Spectroscopy of stripe order in La$_{1.8}$Sr$_{0.2}$NiO$_4$ using resonant soft x-ray diffraction

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Strong resonant enhancements of the charge-order and spin-order superstructure-diffraction intensities in La$_{1.8}$Sr$_{0.2}$NiO$_4$ are observed when x-ray energies in the vicinity of the Ni $L_{2,3}$ absorption edges are used. The pronounced photon-energy and polarization dependences of these diffraction intensities allow for a critical determination of the local symmetry of the ordered spin and charge carriers. We found that not only the antiferromagnetic order but also the charge-order superstructure resides within the NiO$_2$ layers: the holes are mainly located on in-plane oxygens surrounding a Ni$^{2+}$ site with the spins coupled antiparallel in close analogy to Zhang-Rice singlets in the cuprates.

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Doped carriers in strongly correlated oxides are often found to induce ordered periodic arrangements at low temperatures. The first system where such a phenomenon was observed by scattering techniques is hole-doped La$_2$NiO$_4$: Electron and neutron diffraction experiments found in La$_{2-x}$Sr$_x$NiO$_{4+x}$ stripe-like superstructures[1, 2, 3], which were interpreted in terms of charge ordering. The hole-rich stripes form antiphase domain walls for the antiferromagnetic order on the Ni$^{2+}$ ions. Spectroscopic techniques, for instance, have revealed that doping introduces substantial amounts of holes in the oxygen band[3, 4], thereby raising the question whether a description in terms of oxygen hole ordering would be more appropriate. To make things more confusing, there is not even an agreement to what extent and with which symmetry the oxygen holes are bound to the Ni ions[2, 4, 5].

In this paper we present results from a new type of spectroscopic technique, namely resonant diffraction using soft-x-rays. Here the diffraction involves virtual electronic excitations into unoccupied intermediate states[12], which lead to a characteristic modulation of the scattering cross section with photon energy. In particular excitations in the vicinity of the transition metal $L_{2,3}$ (2$p$→3$d$) and rare-earth $M_{4,5}$ (3$d$→4$f$) absorption edges are known to be very sensitive to details of the electronic state of the ions[13, 14, 15].

Resonant diffraction is in fact a combination of spectroscopy and structure determination, and is therefore the most suitable and natural technique to study the electronic structure of superstructures in transition metal and rare-earth systems[14, 17, 18, 19, 20, 21, 22].

We carried out resonant diffraction experiments on La$_{1.8}$Sr$_{0.2}$NiO$_4$ at the Ni $L_{2,3}$ threshold for both the spin-order and charge-order superstructures. We observed pronounced photon-energy and polarization dependences of these diffraction intensities, which allow us to critically determine the local symmetry of the ordered spin and charge carriers. Using a quantitative microscopic theoretical model, we find that the holes are mainly located on the in-plane oxygens surrounding a Ni$^{2+}$ site with the spins coupled antiparallel in close analogy to Zhang-Rice singlets in the cuprates[23].

A single crystal of La$_{1.8}$Sr$_{0.2}$NiO$_4$ was grown by a traveling solvent method and characterized by neutron diffraction at the Orphée reactor, diffractometer 3T.1. The crystal structure at room temperature is tetragonal with I4/mmm symmetry and lattice constants $a = 3.807$ Å and $c = 12.5476$ Å. We will use in the following the larger orthorhombic unit cell with $a_o \approx b_o = \sqrt{2}a$, which is more commonly used in the literature. In this notation the diffraction features with the smallest momentum transfer are the charge-order peak at $(2\pi,0,1)$ and
the spin-order peak at (1-ε,0,0). For the doping level of our sample, ε is 0.278, and both peaks can be reached at the Ni $L_2,3$ and La $M_{4,5}$ resonances (left panel of Fig. 1).

The soft x-ray scattering experiments were performed at the BESSY beamlines U49/2-PGM1 and UE52-SGM1, using the two-circle UHV diffractometer designed at the Freie Universität Berlin [24] in horizontal scattering geometry. The incoming light was linearly polarized either parallel to the scattering plane ($\pi$ polarization) or perpendicular ($\sigma$ polarization) and was monochromatized to an energy resolution of about 300 meV. A silicon-diode photon detector without polarization analysis was used with the angular acceptance set to 1 degree in the scattering plane and 5 degrees perpendicular to it. The sample was cut and polished with a (103) surface orientation and mounted with the [001] and [001] directions in the diffraction plane. At 1010 eV photon energy the (002) structure Bragg peak could be reached and was used together with the superstructure peaks to orient the sample. Reference soft-x-ray absorption measurements on La$_{1.8}$Sr$_{0.2}$NiO$_4$ and LaTiO$_3$ have been performed at the Dragon beamline of the NSRRC in Taiwan.

Fig. 1 shows the position of both superstructure peaks in reciprocal space, together with scans along the [100] (H) and [001] (L) directions, taken with the photon energy tuned into the maximum of the Ni $L_3$ resonance. From the peak widths we determine the correlation length in the $ab$ plane for charge order to about 200 Å and for spin order to about 300 Å. The order along the $c$ direction is less developed with correlation lengths of 50 Å (40 Å) for spin (charge) order.

Fig. 2a) and b) depict the photon-energy dependence of the superstructure intensities across the La $M_{4,5}$ and Ni $L_{2,3}$ edges for two different light polarizations plotted on the same vertical scale. For both superstructure peaks the intensity shows a resonant enhancement mainly for photon energies around 851.6 eV, i.e. in the vicinity of the Ni $L_3$ white line. This is in striking contrast to the shape of the XAS data shown in Fig. 2c), which are dominated by the La $M_{4,5}$ resonance at 833 eV and $M_4$ resonance at 849.2 eV. The gain in contrast for the Ni signal in the diffraction experiment comes from its sensitivity to only the ordered part of the system: The strong enhancement at the Ni resonance for both superstructure signals hence shows directly that not only the antiferromagnetic order, but also the charge-order superstructure originates mainly from the NiO$_2$ layers. Both resonances show a dramatic polarization dependence: For the spin-order peak, the signal for $\sigma$ polarization is only about 10 percent of that for $\pi$ polarization; for the charge-order peak, the maxima at the $L_3$ and $L_2$ resonance when observed with $\sigma$-polarized light are shifted by about 1 eV towards higher photon energies as compared to the data taken with $\pi$-polarized light.

On a closer look, both superstructure peaks show a resonant enhancement at the La $M_{4,5}$ resonances as well. This is, however, a weak effect considering the relative intensities of the Ni and La resonances in the XAS signal. The fact that there is any enhancement of the charge- and spin-order signal at the La resonance indicates a coupling between Ni and La sites, which could be caused by the different bond lengths or by weak hybridization. A possible strong static dopant order in the La/Sr subsystem can be ruled out, since the superstructure peaks decrease above 65 K at both the Ni and La resonances.

The contrast mechanism responsible for the spin-order peak is the different scattering cross section for different
FIG. 3: Comparison between measured data (symbols) and the results of the cluster simulation for the spin-order, \( \sigma \)-polarized light (a); the charge-order superstructure peak, \( \pi \)-polarized light (b) and \( \sigma \)-polarized light (c); and the x-ray absorption signal, \( \pi \)-polarized light (d). The La \( M_4 \) peaks at 849.2 eV, marked by arrows, are not included in the Ni \( L_{2,3} \) simulation.

relative orientations of the electron spins and the polarization directions of the incoming and outgoing photon. From the weakness of the signal observed with \( \sigma \)-polarized light, which in our scattering geometry means that the electric-field vector of the incoming photons is parallel to the stripes, one can conclude, that the Ni spins are essentially (but not perfectly) collinear with the stripes. The contrast for the direct observation of charge order arises from the different energy dependence of the (2p\( \rightarrow \)3d) excitation process for Ni ions with and without the extra holes introduced by doping. The strong resonance found here demonstrates the extreme sensitivity of resonant soft-x-ray diffraction.

While some information can be obtained from a qualitative analysis, e.g., from a comparison of the La and the Ni resonance, the full power of soft x-ray resonant diffraction evolves from a combination with a quantitative microscopic theory. We performed a microscopic modeling based on cluster configuration-interaction calculations \[^{20}\]. The assumed model consists of diagonal stripes with a periodic order Ni\(^{3+}\), Ni\(^{2+}\), Ni\(^{2+}\), Ni\(^{3+}\), Ni\(^{2+}\), Ni\(^{2+}\), Ni\(^{2+}\), with the Ni\(^{3+}\) stripes serving as antiphase domain walls for the antiferromagnetic order of the Ni\(^{2+}\) spins. Such an arrangement produces spin- and charge-order diffraction peaks with \( \epsilon = 2/7 \approx 0.286 \), which is close to the experimental value. In each Ni\(^{2+}\) (Ni\(^{3+}\)) ion site the energy-dependent scattering cross section across the resonance was calculated assuming NiO\(_6^{2-}\) (NiO\(_6^{3-}\)) cluster with the \( D_{4h} \) symmetry, where the ten Ni 3d states and the nearest-neighbor oxygen 2p states are considered. Coulomb and exchange interactions between 3d electrons, 3d spin-orbit interaction, hybridization between the Ni 3d and the oxygen 2p orbitals are taken into account. In the intermediate state of the scattering process, the Coulomb and exchange interactions between the 3d electron and 2p core hole and the 2p spin-orbit interaction are necessary to reproduce the photon energy dependence of the scattering amplitude. For the simulation of the spin-order signal, only the contributions from the Ni\(^{2+}\) sites were considered and the direction of the spins was assumed to be parallel to the stripes. The parameters adopted in the model are \( U_{dd} = 7.0 \) eV, \( U_{dc} = 8.5 \) eV, \( \Delta_{2+} = 6.5 \) eV (for Ni\(^{2+}\)), \( (pd\sigma) = -1.88 \) eV (for the oxygen in the NiO\(_2\) plane), \( (pd\pi) = -1.12 \) eV (for the apical oxygens) and 10\( Dq = 0.5 \) eV. For the value of \( (pd\pi) \), a relation \( (pd\pi) = -\sqrt{3}/4(pd\sigma) \) is assumed. A Lorentzian broadening with widths of 0.15 eV and of 0.2 eV at the \( L_3 \) and \( L_2 \) edges (HWHM), respectively, and a Gaussian broadening with a width of 0.2 eV (HWHM) are applied for the spectra.

With this single set of parameters, we are able to explain the energy and polarization dependences of the spin- and charge-order superstructure peaks, including the relative intensities of the different diffraction signals (Fig. 3). The model also reproduces the experimental Ni contribution to the x-ray absorption spectrum (Fig. 3d), which was determined by subtracting out the La contribution obtained from LaTiO\(_3\). The agreement is particularly good for the data obtained with \( \pi \) polarization even in the details of the shape of the resonance; for \( \sigma \) polarization the agreement in the shape is not that good, but the model reproduces correctly the 1-eV energy shift between \( \pi \) and \( \sigma \) polarization for the charge-order resonance. Our above mentioned interpretation that the spins and stripes are parallel aligned, is confirmed by the calculations since the model gives zero intensity for the spin-order signal with \( \sigma \)-polarized light, reproducing the very weak intensity observed in the experiment.

The model calculations turned out to be very sensitive to the choice of parameters. The quantitative analysis of the spectra provides a detailed understanding of the ground state in the charge-ordered phase: At the Ni\(^{3+}\) sites, where the effective charge-transfer energy \( \Delta_{3+} = \Delta_{2+} - U_{dd} \) is negative, the doped holes reside mainly in the ligand molecular orbital with \( x^2 - y^2 \) symmetry. The 3d electron number at the Ni\(^{3+}\) ions is as high as 7.9, which is surprisingly not much smaller than the value of 8.2 for the 3d electron count on the Ni\(^{2+}\) sites. The spins of the holes on the ligand and 3d orbitals couple antiferromagnetically and form an \( S = 1/2 \) state \[^{22}\] in which the Ni ion with \( t_{6g}^9 e_{g}^2 \) configuration is dressed with a hole in the \( (x^2 - y^2) \) ligand or-
bital. This state is analogous to the Zhang-Rice singlet state in a cuprate superconductor [23]. This assignment is strongly supported by the observation that between the two polarizations there is a strong shift of about 1 eV in the peak maxima in each of the $L_2$ and $L_3$ edges of the $(2e, 0, 1)$ spectrum, which indicates a large energy splitting of the unoccupied $x^2 - y^2$ and $3z^2 - r^2$ levels. Since the polarization vector of $\pi$-polarized light has a finite projection on the $c$-axis, the transition probability of the $2p$-core electron to the low-lying $3z^2 - r^2$ orbital, having lobes along the $c$-axis, is much higher for this polarization than for $\sigma$ polarization, which has the polarization vector perpendicular to the $c$-axis. In the $\sigma$ channel the excitation into the $x^2 - y^2$ orbital dominates. With such a large level splitting, the doped holes can be considered to be well confined within the in-plane oxygens and the system possesses strong two-dimensionality like cuprates.

To conclude, we have observed well developed superstructures in La$_3$Sr$_{0.2}$NiO$_4$ using resonant soft x-ray diffraction. The intensities of the spin-order and charge-order diffraction peaks show strong enhancements when x-ray energies are tuned to the vicinity of the Ni $L_{2,3}$ absorption edges. These observations show directly that not only the antiferromagnetic but also the charge order resides within the NiO$_2$ layers. The photon-energy and polarization dependence of the charge and spin-order diffraction intensity across the Ni $L_{2,3}$ edges can be reproduced by a quantitative microscopic model calculation assuming diagonal stripes of Ni$^{2+}$ and Ni$^{3+}$-like ions, in which the Ni$^{3+}$-like objects are formed of a Ni$^{2+}$ ion accompanied by a hole, which is essentially located at the surrounding in-plane oxygen ions in analogy to a Zhang-Rice singlet in cuprate systems. The good agreement between experiment and calculation indicates that differences in the hole concentration around the Ni ions, i.e., charge ordering, are the cause of the superstructure.

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