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N.B.: When citing this work, cite the original article.

Original Publication:

L.-C. Duda, T. Schmitt, Martin Magnuson, J. Forsberg, A. Olsson, J. Nordgren, K. Okada and A. Kotani, Resonant Inelastic X-Ray Scattering at the Oxygen K Resonance of NiO: Nonlocal Charge Transfer and Double-Singlet Excitations, 2006, Physical Review Letters, (96), 067402.
http://dx.doi.org/10.1103/PhysRevLett.96.067402
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Postprint available at: Linköping University Electronic Press
http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-17408

Resonant Inelastic X-Ray Scattering at the Oxygen K Resonance of NiO: Nonlocal Charge Transfer and Double-Singlet Excitations

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(Received 7 July 2005; published 16 February 2006)

We report high-resolution polarization-dependent resonant inelastic x-ray scattering (RIXS) at the O K resonance of NiO showing a rich excitation spectrum. We perform multisite Ni_6O_{19} cluster model calculations, revealing that solid state effects are substantial. We identify a nonlocal charge transfer excitation at 4–5 eV and double-singlet creation at 1.75 eV, both exhibiting significant scattering geometry dependence. Apart from an intense band of local charge transfer excitations (above 5 eV) also dd excitations at 1 eV are observed. Finally, we point out that O K RIXS of correlated metal oxides allows a quantitative and consistent determination of the charge transfer energy Δ and the Hund coupling energy J_H.

DOI: 10.1103/PhysRevLett.96.067402 PACS numbers: 78.70.En, 71.15.−m, 71.27.+a

NiO is one of the prototypical compounds that has highlighted the importance of correlation effects in transition metal oxides. However, despite several decades of studies there is still no literature consensus on the detailed electronic structure of NiO [1]. Although exhibiting a partially filled $3d$ band and predicted by simple band theory to be a good conductor, NiO has a relatively large band gap (determined to be about 4 eV by optical measurements) that cannot be accounted for in the otherwise successful local density approximation calculations. Even taking magnetic interactions into account, band theory fails to explain the magnitude of the gap satisfactorily. Relying on a combination of two separate electron spectroscopies, Sawatzky and Allen [2] found a (conductivity) gap of 4.3 eV between the onsets of photoelectron spectra (PES) and inverse photoelectron spectra (IPES). The lowest energy states were assigned to $d^8\underline{L}$ (PES) and d^9 (IPES). On the other hand, the correlation gap is defined as the energy for transferring electrons between two Ni sites (Coulomb energy), which is considerably higher (7–9 eV). Also core level spectroscopies bear evidence for the highly correlated nature of low-energy excitations. For instance, the asymmetry of the Ni $2p$ line shape has been attributed to nonlocal charge transfer excitations and multisite cluster calculations show that solid state effects generally are appreciable for correlated materials, such as cuprates and high T_c compounds [3].

In the face of the fact that much of our experimental knowledge about the electronic structure of NiO is based upon combined electron spectroscopies, it is timely to apply a single *charge neutral* spectroscopic probe. Resonant inelastic x-ray scattering (RIXS) is a photon-only technique performed at soft x-ray absorption resonances making it atomically sensitive, orbital symmetry specific, and bulk sensitive and thus complementary in many respects to electron spectroscopy. RIXS is a powerful probe for studying correlated materials and has been described in recent literature [4–8]. In RIXS, the energy loss between the incoming and scattered photons are recorded and correspond to the energies of charge neutral low-energy excitations which obey the selection rule $\Delta l = 0, \pm 2$. In RIXS of correlated oxides local crystal field excitations (which are difficult to observe by other techniques [9]) of the type $(d^8)^*$ (dd excitations) and $d^9\underline{L}$ (local charge transfer excitation) are prominent. Moreover, for cuprates it has been shown that O K RIXS allows the observation of *nonlocal* (Zhang-Rice-like) excitations in certain detection geometries [6]. It would be equally interesting and challenging to be able to study similar excitations in the RIXS of NiO.

In this Letter, we present results from high-resolution polarization-dependent RIXS experiments at the O K resonance of NiO and compare to cluster model calculations using a Ni_6O_{19} cluster shown in Fig. 1. We observe, apart from the main band with a high energy shoulder (HES), previously undetected dd and double-singlet excitations. Previous, lower resolution, studies of NiO using RIXS-related techniques at the Ni L edge [10] and at the O K edge [11,12] either did not reveal the full low-energy excitation spectrum or the analysis was based on band structure calculations which are less appropriate for discussing specific excitations. In contrast, our combination of high energy resolution and polarization-dependent RIXS together with advanced multisite cluster model calculations reveals a rich low-energy excitation spectrum and its connection with the strongly correlated nature of NiO. First, we clarify the origin of known NiO-specific features such as the HES which is found to be due to nonlocal charge transfer (NLCT). Second, our study shows more generally that RIXS is also a powerful probe for investigat-

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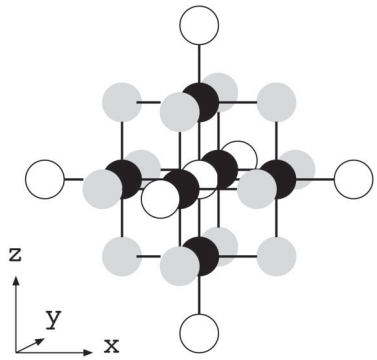

FIG. 1. A schematic perspective view of the Ni_6O_{19} cluster used for our calculations. The black circles represent Ni-ion sites and the white and gray circles represent O-ion sites.

ing nonlocal *magnetic* excitations such as double-singlet creation (DSC) states.

The O K-RIXS measurements have been performed at beam line I511–3 at MAX II (MAXLAB National Laboratory, Lund University, Sweden), based on a modified SX-700 monochromator layout [13]. The detection system was a grazing incidence grating spectrometer in the Rowland geometry [14]. For detecting the O K-RIXS spectra we used the following spectrometer configuration: 1200 lines/mm, 5 m grating in first order of diffraction. The spectrometer resolution was set to about 0.5 eV and the monochromator spectral band width was chosen to have a somewhat smaller value. We used a commercially obtained large single crystal NiO as well as powder samples (with consistent results). All data were taken with the samples at room temperature. The emission energy scale was obtained by recording the Zn $L_{\alpha,\beta}$ emission from a pure Zn foil and the Na K emission from a fresh single crystal of NaCl and using the tabulated wavelengths from literature [15]. The monochromator energy calibration was done by comparing the NiO O K-absorption resonances with literature values [16].

The upper panel of Fig. 2 shows an O K-absorption scan where the lettered arrows indicate the respective excitation energies for the RIXS spectra. The lower panel of Fig. 2 shows the O K-RIXS emission spectra excited (A) on the maximum of the first O K resonance and (B) at 0.5 eV below the maximum on an energy loss scale. When tuning the x-ray energy to the first NiO O K-absorption peak, the O $1s$ electron is excited into empty O $2p$ states strongly hybridized with the Ni $3d$ states. Two different detection geometries are compared: depolarized (polarized) geometry means that the scattered x rays are detected along (perpendicular to) the direction of the electric field vector of the incident x rays [17].

The spectra in Fig. 2 are dominated by an intense broad peak (maximum about 7 eV energy loss) with a high energy shoulder (4–5 eV energy loss). This is consistent with previous observations [11,18], and here we record the elastic peak energy which allows the determination of the corresponding loss energies. Moreover, we observe exci-

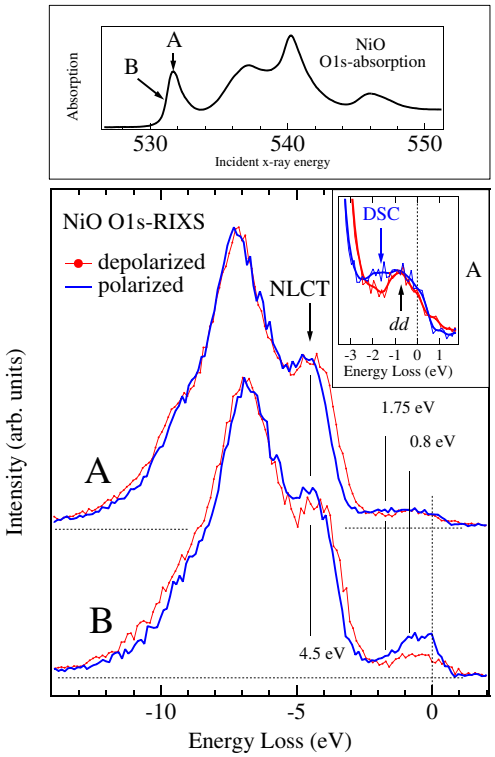

FIG. 2 (color online). Top panel: O K absorption of NiO. The lettered arrows mark the chosen excitation energies for the RIXS spectra. Bottom panel: O K RIXS at the first absorption resonance of NiO (A) and 0.5 eV below (B). The inset gives a magnified view of the excitations below the NLCT energy of spectra at excitation energy A (the heavy lines represent a three-point average of the data).

tations at lower energies (<2 eV), which are shown in detail in the inset of Fig. 2. The main contribution is attributed to dd excitations at about 1 eV which are mediated by the O $1s$-core hole state. This means that $(d^8)^*$ final states of the excited Ni ion are reached, where the asterisk denotes configurations that deviate from the ground state. The dd excitations of NiO have been observed in Ni L-edge RIXS [10] with the strongest component at 1 eV energy loss, which is corroborated by Ni M-edge RIXS at much higher resolution. Note also the extra intensity at about 1.75 eV energy loss that is observed in the polarized geometry but absent in the depolarized geometry. We will discuss the origin of this feature below.

Although some aspects of the NiO O K x-ray emission spectra can be described using a band theoretical approach, we recall that it has been found experimentally [5] and has been described theoretically [19] that O K spectra of correlated materials also can exhibit *many-body* features that have no counterpart in one electron theory. Figure 3 shows the theoretical RIXS spectra S_{mn} calculated at the central O site of the Ni_6O_{19} cluster model, where m (n) represents that the polarization vector of the emitted (incident) x ray is parallel to the m (n) axis. The depolarized spectrum is proportional to S_{zx}, while the polarized one is proportional to the average of S_{xx} and S_{zx}. These spectra are calculated

using the Kramers-Heisenberg formula, taking into account the geometrical arrangement and the incident and scattered photon polarization of the present experiment.

In our Ni_6O_{19} cluster model, the center of the cluster is the O site and it is surrounded with six NiO_6 units (Fig. 1). We assume that the central O atom is excited by an x-ray photon. If the electric field of the x ray is x polarized, the O $2p_x$ hole on the central O site, which is strongly hybridized with Ni $3d$ states, is annihilated in the intermediate state. In the depolarized geometry, an O $2p_y$ or O $2p_z$ electron fills the O $1s$ core hole in the subsequent x-ray emission process. The resultant O $2p_y$ (O $2p_z$) hole may hybridize with the Ni $3d$ states. Thus the Ni-to-Ni charge transfer (CT) occurs via the O $1s$ core hole state. The present Ni_6O_{19} is the minimum size cluster that accounts for the NLCT but the full exact-diagonalization calculation for this cluster model is presently too computer intensive. For simplicity, we disregard the Ni-to-Ni CT path via the gray O sites shown in Fig. 1. In order to concentrate on the charge transfer excitations, we restrict the basis atomic wave functions that describe the Hamiltonian to O $2p_{x,y,z}$ and Ni $3d_{x^2-y^2,3z^2-r^2}$ [20] and the multiplet coupling effects (dd excitations) are disregarded for simplicity. The diagonal matrix elements of the Hamiltonian are described with the charge transfer energy between Ni $3d$ and O $2p$ states ($\Delta = 3.8$ eV), the on-site Coulomb repulsion ($U_{dd} = 7.2$ eV) and Hund coupling on Ni sites ($J_H = 1.3$ eV). The off-diagonal matrix elements are described with the pd hybridization strength [$V(e_g) = 2.2$ eV] and the pp hybridization strength ($t_{pp} = 0.3$ eV).

We find that the spectrum for the depolarized geometry (proportional to S_{zx}) consists of four structures (Fig. 3). Feature $P1$ at -11 eV is due to $d^{10}\underline{L}^2$. Feature $P2$ at -7.5 eV is caused by CT to the antibonding state between $d^9\underline{L}$ and d^8. Feature $P3$ at -6.3 eV can be assigned to the nonbonding type $d^9\underline{L}$ in the single-site model. Compared to experiment, the features $P2$ and $P3$ in Fig. 3 are found at somewhat smaller energy loss and the intensity of $P2$ has too much spectral weight. This is partly because the Ni $3d(t_{2g})$ orbitals are disregarded in the calculation and partly because the cluster size is still too small.

Feature $P4$ at -4.1 eV is a state split off from the nonbonding type $d^9\underline{L}$ due to NLCT excitation, i.e., an excitation involving two Ni sites: $|d^9; d^8\underline{L}\rangle$. This is the RIXS analog to the state described by van Veenendaal and Sawatzky in the Ni $2p$ x-ray photoelectron spectrum (XPS) of NiO [3]. In the Ni $2p$ XPS spectrum, nonlocal excitations lead to a high binding-energy shoulder due to screening of the $2p$ core hole by an electron ($\underline{2p}3d^9$) from a neighboring NiO_6 unit. The energy difference between the unscreened and this screened state is about 2 eV. By contrast, the final state of RIXS has no core hole and we can measure the excitation energy of the $|d^9; d^8\underline{L}\rangle$ NLCT state directly.

The NLCT defines the CT excitation edge and its energy loss is intimately related to the charge transfer parameter

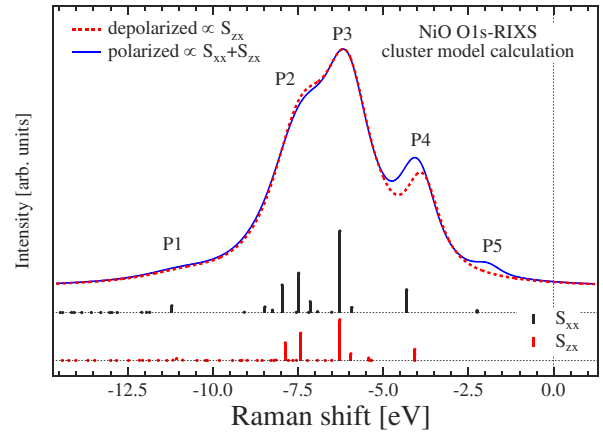

FIG. 3 (color online). The line spectra at the bottom show the polarized RIXS components S_{xx} and S_{zx}. The curves represent the theoretical O K-RIXS spectra for NiO in the depolarized geometry and the polarized geometry as labeled. We applied a variable final state lifetime broadening and a Gaussian broadening to simulate the instrumental resolution of the RIXS spectra.

Δ, which makes the largest contribution to the *superexchange coupling* constant J in NiO [21]. However, the literature estimations for the value of Δ, based on more indirect determination, spans a wide range from 2.0 to 6.5 eV [22]. Experimentally, we observe the charge transfer excitation edge at 4.5 eV, which is in good agreement with our cluster model calculation where we use the charge transfer energy parameter value $\Delta = 3.8$ eV.

The corresponding structures $P1$–$P4$ can also be found in the spectrum for the polarized geometry (proportional to $S_{xx} + S_{zx}$). This indicates that the overall polarization dependence of O K RIXS in NiO is weak due to the high symmetry in the electronic state of the cluster. On the other hand, we find an extra peak $P5$ at -1.9 eV in S_{xx} (forbidden in S_{zx}). This loss energy is roughly twice the intraatomic exchange interaction strength (Hund coupling energy J_H), which indicates that the peak is caused by a DSC excitation [23]. Local spin-flip excitations have been predicted earlier for RIXS at the L and M edges of Cu^{2+} and Ni^{2+} [24]. In that case a single spin-flip leads to an loss peak at relatively low energy, which is presently difficult to resolve instrumentally [25]. In contrast, the DSC excitation is a *nonlocal* type excitation that occurs as a result of exchanging two holes between neighboring Ni sites. Suppose that $|\uparrow\uparrow;\downarrow\downarrow\rangle$ denotes antiferromagnetically aligned spins of two holes on neighboring Ni sites, where $\uparrow$ and $\downarrow$ represent the spin state of each hole. When a $\uparrow$ hole is transferred from the left Ni site to the right, and a $\downarrow$ hole is transferred from the right to the left, $|\uparrow\downarrow;\uparrow\downarrow\rangle$ is realized. In other words, a *double-singlet state* is created as a result of double intersite CT. The DSC excitation energy is characterized by $2J_H$, albeit offset by about 0.7 eV due to the hybridization energy present in NiO.

We also briefly discuss the changes in the spectra when detuning from the first absorption resonance. Experiment-

ally we observe that the *dd* excitations in spectrum *B* (Fig. 2) become strongly enhanced relative to the other excitations, in particular, in the polarized geometry. Detuning in RIXS leads to a faster scattering, suppressing processes taking more time [26]. Thus it is plausible that the nonlocal excitations or changes of x-ray polarization require more scattering time than the local *dd* excitations.

When tuning to energies higher than the first absorption maximum (not shown) the HES moves to about 0.4 eV higher energy. First, the excitation is less selective allowing many more intermediate states leading to a broader appearance of the spectrum. Second, the scattered photon energy no longer reflects the energy difference between the initial and final state since the delocalized excited electron removes part of the atomic energy. Instead, the photon energy is a measure of the energy between the *intermediate* and the final state which is an ionized state similar to a photoemission final state. Thus the nonresonantly excited location of the HES corresponds very closely to the $d^8\underline{L}$-photoemission peak with the lowest binding energy at about 2 eV [2,27].

In conclusion, we find that O *K*-RIXS spectra excited close to the *K*-absorption threshold reflects the energy loss of charge neutral excitations. We perform a multisite cluster calculation and find very good agreement with the salient features of the experimental O *K*-RIXS spectra. Using parameter values $\Delta = 3.8$ eV for the charge transfer energy and $U_{dd} = 7.2$ eV for the Coulomb repulsion corroborates the placement of NiO in the charge transfer regime of the Zaanen-Sawatzky-Allen diagram [28].

In the O *K* RIXS of NiO we assign the resonant high energy shoulder at 4.5 eV to nonlocal charge transfer excitations and a highly anisotropic feature, found experimentally at 1.75 eV energy loss, to double spin flip creation. This excitation is only visible in the RIXS spectrum observed in the polarized geometry, exactly as predicted in our calculations. The nonlocal DSC excitation is a unique and sensitive probe for determining Hund's exchange energy J_H and the influence of covalency effects.

Our results demonstrate that solid state effects of correlated oxides can be identified and the corresponding energies can be accurately determined by combining O *K*-RIXS experiments and multisite cluster calculations. Future higher resolution studies of NiO O *K* RIXS and other correlated materials, will most likely reveal excitations at even lower loss energies (e.g., the two-magnon excitation) and provide theoretical challenges for including collective excitations in model calculations.

This work was supported by the Swedish Research Council (VR) and the Göran Gustafsson Foundation (GGS) and by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology (Japan). The experimental work was performed at MAXLAB in Lund (Sweden). We thank G. Dräger for providing us with the single crystal sample. We gratefully acknowledge the MAXLAB staff for excellent support and working conditions at the beam line.

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