Polarization and momentum dependence of a charge-transfer excitation in Nd_2CuO_4

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We report the polarization and q dependence of 6-eV charge-transfer excitation in Nd_2CuO_4, as studied by resonant inelastic x-ray scattering. The incident polarization is shown to select the intermediate states participating in the resonant process, and resonances associated with $1s \rightarrow 4p_\sigma$ and $1s \rightarrow 4p_\pi$ transitions are resolved. No enhancement is observed for the $\underline{1s}3d^{10}\underline{L}$ well-screened intermediate states in either case. Numerical calculations show that this is the result of nonlocal effects. The intensity and position of the excitation was found to be independent of the momentum transfer along the c axis for $q = 3.5$–7.9 Å^{-1}.

The physics of strongly correlated electron systems is currently attracting enormous attention because it underlies some of the most challenging and important questions in solid-state physics, including high-T_c superconductivity. Of basic interest in these systems is their electronic structure, and in particular the electronic excitation spectrum, which determines the electron dynamics. However, theoretical calculations of such properties are complicated by strong electron correlations, which mean that neither conventional band theories nor local cluster calculations are adequate. Recently, work has begun to extend cluster calculations to larger numbers of atoms in order to correctly account for solid-state (nonlocal) effects.[1,2] While such approaches seem promising, there is a clear need for further experimental tests of these models.

A variety of experimental techniques have been used to probe the electronic excitation spectrum of strongly correlated transition-metal oxides, including x-ray-absorption spectroscopy (XAS) and photoemission spectroscopy. However, these traditional techniques have disadvantages in their application to these materials. In contrast, recent experiments on NiO,[3] Nd_2CuO_4,[4] and other cuprates[5] suggest that resonant inelastic x-ray scattering (RIXS) in the hard x-ray regime may provide a probe of charge-transfer excitations. In particular, it offers bulklike penetration, an absence of effects due to the presence of a deep core hole, and the ability to access any energy transfer. Further, because it is a ''photon-in, photon-out'' process, the technique is equally applicable to metals and insulators and can be performed in applied electric or magnetic fields. Finally, there are suggestions that it is possible to obtain momentum-dependent information.[5,6]

The work on Nd_2CuO_4,[4] in which a charge-transfer excitation at 6 eV was observed with the x-ray energy tuned in the vicinity of the copper K edge, was interpreted in terms of a second-order scattering process, and the electronic structure was calculated within the Anderson impurity model, in which the coupling between the core hole and valence states in the intermediate state was fully taken into account. While this approach accounted for the gross features of the experiment, there were a number of unanswered questions. In particular, of the four distinct features, screened and unscreened pairs of $4p_\sigma$ and $4p_\pi$ resonances, in the Cu K-edge absorption spectrum, the charge-transfer excitation was observed only at one of the $4p_\pi$ resonances. Note that the $4p_\sigma$ orbitals lie in the plane of, and the $4p_\pi$ orbitals lie perpendicular to the plane of, the CuO sheets.

Subsequently, Abbamonte *et al.*[5] suggested quite a different approach, describing their data using a third-order perturbation theory, which treats the observed energy losses as a ''shakeup'' process in between the creation and annihilation of the core exciton created by the resonant process. While these two approaches are attempts to represent the same physics, that of core hole interactions with the valence electron system, they have quite different implications for the data. In particular, the latter approach exhibits peak shifts in the energy-loss feature, as a function of incident energy, and appears to be (in certain limits) reducible to a quantity resembling $S(q,\omega)$, the dynamic structure factor. Given these

differences, and the importance of understanding the scattering process in more detail, there is a clear need for more experimental data.

In this paper, we report the polarization and momentum-transfer dependence of the charge-transfer excitation in Nd_2CuO_4. We show that the presence, or absence, of the $4p_\pi$ and $4p_\sigma$ resonances may be understood as arising simply from the relative orientation of the incident polarization and the $4p$ orbitals. Further, based on extended cluster calculations we show that the absence of the screened $4p_\pi$ resonance is related to nonlocal effects, which suppress the resonance to the localized 6-eV excitation. Finally, the momentum-transfer dependence of the 6-eV excitation was investigated. No significant change in the intensity, position, or width was observed between 3.5 and 7.9 Å^{-1} at the $4p_\sigma$ resonance.

The experiment was carried out at beam line X25 at the National Synchrotron Light Source. The beam line optics consist of a focusing mirror and a double-crystal Si(111) monochromator. The incident photon flux was 5×10^{11} photons s^{-1}, in a spot of size 0.2 mm(V)×0.8 mm(H). The radiation was 98% linearly polarized in the horizontal plane. The scattered radiation was analyzed using a mechanically bent ($r=1$ m) single-crystal Si(553) wafer with an active area of diameter 35 mm.[7] The overall energy resolution was 2.3 eV [full width at half maximum (FWHM)] as measured by the quasielastic scattering from the sample. The experimental setup, including the sample and the analyzer crystal assembly, was enclosed in a helium environment and mounted on a four-circle diffractometer, which allowed scattering angles between 0° and 120° to be reached in both vertical or horizontal scattering geometries. This allowed the direction of incident polarization relative to the crystal orientation, and the magnitude and direction of the momentum transfer, to be varied. The same single crystal of Nd_2CuO_4 was used in this work as that of Ref. 4. It has a c axis parallel to the surface normal and is 0.1 mm thick. All data were taken at room temperature.

We first carried out measurements with the incident polarization aligned in the CuO planes ($\epsilon||ab$ plane) and the momentum transfer perpendicular to the CuO sheets ($q||c$). Energy-loss spectra for a series of incident energies in the vicinity of the Cu K edge were taken at $2\theta=60°$ ($q=4.6$ Å^{-1}). As in the previous experiment,[4] a 6-eV excitation is observed only at certain, resonant, incident energies. The amplitude of the 6-eV excitation as a function of incident energy was extracted by fitting these data to a Gaussian peak on a linear background. The resulting amplitudes are plotted in Fig. 1 (closed circles). The peak positions and widths are almost constant, showing only very slight variations in position and width (the fits are essentially unchanged if the peak position and width are varied or held fixed). Crucially, the fitted peak intensities exhibit a single resonance at 8999.5 eV, of width ≈7-eV FWHM. This is in contrast to the earlier work,[4] for which a resonance was observed at 8990 eV. For completeness, this earlier data are reproduced in Fig. 1 (open circles), scaled by an arbitrary factor for comparison purposes. (In fact, the absolute intensities were a factor of 60 smaller for the original work.[4]) The present results show that with the incident polarization in the CuO planes, a resonant enhancement is observed for $4p_\sigma$ and not for $4p_\pi$ excitations.

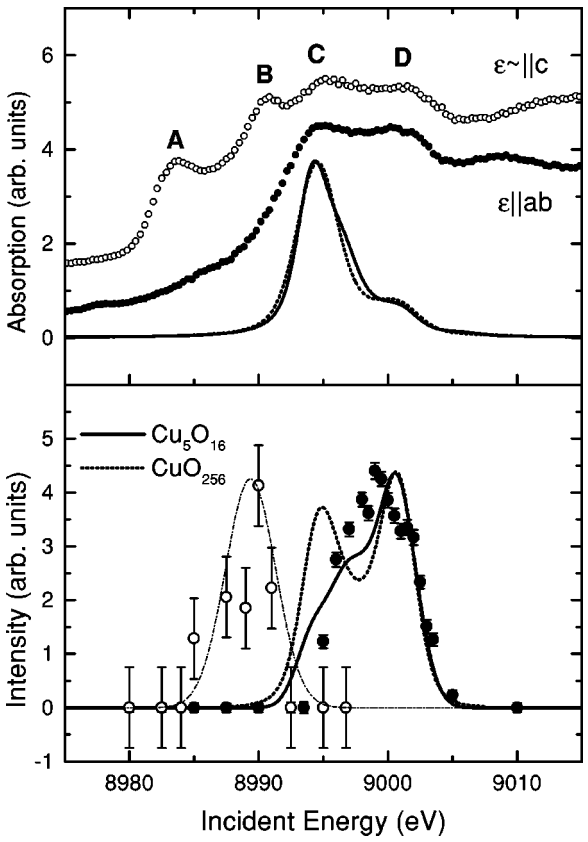

FIG. 1. Top panel: polarization-dependent absorption measured by monitoring the fluorescence yield. Lower panel: the intensity of the 6-eV excitation, extracted by fitting individual energy-loss scans, as a function of incident energy (closed circles). The solid and dashed lines in both panels are the results of numerical calculations for the $1s\rightarrow4p_\sigma$ transitions described in the text. For comparison purposes, the data from Ref. 4 are also included (open circles). These latter data were taken with the incident polarization approximately parallel to c ($1s\rightarrow4p_\pi$ resonance excited). The dash-dotted line through these data is merely a guide to the eye.

Polarized x-ray-absorption spectra, also shown in Fig. 1, provide a natural explanation for these results. These data were obtained by monitoring the intensity of the Cu $K\alpha$ fluorescence from the sample as the incident energy was tuned through the K edge. Note that while the sample geometry made it possible to place the incident polarization solely in the ab plane (vertical scattering geometry), in the horizontal scattering geometry the polarization was in fact 30° off the c direction.

These absorption spectra duplicate previously published results,[8,9] and exhibit four distinct features at 8983, 8990, 8995, and 9002 eV, labeled *A*, *B*, *C*, and *D*, respectively. Features *A* and *B* are associated with the dipole transitions to the $4p_\pi$ orbitals, and Fig. 1 shows that they are preferentially excited when the incident polarization is along the c direction. Conversely, features *C* and *D* are associated with $1s\rightarrow4p_\sigma$ transitions and, correspondingly, these are most prominent when the incident polarization is in the ab plane.

In the present context, the significance of these data is that the *final* state of the XAS process is the *intermediate* state in

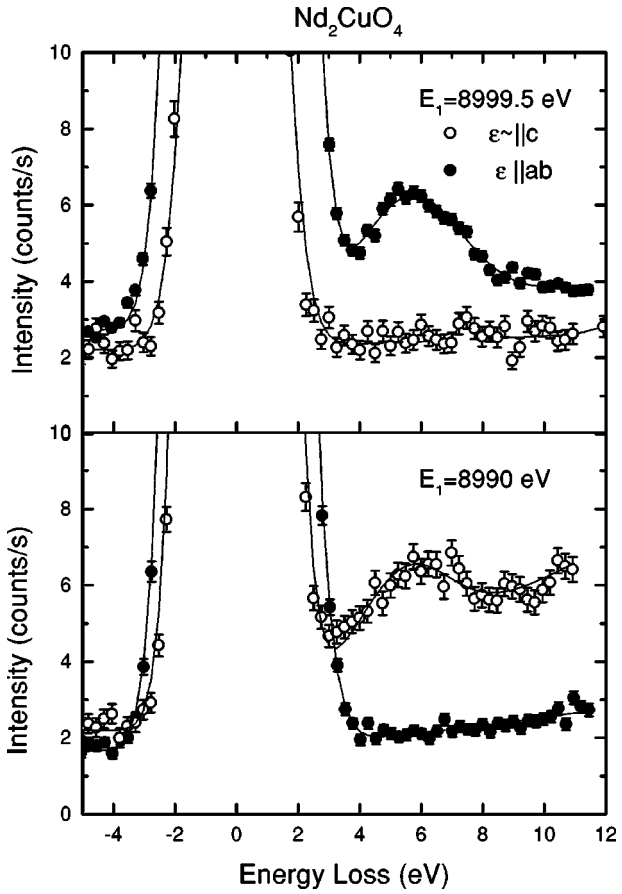

FIG. 2. Top panel: inelastic scattering for an incident energy of 8999.5 eV. Closed circles: incident polarization in the ab plane; open circles: incident polarization approximately along c. Bottom panel: same as top, with incident energy set to 8990 eV [$\epsilon||c$ data (open circles) are multiplied by 5 to highlight the peak].

the RIXS process. For a significant resonant enhancement to occur, it is necessary that the intermediate state be strongly excited. The polarized XAS results show that the $4p_\sigma$ intermediate states are strongly excited (and the excitation transitions $1s \rightarrow 4p_\pi$ strongly suppressed) when the polarization is in the CuO planes. This suggests that it is this polarization dependence of the excitation process which is responsible for the presence or absence of resonant enhancements at the $4p_\sigma$ and $4p_\pi$ positions.

To confirm this, we carried out measurements in the two scattering geometries at two energies, 8990 and 8999.5 eV. In both cases, the momentum transfer is of the same magnitude ($q=4.6$ Å^{-1}) and direction ($q||c$); only the relative orientation of the incident polarization is altered. Figure 2 shows that with the incident energy set to 8999.5 eV ($4p_\sigma$ resonance), an inelastic feature is observed when the incident polarization is in the CuO plane, and not when it is perpendicular to the plane. Conversely, at 8990 eV ($4p_\pi$ resonance), an inelastic feature is observed with the incident polarization (approximately) parallel to the c axis, and not with it in the plane. In each case, the same excitation is observed, at 6 eV. These data thus confirm the above interpretation.

While a strong excitation to the intermediate state is a necessary condition for observing a resonant enhancement, it is not sufficient, as demonstrated by the absence of resonances associated with the $1s3d^{10}\underline{L}$ intermediate states. We next address this puzzle.

Calculations of electronic structure and the RIXS process, based on a single copper site, correctly predict the incident polarization dependence. However, they fail to account for the systematic absence of any $1s3d^{10}\underline{L}$ resonances (features A and C). In both experimental geometries, resonances are only observed for $3d^9$ intermediate states (features B and D), as illustrated in Fig. 1. In contrast, the single-site calculations predict resonant inelastic enhancements for all intermediate states. This failure of the single-site calculation led to speculation[4] that the suppression of the $1s3d^{10}\underline{L}$ resonances was due to nonlocal effects active in the intermediate state, following ideas developed originally in the context of photoemission experiments.[1] Specifically, in the intermediate state the $\underline{L}$ hole is thought to be repelled by the core hole, and to move off elsewhere in the CuO plane, where it forms a Zhang-Rice singlet.[10] This extended state has very little overlap with the charge-transfer-excited state at 6 eV, which is nearly local, and there is thus no resonant enhancement of the inelastic scattering associated with these intermediate states (A and C).

In order to show explicitly that this is a nonlocal screening effect, we have improved upon the earlier calculations, modeling the RIXS with a Cu_5O_{16} cluster model, in which five CuO_4 plaquettes are arranged in the ab plane with D_{4h} symmetry. On each Cu site we take into account a Cu $3d_{x^2-y^2}$ orbital, and on each O site we consider an O $2p_x$ or $2p_y$ orbital which hybridizes with the neighboring Cu $3d_{x^2-y^2}$ orbital. Parameter values in the cluster model are taken as follows: the charge-transfer energy $\Delta=2.5$ eV, the electron hopping energy between neighboring Cu $3d$ and O $2p$ orbitals $T_{pd}=1.21$ eV, that between the neighboring O $2p$ orbitals $T_{pp}=0.55$ eV, the on-site Coulomb interaction between Cu $3d$ electrons $U_{dd}=8.8$ eV, and the Cu $1s$ core hole potential acting on the Cu $3d$ hole $U_{dc}=7.5$ eV. For the Cu $4p$ orbitals, we consider nearest-neighbor hopping as represented by the Slater-Koster parameters $(pp\sigma)=0.24$ eV and $(pp\pi)=-0.8$ eV, the on-site Coulomb interaction between Cu $4p$ and $3d$ states $U_{pd}=3.3$ eV, and the on-site Coulomb potential of the core hole acting on $4p$ electron $-U_{pc}=-4.0$ eV. The RIXS spectra are calculated with a coherent second-order optical formula,[11] following an exact diagonalization of electronic states of the cluster.[2] The detailed description and discussion of the computational model and the parameters related to this work is published elsewhere.[12]

The calculated result for the 6-eV amplitude at the $1s \rightarrow 4p_\sigma$ transition is shown in Fig. 1 (solid curve). The calculation is broadened by the resolution of 2.3 eV in order to approximate the experimental results. A strong resonance is seen only at the higher-energy XAS feature ($1s3d^9$), in broad agreement with the experimental result. For comparison, the results of the Anderson impurity model calculation for a large cluster with a *single* Cu site and many O sites (256) are shown by the dashed curve. It exhibits resonances at both the $1s3d^9$ and $1s3d^{10}\underline{L}$ energies.[13] Taken together, then, these calculations demonstrate that the suppression of the resonant enhancement associated with the $1s3d^{10}\underline{L}$ intermediate states results from the presence of multi-Cu sites, and does indeed reflect nonlocal effects.

Specifically, the calculation confirmed that in the intermediate state, the $1s3d^{10}\underline{L}$ configuration is unstable and that the

hole on the ligand sites is pushed out to the edges of the cluster by the Coulomb interaction with the core hole, where it forms a Zhang-Rice singlet state with a Cu $3d^9$. This fully relaxed intermediate state is an extended, nonlocal state with a Zhang-Rice singlet and, as mentioned above, has a very small transition probability for de-excitation into the charge-transfer-excited state, and thus the resonant enhancement of the inelastic scattering is suppressed. In contrast, in the single Cu site calculation, the $\underline{L}$ hole, which moves along the relatively strong hybridization path O $2p \rightarrow$ Cu $3d \rightarrow$ O $2p$ in the multisite case, is confined mainly to the central plaquette where the core hole was created, and thus the intermediate state is also localized; no Zhang-Rice singlet is formed, and there is a strong overlap with the charge-transfer excitation, resulting in a prediction of a resonant enhancement.

Finally, we note that with the higher quality data of the present work, we are able to accurately place the energy of this excitation at $E_{CT}=5.7$ eV. This is in very good agreement with the multisite calculation $E_{CT}=5.7$ eV. Such quantitative comparisons highlight the potential for RIXS measurements to provide sensitive tests of electronic structure calculations for these materials.

We have also investigated the q dependence of the scattering. Data were taken in a vertical geometry, i.e., with the polarization in the ab plane, and at the peak of the resonance ($E_1=8999.5$ eV). Spectra were recorded at four different scattering angles corresponding to momentum transfers of 3.5, 4.6, 6.5, and 7.9 Å^{-1}, respectively (Fig. 3). No dispersion in the peak position or width is observed, within the experimental error. Furthermore, the spectra have identical peak intensities, to within experimental uncertainties. We conclude that there is no significant dispersion along c axis in intensity, position, or width of the excitation between 3.5 and 7.9 Å^{-1}.

As emphasized above, this charge-transfer excitation is a nearly local excitation and thus would not be expected to exhibit much dispersion. It is therefore not possible to comment from these data on the speculations of Refs. 5,6 that q-dependent information can be obtained with this technique. However, these data do rule out any strong angular intensity dependence in the resonant cross section in this geometry.

In summary, we have measured the polarization and q dependence of a charge-transfer excitation in Nd_2CuO_4 using resonant inelastic x-ray scattering. In contrast to recent data on La_2CuO_4 and $Sr_2CuO_2Cl_2$,[5] we are able to explain all aspects of the data within a second-order scattering formalism. Improved cluster calculations of the electronic structure correctly predict the suppression of resonant inelastic scattering for nonlocally screened intermediate states, and we show that the incident polarization dependence of the excitation process may be exploited to select the intermediate state of the resonance. Finally, no q dependence of the 6-eV charge-transfer excitation is observed in our measurements.

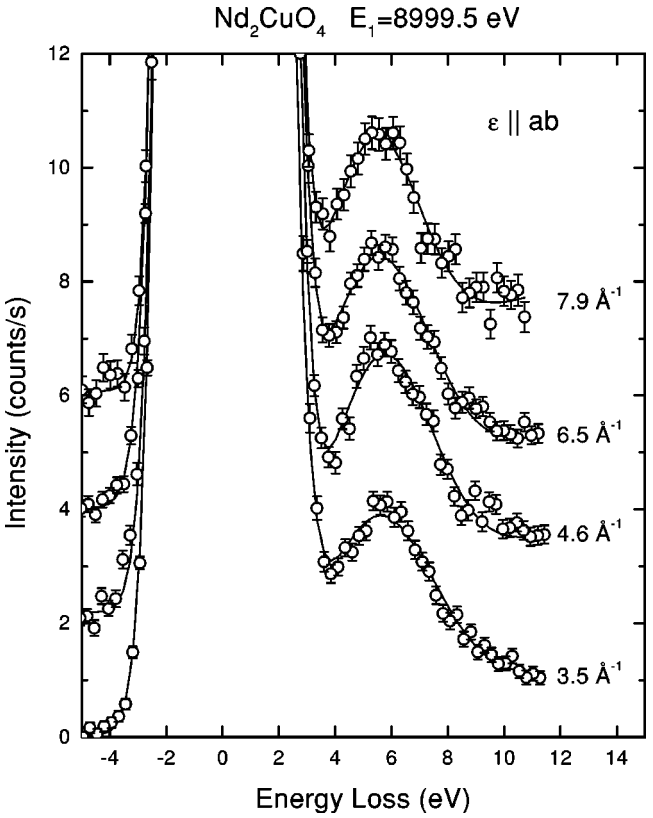

FIG. 3. Energy-loss spectra recorded at the $1s \rightarrow 4p_\sigma$ resonance for different momentum transfers along the c axis. The different q values correspond to scattering angles of 45°, 60°, 90°, and 120°, respectively.

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