d-d excitations and charge ordering in $La_{5/3}Sr_{1/3}NiO_4$

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We report the temperature dependence of the crystal-field-excitation spectrum in $La_{5/3}Sr_{1/3}NiO_4$ by resonant inelastic x-ray scattering at the Ni *K* edge. Two distinct excitations are observed in the 1–3 eV energy range, in agreement with optical conductivity studies. The temperature dependence of the low-energy spectral weight is found to be closely related to the appearance and suppression of charge ordering. The relation between these crystal-field excitations and the stripe ordering is discussed.

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I. INTRODUCTION

Strongly correlated transition-metal oxides (TMO) display a wide array of fundamentally and technologically important properties ranging from colossal magnetoresistance to high-temperature superconductivity. The orbital degrees of freedom play a key role to describe physical properties of these systems. In fact the correlated nature of the 3*d* orbitals seems to be responsible for many of the fascinating properties observed in the 3*d* TMO. In particular, the 214-type nickelates and cuprates (M_2AO_4, A=Cu,Ni and M=La/Sr) contain Ni or Cu atoms with a formal 2+ oxidation state and the electrons around the Fermi level are mainly contributed by Ni or Cu 3*d* orbitals. In the doped 214-systems, the transition-metal oxidation state and the crystal structure are partially changed, thus modifying the electronic structure of the 3*d* orbitals. These systems exhibit charge-stripe order appearing in the MO plane, in which the doped holes segregate to form hole-rich domain walls separated by antiferromagnetically ordered spins. It has been demonstrated that the ordering has electronic or magnetic origins.[1] In order to shed light on the complex interplay between the spin-charge-lattice degrees of freedom, it is thus important to investigate the energetics of the 3*d* levels and their correlation with the stripes formation.

The resonant inelastic x-ray scattering (RIXS) technique is one of the most powerful probes to measure the charge and spin correlation function multiplied by a resonant enhancement factor.[2,3] RIXS in the hard and soft x-ray regimes is rapidly developing at third generation synchrotron radiation sources and is currently utilized to study various types of excitations in strongly correlated electron systems.[4–14] In particular, in the case of 214-type nickelates, the study of *d-d* excitations using RIXS in the soft x-ray range is difficult due to the superposition of the Ni *L* edge with the La *M* edge. Hard x-ray RIXS can instead be used to access these excitations and to follow their temperature dependence, permitting to explore their relation with the stripe-ordering phenomenon.

Among the 214-nickelates, a substantial amount of work has been dedicated to $La_{5/3}Sr_{1/3}NiO_4$ due to the fact that the charge ordering at this doping level is stable, nearly commensurate, and visible to most of the experimental probes, making it a model system to address charge ordering and stripe correlations in TMO perovskites.[15–19] In this system the ordering process occurs in a very large temperature range (100–240 K) and it can be described as a continuous two-dimensional (2D) transition.[20] Exploiting the specific advantages of RIXS, Wakimoto *et al.*[14] have recently investigated the wave number (**q**) dependence of the low-energy-excitation spectra of $La_{5/3}Sr_{1/3}NiO_4$. In this paper, we present studies on the temperature dependence of the *d-d* electronic excitations in $La_{5/3}Sr_{1/3}NiO_4$. In order to investigate the role of the energetics of the 3*d* orbitals in the stripe phenomenon, we compare the RIXS results with the temperature dependence of the superstructure peak, measured by x-ray diffraction on the same sample.[20] We find a clear change in the RIXS spectra across the charge ordering temperature, pointing toward a correlation between the low-energy crystal-field excitations and the charge ordering phenomenon.

II. EXPERIMENTAL DETAILS

The single-crystal sample of $La_{5/3}Sr_{1/3}NiO_4$ was grown at Bell Laboratories using the floating-zone method.[17] The RIXS experiments were performed at the Ni *K* edge using the ID16 beamline of the ESRF.[21] The incident x-rays were monochromatized using a Si(111) premonochromator and a Si(444) channel-cut crystal to a bandwidth of 80 meV at 8.3 keV. The scattering plane was horizontal and parallel to the linear polarization vector. The focused beam spot size on the sample was about $50\times130(V\times H)$ μm^2. The spectrometer was based on a Si(551) analyzer crystal (bending radius R =1 m) and a pixelated position-sensitive Medipix2 detector.[22,23] We carried out measurements with two different setups. First, a low-resolution overall measurement of the 2D RIXS plane was performed with a bent analyzer crystal resulting in a total energy resolution of 880 meV full width at half maximum (FWHM). For more detailed measurement of the *d-d* excitations, we carried out high-resolution measurements with a diced analyzer crystal yielding a total energy resolution of 130 meV FWHM.[21,22]

The spectra shown here were carried out fixing the momentum transfer to $q_s=(2\pi/3,2\pi/3,2\pi n)$, where n was chosen so that the scattering angle $2\theta\approx90°$ in order to minimize the nonresonant quasielastic scattering. The sketch of

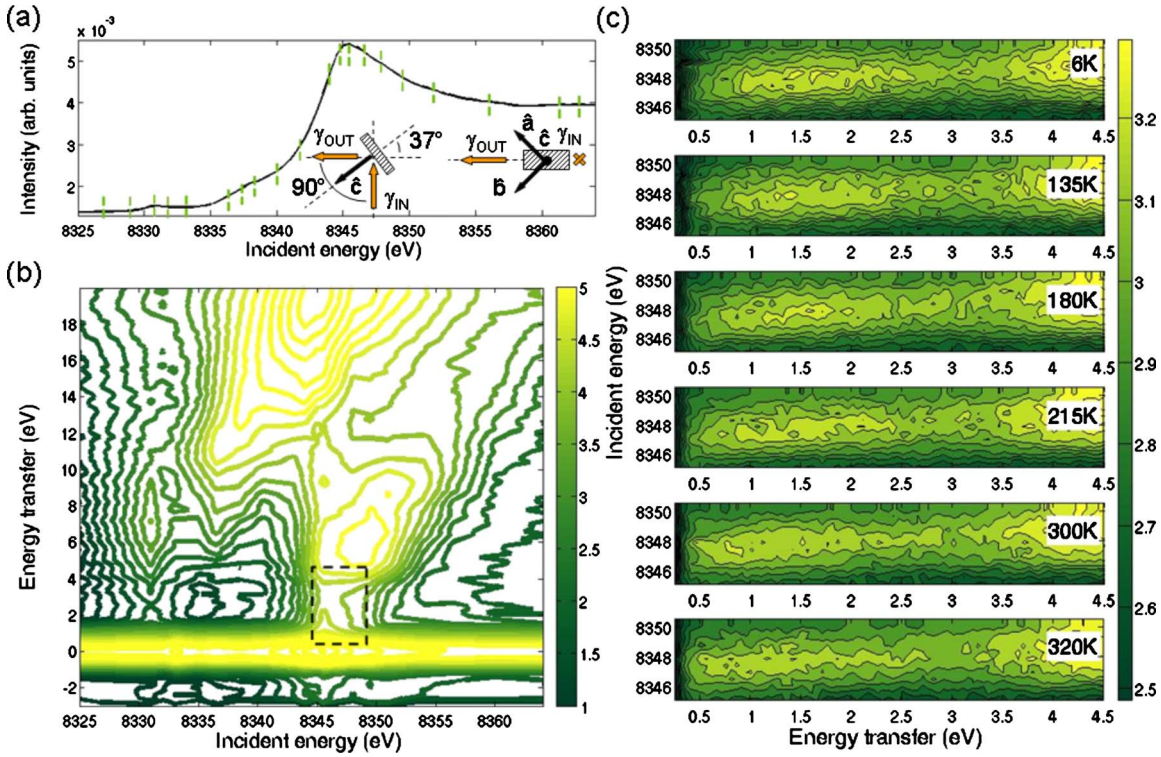

FIG. 1. (Color online) (a) X-ray absorption spectrum measured using total fluorescence yield, where the insert shows a sketch of the sample orientation as seen from above (left) and from the incoming beam perspective (right). The green vertical lines represent the incident photon energies chosen for the energy map (b), where a low-resolution ($\Delta E = 880$ meV) contour plot of the logarithm RIXS intensity is reported. We focused our attention on the temperature dependence of the *d-d* excitations at the main Ni *K* edge (black dashed rectangle). (c) High-resolution ($\Delta E = 130$ meV) energy maps of the logarithm RIXS intensity, after the subtraction of the quasielastic contribution, collected around the main Ni *K* edge at different temperatures.

the sample orientation is shown in the inset of Fig. 1, upper left panel.

III. RESULTS AND DISCUSSIONS

First of all, we characterized the different electronic excitations accessible in the energy range around the Ni *K* edge using the low-resolution setup. To begin with, Fig. 1(a) shows the absorption spectrum of $La_{5/3}Sr_{1/3}NiO_4$ measured using total fluorescence yield. The vertical green lines indicate the chosen incident-photon energies E_1 for the measurements of a 2D RIXS map [Fig. 1(b)], showing the logarithm of the measured scattering intensity as a function of E_1 and energy transfer. A number of different electronic excitations resonate at different values of E_1. Tuned to the prepeak present in the absorption edge at 8331 eV a distinct resonance of an inelastic feature around 7 eV is found. At higher E_1 values, fluorescence starts to dominate the spectra for energy transfers higher than 10 eV. Two evident inelastic peaks resonate at the main edge (8346 eV), with energy-transfer values of 5.5 and 9.5 eV. These features are known to be the charge excitations across the charge-transfer (CT) gap.[9] Finally, a weak inelastic feature around 2 eV resonates mainly at the main edge. It has been assigned to crystal-field (*d-d*) excitations.[9,14]

We focus our attention to the low-energy excitations, in the typical energy range of *d-d* excitations (1–5 eV), indicated by a rectangle in Fig. 1(b). Unlike in a previous report,[14] we didn't find dependence on **q** in the low-energy range of the spectra collected with q parallel to the *c* axis (lattice parameter orthogonal to the Ni-O planes) and perpendicular to the stripes direction in the Ni-O plane $[q_s = (2\pi/3, 2\pi/3, 2\pi n]$ at three different temperatures (10, 100, and 300 K). We have collected high-resolution RIXS maps at different temperatures [Fig. 1(c)] in the *d-d* excitation range. The remaining quasielastic-peak tail has been subtracted from all spectra, fitting it with a Pearson VII curve from 0.05 to 0.25 eV, which takes explicitly into account all possible thermal broadening effects of the quasielastic line. Looking at the RIXS maps it is possible to identify a gradual transfer of spectral weight toward lower energy on increasing the temperature. Integrating over E_1 we obtain RIXS spectra in the traditional presentation, i.e., intensity versus energy transfer. In Fig. 2(a) we report such spectra for 135, 180, and 300 K. A clear temperature effect is seen. On decreasing the temperature, a part of the low-energy spectral weight is suppressed and transferred to higher energies, consistently with optical conductivity studies.[24,25] It results in a systematic energy shift of the feature around 1.6 eV as a function of the temperature.

In order to quantify this temperature effect, we have attempted to fit the spectra with two Gaussians, one representing the CT and one corresponding to the 1–2 eV feature. The temperature dependence at the CT excitation was found to be

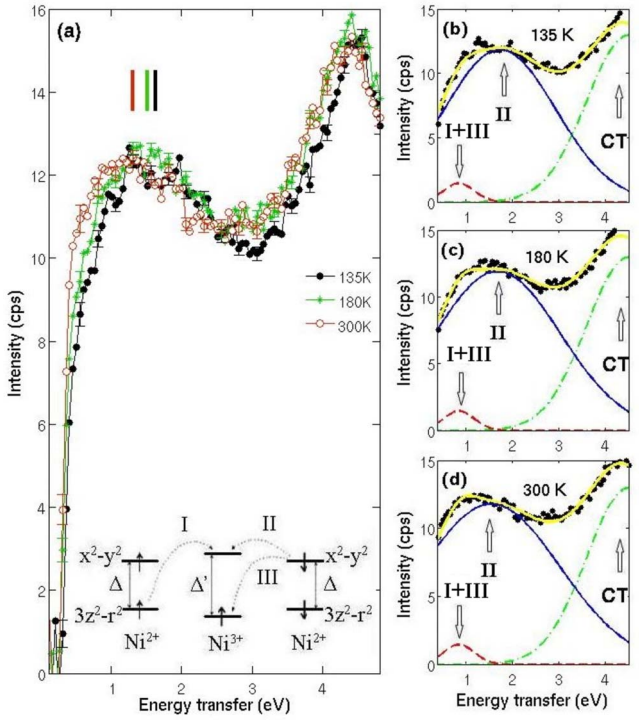

FIG. 2. (Color online) (a) RIXS spectra collected at three representative temperatures, 135 180, and 300 K, analyzed in terms of the model sketched at the bottom of the figure. A clear temperature effect is visible. The three bars on the top of the low energy peaks (≈1.6 eV) underline the evident energy shift. [(b)-(d)] Fits (yellow thick line) to the RIXS spectra collected at 135, 180, and 300 K. These fits correspond to a three Gaussian model: a fixed CT contribution (green dash dotted line), a first temperature-independent low-energy contribution (I+III) (red dashed line) and a second temperature-dependent component (II) (blue line).

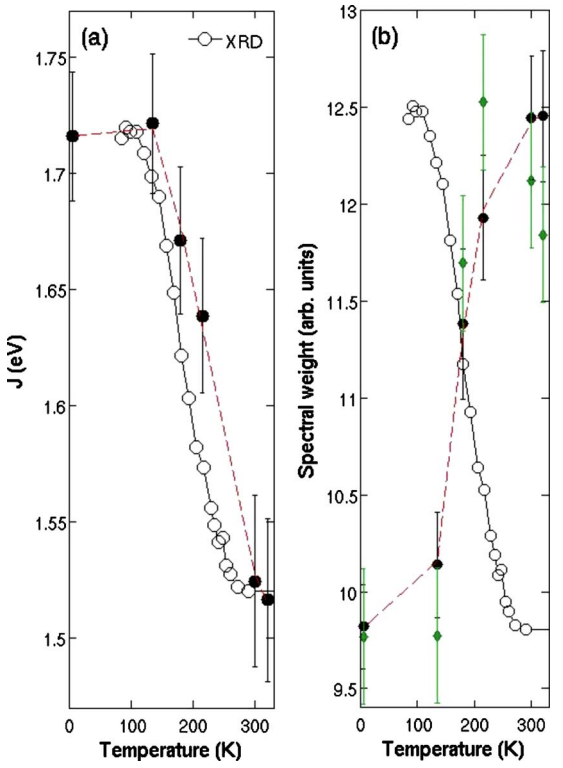

FIG. 3. (Color online) Comparison between the evolution of the integrated intensity of the charge order superlattice peak (open circles) obtained by x-ray diffraction (Ref. 20) and the behavior of (a) the energy and (b) the spectral weight (filled dots) of the temperature-dependent RIXS component (II) as a function of temperature. The green rhombi represent the evolution of the renormalized integrated intensity between 0 and 2.8 eV. The red dashed lines are guides for the eye.

small compared to the strong temperature-induced variations in the 1–2 eV feature.

Assuming a temperature-independent CT excitation, the data are described by a fixed high-energy (≈4.5 eV) Gaussian and a variable low-energy (≈1.6 eV) component. Because of the apparent asymmetry of the lower energy part of the spectra, the fits with two symmetric line shapes are not able to reproduce the data perfectly. Reasonable fits can be obtained using a fixed CT component and two low-energy excitations, one being temperature independent and the other one strongly temperature dependent. However, the results do not depend on the fitting procedure. In particular, the temperature dependence of the fit results with one or two low-energy components was found to be the same except for a rigid shift in the absolute values. Figs. 2(b)–2(d) show the fits to the spectra collected at three representative temperatures (135, 180, and 300 K).

In order to understand the nature of these two excitations, we have to consider the electronic configurations of the Ni^{2+} and Ni^{3+} ions as proposed to interpret the optical conductivity spectra of $La_{3/2}Sr_{1/2}NiO_4$ and shown in the inset in Fig. 2(a).[25] The Jahn-Teller distortion in the system causes the e_g orbitals to split by Δ. On the Ni^{3+} sites the e_g orbital splitting, Δ′, can be slightly larger.[26] The difference between Δ and Δ′ might be too small to be detected here.[27] We have considered the three electronic transitions displayed in the insert of Fig. 2(a). Transitions I, II, and III require an energy of about $(\Delta+\Delta')/2$, $J+(\Delta'-\Delta)/2$, and $J-(\Delta+\Delta')/2$ respectively, where J represents the exchange energy. Within this simplified model J contains all the complex magnetic contributions present in this highly correlated system, including contributions of superexchange and hybridization. The strengths of the transitions I and III are expected to be smaller than that of transition II. In fact, while the transitions I and III occur between different types of orbitals, in the transition II the electron in the filled $d_{x^2-y^2}$ level in the Ni^{2+} site moves to the unfilled $d_{x^2-y^2}$ level in the Ni^{3+} site.

The excitations I and III are indistinguishable in the present study due to the very small energy difference since the value of J turns out to be $\sim 2\Delta$. Following the optical conductivity study,[25] we can assign the first lower energy excitation around 0.85 eV to the transitions I and III and the second one to the transition II. From these assignments, we can extract the value of $\Delta \approx 0.85$ eV in $La_{5/3}Sr_{1/3}NiO_4$. The temperature independence of the feature at ~0.85 eV that seems to emerge from the fit within the experimental accuracy, is consistent with the temperature evolution of the crystal structure.[28] In fact, the variations in the Jahn-Teller distortion effect as a function of temperature are too small to be

detected in this work. Moreover, the energy of the excitation II corresponds approximately to J. In principle, this energy value is close to $10Dq$ for this system.[29] However, its observed strong temperature dependence [Fig. 3(a)] contrasts with the expected weak temperature dependence of $10Dq$ derived from the lattice contraction.[28] This excludes the possibility of the feature II being due to an excitation from t_{2g} to e_g orbitals and supports its assignment to J.

Let us now compare the results obtained by RIXS with the ones obtained by x-ray diffraction (XRD) on the same crystal.[20] In fact by XRD it is possible to monitor the occurrence of the charge ordering following the increase in the integrated intensity of the superlattice peak on decreasing the temperature. In Figs. 3(a) and 3(b) we compare the behavior of the energy J and of the spectral weight of the temperature-dependent RIXS feature II (filled dots) with the behavior of the superlattice peak intensity (open circles). Charge ordering starts at 240 K. As temperature decreases the diffraction peak intensity continues to grow down to 100 K where saturation is observed. With decreasing temperature and an increasing charge ordering the energy J increases with a similar behavior to the XRD data. At the same time, the hopping between neighboring Ni sites with different oxidation states is suppressed with an increasing charge ordering. In Fig. 3(b) we report additionally the integrated intensity of the spectra between 0 and 2.8 eV. The rough estimate of the spectral weight evolution is in good agreement with the one obtained by our RIXS results. Our data reveal the clear correlation between the temperature dependence of the RIXS spectra and the stripe formation.

Finally we can relate our results to the ones obtained by studying the temperature dependence of the electrical resistivity ρ on the same system.[1,30] The sudden increase observed in ρ below the charge ordering transition is associated to the charge ordering. The behavior of J as a function of temperature is very similar to that of ρ. The suppression of the hopping between neighboring Ni sites can therefore be an ingredient of the detected resistivity increase on increasing the charge ordering.[1,30]

IV. SUMMARY AND CONCLUSIONS

In conclusion, we have investigated the temperature dependence of the d-d excitations in $La_{5/3}Sr_{1/3}NiO_4$ by RIXS in the hard x-ray regime. We detected two low-energy excitations, and obtained approximate values for the e_g splitting ($\Delta \approx 0.85$ eV) and the exchange energy J ($\approx 1.5-1.7$ eV). We have followed the temperature dependence of the RIXS spectra and compared it with x-ray scattering results.[20] We find a clear correlation between the temperature dependence of the exchange energy J and the occurrence of charge ordering, suggesting that the hopping between neighboring Ni sites leads to stripe formation and to the related resistivity increase. Such detailed information on the correlation between d-d excitations and stripe ordering obtainable via this experiment may shed a new light on the magnetic and electronic properties of highly correlated systems, such as, for example, cuprates, where the discussed relation between high T_c superconductivity and stripe ordering requires the understanding of the charge stripes formation studied here.

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