Resonant Inelastic X-Ray Scattering in Nd_2CuO_4

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We report inelastic x-ray scattering studies of charge excitations in insulating Nd_2CuO_4 as a function of incident photon energy. An excitation of $\sim$6 eV is observed when the incident photon energy is tuned through the Cu K edge. This is interpreted as resonantly enhanced inelastic x-ray scattering. Numerical calculations identify the 6 eV feature as a charge-transfer excitation to the antibonding state and suggest that nonlocal effects play a role in determining the shape of the resonance. [S0031-9007(98)06181-X]

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Understanding the normal state electronic properties of the high-T_C copper oxides is an important prerequisite for a theory of high temperature superconductivity. In addition, the properties themselves are highly unusual, exhibiting non-Fermi-like behavior [1] and they have therefore attracted much interest from the more general perspective of understanding electronic behavior in strongly correlated transition metal oxides.

A useful theoretical approach has been to treat the copper oxide planes within the framework of a microscopic electronic Hamiltonian, such as the extended Hubbard model [2]. The strong electron correlations preclude the possibility of successful band structure calculations, and a variety of numerical techniques have therefore been applied, utilizing small clusters of ions for which on-site interactions can be treated explicitly [3], for example, impurity and cluster interaction models [4,5]. These models are typically local, that is, the translational symmetry of the lattice is neglected. However, as first emphasized by Veenendaal, Eskes, and Sawatzky [6], solid state (nonlocal) effects can be important, and recently calculations have been performed for a number of clusters connected in a planar geometry for which some degree of translational symmetry is restored [7].

A crucial test of such treatments is to compare their predictions with measurements of the electronic excitation spectrum. To this end a variety of spectroscopies have been applied to the cuprates. However, each has its limitations. For example, photoemission experiments only probe to the photoelectron escape depth and it can be difficult to ensure that bulklike properties are measured. Also final-state effects (i.e., those due to the presence of a core hole in the final state) are large, and electrostatic charging may be a problem for insulators. X-ray absorption spectroscopy (XAS) offers bulklike penetration, but still suffers from a final-state core hole, and optical spectroscopies are essentially limited to $q = 0$ properties and energy transfers of a few eV. There remains a clear need for new spectroscopies to elucidate the electronic excitation spectrum of the high-T_C cuprates.

Inelastic x-ray scattering in the hard x-ray regime exhibits none of the above disadvantages. The scattering process is charge neutral so that final-state effects are eliminated and the excitation spectrum is measured directly. Further, bulklike properties are measured. It would thus seem an ideal tool in this endeavor. Unfortunately, the cross section is in general small, limiting studies to low-Z materials, for which the absorption is weak. Very recently, however, Kao *et al.* discovered a large enhancement ($\sim 100\times$) in the inelastic x-ray cross section of NiO, on tuning the incident photon energy through the Ni K edge [8]. These measurements suggest the possibility of performing resonant inelastic x-ray scattering studies in highly absorbing materials, such as the cuprates. In addition, such scattering is element specific allowing, for example, excitations associated with the copper orbitals to be probed by tuning to the Cu K edge.

In this Letter, we report the first observation of inelastic x-ray scattering with hard x rays from a high-T_C cuprate. The work was carried out on Nd_2CuO_4, the parent compound of the electron doped high-T_C family, $Nd_{2-x}Ce_xCuO_4$. A resonantly enhanced excitation of two counts per minute was observed when the incident photon energy was tuned through the Cu K edge. On the basis of numerical calculations, we interpret this excitation as a charge-transfer process and conclude that the antibonding state in the CuO planes is 6 eV above the ground state. This work demonstrates the importance of nonlocal effects in determining the excitation spectrum, as evidenced by the incident energy dependence of the scattering, and that this technique is preferentially sensitive to charge-transfer excitations and is thus complementary to existing soft x-ray methods in these materials.

The experiments were carried out at beam line X21 at the National Synchrotron Light Source. The incident energy resolution was determined by a monochromator

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comprised of two channel-cut Si(220) crystals and had a width of 0.2 eV, full width at half maximum (FWHM). The incident flux was 5×10^{10} photons s^{-1}, in a 0.5 mm $\times$ 0.5 mm spot. The horizontally scattered radiation was collected by a spherically bent ($R = 1$ m) Si(553) analyzer. The overall energy resolution, as determined from the quasielastic scattering from the sample, was well described by a Gaussian of 1.9 eV FWHM. The data were taken at room temperature at a momentum transfer of $q = 4.55$ Å^{-1}, with q parallel to the c axis. The incident beam was predominantly horizontally polarized, and hence there was a component of the electric field in both the c direction and in the a-b plane, with 75% of the intensity along the c direction. A single crystal of Nd_2CuO_4 was studied, chosen for its excellent mosaic (0.014° FWHM) to minimize the quasielastic scattering. It was $\approx$0.1 mm thick, with a c axis surface normal.

The inelastic scattering observed with an incident photon energy of $E_i = 8989$ eV is plotted in Fig. 1. Two peaks are present, in addition to the elastic scattering. Each has a distinct incident energy dependence. The peak at 8975 eV disperses approximately linearly with incident energy below threshold. Above threshold, it appears at a fixed final energy, $E_f = 8976$ eV, with an amplitude of $\sim$15 counts per minute. These characteristics identify it as resonant Raman scattering from the Cu $K\beta_5$ emission line and it will not be considered further here.

In contrast, the peak at 8983 eV exhibits quite different behavior, as shown in Figs. 2 and 3. The scattered intensity is plotted as a function of energy loss $(E_i - E_f)$ for incident photon energies around the Cu K edge in Fig. 2. Each data set took approximately 24 hours to collect. The excitation at 6 eV is observed only for incident energies in the vicinity of 8990 eV, and remains at an approximately fixed energy loss for all incident energies. As discussed below, we believe that this scattering arises from a charge-transfer-type excitation.

The amplitude of the 6 eV excitation was extracted by fitting the energy loss scans to a Gaussian peak on a sloping background (to account for the tails of the $K\beta_5$ line) and is plotted in Fig. 3 as a function of incident photon energy. Resonant behavior is clearly observed, with a peak at 8990 eV. Even at resonance, the count rates remain small, on the order of a few counts per minute. The q dependence of the scattering was not investigated.

To identify the origin of the enhancement, the absorption of Nd_2CuO_4 powder, ground from crystals obtained from the same growth batch as the sample, was measured and is shown, together with the absorption from a Cu foil, in Fig. 3. The Cu K edge, located by the first point of inflection in the metal foil spectrum is at 8979 eV. The powder absorption is in quantitative agreement with data

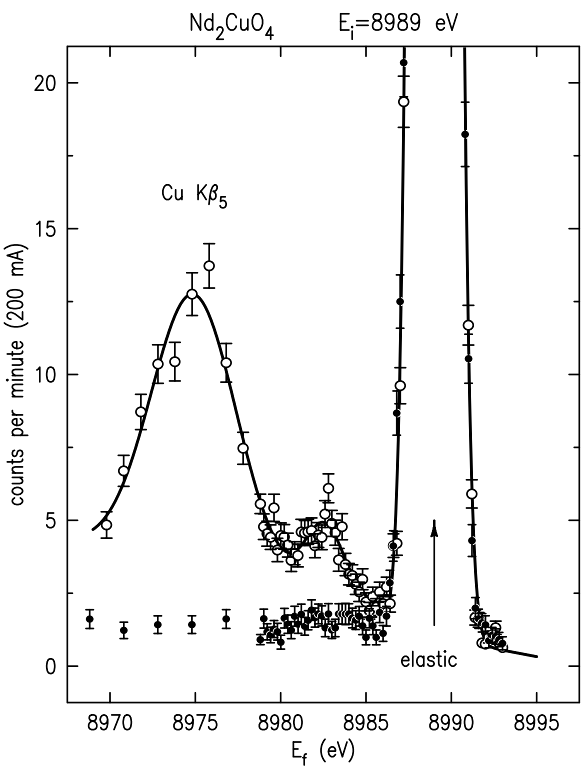

FIG. 1. Scattered intensity as a function of final energy, E_f for a fixed incident energy, $E_i = 8989$ eV. The solid line is a guide to the eye. Solid symbols: Data taken well above resonance ($E_i = 9020$ eV) to characterize inelastic background. Elastic energy is shifted for comparison.

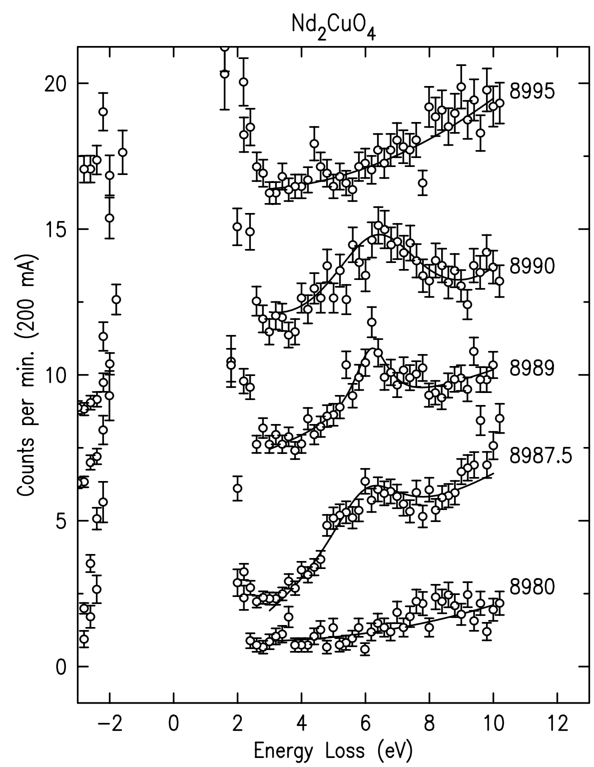

FIG. 2. Scattered intensity as a function of energy loss $(E_i - E_f)$ for a number of incident energies. Data are offset vertically for clarity and solid lines are guides to the eye.

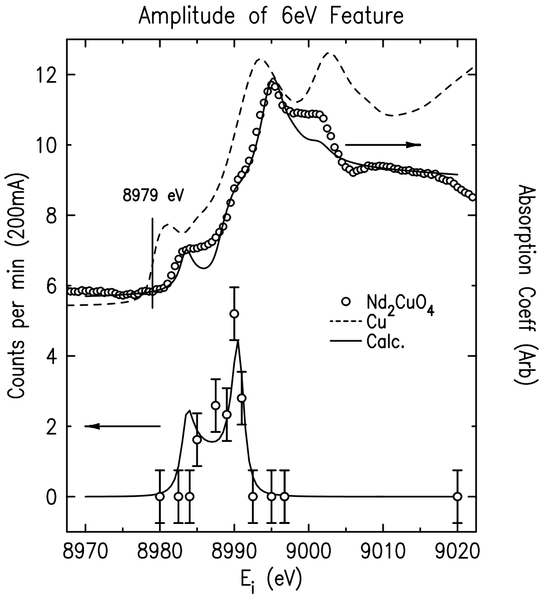

FIG. 3. The amplitude of the 6 eV excitation, as a function of incident energy, showing a resonance in the vicinity of 8990 eV (open circles). The solid line is the result of a numerical calculation described in the text. The top half of the figure displays the absorption measured for powdered Nd_2CuO_4 (open circles), together with a calculation using the same parameters as for the scattered intensity. The absorption from Cu foil (dashed line) is shown for reference.

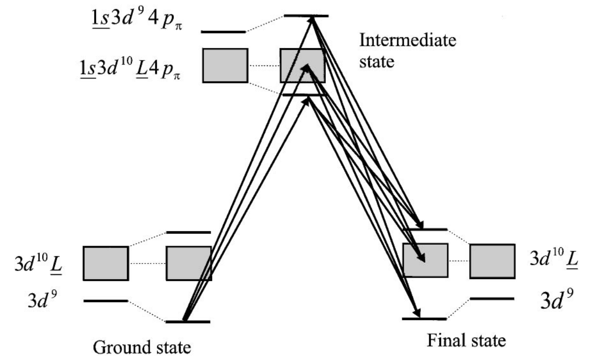

FIG. 4. Schematic energy level diagram for inelastic scattering from a copper site. Arrows indicate processes summed over in the calculation of the scattered intensity.

of others [9,10] and shows features at 8983, 8990, 8995, and 9002 eV. These have been interpreted as arising from two sets of dipole transitions [9–11]. The first two (lower energy pair) are the $1s \rightarrow 4p_\pi$ transition ($4p$ orbitals perpendicular to the CuO planes) and the second two are the $1s \rightarrow 4p_\sigma$ transition (in-plane $4p$ orbitals).

Figure 3 shows that the resonant enhancement is associated with the $1s \leftrightarrow 4p_\pi$ transition. There is no apparent enhancement at the $1s \leftrightarrow 4p_\sigma$ transition. This may in part be explained by the incident polarization, which ensures that this transition is not strongly excited, and the fact that the absorption is maximum here. In NiO, for which the count rates were significantly larger, resonances were observed at each feature in the absorption spectrum [8].

We now consider the scattering process and the electronic structure of the CuO planes in more detail, in order to elucidate the nature of the observed excitation.

At resonance, the scattering is a second order process, proceeding via a short-lived intermediate state involving a $\underline{1s}$ core hole. This state may decay radiatively, either to the ground state, (elastic scattering) or to an excited state for which a net energy loss is seen. (Note that in the final state there is no core hole present and thus there are no "final-state effects," in the sense referred to previously, to complicate the excited state spectrum.) A schematic energy level diagram of this process is shown in Fig. 4.

In the CuO planes, the Cu $3d^9$ configuration hybridizes with $3d^{10}\underline{L}$, where $\underline{L}$ represents a O $2p$ ligand hole and has a finite bandwidth. As described by the Anderson impurity model [12,13], this results in discrete bonding and antibonding states composed of a mixture of $3d^9$ and $3d^{10}\underline{L}$ configurations, with a continuous band between them (Fig. 4). The ground state is then the bonding state with about 60% of the $3d^9$ configuration. The lowest edge of the continuous band is about 2 eV above the ground state, and this is usually denoted as the charge-transfer gap [14]. The antibonding state is near the highest edge of the band. Our calculations (below) place this ~6 eV above the ground state.

Now, in the intermediate state a Cu $1s$ electron is excited to the Cu $4p_\pi$ conduction band, and the core hole potential reverses the balance between the $3d^9$ and $3d^{10}\underline{L}$ configurations. The bonding state, now of predominately $\underline{1s}3d^{10}\underline{L}4p_\pi$, is then about 7 eV lower than the antibonding state, $\underline{1s}3d^9 4p_\pi$, and they form the 8983 and 8990 eV features of the Cu K-edge XAS. (The $1s \rightarrow 4p_\sigma$ is similarly split.) Note, in Fig. 4, the Cu $4p_\pi$ bandwidth is taken to be zero for simplicity; in the calculations a value of 2.0 eV was used. If either of these intermediate states decays into the antibonding excited state, a 6 eV energy loss would result and we believe that this is the origin of the observed scattering.

To support this picture, we have carried out numerical calculations of the inelastic x-ray scattering, calculating the electronic structure within the Anderson impurity model and the scattering as a coherent second order dipole process [12]. The parameters used were essentially the same as in [12]. The calibration of the incident energy was obtained by simulating the powder XAS within the same model (solid line, Fig. 3, top). At 8990 eV, the calculated inelastic scattering indeed exhibits a feature at about 6 eV, reminiscent of the experimental data. (Transitions to the continuous band are suppressed because the band is largely $3d^{10}\underline{L}$ in character and thus has very little overlap with the intermediate state, when $E_i = 8990$ eV.) Further, the calculated incident energy intensity dependence of the 6 eV energy loss is in approximate agreement with the observed behavior (solid line, Fig. 3, bottom). Specifically, a resonance is observed at 8990 eV, and we conclude that the 6 eV feature is indeed the charge-transfer excitation to the antibonding state.

The theory also predicts a resonance at 8983 eV (i.e., an enhancement is expected for both the bonding and antibonding intermediate states), which is absent in the data. This discrepancy may arise from nonlocal screening in the intermediate state. As first pointed out by Veenendaal, Eskes, and Sawatzky [6], solid state effects play an important role in the final state of Cu $2p$ photoemission spectra of systems with a linear chain of CuO_4 plaquettes. They showed that while a $3d^{10}$ state is required to screen the $\underline{2p}$ core hole, the lowest energy state is one in which the $\underline{L}$ hole, repelled by the $\underline{2p}$, moves onto another CuO_4 plaquette, where it forms a Zhang-Rice (ZR) singlet [15]. Recent calculations have extended such conclusions to 2D clusters [7].

This photoemission final state is analogous to the intermediate state formed when $E_i = 8983$ eV in the present paper, and one might therefore expect a ZR singlet to be formed here also. In contrast, the 6 eV excitation has a *local* character with no ZR singlet (even in large cluster systems), and the 6 eV intensity would thus be suppressed at 8983 eV because of the small transition probability between states with and without a ZR singlet. Preliminary calculations on a system with three CuO_4 plaquettes support this idea, but more detailed work is required before any quantitative statements may be made.

The numerical work discussed above highlights an essential difference between the K-edge inelastic spectra presented here and those obtained in the soft x-ray regime, arising from the different core holes created. Previous calculations of scattering at the Cu $L_{\mathrm{II,III}}$ edge in La_2CuO_4 [13] showed that the main inelastic structure arose from crystal field excitations of the Cu $3d$, with little contribution from charge-transfer excitations. Recent experiments support this view [16]. In contrast, for the Cu K-edge resonance, both the $\underline{1s}$ hole and $4p_\pi$ electron have almost no interaction with the Cu $3d$ states, which therefore retain their ground state symmetry B_{1g} in both the intermediate and final states. There is then no $d - d$ excitation in the inelastic spectrum. Thus our hard x-ray results complement soft x-ray resonance techniques and preferentially probe the charge-transfer excitations.

Finally, we comment on the resonant inelastic cross section. For NiO, intensities of $\sim$50 times those reported here were observed [8]. Taking into account the differences in absorption, number density, and fraction of the total cross section contributed by the resonant ions, one would expect a factor of $\sim$30, broadly consistent with that observed. This suggests that the resonant cross section per ion is similar at the Ni and Cu K edges. Thus other highly correlated systems should be amenable to study with this technique. The quantum 1D magnet $CuGeO_3$, for example, should give relatively high count rates.

In summary, we have observed resonantly enhanced inelastic scattering from Nd_2CuO_4, with the incident photon energy tuned to the Cu K edge. The excitation observed was of a charge-transfer-type, involving the oxygen $2p$ and Cu $3d$ orbitals. The results broadly confirm recent cluster calculations for the CuO planes in high-T_C materials and suggest nonlocal effects play a role in controlling the resonance phenomena.

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