

## Crystal-field excitations in NiO studied with hard x-ray resonant inelastic x-ray scattering at the Ni *K* edge

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Charge-neutral *dd* excitations in NiO have been studied using resonant inelastic x-ray scattering (RIXS) at the quadrupolar pre-edge of the Ni *K* absorption edge (8331 eV) with an energy resolution of 250 meV. The results agree well with calculations performed using the atomic multiplet model for the Ni<sup>2+</sup> ion including crystal-field effects. Most notably the first  $t_{2g} \rightarrow e_g$  excitation at 1.05 eV was observed clearly and its energy determined with a high accuracy. The remaining differences between the theoretical and the experimental results, especially in the incident-photon-energy dependence, are suggested to be due to lattice distortions. This study demonstrates that bulk sensitive, high-resolution hard-x-ray RIXS can open up possibilities in studies of highly correlated materials.

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The electronic properties of strongly correlated materials are still far from being understood despite almost a century of intense research. This constitutes an important field of study since strong correlation brings up several important phenomena, for example, high- $T_C$  superconductivity, colossal magnetoresistance, and metal-to-insulator transitions. Electronic excitation energies, dispersion, and line shapes provide information on both occupied and unoccupied electronic levels. In particular, the so-called *dd* (or crystal-field) excitations, in which only the occupation of the *3d* orbitals of a transition-metal (TM) ion changes, are sensitive to the local coordination, providing information on the fine structure of the energy levels of electrons involved in, e.g., metal-insulator transitions.

The *dd* excitations, whose energies are typically  $\leq 5$  eV, have been successfully studied using optical techniques,<sup>1</sup> electron-energy-loss spectroscopy,<sup>2</sup> and resonant inelastic x-ray scattering (RIXS), typically in the soft-x-ray region at the *L* absorption edge of the *3d* TM ion or the *K* edge of oxygen.<sup>3</sup> Soft-x-ray techniques are very well suited for these studies due to their direct dipolar coupling (especially in  $2p$ - $3d$ - $2p$  absorption and emission channels), but while the strong  $2p$ - $3d$  interaction causing intra-atomic multiplet effects renders the spectra rich in information, it also makes their analysis challenging. In the case of hard-x-ray RIXS studies of *dd* excitations, the absorption and emission channels can be either dipolar ( $1s$ - $4p$ ) or quadrupolar ( $1s$ - $3d$ ) in character, although hybridization of the *3d* orbitals with ligand  $2p$  states may bring a dipole character to an otherwise quadrupolar  $1s3d$  process. In any case, at *K*-edge resonance the *dd* excitations are typically much weaker than at the corresponding *L*-edge resonance. Bulk sensitivity, higher energy resolution, and the possibility to study samples in demanding environments such as high-pressure cells renders *K*-edge RIXS a very appealing technique for these studies. However, the order-of-magnitude weaker coupling between initial, intermediate, and final states has made well-resolved *K*-edge RIXS *dd*-excitation studies rare compared to those of soft-x-ray RIXS.<sup>4-7</sup>

Perhaps the most important benchmark system among all highly correlated oxides is the antiferromagnetic NiO, in which hard-x-ray RIXS was in fact first utilized by Kao *et al.*<sup>8</sup> NiO is a charge-transfer insulator with a band gap of  $\sim 4$  eV. It has a rocksalt structure but the antiferromagnetic ordering, the magnetization axis being along (111), causes a rhombohedral lattice distortion below the Néel temperature (523 K), above which the crystal becomes perfectly cubic.<sup>9</sup> Charge-transfer and *dd* excitations in NiO have been a subject of intense study both with x-ray techniques and theoretical methods.<sup>5,10-19</sup> The energy difference of the spectral peaks is a direct consequence of the splitting of the final *3d* levels by the crystal local field and *dd* interaction and gives important information on the electronic structure of the material, especially on the crystal-field splitting parameters  $Dq$ ,  $Ds$ , and  $Dt$ . Furthermore, with an increasing resolving power the effects of spin-orbit coupling, exchange interaction, and lattice distortions can be studied.

The purpose of this Rapid Communication is twofold. First, we demonstrate the power of TM *K*-edge RIXS in the study of *dd* excitations, thanks to the recent developments in synchrotron-based experimental facilities. This gives a new high-resolution and bulk-sensitive method to study the electronic structure of highly correlated systems. Second, we obtain highly accurate data of the *dd* excitations in NiO with few multiplet effects, giving a direct and accurate insight into the electronic structure of NiO.

The emission spectra of single-crystal NiO were measured with a resolution of 250 meV up to an energy-transfer range of 5 eV using resonant inelastic x-ray scattering in the hard-x-ray regime (Ni *K* edge at 8331 eV). The experiments were performed at the beamline ID16 of the European Synchrotron Radiation Facility. The sample was a nearly black single crystal with faces oriented along the main crystallographic axes. The novel experimental setup has been described in Refs. 20 and 21. The incident-photon beam was monochromatized by a combination of a Si(111) premonochromator and a Si(444) channel cut to a bandwidth of 100 meV. The beam was focused to a spot size of 50

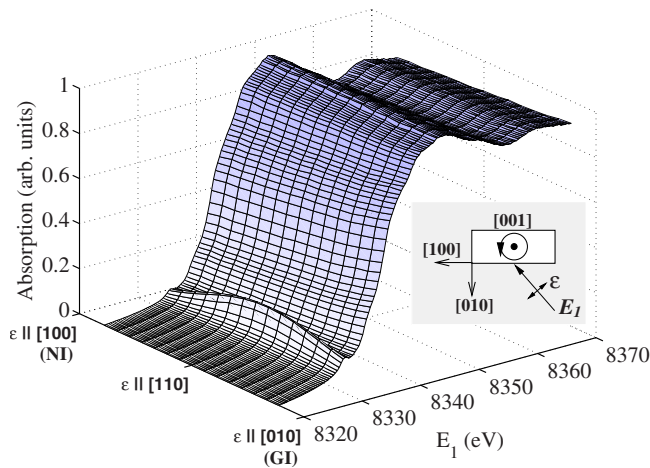


FIG. 1. (Color online) Ni  $K$  edge absorption spectra from single-crystalline NiO measured as a function of the direction of the linear polarization vector from normal incidence (NI) to grazing incidence (GI). The measurement geometry as seen from the top is shown in the inset.

$\times 120 \mu\text{m}^2$  ( $V \times H$ ) with a toroidal Rh-coated mirror. The incident-photon flux was  $10^{12}$  photons/s. The spectra were measured using a spectrometer based on a diced Si(551) analyzer crystal and a position-sensitive pixelated detector Medipix2.<sup>22</sup> The final energy resolution was measured using the elastic line from a Kapton foil and was 250 meV full width at half maximum. All measurements were performed at room temperature. The scattering plane was horizontal, i.e., parallel to the linear polarization vector. The momentum-transfer dependence of the excitations was studied in the range of 2.5–6.0  $\text{\AA}^{-1}$ , but as no dependence of the spectra as a function of momentum-transfer magnitude was found, the emission spectra presented here were measured with scattering angle  $2\theta=90^\circ$  to minimize the intensity of the quasielastic line. The spectra were corrected for changes in the sample self-absorption due to changing angles for incident and scattered photons with respect to the sample surface. No energy-dependent absorption corrections were made to the spectra. The experimental scheme was found to improve the resolving power and throughput of the spectrometer considerably and the present study should pave the way for even more improved experimental studies in the future, especially in demanding sample environments such as high pressure.<sup>19</sup>

Figure 1 presents the absorption spectra of NiO as measured using total fluorescence yield in selected directions of the linear polarization vector  $\epsilon$  of the incident x-ray beam with respect to the crystal lattice. The incident beam was kept always perpendicular to [001], which was the vector around which the sample was rotated. Each spectrum was corrected for a constant background and normalized to unity at maximum. All spectra represented here were measured with incident-photon energy ( $E_1$ ) tuned to the vicinity of the weak prepeak at 8331 eV, which corresponds to the local transition  $\text{Ni } 1s^2 3d^8 \rightarrow 1s^1 3d^9$ . It can be clearly seen how sensitive this peak is to the relative orientation of the polarization vector  $\epsilon$  with respect to the sample, exhibiting a period of  $90^\circ$  and a maximum when  $\epsilon$  is aligned along [110]. In

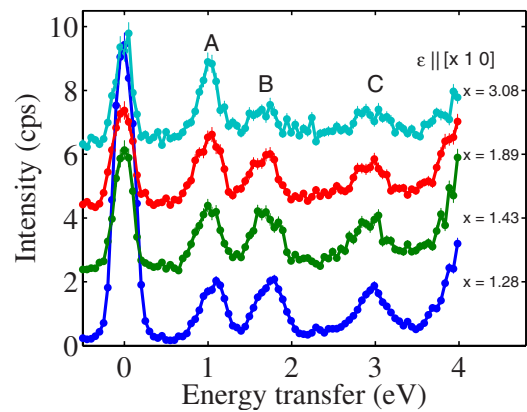


FIG. 2. (Color online) Measured emission spectra of NiO with four different sample orientations. The direction of the linear polarization vector  $\epsilon$  of the incident beam is given with respect to the crystallographic orientation of the sample, as in Fig. 1. The zero-energy-loss peak is the quasielastic line, strengthening in intensity toward  $\epsilon \parallel [110]$  due to the vicinity of the NiO(200) reflection.

the case of dipolar transitions the transition probability would be expected to maximize when  $\epsilon$  is aligned along the empty orbitals.<sup>23</sup> In the case of NiO the only empty states are of  $e_g$  character, aligned along the main crystallographic axes, but the intensity is *minimized* when  $\epsilon$  is along those directions. This is due to the quadrupolar transition operator which results in a more complicated intensity distribution than the simple dipolar operator.<sup>10</sup> This and the  $90^\circ$  period of the prepeak intensity in the sample coordinate frame suggest a strong quadrupolar character of the prepeak in NiO in accordance with previous studies.<sup>24–29</sup>

The measured emission spectra, averaged over  $E_1$  around the absorption prepeak, are presented in Fig. 2. First of all, the charge-transfer gap is observed as a steep increase in intensity starting at 3.5 eV. If defined as the energy where the spectral intensity has reached 50% of the first maximum of the charge-transfer band, the charge-transfer energy was found to be  $3.8 \pm 0.2$  eV, in good agreement with previous results.<sup>19</sup> More interestingly, three peaks due to crystal-field ( $dd$ ) excitations, labeled A, B, and C, can be clearly distinguished within the charge-transfer gap. Their energies were found to be 1.05, 1.70, and 2.95 eV, respectively. No dispersion of their energies was observed as a function of momentum-transfer magnitude, as can be expected for localized  $dd$  excitations. All three excitations have been observed previously in soft-x-ray RIXS (Refs. 12–16) but only B and C in hard-x-ray RIXS and nonresonant IXS (NRIXS).<sup>5,11</sup> The excitation A is the lowest-lying  $dd$  excitation in NiO and its energy corresponds roughly to the crystal-field splitting parameter  $10Dq$ . To the authors' knowledge, this is the first well-resolved observation of excitation A in hard-x-ray IXS. In Fig. 2 spectra are presented for four different incidence angles. It can be seen that while the intensity of peak A is little dependent on the direction in the studied angular range, peaks B and C get progressively weaker when  $\epsilon$  approaches the [100] direction. This is in excellent agreement with the intensity distribution observed by Larson *et al.*<sup>11</sup> in NRIXS. The energies and intensities of the three peaks are collected in Table I.

TABLE I. The energies  $E^{A,B,C}$  and intensities  $I^{A,B,C}$  of the three observed excitations labeled A, B, and C, respectively, as a function of the direction of the polarization vector  $\epsilon$  along crystallographic axes of the sample. The energies are in eV and intensities in units normalized to the intensity of the first excitation peak in the first row.

$\epsilon \parallel$	$E^A$	$E^B$	$E^C$	$I^A$	$I^B$	$I^C$
[1.28 1 0]	1.06	1.73	2.96	1.0	1.1	0.8
[1.43 1 0]	1.00	1.68	2.92	1.0	1.0	0.7
[1.89 1 0]	1.01	1.66	2.92	1.2	0.8	0.5
[3.08 1 0]	1.01	1.64	2.95	1.0	0.4	0.3

Atomic multiplet calculations of the transitions were performed using Thole's version of Cowan's code together with the MISSING interface.<sup>30</sup> The calculations were done in the  $D_{4h}$  symmetry, and the best fit with experimental data was obtained with the crystal-field parameter  $10Dq=1.05$  eV. A Slater-Condon parameter reduction factor of 63% was needed to obtain a good fit of the energies of all three measured spectral lines. The reduction factor partly incorporates correlation effects, and the relatively important reduction used here brings the results closer to those obtained with configuration-interaction calculations.<sup>12</sup> The spin-orbit coupling constant was obtained to be 84 meV and the value of 1.39 eV was used for the core-hole lifetime.<sup>31</sup> Changing the crystal-field parameters  $Ds$  or  $Dt$  was found not to improve the agreement considerably so in the following they are kept at  $Ds=Dt=0$ . The calculated emission spectrum and the experimental result at  $\epsilon \parallel [1.28 1 0]$  (both averaged over  $E_1$  around the prepeak region) are presented in Fig. 3. It can be seen that the agreement on the energies of the calculated three peaks is good. The existence of the predicted small shoulderlike feature at 2.5 eV is difficult to confirm in the present experiment due to its weakness, but the experimental spectrum does seem to have an excess of intensity between peaks B and C. It is also possible that an indication of splitting of peak B is visible in the experimental spectrum. Higher resolution would be desirable to confirm these features.

The  $E_1$  dependence of the spectra is shown in Fig. 4,

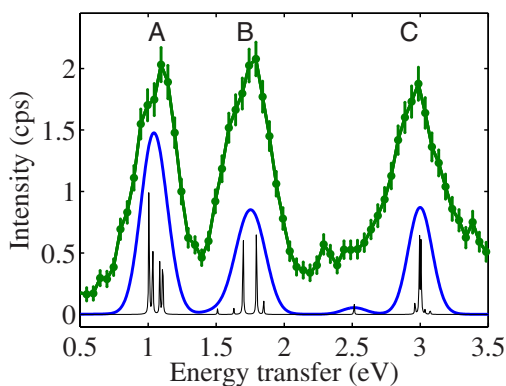


FIG. 3. (Color online) Measured crystal-field excitation spectra of NiO at  $\epsilon \parallel [1.28 1 0]$  (points connected with a solid line). Results of a calculation based on the atomic multiplet approach as a stick diagram and taking the experimental resolution into account are shown as the solid line.

which shows the observed intensity as a function of  $E_1$  and energy transfer, measured with  $\epsilon \parallel [1.28 1 0]$ . Both the experimental and theoretical result show one main absorption channel at 8331.1 eV. This two-dimensional map shows perhaps the most important results of this work. While all excitations are concentrated in a single well-defined region, peak A appears in the experiment to have shifted to higher energy by about 140 meV. Our calculations for tetragonal distortion, carried out by changing the crystal-field parameters  $Dt$  and  $Ds$ , showed that the resonance energy of peak A is very sensitive to possible distortions. However, it was found that its resonance shifts preferably toward lower  $E_1$  with nonzero tetragonal distortion parameters, in contrast with the experimental observation, so the agreement with the experimental result was not found to improve upon nonzero  $Dt$  and  $Ds$  parameters. The measured relatively large shift toward higher energy may be due to the fact that the distortion is rather rhombohedral than tetragonal. This is most probably due to the antiferromagnetic lattice distortion which lifts the degeneracy of the  $e_g$  orbitals.<sup>1,32,33</sup> Nevertheless, similar calculations performed in the cubic  $O_h$  symmetry confirm the existence of only one absorption channel in the absence of any splitting of the  $e_g$  orbitals, supporting the hypothesis that the difference in resonance energies might be due to lattice distortions. Other possible explanations could be effects due to the hybridization of the O 2p and Ni 3d orbitals or non-stoichiometry effects due to the probable excess of oxygen in the sample.<sup>34</sup> Understanding these effects will require more sophisticated calculations.

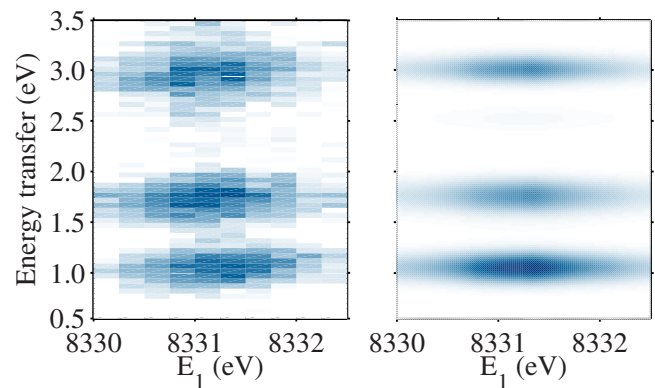


FIG. 4. (Color online) Measured (left) and calculated (right) crystal-field excitation spectra of NiO as a function of  $E_1$  and energy transfer. The theoretical result in the right panel is broadened to reflect the experimental resolution. As in Fig. 3, the experimental data were measured with  $\epsilon \parallel [1.28 1 0]$ .

The  $E_1$  dependence of the spectra is rather simple as compared to  $2p$  core-level spectroscopies due the absence of an orbital angular momentum in the  $1s$  core hole. Also, the overlap of the radial part of the atomic wave functions of the  $1s$  core hole and the hole of the excited  $3d^9$  shell is very small. This results in fewer and smaller Slater-Condon integrals and thus a simpler multiplet splitting than observed in  $L$ -shell spectroscopy. To a good approximation there is only one resonance energy in the case of NiO, and possible fine structure may be due to lattice distortion, hybridization effects, or oxygen excess in the sample. This would suggest that  $K$ -edge RIXS is a very appealing spectroscopic choice for studying  $dd$  excitations. Although the coupling of the probe to the  $dd$  excitations is weaker than in soft-x-ray RIXS, in view of the recent breakthroughs in spectroscopic methods and the continuous increase in the obtainable photon flux at modern synchrotron-radiation sources, this limitation can be overcome as is shown in this study.

In conclusion, high-resolution energy-loss spectra of single-crystal NiO have been measured using resonant in-

elastic x-ray scattering at the Ni  $K$  edge. Three nondispersing energy-loss features were observed, located at 1.05, 1.70, and 2.95 eV. The excitations are assigned to  $dd$  excitations and the results are in good agreement with results of the atomic multiplet model. The spectra are shown to exhibit few competing multiplet effects, rendering the spectral analysis straightforward and simple and resulting in an accurate determination of parameters relevant to the electronic structure of a highly correlated system. The experimental setup has allowed a significant breakthrough in increasing the resolving power and efficiency of the hard-x-ray IXS spectrometers, fully elucidating the power of truly bulk sensitive high-resolution hard-x-ray inelastic x-ray scattering in the studies of highly correlated materials.

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