Observation of a 500 meV Collective Mode in $La_{2-x}Sr_xCuO_4$ and Nd_2CuO_4 Using Resonant Inelastic X-Ray Scattering

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Utilizing resonant inelastic x-ray scattering, we report a previously unobserved mode in the excitation spectrum of $La_{2-x}Sr_xCuO_4$ and Nd_2CuO_4 at 500 meV. The mode is peaked around the (π, 0) point in reciprocal space and is observed to soften, and broaden, away from this point. Samples with $x = 0$, 0.01, 0.05, and 0.17 were studied. The new mode is found to be rapidly suppressed with increasing Sr content and is absent at $x = 0.17$, where it is replaced by a continuum of excitations. This mode is only observed when the incident x-ray polarization is normal to the CuO planes.

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The high-frequency dynamics ($\hbar\omega \gtrsim J$) of the cuprate superconductors are presently attracting intense interest for a number of reasons. First, attempts to understand the dynamics within the context of effective, spin-only Hamiltonians have raised several outstanding questions, including understanding the importance of higher-order corrections to the nearest-neighbor Heisenberg Hamiltonian [1–4]. Further, interest in the optical community has been focused on the same mid-IR energy regime, following claims that the Ferrell-Glover-Tinkham sum rule is violated in several materials [5–8]. While it is not yet clear what the ultimate significance, if any, of these various results will be in understanding the mechanism of high-T_c superconductivity, it is clear that further experimental investigations of this energy regime are vital. Here it will be of particular value to investigate the momentum dependence of the high-energy excitations.

Motivated by this, we have carried out a resonant inelastic x-ray scattering (RIXS) study of the mid-IR region as a function of momentum transfer and doping in the $La_{2-x}Sr_xCuO_4$ system, and the related cuprate Nd_2CuO_4. This technique, which probes the electronic excitations associated with the copper site, provides momentum-resolved, bulk property information and is therefore an ideal probe for this endeavor. In the parent compound ($x = 0$), we find a previously unobserved excitation, peaked in **q** space around the (π, 0) point at 500 meV ($\sim$4000 cm^{-1}). On moving away from the zone boundary, the excitation is observed to soften and broaden. It is not observed at either the zone center (0, 0) or the antiferromagnetic point (π, π). As a function of Sr concentration, the excitation is rapidly suppressed, broadening and weakening successively for $x = 0.01$ and $x = 0.05$. For $x = 0.17$, only the particle-hole continuum is observed. Further, we find that the excitation has strong photon polarization dependence—it is only observable when the incident polarization is along the c axis and not when it is in the ab plane. Finally, investigations of the related cuprate, Nd_2CuO_4, show a similar feature at 500 meV. Possible origins for this excitation are discussed.

The experiments were performed at beam line 9IDB, at the Advanced Photon Source. A Si(111) monochromator and a Si(444) secondary monochromator provided an incident flux of 5×10^{11} ph s^{-1}, in a 0.1 mm $\times$ 0.8 mm (v $\times$ h) spot. The scattered radiation was analyzed by a Ge(733) crystal. The overall resolution was 120 meV (FWHM) [9]. The samples were cooled to 20 K to reduce the phonon contribution to the elastic scattering. Four samples of $La_{2-x}Sr_xCuO_4$ ($x = 0$, 0.01, 0.05, and 0.17) and Nd_2CuO_4 were studied. Except where noted, the incident (horizontal) polarization was along the c axis of the crystal.

Data were taken with the incident photon energy tuned to the peak of the fluorescence following $1s \rightarrow 4p_\pi$ transitions ($E_i = 8992.5$ eV), where the $4p_\pi$ orbitals are perpendicular to the CuO_2 plane [10]. Throughout this Letter, we use the tetragonal notation, that is $a = b \approx 3.79$ Å with **Q** = (100) parallel to the Cu-O-Cu bond direction. The $x = 0$ and 0.17 samples had surface normals along the (100) direction, and the $x = 0.01$ and 0.05 samples had (110) surface normals. In all cases, we report scattering in terms of the reduced wave vector **q**, where **Q** = **G** + **q**, with **Q** the total momentum, and **G** a reciprocal lattice vector [11]. Most of our measurements were carried out near **G** = (3, 0, 0).

In Fig. 1, we show the resonant inelastic scattering intensity in the range 0.2–0.8 eV (closed symbols) at (π, 0) in La_2CuO_4. A clear peak of $\sim$0.2 counts per second is

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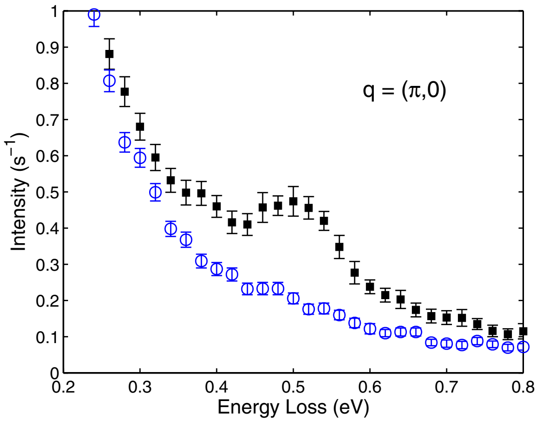

FIG. 1 (color online). (a) Inelastic x-ray scattering in La_2CuO_4 observed at the (π, 0) point, $\mathbf{Q} = (2.5, 0, 0)$, on and off resonance (closed and open symbols, respectively). A clear peak is observed at 500 meV on resonance.

observed at 500 meV, on a sloping background. The background arises from the tails of the elastic scattering, which is 110 counts/s at zero energy loss. In order to examine the peak in more detail, we subtract off this elastic scattering—which arises from static disorder and a small amount of thermal diffuse scattering. This is achieved by tuning the incident photon energy to 8980 eV, far from resonance. For all practical purposes, this "turns off" the inelastic scattering and provides a clean measure of the elastic scattering. We then subtract off this elastic scattering, appropriately scaled, to obtain the resonantly enhanced inelastic signal. This is shown in Fig. 2(c), which is described reasonably well by a Lorentzian-like peak at 500 meV, of width 200 meV (FWHM).

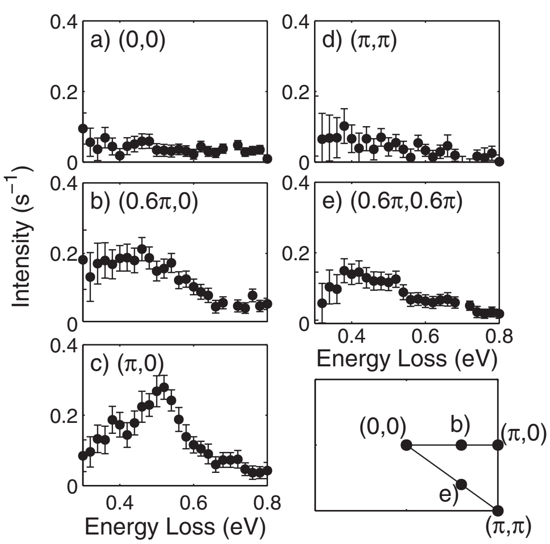

FIG. 2. Momentum dependence of the 500 meV feature in La_2CuO_4. The figure shows the inelastic data, with the elastic scattering subtracted off, for 5 different momenta in the 2D Brillouin zone.

In Fig. 2, we show the momentum dependence of this mode. Significantly, the mode is not observed at the zone center (0,0) or at the antiferromagnetic point (π, π). Either the peak is absent at these points, or it has dispersed to lower energies and is unobservable with the present resolution. On moving away from (π, 0), the peak is seen to soften slightly and broaden, with a peak position of 430 meV at (0.6π, 0) and (0.6π, 0.6π) and a full width at these points of 360 and 280 meV, respectively. Since these peaks are quite broad and weak, it is difficult to extract the dispersion relation of the excitation unambiguously at this point. Nevertheless, our momentum-dependence study clearly demonstrates the nonlocal nature of the observed excitation.

The doping dependence of the 500 meV feature is presented in Fig. 3, in which the scattering intensity at (π, 0) is shown for each of the four samples. The peak rapidly broadens and weakens with increasing Sr content, while its position does not change. There is no measurable peak in the $x = 0.17$ compound, where the particle-hole continuum due to metallic electronic structure is observed. We note that for $x = 0.01$ and $x = 0.05$, the same systematics in the momentum dependence of the peak were observed as in the undoped compound, and preliminary data at $x = 0.07$ show similar behavior to $x = 0.05$. The polarization dependence of the scattering was also investigated. In Fig. 4, data are shown for La_2CuO_4 with the incident photon polarization parallel to c ($\epsilon \parallel \hat{c}$) and for $\epsilon \perp \hat{c}$. The mode at 500 meV is only observed when the incident polarization is along the c axis, that is when the photoelectron is excited to the Cu $4p_z$ orbital in the intermediate state.

We now discuss possible origins for this new feature. First, this mode is not directly related to the mid-IR peaks seen in the optical conductivity [12], because the strength of this feature increases as the Mott-Hubbard insulator state is approached, in contrast to the doping dependence

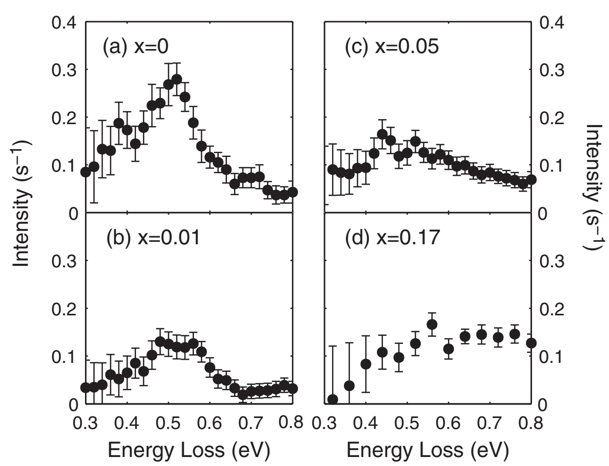

FIG. 3. Doping dependence of the 500 meV feature. Data are taken at (π, 0) and have the elastic scattering subtracted off.

of the optical measurements [13]. These same systematics also rule out the possibility that the peak arises from charge excitations associated with any electronic inhomogeneity of the doped carriers [14]. Finally, one could postulate that the peak results from transitions to impurity-derived, midgap states. However, such states would be expected to be highly localized and it is difficult to explain the momentum dependence, or the observed doping dependence. We conclude that this scattering is unlikely to arise from such states. This leaves two plausible origins for this new mode: (i) a $d-d$ excitation, and (ii) a multimagnon excitation.

(1) *d-d excitation.*—While most calculations put all *d-d* excitations at significantly higher energies than discussed here (e.g., 1 eV [15]), it has been suggested that at least one transition is at much lower energy. Perkins *et al.* explained a broadband mid-IR absorption peak in terms of a low energy (0.4 eV) *d-d* excitation together with phonon and magnon sidebands [16] and Ghiringhelli *et al.* recently calculated the $d_{x^2-y^2} \rightarrow d_{3z^2-r^2}$ excitation to be 0.4 eV in La_2CuO_4 [17]. Such a low energy is controversial, however, and most have argued that this *d-d* excitation is at much higher energy, although there has been no direct observation [18]. If the 500 meV peak is indeed due to this *d-d* excitation, the observed doping dependence might be explained as the result of an increased hybridization of the *d* states as the metallic state is approached [19]. The observed q dependence is more problematic for this picture, since one would expect such a local excitation to show no dispersion, though it could arise from anisotropic hopping.

To further explore this explanation for the 500 meV mode, we carried out a study of Nd_2CuO_4, which lacks the apical oxygens of La_2CuO_4 and has a 4% larger in-plane CuO distance. One might expect that this would shift the $d_{3z^2-r^2}$ orbitals to much higher energies. In Fig. 4, we show the results for Nd_2CuO_4. Just as in La_2CuO_4, a weak peak is observed at 500 meV. In view of this observation, the *d-d* excitation interpretation is unlikely, though it cannot be ruled out completely.

(2) *Multimagnon excitation.*—In-plane two-magnon spin exchange have been studied by optical resonant Raman scattering. In these experiments, a peak is observed at 375 meV and is associated with the creation of two zone-boundary magnons with an energy reduced to ~2.7 J by magnon-magnon interactions [20–25]. Raman experiments probe the $\mathbf{q} = 0$ response (i.e., the total momentum of the magnon pair is zero) and should not be directly compared to the present peak at $(\pi, 0)$. One can calculate the momentum dependence of the noninteracting two-magnon density of states (DOS) from the single magnon dispersion [2]. This does show a peak at 500 meV at $(\pi, 0)$ [26] and it is tempting to associate the present x-ray peak with this process. The two-magnon DOS also has strong peaks at 600 meV at (0, 0) and (π, π) [26], which are not

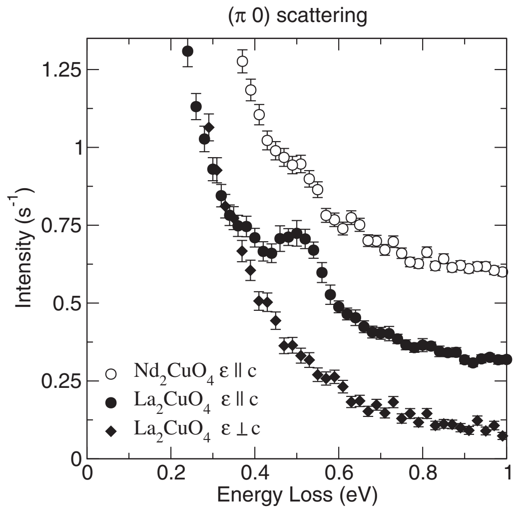

FIG. 4. Polarization dependence of the 500 meV peak in La_2CuO_4 (closed symbols). The peak is only observed with the incident polarization parallel to the c axis. Data taken for Nd_2CuO_4 (open circles) show a weak peak at the same energy. Scans are shifted vertically for clarity.

seen in our data, possibly due to the effect of RIXS matrix element. In fact, recent calculations suggest that the two-magnon RIXS cross section is zero or greatly reduced for these points [27–30].

If this mode is indeed magnetic in origin, then it is natural to ask how does RIXS couple to magnetic excitations. Figure 5 shows one possible scattering mechanism. The system begins in the ground state, with nearest-neighbor $3d^9$ spins at sites 1 and 2 antiferromagnetically coupled: $|\downarrow_1;\uparrow_2\rangle$. In the intermediate state, a $1s$ core hole is created at site 1, repelling the Cu spin to the neighboring site, site 2. When the $4p$ decays, instead of the original "down" spin, the "up" spin on site 2 hops back, and the net effect is to flip two spins, leaving the system in a final state $|\uparrow_1;\downarrow_2\rangle$. Other two-magnon processes are also possible [31], though since these involve quadrupole transitions, we deem them less likely.

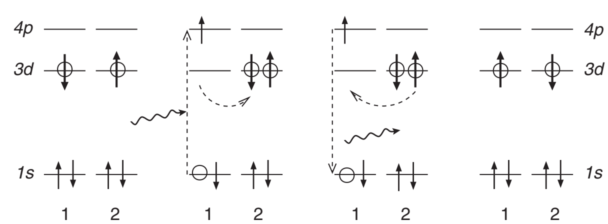

FIG. 5. Possible resonant scattering process resulting in the creation of two magnons. The Cu (hole) spin on site 1 is repelled onto a neighboring site, site 2, by the 1s core hole in the intermediate state. Following the decay of the core hole, the "other" spin hops back resulting in spin flips on both sites. Note the two sites could, in principle, be in neighboring layers.

The doping dependence of the excitation at (π, 0) supports a multimagnon identification. In particular, the Raman data of Sugai [32] show a similar doping dependence for the two-magnon scattering in $La_{2-x}Sr_xCuO_4$ as observed here for the x-ray data, suggesting that both x-ray and Raman modes may arise from related processes [33]. We note that in their oxygen K-edge RIXS study of $Sr_2CuO_2Cl_2$, Harada *et al.* observed a feature around 0.5 eV excitation energy, which was also interpreted as the two-magnon excitation [34].

One problem with assignment of the 500 meV mode to in-plane spin exchange process is that the peak occurs at the energy expected for noninteracting magnons. Lorenzana and Sawatzky have shown that a finite momentum magnon-magnon interaction can result in a bound two-magnon resonance [24]. This gives a sharp quasi-particle-like peak at (π, 0). However, the proposed resonance does not appear to explain the present **q**-resolved data, since the "bimagnon" resonance at (π, 0) occurs at 2.7 J ~ 375 meV. On the other hand, an interlayer spin exchange process resulting from two spin flips occurring in adjacent CuO_2 layers is consistent with the incident polarization of experiment. Because of small interlayer coupling the resulting interlayer two-magnon mode is expected to occur almost at the noninteracting value, which is in agreement with experimental observations.

Finally, we note that, motivated by the present experimental work, a number of authors have investigated the magnetic inelastic x-ray scattering cross section [27–30]. All find qualitative similarities with the symmetries of the present data.

In summary, we have observed a new collective excitation at about 500 meV in $La_{2-x}Sr_xCuO_4$ and Nd_2CuO_4 using resonant inelastic x-ray scattering. We show that the mode is peaked at the (π, 0) point, and it is broadening and softening away from the zone boundary. The mode is rapidly suppressed on doping with Sr. It is only present with the incident polarization along the c axis. We suggest that this mode is either $d_{x^2-y^2} \rightarrow d_{3z^2-r^2}$ orbital excitation or a two-magnon excitation, with perhaps the preponderance of evidence in favor of an (interlayer) x-ray induced spin exchange process. While definitive identification of this mode will have to wait further experimental and theoretical investigations, the significance of this result lies in the observation of this new mode in this important energy regime and the potential for new insights on the high-energy Hamiltonaian that understanding such a mode will provide.

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