

Localized and Delocalized Excitons: Resonant Inelastic X-Ray Scattering in $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

E. Collart,¹ Abhay Shukla,^{1,*} J.-P. Rueff,² P. Leininger,² H. Ishii,³ I. Jarrige,³ Y. Q. Cai,³ S.-W. Cheong,⁴ and G. Dhalenne⁵

¹*Institut de Minéralogie et de Physique des Milieux Condensés, Université Pierre et Marie Curie, case 115, 4 place Jussieu 75252 Paris cedex 05, France*

²*Laboratoire de Chimie Physique, 11 rue Pierre et Marie Curie, 75231 Paris cedex 05, France*

³*National Synchrotron Radiation Research Center, Hsinchu Science Park, Hsinchu 30076, Taiwan*

⁴*Rutgers Center for Emergent Materials and Department of Physics & Astronomy, Rutgers, Piscataway, New Jersey 08854, USA*

⁵*Laboratoire de Physico-Chimie de l'Etat Solide, B.410, Université Paris XI, 91405 Orsay Cedex, France*

(Received 15 November 2005; published 20 April 2006)

The dynamics of doped charge in an antiferromagnetic lattice is central to the description of the insulator-metal transition that occurs on doping the parent high T_c compounds. In this work we use high resolution resonant inelastic x-ray scattering to investigate the dynamics of the charge-transfer exciton by measuring its energy dispersion in two prototype compounds, La_2CuO_4 and La_2NiO_4 . We show that this behavior is radically different in the cuprate with respect to a system known to exhibit strong polaronic behavior, namely, the nickelate: the exciton is mobile in the cuprate while it is well localized in the nickelate. Using a simple Wannier-Mott model we can estimate the total hole plus electron effective mass in the cuprate to be $3.5 \pm 0.3m_e$ which would exclude strong localization in the undoped cuprate.

DOI: 10.1103/PhysRevLett.96.157004

PACS numbers: 74.25.Jb, 71.20.Be, 74.72.Dn, 78.70.Ck

The nature of the insulator-metal transition in cuprates is closely linked to the nature of the Zhang-Rice (Z-R) band at the top of the valence band and the upper Hubbard band which are, respectively, occupied and unoccupied in the undoped insulating state. In hole doped compounds, the Z-R band is progressively emptied of electrons on doping. An open question remains about the nature of these two bands in the insulator. Are they localized with a corresponding elevated effective mass for the carriers or are they dispersive with a correspondingly small effective mass? Recent work [1] using angle-resolved photoemission spectroscopy in cuprates has raised the possibility that the Z-R band is nearly invisible and nondispersive due to polaronic localization resulting from electron-phonon coupling. High energy core level photoemission experiments [2] show that the Z-R band is visible in the bulk but that the signal disappears when surface sensitive soft x rays are used. More generally, the dynamics of a charge-transfer generated bound state in an undoped cuprate lattice has been discussed by Zhang and Ng [3]. They predicted that such an exciton formed from a hole in the Z-R band and an electron in the UHB would be dispersive because of coupling with an adjacent Z-R singlet to form twin spin zero Cu sites. This spin zero pair could move through the lattice without disturbing the antiferromagnetic motif. In this work we use resonant inelastic x-ray scattering (RIXS) to measure the dispersion of the exciton through the Brillouin zone at the Cu-K absorption edge in La_2CuO_4 and at the Ni-K absorption edge in La_2NiO_4 . The cuprate and the nickelate are almost completely isostructural but with remarkably different physical properties. No superconductivity has been reported in the nickelate and metallic behavior arises at very high doping, $x = 0.8$ [4] as opposed

to $x = 0.05$ in cuprates. We find dispersive behavior for the exciton in the cuprate in very good agreement with the prediction of Zhang and Ng [3]. The dispersion differs markedly from that given in earlier measurements [5]. In the nickelate we show for the first time that the exciton is nondispersive and localized. Here, the antiferromagnetic correlations are stronger and doped charge is known to exhibit polaronic localization. These results imply that the Z-R and upper Hubbard bands in the cuprate cannot be strongly localized.

In our experiment the incident photon energy is chosen in the region of an absorption edge. This choice also determines the intermediate state of the scattering process which involves a core hole generated by the incident photon. Electronic decay follows which fills the core hole but may leave the system in an excited final state, resulting in inelastic features. Since the photon can exchange sizeable momentum with excitations in the system, their dispersion can be measured. The method is bulk sensitive, with an enhanced cross section due to the intermediate-state core-hole. Excitations in the eV range have been measured in several cuprates and different interpretations have been put forward as to their origin [5,6]. The Cu-K (Ni-K) edge of La_2CuO_4 (La_2NiO_4) shows features [7] which are related to $1s - np$ dipolar transitions with, preponderantly, $n = 4$ [Figs. 1(a) and 1(b)]. When the photon polarization is parallel to the c axis only Cu(Ni) $1s - np_\pi$ transitions are observed. Two peaks are seen related to the presence of a charge-transfer process [8]. In the cuprate (nickelate) the Cu (Ni) $3d$ filling is nominally 9 (8) but when one considers the charge-transfer process in the Cu-O (Ni-O) plane one obtains, in addition to the expected $1s - np3d^9(1s - np3d^8)$ transition

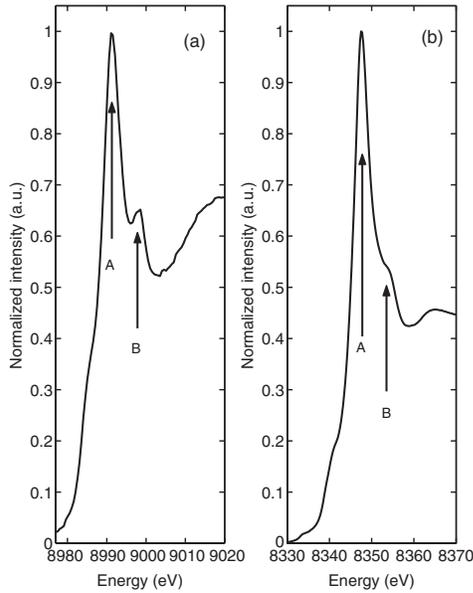


FIG. 1. Total fluorescence yield Cu-K edge absorption in (a) La_2CuO_4 (photon polarization at 15° from c axis and (b) La_2NiO_4 (polarization parallel to c axis).

(peak B), a contribution from the $1s - np3d^{10}\underline{L}(1s - np3d^9\underline{L})$ transition (peak A) where \underline{L} is a hole in an O $2p$ orbital. The resonance chosen for both materials is peak A, generated by an incident photon of energy 8992 keV (8348 eV for the nickelate) and chosen so as to amplify transitions related to the charge-transfer process. The measurements were carried out at Spring-8 on the undulator beam line BL12XU (NSRRC ID) [9]. Spherically bent 2 m radius Si analyzers (Si 553 for the Cu-K edge and Si 551 for the Ni-K edge) were used to reach a total resolution of 300 meV for the experiments [10]. Because of the horizontal scattering geometry we cannot access dispersion in the a/b plane while keeping the polarization strictly parallel to the c axis [5] but we can ensure, by using a large scattering angle, that the polarization always has a dominant component parallel to the c axis. The angle between the polarization and the c axis for all following measurements varies approximately from 25° for measurements at the Brillouin zone (BZ) center to 35° at the BZ edge.

Figure 2(a) shows the measured RIXS parallel to the $[100/010]$ axis in a twinned sample of undoped La_2CuO_4 . The scans are taken at various points in the BZ, between $[4.5\ 0\ 0]$ and $[5\ 0\ 0]$ and have been displaced vertically for clarity. From top to bottom, the momentum transfer varies from the center of the zone to the edge. The zone edge smoothed spectrum is used as a background for highlighting the behavior of the lowest energy inelastic feature as explained below. Between the elastic line (zero energy transfer) and about 2 eV no inelastic features are present and this situation corresponds to the measured optical gap in La_2CuO_4 [11] which is of the charge-transfer type. This charge transfer and other processes across the charge-transfer gap result in the hump constituting the inelastic

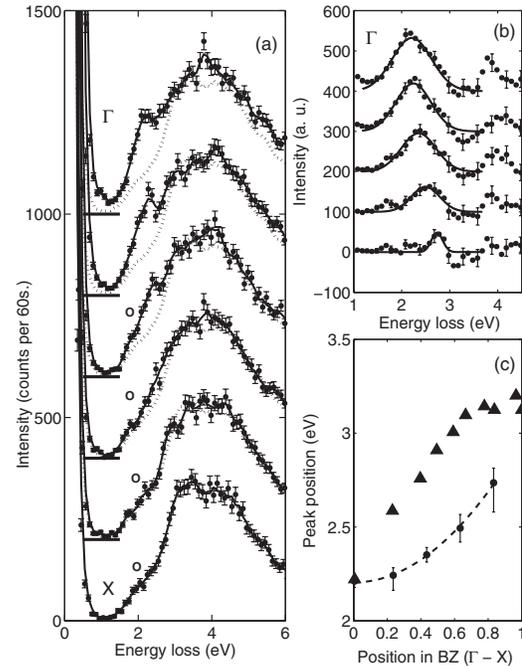


FIG. 2. (a) RIXS dispersion in La_2CuO_4 along the $[100/010]$ direction. The spectra have been shifted vertically, the baseline is indicated for each spectrum. Solid line: 3 point smoothed guide for the eye; dotted line: BZ edge spectrum; open circles label crystal field excitations. (b) Differences between smoothed spectra at various points in the BZ and the BZ edge spectrum from (a). (c) Dispersion of the exciton as determined from our data (solid circles) and as determined by Kim *et al.* [5] (triangles).

signal which probably has several resolution limited peaks superimposed on it.

At an energy loss of 2.2 eV a peak is seen in the scans near the center of the BZ. As the momentum transfer decreases from the zone center to the zone edge, the peak at 2.2 eV disperses to higher energy loss. However, the intensity of this peak also decreases at the same time and at the zone edge it is invisible. In Fig. 2(b), we subtract the 3 point smoothed spectrum taken at the BZ edge [dotted line in Fig. 2(a)] from spectra taken at various other points in the BZ. These differences clearly show both the dispersion as well as the variation in intensity of the peak which we assign to the fundamental charge-transfer exciton. Another peak is seen at 4 eV energy loss, does not disperse but also loses intensity from zone center to zone edge. The dispersion of the low energy peak is estimated from Fig. 2(b) by fitting a Gaussian line shape and shown in Fig. 2(c). The gain in resolution with respect to the earlier experiment by Kim *et al.* [5] clearly shows that the dispersion is markedly different from their measurement [triangles in Fig. 2(c)]. Over the observed range the exciton disperses quadratically by about 0.5 eV implying free-particle-like behavior. For the scans near the zone edge where the 2.2 eV peak is weak or absent, a shoulder shown by open circles [Fig. 2(a)] is seen just below 2 eV.

We interpret this as a localized excitation of the crystal field [12].

A possible interpretation of the dispersive feature seen in the in-plane dispersion is given by Zhang and Ng [3] who use a local model and find bound electron-hole states in the Cu-O plane. Zhang and Ng find four propagational modes of which only two should be visible in an electron-energy-loss spectroscopy experiment. The first one, with p symmetry, has an energy of about 2 eV at the zone center and disperses by about 0.5 eV to higher energy, while its intensity decreases to zero in going to the zone edge in the [100] direction. This behavior matches the excitation that we see at 2.2 eV at the BZ center in La_2CuO_4 . The second one with s symmetry is placed at 4 eV, does not disperse, but increases in intensity, from zone center (zero intensity) to zone edge. Though in Fig. 2(b) we detect an excitation at an energy loss of about 4 eV, its behavior needs to be characterized with measurements with higher statistics. Existing theoretical works use among other approaches, multisite cluster models ([13], in the case of one dimensional compounds) or next nearest neighbor Hubbard models [14] for theoretical interpretation of RIXS spectra. Both present difficulties for applications such as our experiment. For a square two dimensional lattice, a multisite model is limited to only four sites given current computational possibilities. This rules out the calculation of reliable theoretical spectra because only the behavior at the two extremities of the BZ can be evaluated. A Hubbard model approach on the other hand is valid for predicting dynamics on an energy scale which is lower than the one of our experiment [15].

Figure 3(a) shows the measured RIXS parallel to the a/b axis in a twinned sample of undoped La_2NiO_4 . The scans are taken at similar points in the BZ as for La_2CuO_4 (between [4.5 0 0] and [5 0 0]) and have been displaced vertically for clarity. From top to bottom, the momentum transfer varies from the center of the zone to the edge. The charge-transfer excitation gap measured by RIXS is about 4 eV, and compares well with the measured optical gap in La_2NiO_4 [16]. Though no clearly resolved peak emerges, closer inspection of Fig. 3(a) reveals that the scans nearer the zone center show a low energy shoulder which vanishes near the zone edge. Following the analysis for La_2CuO_4 , three point smoothed differences of the RIXS scans at different points of the BZ with respect to the zone edge scan [dotted line in Fig. 3(a)] are shown in Fig. 3(b). A peak exists at about 3.6 eV, and loses intensity in going from zone center to edge. This behavior mirrors to a certain extent that seen in La_2CuO_4 , except for the notable fact that no dispersion is seen. This is direct evidence for the complete localization of the charge-transfer exciton in La_2NiO_4 . In Fig. 2(c) the excitonic peak positions are plotted and the lack of dispersion is evident. Weak non-dispersive features in the charge-transfer gap shown by open circles [Fig. 3(a)] are localized excitations of the crystal field (similar structure is observed in measurements in NiO) and will be discussed elsewhere. Figure 4(a) shows

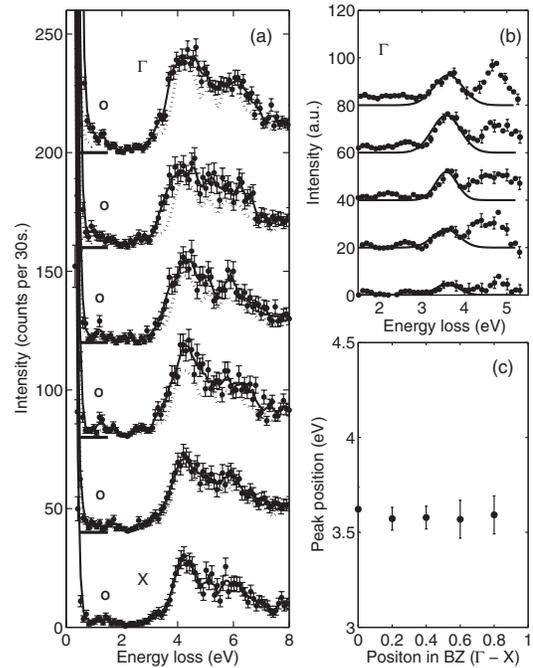


FIG. 3. (a) RIXS dispersion in La_2NiO_4 along the [100/010] direction. The spectra have been shifted vertically, the baseline is indicated for each spectrum. Solid line: three-point smoothed guide for the eye; dotted line: BZ edge spectrum; open circles label crystal field excitations. (b) Differences between smoothed spectra at various points in the BZ and the BZ edge spectrum from (a). (c) Dispersion of the exciton as determined from our data.

energy loss scans at the same point near the BZ center (Γ), for La_2CuO_4 and $\text{La}_{1.93}\text{Sr}_{0.07}\text{CuO}_4$. Figure 4(b) shows a similar comparison at the BZ center between La_2NiO_4 and $\text{La}_{1.9}\text{Sr}_{0.1}\text{NiO}_4$, where the spectrum of the underdoped sample has been multiplied by a factor of 2 to ease comparison. In both underdoped samples features that were identified with excitonic peaks have disappeared. $\text{La}_{1.93}\text{Sr}_{0.07}\text{CuO}_4$ is weakly metallic and the interpretation of damped excitations due to screening from the doped charge is reasonable. However, $\text{La}_{1.9}\text{Sr}_{0.1}\text{NiO}_4$ is still strongly insulating and the reason for the suppression of the excitonlike features is probably due to the fact that hole doping suppresses the charge-transfer channel because it provides an alternative mechanism for hole creation in the ligand orbitals.

We thus observe well-defined excitations at the charge-transfer gap both in La_2CuO_4 and in La_2NiO_4 . These are identified as charge-transfer excitons and their dispersion provides, for the first time, a direct and simple justification of proposed exciton hopping mechanisms in the antiferromagnetic Cu-O plane [Fig. 4(c) as discussed below]. In La_2CuO_4 , the CuO_2 unit cell in the plane contains one hole on the Cu site. If we consider a plaquette consisting of a central Cu atom and four surrounding O atoms in the CuO_2 planes, charge transfer is invoked by the transfer of one electron from the O $2p$ orbitals on the plaquette to a

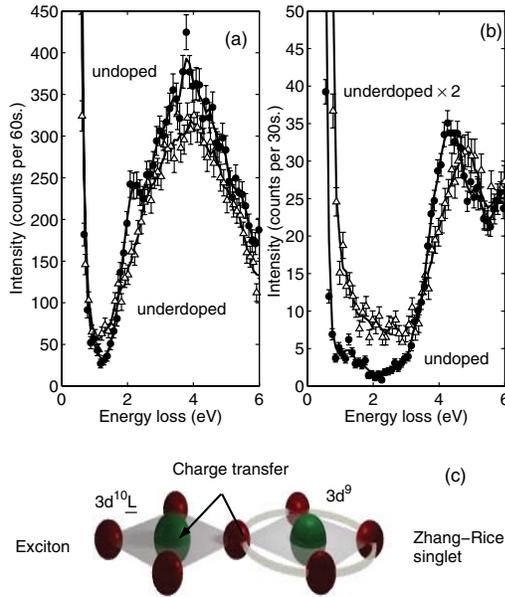


FIG. 4 (color online). (a) RIXS spectra of $\text{La}_{1.93}\text{Sr}_{0.07}\text{CuO}_4$ (open triangles) and La_2CuO_4 (solid circles) at the BZ center. (b) RIXS spectra of $\text{La}_{1.9}\text{Sr}_{0.1}\text{NiO}_4 \times 2$ (open triangles) and La_2NiO_4 (solid circles). Here, spectra have been summed over the BZ to increase statistics. Solid lines: three-point smoothed guides for the eye. (c) Schematics of formation of twin spin zero Cu sites in the CuO_2 planes. The bigger central sphere represents Cu while the surrounding smaller spheres represent O atoms on a CuO_2 plaquette. Charge transfer results in an exciton and a Cu $3d^{10}$ spin zero configuration on the left while the hole spins form a spin zero Z-R singlet on the right.

neighboring Cu site which then assumes the Cu $3d^{10}$ configuration. The O $2p$ hole on the plaquette and the electron on the neighboring Cu site can then form a bound exciton. The binding energy of this exciton and its dynamics in the CuO_2 plane depend also on the interaction of the O $2p$ hole and the Cu $3d^9$ hole on the plaquette. These two can, in principle, interact to form a singlet state or a triplet state. An important consequence of singlet formation on the plaquette is that the exciton which consists of two spinless Cu sites (Cu $3d^{10}$ and the Cu-O hole singlet) moves through the CuO_2 plane without upsetting the antiferromagnetic (AF) $S = 1/2$ background [3]. We measure a quadratic dispersion corresponding to this real-space mobility. In a simple Wannier-Mott excitonic model for a cubic crystal with spherical band edges, $E(q) = E(q = 0) + \hbar^2/2(m_e^* + m_h^*)q^2$. Notwithstanding the fact that this expression is not completely adequate, we find, using the measured coefficient of q^2 ($1.1 \pm 0.1 \text{ eV \AA}^2$), that $m_e^* + m_h^* = (3.5 \pm 0.3)m_e$. This value excludes strong localization of the concerned Z-R and upper Hubbard bands.

In the nickelate the situation undergoes a radical change. Charge transfer can potentially result in the formation of a

bound exciton as in the case of the cuprate and a spin zero Ni site for a singlet coupling between the spins of the Ni $3d^9$ ($S = 1/2$) hole and the ($S = 1/2$) O $2p$ hole. But, in contrast to the cuprate where the central Cu site is spin zero due to the formation of a spin singlet with the O $2p$ hole, the central Ni site with a $3d^8$ configuration is high spin ($S = 1$) [17]. The direct consequence of this difference should be an observable change in exciton dynamics: the single spin zero site in the $S = 1$ NiO_2 AF lattice can only hop by disrupting the AF order [18] and thus should have reduced mobility with respect to the twin spin zero Cu sites in the $S = 1/2$ CuO_2 AF lattice. This nondispersive behavior is akin to that of the crystal field excitations mentioned earlier, which are, in fact, very localized excitons on a given Ni site. It is also worth remarking that in the nickelate doped charge is known to localize.

In conclusion, our measurements of a dispersive exciton in the undoped cuprate and the estimation of the combined hole-electron effective mass is not indicative of strong localization. In the undoped nickelate, on the other hand, no dispersion is measured indicating localization of the excitation.

We acknowledge discussions with M. Calandra, A. Kotani, and K. Okada. This work benefited from CNRS/JSPS Grant No. 16030 and was partly supported by NSRRC and NSC of Taiwan and by NSF-DMR-0405682 at Rutgers.

*Corresponding author.

Electronic address: Abhay.Shukla@impmc.jussieu.fr

- [1] K. M. Shen *et al.*, Phys. Rev. Lett. **93**, 267002 (2004); O. Rosch *et al.*, Phys. Rev. Lett. **95**, 227002 (2005).
- [2] M. Taguchi *et al.*, Phys. Rev. Lett. **95**, 177002 (2005).
- [3] F. C. Zhang and K. K. Ng, Phys. Rev. B **58**, 13 520 (1998).
- [4] H. Eisaki *et al.*, Phys. Rev. B **45**, 12 513 (1992).
- [5] Y. J. Kim *et al.*, Phys. Rev. Lett. **89**, 177003 (2002).
- [6] M. Z. Hasan *et al.*, Science **288**, 1811 (2000).
- [7] Abhay Shukla *et al.*, Phys. Rev. Lett. **96**, 077006 (2006).
- [8] H. Tolentino *et al.*, Phys. Rev. B **45**, 8091 (1992).
- [9] Y. Q. Cai *et al.*, in *Optical Design and Performance of the Taiwan Inelastic X-Ray Scattering Beamline*, edited by T. Warwick, J. Arthur, H. A. Padmore, and J. Stöhr, AIP Conf. Proc. No. 705 (AIP, New York, 2004), p. 340.
- [10] E. Collart *et al.*, J. Synchrotron Radiat. **12**, 473 (2005).
- [11] S. Uchida *et al.*, Phys. Rev. B **43**, 7942 (1991).
- [12] G. Ghiringhelli *et al.*, Phys. Rev. Lett. **92**, 117406 (2004).
- [13] Kozo Okada *et al.*, J. Phys. Soc. Jpn. **74**, 653 (2005).
- [14] Kenji Tsutsui *et al.*, Phys. Rev. Lett. **91**, 117001 (2003).
- [15] A. Macridin *et al.*, Phys. Rev. B **71**, 134527 (2005).
- [16] T. Ido *et al.*, Phys. Rev. B **44**, R12094 (1991).
- [17] V. I. Anisimov *et al.*, Phys. Rev. B **59**, 7901 (1999).
- [18] J. Zaanen and P. B. Littlewood, Phys. Rev. B **50**, 7222 (1994).