Pressure dependence of the superexchange interaction in antiferromagnetic La_2CuO_4

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Using high-pressure Raman scattering, we have directly measured the pressure dependence of the in-plane superexchange interaction J in antiferromagnetic La_2CuO_4 between 1 bar and 100 kbar. We find that J has a substantially weaker pressure dependence than in conventional magnets. We also show that the Hubbard-model parameters describing the low-energy electronic structure are significantly influenced by out-of-plane compositional and structural variations. Finally, we show that the relationship between J and the Neél temperature T_N is poorly described by current theory.

One of the current challenges of condensed-matter physics is developing a better understanding of the electronic structure of the high-T_c superconductors and their insulating parent compounds. The low-energy electronic structure of these materials seems to be well described by single- or multiband Hubbard models,[1] incorporating hybridized Cu $d_{x^2-y^2}$ and O p_σ orbitals. Constrained density-functional theory[2,3] and exact diagonalization studies of finite-size clusters[3,4] have been used to calculate not only such Hubbard-model parameters as the charge-transfer energy gap Δ, the Cu-O hopping energy t_{pd}, and the on-site Coulomb interactions U_p and U_d, but also the in-plane superexchange interaction J.

There is currently considerable debate[5-10] as to how structural variations among different high-T_c materials influence the Hubbard-model parameters. Based on spectroscopic measurements on different members of the 2:1:4 family, it has been argued that J and Δ depend predominantly on the in-plane Cu-O spacing r.[7-10] However, such comparisons alone cannot uniquely distinguish the effects of variations in r from those due to variations in out-of-plane composition and atomic positions. Spectroscopic measurements of J and Δ as a function of applied pressure, and their comparison with the results of material variation studies, can provide new insight into this issue. In addition, high-pressure spectroscopic measurements, in combination with electronic-structure calculations, are essential for understanding the underlying mechanisms responsible for the remarkable pressure sensitivities of the superconducting[11] and magnetic ordering[12] transitions, as well as for explaining qualitative details and trends of the electronic structure among different Cu-O materials.

In this paper we report measurements of the pressure dependence of J in a copper oxide, focusing on antiferromagnetic La_2CuO_4 as the archetype of this class of compounds. Compared to more prosaic transition-metal magnets we find that J has an anomalously weak pressure dependence. We also show that variations in J and Δ among different members of the 2:1:4 family are significantly influenced by out-of-plane compositional and structural variations, contrary to previous interpretations.[7-10] Finally, we compare the pressure dependences of J and the three-dimensional (3D) magnetic ordering temperature T_N and find that their relationship is poorly described by current theory.

Two-magnon Raman scattering has provided a direct determination of J in a number of high-T_c materials.[13] However, high-pressure Raman measurements on opaque materials have been extremely limited.[14] The two-magnon Raman spectrum of La_2CuO_4 presents particular difficulty as it is weak and very broad, necessitating the virtual elimination of the strong Raman scattering and fluorescence from the diamond anvils for an accurate determination of J. We accomplished this by developing a new diamond-anvil cell design which allows for more efficient spatial filtering of the collected light compared to previous approaches.[15] Our technique[16] greatly expands the range of weakly scattering opaque materials accessible to high-pressure Raman scattering.

The Raman-scattering measurements were performed on a single crystal of La_2CuO_4,grown from CuO flux. The as-grown crystal was annealed in nitrogen at 750 °C for 9 h, a procedure which reduces the oxygen doping level to yield an antiferromagnetic sample with T_N of 308 K, measured by magnetic susceptibility. After mechanically polishing the sample to a thickness of 20 μm along the c axis, it was cleaved along the a and b axes with dimension of 60×180 μm^2 in the a-b plane. The oriented sample was loaded into the diamond-anvil cell using krypton as the pressure transmitting medium. The 7-mW incident laser beam was focused into a 50×100 μm^2 line on the sample. The Raman scattered light was analyzed with a Spex triple spectrometer and a charge-coupled-

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device (CCD) detector. The pressure inside the cell was determined from the shift of the fluorescence peaks of a small ruby chip placed next to the sample.[14]

In Fig. 1 we show the room-temperature B_{1g} symmetry Raman spectra for pressures ranging from 1 bar to 100 kbar. There was no significant scrambling of the polarizations by the strain birefringence of the diamond. The data have been corrected for the wavelength-dependent response of the collection optics, spectrometer, and detector. A linear fluorescence background from the samples has been subtracted. No pressure dependence of the resonance enhancement[7] of the two-magnon scattering was evident, so we present results only for an incident wavelength of 4579 Å.

The pressure dependence of J can be extracted[17] from the first and second moments $M_1 = 3.58J$ and $M_2 = 0.81J$ of these spectra. These relations differ significantly from the corresponding classical ones, reflecting the strong quantum fluctuations of this two-dimensional (2D) spin-$\frac{1}{2}$ Heisenberg system. We find at all pressures that $M_2/M_1 = 0.20 \pm 0.01$, in good agreement with the renormalized spin-wave value of 0.23. We conclude that describing La_2CuO_4 with a Heisenberg model seems reasonable at all pressures.

The value of J calculated from M_1 increases monotonically with pressure, as shown in Fig. 2. Since the dominant superexchange path involves only the nearest neighbor in-plane Cu-O spacing, r, we plot in Fig. 3 the logarithm of J as a function of the logarithm of r taken from high-pressure x-ray measurements.[18] At the lowest pressures we find $J \simeq 1/r^n$ with $n = 6.4 \pm 0.8$, with a somewhat weaker variation at the highest pressures. The reduced sensitivity of J to r at the highest pressures may arise from modifications to the crystal structure as the pressure-dependent orthorhombic-tetragonal phase transition drops below room temperature at ~ 40–60 kbar.[19]

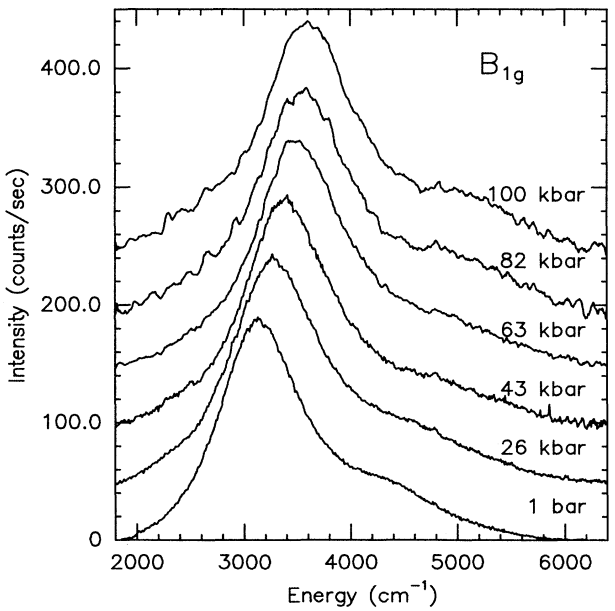

FIG. 1. The pressure dependence of the room-temperature Raman spectrum of La_2CuO_4 (B_{1g} symmetry). The data have been vertically offset from one another by 50 counts/sec each for clarity.

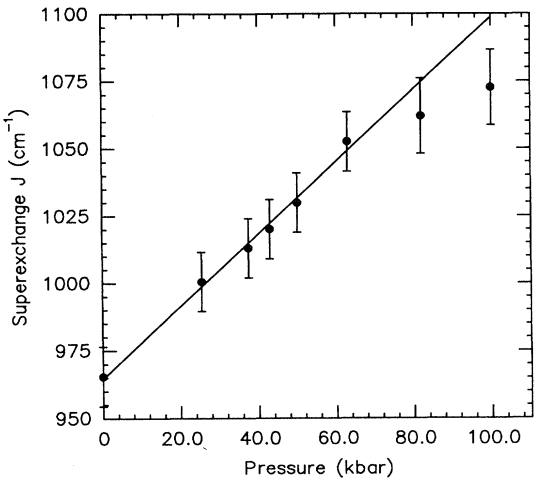

FIG. 2. Pressure dependence of the in-plane superexchange J. Solid line is a fit to the data for pressures ≤ 60 kbar. The fit gives $J(P) = 965\ \mathrm{cm}^{-1} + 1.34\ (\mathrm{cm}^{-1}/\mathrm{kbar})P$.

The surprising nature of our results can be appreciated by contrasting them with the pressure dependence of J in conventional transition-metal oxide and halide magnets. A variety of experiments[20–22] on such materials have shown that J depends exclusively on the superexchange path r, varying as $J \simeq 1/r^n$ with $10 \lesssim n \lesssim 12$, substantially stronger than the path-length dependence which we find for La_2CuO_4. To gain insight into this result we consider the perturbative expression for J derived from the two-band Hubbard model in the limit $t_{pd} \ll \Delta$, U_p, U_d (Ref. 23)

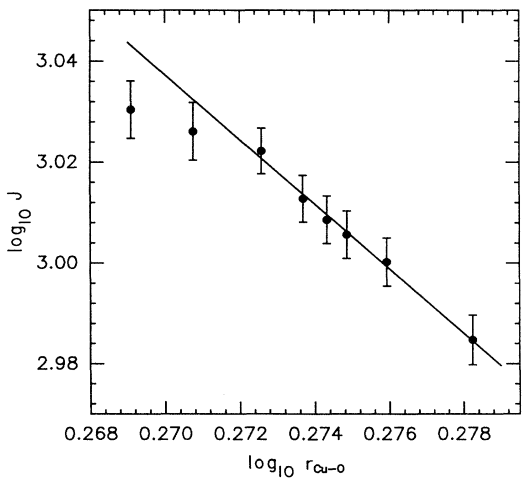

FIG. 3. Double log plot of in-plane J versus the nearest-neighbor Cu-O spacing r, taken from high-pressure x-ray measurements (Ref. 18). The solid line is a fit for pressures ≤ 60 kbar and gives $J \simeq 1/r^n$, $n = 6.4 \pm 0.8$.

$$J = 4\frac{t_{pd}^4}{\Delta^2}\left[\frac{1}{U_d}+\frac{1}{2\Delta+U_p}\right]. \quad (1)$$

Numerical calculations[24,25] of $3d$-$2p$ overlaps have found that $t_{pd}\simeq 1/r^n$ with $2.5\lesssim n\lesssim 3.0$. Thus, the pressure dependence of J in these magnets arises from that of t_{pd}, while Δ, U_p, and U_d are essentially pressure independent.

The anomalous apparent dependence of J on the superexchange path length in La_2CuO_4 suggests either that Δ and/or t_{pd} may have anomalous path-length dependence, or that they do not depend exclusively on the Cu-O spacing, but also on the interplanar structure. Addressing the first possibility, high-pressure reflectivity measurements[26] find that Δ depends only weakly on r, varying as $1/r^n$ with $n=0.4\pm0.4$. Using Eq. (1) to combine the measured apparent dependence of J and Δ on r with constrained LDA band-structure estimates[2] for U_p and U_d, we find that $t_{pd}\simeq 1/r^n$ with $n=1.8\pm0.2$. In contrast, tight-binding fits to LAPW band structures for La_2CuO_4 at two different lattice constants,[27] as well as atomic overlap calculations[25] predict the much stronger dependence $t_{pd}\sim 1/r^n$ with $2.5\lesssim n\lesssim 3.0$. This discrepancy may reflect the inadequacy of mean-field density functional calculations for fully including correlation effects. However, we note that LDA estimates of $t_{pd}=1.3$ eV and $\Delta=3.6$ eV do not satisfy $t_{pd}\ll\Delta$, so the perturbation theory expression for J may itself be invalid. Exact diagonalization studies of small Cu-O clusters qualitatively support this conclusion, giving a significantly weaker dependence of J on t_{pd} than Eq. (1). Constrained LDA band-structure calculations at several lattice spacings combined with exact diagonalization studies of larger clusters are required to definitively rule out an anomalously weak path-length dependence for t_{pd}.

The second possibility is that the Hubbard-model parameters are sensitive to variations in interplanar structure. Comparing the apparent dependences of J and Δ on Cu-O spacing extracted from pressure measurements with those deduced from measurements[7-10] on different 2:1:4 compounds supports this possibility. For example, the material variation studies of Cooper *et al.*[9] deduced that $J\sim 1/r^n$ with $n=4\pm2$, in mild disagreement with the apparent dependence derived from our pressure measurements of $n=6.4\pm0.8$. Furthermore, the weak apparent dependence of Δ on Cu-O spacing deduced from pressure measurements on La_2CuO_4,[26] is in dramatic contrast to the very strong apparent dependence of $1/r^n$ with $n=6\pm2$ found in material variation studies.[9]

Applying pressure or varying the out-of-plane composition and atomic positions both result in simultaneous changes in the intra- and interplanar distances, albeit in different ways. Nevertheless, if the in-plane Cu-O spacing is the single relevant length scale for determining low-energy electronic structure, then $J(r)$ and $\Delta(r)$ should be identical for the pressure and material studies. The extent of the disagreement demonstrated here clearly indicates that this is not the case. While a Hubbard-model description involving Cu and O orbitals originating in the plane seems to be a valid simplification of the low-energy electronic structure, our results indicate that the Hubbard-model parameters depend on the full 3D structure of the material. Although our data do not provide an indication of what the most important out-of-plane structural features are, we note that recent theoretical work[5,6] has found for a large number of high-T_c materials that the Madelung potential contributions to Δ depend significantly on the out-of-plane structure.

Measurements of the pressure dependence of J can be combined with high-pressure neutron-diffraction measurements[12] of T_N to estimate the dependence of the effective interplanar coupling $J_\perp$ on the interplanar spacing R. As a result of the interlayer coupling, domains in adjacent layers order in 3D at a Néel temperature T_N, which is a function of the domain size ξ^2, the reduced moment M^2, and $J_\perp$, given self-consistently by

$$T_N \approx J_\perp M^2 \xi^2(T_N). \quad (2)$$

The temperature dependence of the 2D correlation length ξ has the form[28]

$$\xi(T_N)=C_\xi a \exp\left[\frac{2\pi\rho_s}{k_B T_N}\right], \quad (3)$$

where a is the lattice constant, $C_\xi=0.5$, and the spin-wave stiffness $2\pi\rho_s=0.94J$.

The pressure dependence of $J_\perp$ is extracted from Eqs. (2) and (3) by combining our measurements of $J(P)$ with those of $T_N(P)$ (Ref. 12) and ambient pressure M^2,[29] both measured by neutron scattering on samples of La_2CuO_4 with a somewhat higher oxygen doping level and lower T_N than our sample. The calculated $J_\perp$ is extraordinarily sensitive to pressure, increasing about a factor of 20 in 100 kbar. While $J_\perp$ should increase as R decreases, we regard the extracted pressure dependence to be unphysically strong. It is likely instead that Eq. (2) is incomplete, omitting such potentially important contributions as the in-plane anisotropy, more distant neighbor interactions, and a pressure-dependent orthorhombic-tetragonal transition[19] which are comparable in magnitude to $J_\perp$. Clearly, a more detailed microscopic model for the effective interplanar coupling and the 3D magnetic ordering of the 2:1:4 layered compounds needs to be developed.

To summarize, we have shown that the superexchange interaction J in La_2CuO_4 has an anomalously weak-pressure dependence. Our work demonstrates the need for nonperturbative calculations of J in the two-band Hubbard model, as well as for constrained density-functional calculations combined with exact diagonalization studies as a function of lattice constant. We further found that the Hubbard-model parameters describing the low-energy electronic structure are significantly influenced by the out-of-plane composition and atomic positions. Finally, we conclude that the existing self-consistent theory does not adequately describe the 3D magnetic ordering in La_2CuO_4. The improvements in high-pressure Raman-scattering techniques reported here allow the application of these powerful pressure studies to a substantially wider class of materials than has been

possible previously.

Ohta, Tohyama, and Maekawa[30] recently reported a theoretical analysis of the material dependence of J and Δ which supports our conclusions. However, we do not agree with their suggestion that the weak-pressure dependence of J results from a cancellation of the pressure dependencies of t_{pd} and Δ. Instead, we believe, as discussed above, that it arises because either (a) the large value of t_{pd}/Δ leads to a reduction in γ from the perturbation theory result that $\gamma=4$, where $J\sim t_{pd}^{\gamma}$or (b) t_{pd} has an anomalously weak dependence on te Cu-O spacing.

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