Charge and Orbital Excitations in Li_2CuO_2

Y.J. Kim,[1] J.P. Hill,[1] F.C. Chou,[2] D.M. Casa,[3] T. Gog,[3] C.T. Venkataraman[3]
[1]Brookhaven National Laboratory, Upton, NY, U.S.A.
[2]Massachusetts Institute of Technology, Cambridge, MA, U.S.A.
[3]Argonne National Laboratory, Argonne, IL, U.S.A.

Introduction

Spectroscopic studies of electronic structure and excitations can provide important information for an improved microscopic understanding of magnetism in insulating copper oxides. Li_2CuO_2 has been frequently modeled as an edge-sharing chain compound; that is, the copper-oxygen plaquettes in this material are connected by their edges with the Cu-O-Cu bond angle close to 90° [1]. Electronic properties of Li_2CuO_2 have been studied by various experimental methods [2-4]. The consensus from these experiments as well as from spin-polarized local density approximation (LDA) calculations [5] is that Li_2CuO_2 is a charge-transfer (CT) insulator, with a CT gap of 2.2 to about 2.7 eV. Another important observation from these studies is that several exchange paths exist between the copper spins and that none of these exchange interactions dominate; as a result, Li_2CuO_2 cannot be described as a simple Heisenberg spin chain [3, 4].

In the present work, we have carried out resonant inelastic x-ray scattering (RIXS) experiments to study the electronic excitations of Li_2CuO_2. We have observed two types of excitations, one type at 2.1 eV that we attribute to a localized d-d type orbital excitation, and excitations at 5.4 eV and 7.6 eV that we believe arise from CT-type processes in the Cu-O plaquettes. A small, but finite, dispersion of the latter along the direction perpendicular to the chain direction suggests that the interchain coupling is nonzero, supporting the conclusions from previous studies of magnetic interactions.

Methods and Materials

The RIXS technique provides a bulk-sensitive, element-specific, and momentum-resolving spectroscopic tool for measuring particle-hole pair excitations [6-8]. The experiment was carried out at CMC-CAT beamline 9-ID at the APS with a double-bounce Si(333) monochromator. A spherical, diced, Ge(733) analyzer was used to obtain an overall energy resolution of ~0.4 eV (full width at half-maximum [FWHM]). The polarization of the incident x-ray was kept close to the crystallographic c-direction. A single crystal sample of Li_2CuO_2, grown with the floating-zone method, was used in our experiments. In our measurements, the incident photon energy E_i was fixed at either 8997 or 8987 eV, while the final photon energy was varied to produce spectra as a function of energy transferred to the electron system.

Results

We measured the energy spectra at two different incident energies, as shown in Fig. 1. We attribute the strong peak around 5.4 eV to a charge-transfer-type excitation on a single copper-oxygen plaquette; specifically, we believe that it represents the energy difference between a bonding state and an antibonding state. The smaller peak at 7.6 eV could arise from excitation of electrons from different bands than those for the 5.4 eV feature. Alternatively, in the localized excitation picture described above and in Ref. 4, there can be different excitation modes depending on the symmetry of the four oxygen orbitals in the plaquette. Further studies of polarization dependencies might be able to distinguish between these two possibilities.

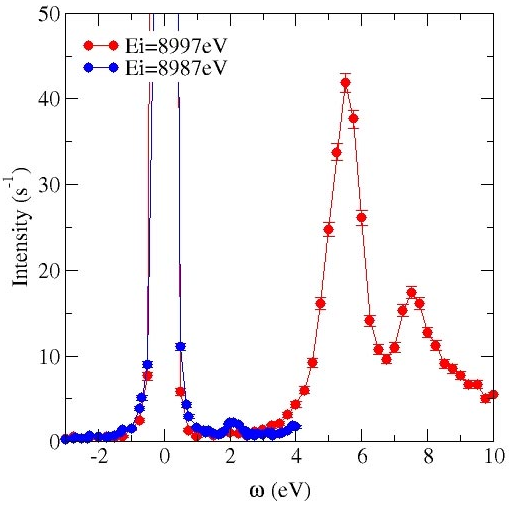

FIG. 1. Resonant inelastic scattering spectra obtained for Li_2CuO_2 with fixed incident energies as noted.

The weak peak at 2.1 eV exhibits resonant behavior when the incident photon energy is at 8987 eV. In contrast to the higher-energy features, the

2.1-eV feature is found to be resolution limited and clearly dispersionless, which implies that this excitation is localized and has a long lifetime. On the basis of these observations, we associate the 2.1-eV feature with a dd type orbital excitation; that is, an excitation corresponding to exciting holes from the d_{yz} orbital to higher-energy d-orbitals. According to the calculation of Tanaka et al. [9], the energy splitting between the ground state d_{yz} and the excited levels of d_{xy}, d_{zx}, $d_{3x^2-r^2}$ in Li_2CuO_2 is ~2 eV, which is consistent with our value of 2.1 eV.

Discussion

We also observe apparent dispersion of the 5.4-eV feature along the a-direction. One needs to go beyond the simple picture of a localized excitation to understand this observation. This observation suggests that the interchain coupling along the a-direction is not negligible. However, according to the calculation by de Graaf et al. [10], the superexchange interaction via Li and O orbitals is too small to account for the nonzero dispersion behavior along this direction. A different exchange mechanism, such as direct exchange between Cu orbitals, may need to be considered to understand this.

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References

[1] F. Sapina et al., Solid State Commun. **74**, 779 (1990).
[2] Y. Mizuno et al., Phys. Rev. B **57**, 5326 (1998).
[3] R. Neudert et al., Phys. Rev. B **60**, 13413 (1999).
[4] S. Atzkern et al., Phys. Rev. B **62**, 7845 (2000).
[5] R. Weht and W.E. Pickett, Phys. Rev. Lett. **81**, 2502 (1998).
[6] C.-C. Kao et al., Phys. Rev. B **54**, 16361 (1996).
[7] J. P. Hill et al., Phys. Rev. Lett. **80**, 4967 (1998).
[8] Y. J. Kim et al., Phys. Rev. Lett. **89**, 177003 (2002).
[9] N. Tanaka et al., J. Phys. Soc. Japan **68**, 1684 (1999).
[10] C. de Graaf et al., Phys. Rev. B **66**, 014448 (2002).