temperature smoothly evolves with the size of the rare earth from $T_N=130$ K for Lu to $T_N=225$ K for Sm, and $T_N\equiv T_{MI}$ for Nd and Pr. Moreover, based on the discovery of an unprecedented magnetic ordering of spin-$\frac{1}{2}$ Ni moments in $PrNiO_3$ and $NdNiO_3$, a *nonuniform* orbital occupancy of the single e_g electron in the low-spin Ni^{3+} configuration has been predicted.[10] In these two compounds, $T_N=T_{MI}$, and the magnetic structure has an unexpected propagation vector, $q=(\frac{1}{2},0,\frac{1}{2})$, corresponding to an ↑↑↓↓ stacking of ferromagnetic planes along the (1,1,1) direction of the pseudocubic lattice. This magnetic symmetry is not compatible with nearest-neighbor exchange coupling of the same sign and requires alternating ferromagnetic and antiferromagnetic Ni–O–Ni couplings along the three pseudocubic axes. This can be achieved if a $d_{x^2-y^2/d_{z^2}}$ orbital ordering exists in the crystal, that breaks down the inversion center at the Ni site. However, no structural distortion originating from orbital ordering has been observed so far. Moreover, Hartree–Fock calculations have showed that the orbital ordered state has a relatively high energy and thus suggested that this possibility is very unlikely to explain the observed magnetic order.[11,12]

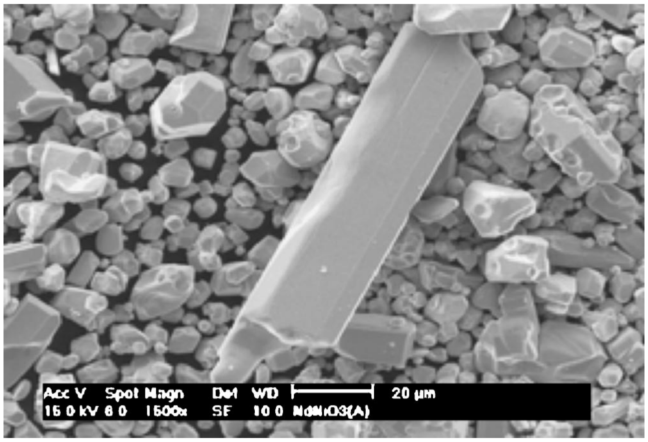

FIG. 1. Electron microscopy image of small single crystals of $NdNiO_3$ obtained under pressure (see Ref. 18).

Charge order disproportionation in the form $Ni^{+3+\delta}$–$Ni^{+3-\delta}$, with $\delta \approx 0.3e^-$, has been invoked to be present in all the small rare-earth RNiO$_3$ (R=Ho$\cdots$Lu and Y) compounds on the basis of a bond valence analysis of the structure in the insulating state.[5,13] This empirical analysis of the charge *usually* yield appropriate results. However, RNiO$_3$ are generally viewed as charge transfer insulators, and along this line one may expect that the JT energy of the doubly degenerated e_g level is raised, not by an *often* large JT distortion, but rather by getting rid of the electron degeneracy in this orbital. According to this simple view, the charge would go either to the ligand oxygen (also known as bond charge ordering), following the well-known scheme $3d^7+2p^6 \rightarrow 3d^8+2p^5$, or it will remain disproportionated in the metal ions $3d^7+3d^7 \rightarrow 3d^6+3d^8$. Recent Hartree–Fock calculations on RNiO$_3$ perovskites have shown that it is difficult to assert which option is the best, or even if it does change from, for instance, bond order in the larger rare-earth to metal-site ordering in the smaller ones.[14]

RNiO$_3$ perovskite compounds have been known for many years, and quite a lot of experimental as well as theoretical work has been accumulated (see Ref. 15 for a recent review). All experiments aiming at a precise determination of the structure(s), including synchrotron and neutron diffraction, have been carried out in polycrystalline samples, except for a very recent work on 500-Å-thick thin films of $NdNiO_3$, to determine the amount charge ordering at the M-I phase transition.[16,17] Both x-ray and neutron powder diffraction have shown no sign of orbital ordering (superstructure reflections should be 10^4 times smaller than the largest nuclear reflection), which speaks in favor of a very small lattice distortion. We have now grown small single crystals of $NdNiO_3$ (Ref. 18) (see Fig. 1) large enough to carry out diffraction experiments at synchrotron light sources. With this high quality single crystals it will be then possible to test many ideas on the origin of magnetism in this compound and the very intriguing possibility of a *pure* orbital ordering; i.e., without an accompanying lattice distortion. As we shall see, orbital ordering Bragg reflections in the predicted positions are systematically absent. It is then natural to turn to the charge ordering as the origin of the elusive magnetic ordering observed in this compound. These are the goals of the work developed in this paper.

II. EXPERIMENTAL CONDITIONS

Resonant (also called anomalous) x-ray scattering (RXS) techniques have proved to be very powerful to unravel orbital (and charge) orderings and its likely relation with magnetic orderings.[8] RXS consists of measuring the intensity of some *selected* Bragg reflections as a function of the incident photon energy around the absorption edge of one of the atomic species. There are several different ways to proceed with this technique, depending upon whether the information sought is crystallographic or, rather, spectroscopic.[19] In all the cases, the key point of the technique is that for incident photon energies in the vicinity of an absorption edge, the x-ray scattering factor of the anomalous atom becomes complex $[f_i'(E)+if_i''(E)]$ and displays a nontrivial energy dependence. This complex structure factor interferes with the phase factor of the given reflection ($\mathbf{Q}$) in a manner described by the following equation:

$$I(\mathbf{Q},E) \propto \left| \sum_i [f_{0i} + f_i'(E) + if_i''(E)] e^{i\mathbf{Q}\cdot r_i} e^{-W_i(\mathbf{Q})} \right|^2, \qquad (1)$$

where $W_i(\mathbf{Q})$ is the temperature factor, f_{0i} is the atomic scattering factor, f' and f'' are rank-2,3,4, ... tensors in their most general form (including magnetic as well as nonmagnetic scattering factors) projected over the incoming and outgoing photon polarization direction, respectively. For all the purposes of this paper, we will be exclusively interested in the dipole–dipole (E1E1) transition at the Ni K edge ($1s \rightarrow 4p$ transition) whose operator can be written in the form of a rank-2 tensor (or a matrix). In order to comprehend how RXS can explore the *purely electronic orderings* in a solid, it is important to notice the following: (i) the exact value of the absorption edge depends on the electronic *charge* that the resonant atom experiences, and along this line the different charge states of the resonant atom are characterized by slight changes of the position of the absorption edge. (ii) The electronic transition probes the *empty* 3d orbital states via quadrupole–quadrupole (E2E2) processes of the type $1s \rightarrow 3d$. If the orbital ordering is stabilized without site symmetry breaking, i.e., no lattice distortion (no cooperative JT effect), one should expect a new periodicity, exclusively electronic, that might be observable precisely at the energy corresponding to the nonoccupied degenerate orbitals. This latter form of ordering has been suggested in a number of systems but, unfortunately, orbital orderings have been invariably observed to be stabilized by local symmetry breaking. Due to that, the anisotropy induced in the neighboring 4p states is rather strong, and it has been observed that the E1E1 process prevails against the purely orbital ordering signal at the K edges of 3d transition metals. This conclusion results both from simulations of the measured spectra in the giant magnetoresistance manganites[20] and more recently from detailed experimental studies on thin films.[21] It has been speculated that $NdNiO_3$, by virtue of its unexpected magnetic ordering wave vector and the absence of lattice distortions, might be a candidate to further explore the so far theoretical concept of orbital ordering stabilized by magnetic interactions alone. Below we will pursue this discussion of the tensor scattering factors by introducing the site symmetry of Ni ions in the lattice and we will show that the geometrical conditions have to be taken into account in order to properly disentangle *electronic orderings* from local anisotropy in the diffraction spectra.

The RXS experiment was carried out at the ESRF in the magnetic scattering beamline ID20 (Ref. 22) at photon energies in the close vicinity of the Ni K edge. The absorption edge is located at 8.343 eV ($\lambda = 1.486$ Å) in $NdNiO_3$. For comparison the edge in Ni metal lies at lower energies, 8.333 eV. A sample of dimensions $20 \times 20 \times 50$ μm^3 was glued on top of a quartz whisker and then placed onto the cold finger of a closed-cycle He refrigerator. The setup was installed on a four-circle goniometer and the scattering plane is vertical. Sample quality can be considered as excellent in view of the value of the Bragg peaks rocking width, of the order of 0.02°. The count rate at the (004) reflection was 5×10^8counts/sec. In order to discriminate the polarization of the scattered photons (either parallel to the scattering plane, π, or perpendicular, σ) a Cu(222) analyzer crystal was placed before the detector, a NaI scintillator. The polarization leakage (σ-$\sigma \rightarrow {}_{\tau}\sigma$-$\pi$) was measured to be $\tau = 0.005$. As expected for a low-symmetry perovskite compound, $NdNiO_3$ single crystals are twinned even at room temperature. The actual structure is orthorhombic *Pbnm* with lattice parameters $a = 5.389$ Å, $b = 5.3863$ Å, $c = 7.6078$ Å.[4] Because of the twins, a pseudocubic lattice with average lattice parameter $a = 7.6$ Å was preferred. The reciprocal space transformation rule between both settings is $h_o = \frac{1}{2}(h_c + k_c)$, $k_o = \frac{1}{2}(h_c - k_c)$, and $l_o = l_c$, and the two corresponding axes permutations. Therefore, the cubic $(115)_c$ reflection will contain the superposition of the $(105)_o$ and $(015)_o$ reflections. The four remaining domains are found by cyclic permutations of the indices h_c, k_c, l_c. The low-temperature structure (monoclinic $P2_1/n$) arising from the M-I phase transition at T_{MI} multiplies the number of domains by a factor of 2, albeit without changing the unit cell volume.

Absorption is an important issue in this compound. Indeed, the three Nd L edges happen to be at lower energies (6.208, 6.721, and 7.126 keV) and their contribution dominates the absorption coefficient both below ($\mu = 1734$ cm^{-1}) and above ($\mu = 2158$ cm^{-1}) the Ni edge. Therefore, and despite that the whole sample is bathed by the x-ray beam, absorption limits the penetration depth to 6 µm below the Ni edge and to 4.6 µm above. These values, smaller that the size of the sample, lead us to cast serious doubts on how the domain structure is going to appear in our diffraction spectra and therefore on the intensity of the different peaks.

III. METAL-INSULATOR PHASE TRANSITION

Temperature scans were carried out in order to characterize the thermal evolution of the sample and check the appearance of a phase transition. The photon energy for these experiments was chosen to be 10 eV below the Ni absorption edge. Figure 2 shows a contour plot of the diffraction angle θ_B of the $(115)_c$ Bragg reflection for a series of temperatures above and below T_{MI}. Only one peak is visible above T_{MI}, whereas at least four develop below, although this has seen to be dependent of the thermal history. Clearly, a first-order structural phase transition induced by the charge ordering occurs in $NdNiO_3$, in much the same way as it has been observed for the small rare-earth analogues. Our data, and in particular the fact that Bragg peaks above T_{MI} turned out to be splitted below, are in good agreement with the change in the lattice symmetry below 200 K ($Pbnm \rightarrow P2_1/n$) reported by electron diffraction experiments.[8] The transition temperature was determined from the onset of the splitting of the diffraction peak to be 195 K, and pretransitional effects have been observed as well. A refinement of the structure, based on single-crystal data, above and below T_{MI} is presently underway.[23]

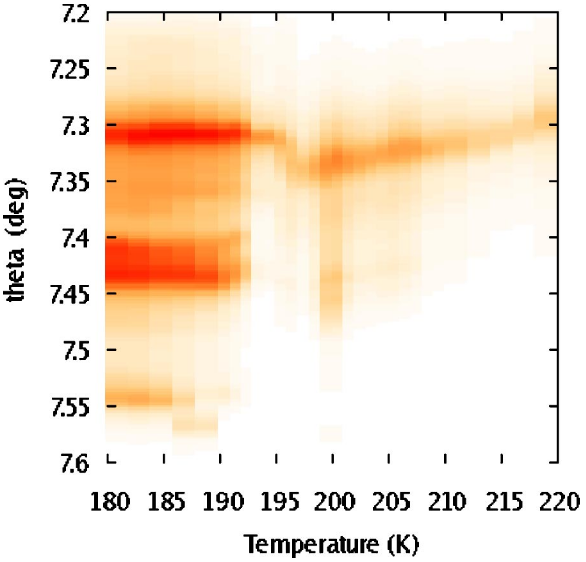

FIG. 2. (Color online) Variation of the diffraction angle θ_B as a function of temperature around the M-I phase transition, $T_{MI} = 195$ K, of the $(115)_c$ reflection. Data were taken on a heating run. The reflection that appears at around $\theta_B = 7.31$ below T_{MI} appears to be the continuation of the scattering observed above and therefore is identified as the allowed $(105)_o$. The reflection centered at $\theta_B = 7.42$ abruptly appears below T_{MI} and is attributed to the $(015)_o$, extinct above T_{MI}.

The lattice distortion occurring below T_{MI} corresponds to the charge ordering mechanism. The magnitude of this distortion is sensibly smaller than that observed for the Ho…Lu nickelates and it has been overlooked is previous diffraction experiments in powder samples.[4] In view of this, the determination of the charge ordering itself by using direct methods, such as RXS, is certainly of paramount importance. As we have mentioned above, it is not excluded that different types of CO as a function of the size of the rare earth may occur. We have carried out preliminary RXS experiments in $NdNiO_3$ and part of the results are shown in Fig. 3. Once corrected for absorption, our anomalous scattering measurements display identical features as in Ref. 13, where the use of thin films makes the absorption correction unnecessary. The energy dependence of the spectra reflects the presence of slightly anisotropic octahedra (we call this *dichroic effect*, as we shall explain in Sec. IV, below) rather than a charge or-

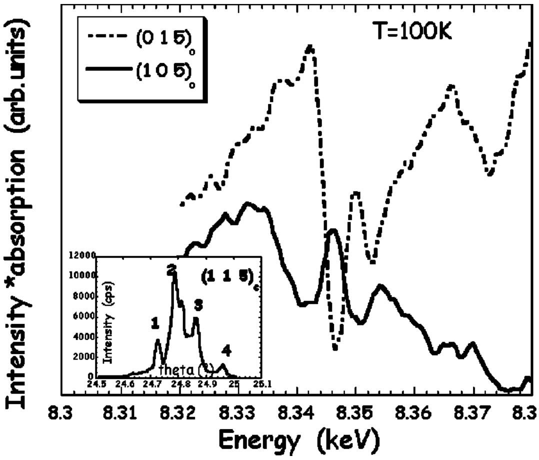

FIG. 3. Energy variation of the $(015)_o$ and $(105)_o$ reflections around the Ni K edge. The quality of these data is poorer than that of Fig. 2 in Ref. 13. The inset shows a theta scan of the $(115)_c$ reflection, where at least four peaks are visible. From their respective energy dependence we have evidenced that peaks 1 and 3 correspond to the $(105)_o$ whereas 2 and 4 correspond to the family $(015)_o$.

dering itself. Unfortunately, these data do not have a convincing quality and little else can be said. We believe that our data are suffering from a proper incident beam correction as a function of energy. The present beamline configuration, having the slits and the beam monitor 1 m apart from the sample, is very likely inadequate for this type of experiment, in which the incident slits and monitor should be as close to the sample as possible to perform a proper normalization of the incident beam.

One of the goals of this work was to check whether a postulated orbital ordering develops concomitantly to the charge and magnetic orderings. A systematic check for reflections indexed by $\mathbf{q}=\left(\frac{1}{2}\,0\,\frac{1}{2}\right)_o$ has been carried out at $T=10$ K and at different Brillouin zones, ending with a null result. This search was carried out at different energies around the Ni absorption edge in $NdNiO_3$. From the measurement of the background and of the intensity of different Bragg peaks we can conclude that such orbital ordering does not exists, or the corresponding peaks are at least 10^8 times weaker than the fundamental ones. Based on this figure, a very simple minded calculation of the magnitude of the atomic distortions that an orbital ordering might induce locates an upper limit at around $\epsilon \approx 5\times 10^{-5}$ Å. The magnitude of the distortion observed at Bragg peaks developing below T_{MI}, although too small to be observed in previous powder diffraction experiments, is far greater than the putative orbital ordering peaks. No sign of magnetic ordering was found in our spectra, which certainly reflects the smallness of the magnetic scattering cross section for x rays.

IV. RXS EXPERIMENTS ON CHARGE ORDERING

In the absence of orbital ordering (in the sense of a cooperative JT distortion) it is not therefore unreasonable to turn our attention to the charge ordering as the key concept to explain both the M-I transition as well as the magnetic ordering. In view of the relevant conclusions that RXS can disclose, we believe that it is important to understand in full detail what difficulties this technique may encounter with respect to CO in this specific compound. Charge ordering in the form $Ni^{+3+\delta}-Ni^{+3-\delta}$, with $\delta \approx 0.2$, (or Ni^1-Ni^2) was claimed based on the observation of anomalous scattering in reflections $(015)_o$ and $(105)_o$.[16,17] Whether or not charge ordering of this magnitude is actually present in this compound, or even if it is bond centered, a detailed analysis of the local structure of the Ni site and how this local structure is going to influence the above-mentioned reflections in the neighborhood of the Ni K edge is lacking. In the following we will describe such calculation, which can be easily extended to most of the 3*d* transition metal oxides perovskite structures.[24]

The structure factor in Eq. (1) (using rank-2 tensors) for these two reflections mixes, through the phase factor, different components of the local scattering tensor. Particularly dangerous is the case where the structure factor results from the *difference* of two distinct elements of the tensor. This is the so-called *dichroic effect*. In the case of the present octahedral environment, each one of the O–Ni–O bonding represents a principal direction of the local anomalous scattering tensor of the metal. The dichroic effect can easily pictured by noticing that not all the O–Ni–O distances are equal, and thus their corresponding components of the tensor are expected to be slightly shifted in energy. As we shall see below, it can give rise to *strikingly similar* diffraction patterns and therefore this dichroic effect can be easily misinterpreted as the signature of a charge ordering. Here we discuss a full tensor calculation of the structure factor of the anomalous Ni in the dipole–dipole approximation and under different polarization conditions. For the sake of completeness we have included the azimuthal angle ϕ, and the Bragg angle of the reflection θ_B.

In the following, we shall concentrate on reflections $(105)_o$ and $(015)_o$ exclusively. From the calculations displayed in Table I, the only element of the structure factor tensor that contributes to these reflections at high temperature is $D_{xz}(D_{xz}\approx D_{yz}\approx 7D_{xy})$.[24] This resonant scattering tensor element can be calculated from the original diagonal elements of the NiO_6 distorted octahedra; i.e., extracting the scattering factors along the three Ni–O directions (f_{x+y}, f_{x-y} and f_z). Once the tilts of the octahedra are considered, D_{xz} can be expressed to a good approximation as

$$D_{xz}(E) = 0.103 f_{x+y}(E) + 0.031 f_{x-y}(E) - 0.134 f_z(E).$$

The position of the absorption edge for each f depends linearly on the Ni–O distance along each direction. In order to *quantitatively* estimate this magnitude one should use an adequate simulation code, such as FDMNES.[25] Here, we shall restrict our discussion to symmetry considerations and take advantage of the nearly octahedral coordination of Ni. Nevertheless we want to stress that the theoretical discussion here has been double-checked with simulations carried out with the above-mentioned code. As $d(\mathrm{Ni-O})$ distances along $x+y$ and $x-y$ are the same within the error bar (at RT),[4] one can readily see that $D_{xz}\approx 0.135(f_{x+y}-f_z)$ and therefore the

TABLE I. Partial structure factor of Ni in the *Pbnm* structure (above T_{MI}) and in the $P2_1/n$ (below) including a charge order shift Δ. Below T_{MI}, we have performed the approximation of small and isotropic charge order defined as $\Delta = D^1_{xx} - D^2_{xx} \equiv D^1_{yy} - D^2_{yy} \equiv D^1_{zz} - D^2_{zz}$. The dichroic term is supposed unchanged, $D_{xz} \equiv \frac{1}{2}(D^1_{xz} + D^2_{xz})$. The first row is the full matrix operator corresponding to the dominant E1E1 resonant process, above $T_{MI} \rightarrow$ below T_{MI}. For the sake of completeness we have included the structure factor already projected for selected incoming and outgoing photon polarizations and as a function of the azimuthal angle ϕ.

	(0 1 5)	(1 0 5)
F^{Ni}	$\begin{pmatrix} 0 & 0 & 8D_{xz} \\ 0 & 0 & 0 \\ 8D_{xz} & 0 & 0 \end{pmatrix} \rightarrow \begin{pmatrix} 4\Delta & 0 & 8D_{xz} \\ 0 & 4\,\Delta & 0 \\ 8D_{xz} & 0 & 4\Delta \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & -8D_{xz} \\ 0 & 0 & 0 \\ -8D_{xz} & 0 & 0 \end{pmatrix} \rightarrow \begin{pmatrix} -4\Delta & 0 & -8D_{xz} \\ 0 & -4\Delta & 0 \\ -8D_{xz} & 0 & -4\Delta \end{pmatrix}$
$F^{\mathrm{Ni}}_{\sigma\sigma}$	$4\Big[\Delta - \sqrt{\frac{2}{13}} D_{xz} \sin(2\phi)\Big]$	$-4\Delta + \frac{40}{13} D_{xz} \sin^2(\phi)$
$F^{\mathrm{Ni}}_{\sigma\pi}$	$-4\sqrt{\frac{2}{13}} D_{xz}[5\cos(\theta_B)\cos(\phi) - \cos(2\phi)\sin(\theta_B)]$	$\frac{8}{13} D_{xz}[12\cos(\theta_B) - 5\cos(\phi)\sin(\theta_B)]\sin(\phi)$
$F^{\mathrm{Ni}}_{\pi\sigma}$	$-4\sqrt{\frac{2}{13}} D_{xz}[5\cos(\theta_B)\cos(\phi) + \cos(2\phi)\sin(\theta_B)]$	$\frac{8}{13} D_{xz}[12\cos(\theta_B) + 5\cos(\phi)\sin(\theta_B)]\sin(\phi)$
$F^{\mathrm{Ni}}_{\pi\pi}$	$4\Big[\Delta\cos(2\theta_B) - \sqrt{\frac{2}{13}} D_{xz}\sin^2(\theta_B)\sin(2\phi)\Big]$	$-4\Delta\cos(2\theta_B) - \sqrt{\frac{40}{13}} D_{xz}[\cos^2(\theta_B) + \cos^2(\phi)\sin^2(\theta_B)]$

anomalous contribution at both reflections contains a dichroic effect! As the distortion of the octahedra is small[4] ($\Delta d_{(\mathrm{Ni-O})} \sim 0.007$ Å) the magnitude of the dichroic effect is small ($\Delta E \leqslant 0.4$ eV), but the energy dependence signature should be nearly identical to that expected for a charge order process developing below T_{MI}. Let us now examine the low temperature structure. Very likely, the space group below T_{MI} is $P2_1/n$,[8] with two different positions for Ni (Ni$_1$ at site 2*d* and Ni$_2$ at site 2*c*)[26] and therefore the atomic coordinates remain unchanged. Both positions are symmetry related in *Pbnm* through a 90° rotation around the *z* axis [plus translation $(0,0,\frac{1}{2})$]. Identical calculations as before can be carried out for both Ni$_1$ and Ni$_2$. Now the diagonal elements, D_{xx}, D_{yy}, and D_{zz}, for each one of the Ni have opposite signs, and their total contribution to the scattering tensor is zero in the absence of charge ordering. As for D_{xz} above, the diagonal elements can be defined in terms of the proper Ni−O principal axis:

$$D^{1,2}_{xx} = 0.295 f^{1,2}_{x+y} + 0.686 f^{1,2}_{x-y} + 0.019 f^{1,2}_{z},$$

$$D^{1,2}_{yy} = 0.668 f^{1,2}_{x+y} + 0.312 f^{1,2}_{x-y} + 0.019 f^{1,2}_{z},$$

$$D^{1,2}_{zz} = 0.036 f^{1,2}_{x+y} + 0.001 f^{1,2}_{x-y} + 0.962 f^{1,2}_{z},$$

where the superindex stands for Ni$_1$ or Ni$_2$ sites. Note that both diagonal and off-diagonal elements of the anomalous structure factor are expressed in the same basis $f_{x+y}(E)$, $f_{x-y}(E)$, and $f_z(E)$ and, therefore, comparison between expected results at different Bragg reflections (not done in this paper) can be easily carried out. Moreover, the atomic scattering factors are strictly proportional to tabulated $f'(E)$ and $f''(E)$ for energy values sufficiently different than the absorption edge energy.

The first-order effect of the charge ordering at the K–edge of 3*d* transition metal ions is to shift the 1*s* level[27] by an amount $\Delta E/2$ proportional to the charge itself (δ). Moreover, the effect of the CO at the K–edge is independent of the extension of the final states, and therefore it can be considered as isotropic in a first approximation. After some trivial algebra, it is easy to realize that reflections $(015)_o$ and $(105)_o$ [or identically $(015)_m$ and $(105)_m$] have non-null diagonal elements below T_{MI} as now Ni$_1$ and Ni$_2$ have slightly different charge states $[D^1_{xx}(E+\Delta E) \approx D^2_{xx}(E), \ldots]$, and therefore the total contribution does not exactly cancel out. We define the isotropic shift due the different charge states at Ni$_1$ and Ni$_2$ as $\Delta \equiv \Delta_1 = D^1_{xx} - D^2_{xx} \equiv \Delta_2 = D^1_{yy} - D^2_{yy} \equiv \Delta_3 = D^1_{zz} - D^2_{zz}$, which is nothing else but the *derivative effect* $[\Delta \propto \Delta E \cdot \partial D_{xx}(E)/\partial E]$ already mentioned in the literature by several groups. Note that this approximation assumes that the diagonal elements $D_{xx}, \ldots$ have the same energy dependence except for a small shift. This approximation remains valid in NdNiO$_3$ but it does not in, for instance, α-NaV$_2$O$_5$,[28] where the local coordination of V is a pyramid, with $d(\mathrm{V-O})$ distances ranging between 1.611 and 1.965 Å ($\Delta d_{(\mathrm{V-O})} \sim 0.35$ Å). From Table I, the result of the charge ordering appears in the structure factor as a shift of the Ni partial structure factor, with *no azimuthal dependence*! The second interesting conclusion is that the charge ordering does not appear in the cross-channels σ-π and π-σ. It will be evidenced in these channels in a second-order approximation if the charge order parameter cannot be considered as isotropic.[24] This finding is to be compared with the results shown in Fig. 2 in (Ref. 14), where an azimuthal dependence has been found in the intensity of the $(105)_o$ reflection in the σ-π channel. Very likely, these results reflect the azimuthal dependence of the dichroic effect rather the CO itself. Another possibility is that the observed dependence contains some *anisotropic* charge ordering, which is expressed under the condition $\Delta_1 \neq \Delta_2 \neq \Delta_3$. Further experimental work has to be carried out to elucidate this latter hypothesis.

Another issue raised in[16,17] is the magnitude of the σ-π diffracted intensities at both $(015)_o$ and $(105)_o$. The diffracted intensities are written as

$$I_{\sigma\sigma}(E) \propto |[F_{NR} + F^{\mathrm{Ni}}_{\sigma\sigma}(E)](1-\tau) + F^{\mathrm{Ni}}_{\sigma\pi}(E)\tau|^2,$$

$$I_{\sigma\pi}(E) \propto |[F_{NR} + F^{\mathrm{Ni}}_{\sigma\sigma}(E)]\tau + F^{\mathrm{Ni}}_{\sigma\pi}(E)(1-\tau)|^2,$$

where, as mentioned earlier, $\tau=0.005$ is the polarization leakage factor between the two polarization channels, and $F_{NR}=F^{\mathrm{O}}+F^{\mathrm{Nd}}+F^{\mathrm{Ni}}_{NR}$ is the nonresonant contribution to the diffraction.[29] Interestingly, the intensity in the σ-σ channel is expected to be orders of magnitude larger than that of the σ-π, despite the fact that $F^{\mathrm{Ni}}_{\sigma\sigma}$ and $F^{\mathrm{Ni}}_{\sigma\pi}$ are of the same order of magnitude.

Finally, several other RXS experiments at different Bragg reflections will yield important understanding. For instance, a dichroic effect between $f_{x+y}(E)$ and $f_{x-y}(E)$ arising from the monoclinic distortion can be suitably studied at $h+k+l=2n$ reflections, extinct for Ni_1 and Ni_2, where the signature of the charge ordering of the type described above should be absent. It will be very interesting to check for the possibility of an anisotropic CO and explore the concept of charge transfer (bond order) vs charge disproportionation at the metal site and properly quantify each one of the solutions. RXS is very powerful and certainly can answer this conundrum, once the dichroic effects have been thoroughly considered.

In conclusion, one should be *very* cautious in claiming that the observed effect in the forbidden (extinct by the nonsymmorphic operations of the space group, *n* and *b*) reflections of $\mathrm{NdNiO_3}$ is the result of charge ordering alone. Charge ordering and dichroic effects can be disentangled through azimuthal scans ϕ; the former is independent of the azimuthal angle, whereas the latter do shows a significant variation. Signatures of the charge ordering are best observed in Bragg peaks corresponding to new lattice periodicities (if any), as it has been the case in α-$\mathrm{NaV_2O_5}$.[28] In the case where the unit cell remains unchanged, one should seek for weak reflections where atoms of supposedly different charge contribute out-of-phase, but this procedure might lead to misleading results if the space group is nonsymmorphic.

V. CONCLUSIONS

In this paper, we have shown that $\mathrm{NdNiO_3}$ exhibits a small but noticeable lattice distortion at T_{MI} that is identified as the charge ordering transition, in a manner similar to other rare-earth nickelates. We have carried out resonant x-ray scattering experiments on $\mathrm{NdNiO_3}$ single crystals in view of proving or disproving a longstanding hypothesis[10] that an orbital ordering should occur in this compound that may explain the presence of a magnetic ordering characterized by a wave vector $\mathbf{q}=(\frac{1}{2}\ 0\ \frac{1}{2})$. All our experimental efforts have yielded a null result and if there exists such orbital ordering the Bragg peaks originating from the concomitant lattice distortion should be 8 orders of magnitude weaker than those of the average *Pbnm* structure. A signature of an exclusively electronic ordering might be seen in our resonant scattering spectra, but we did not find any. It rather seems that the charge ordering, either in the form of charge disproportionation at the metal sites or a ligand hole ordering (bond center ordering), triggers the magnetic ordering and further stabilizes the magnetic structure. Data obtained in RXS experiments in single crystals, are hindered by absorption and by the small size of the crystals. Clearly future work aimed at an understanding of the charge ordering and of the related points raised in this paper has to be carried out in thin films. Finally, we have completely worked out the data analysis that one should apply in order to directly quantify the magnitude of the charge ordering as measured by RXS experiments. The effect of the charge ordering as seen in the energy dependence of the RXS is exactly the same as dichroic effects arising from the slight anisotropy of the $\mathrm{NiO_6}$ octahedra, which have been disregarded in previous experiments.[16,17] We have developed the scattering equations in the presence of a charge ordering that include the dichroic effect as well. These equations have been derived from the symmetry of both high- and low-temperature phases, and contain a minimum number of assumptions. In the absence of a very detailed study of the resonance, a commensurate $q=0$ charge ordering contribution can be misinterpreted with dichroic effects arising from the anisotropy of the anomalous atom scattering tensor. We have made predictions on the observability of this effect and we have described proper ways to disentangle both contributions. Whereas an azimuthal dependence is expected for the dichroic signal, the contribution of the CO is independent of the azimuth angle, and it is absent of the photon polarization crossed-channels σ-π and π-σ. These calculations can be straightforwardly extended to other perovskite-type structure compounds, such as the colossal magnetoresistance manganites.

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[29] Strictly speaking, one should consider two sources of leakage: τ_1 related to the polarization of the incoming beam and τ_2 associated with the efficiency of the polarization analyzer. In this paper, we have disregarded the first contribution, and therefore $\tau \equiv \tau_2$.