Pressure dependence of the superexchange interaction in antiferromagnetic \( \text{La}_2\text{CuO}_4 \)

M. C. Aronson and S. B. Dierker

The Harrison M. Randall Laboratory of Physics, University of Michigan, Ann Arbor, Michigan 48109-1120

B. S. Dennis and S-W. Cheong

AT&T Bell Laboratories, Murray Hill, New Jersey 07974-2070

Z. Fisk

Los Alamos National Laboratory, Los Alamos, New Mexico 87545

(Received 26 April 1991)

Using high-pressure Raman scattering, we have directly measured the pressure dependence of the in-plane superexchange interaction \( J \) in antiferromagnetic \( \text{La}_2\text{CuO}_4 \) 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 Neel 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, incorporating hybridized Cu \( d_{\pi-\gamma} \) and O \( p_{\sigma} \) orbitals. Constrained density-functional theory \(^3,3\) 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 \( \Delta \), 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 \(^5\) to \(^10\) 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 \( \Delta \) depend predominantly on the in-plane Cu-O spacing \( r \).\(^7\)\(^\text{-}10\) 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 \( \Delta \) 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\(^1\) and magnetic ordering\(^1\) 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 \( \text{La}_2\text{CuO}_4 \) 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 \( \Delta \) among different members of the 2:1:4 family are significantly influenced by out-of-plane compositional and structural variations, contrary to previous interpretations.\(^7\)\(^\text{-}10\) 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.\(^1\) However, high-pressure Raman measurements on opaque materials have been extremely limited.\(^1\) The two-magnon Raman spectrum of \( \text{La}_2\text{CuO}_4 \) 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.\(^1\)\(^5\) Our technique\(^1\)\(^6\) 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 \( \text{La}_2\text{CuO}_4 \), 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 \( \mu \)m along the \( c \) axis, it was cleaved along the \( a \) and \( b \) axes with dimension of \( 60 \times 180 \mu \text{m}^2 \) 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 \( \times \) 100 \( \mu \text{m}^2 \) line on the sample. The Raman scattered light was analyzed with a Spex triple spectrometer and a charge-coupled-
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 enhancement7 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 extracted17 from the first and second moments $M_1 = 3.58J$ and $M_2 = 0.81J$ of these spectra. These relations differ significantly from those 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$_2$CuO$_4$ 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 $J \approx 1/r^n$ 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 $\sim 40$-60 kbar.19

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 experiments20-22 on such materials have shown that $J$ depends exclusively on the superexchange path $r$, varying as $J \approx 1/r^n$ with $10 \leq n \leq 12$, substantially stronger than the path-length dependence which we find for La$_2$CuO$_4$. To gain insight into this result we consider the perturbative expression for $J$ derived from the two-band Hubbard model in the limit $t_{pd} \ll \Delta, U_\rho, U_d$ (Ref. 23)

![FIG. 1. The pressure dependence of the room-temperature Raman spectrum of La$_2$CuO$_4$ ($B_{1g}$ symmetry). The data have been vertically offset from one another by 50 counts/sec each for clarity.](image1)

![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 $J(P) = 965 \text{ cm}^{-1} + 1.34 (\text{cm}^{-1}/\text{kbar})P$.](image2)

![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 $J \approx 1/r^n, n = 6.4 \pm 0.8$.](image3)
Numerical calculations\textsuperscript{24,25} of 3d-2p overlaps have found that 
\( t_{pd} \approx 1/r^n \) with \( 2.5 \leq n \leq 3.0 \). Thus, the pressure 
dependence of \( J \) in these magnets arises from that of \( t_{pd} \), 
while \( \Delta_r, U_p, \) and \( U_d \) are essentially pressure independent.

The apparent anomalous dependence of \( J \) on the superexchange 
path length in LazCu\textsubscript{04} suggests either that \( \Delta \) 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\textsuperscript{26} find that \( \Delta \) depends only weakly on \( r \), 
varying as \( 1/r^n \) with \( n=0.4 \pm 0.4 \). Using Eq. (1) to combine 
the measured apparent dependence of \( J \) and \( \Delta \) on \( r \) 
with constrained LDA band-structure estimates\textsuperscript{3} for \( U_p \) 
and \( U_d \), we find that \( t_{pd} \approx 1/r^n \) with \( n=1.8 \pm 0.2 \). In 
contrast, tight-binding fits to LAPW band structures for 
LazCu\textsubscript{04} at two different lattice constants,\textsuperscript{27} as well as 
avtomic overlap calculations\textsuperscript{28} predict the much stronger 
dependence \( t_{pd} \approx 1/r^n \) with \( 2.5 \leq n \leq 3.0 \). This discrepancy 
may reflect the inadequacy of mean-field density functional 
calculations for fully including correlation effects. However, we note that LDA estimates of \( t_{pd} \approx 1.3 \, \text{eV} \) and 
\( \Delta \approx 3.6 \, \text{eV} \) do not satisfy \( t_{pd} << \Delta \), 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 \( \Delta \) on 
Cu-O spacing extracted from pressure measurements with 
those deduced from measurements\textsuperscript{7-10} on different 
2:1:4 compounds supports this possibility. For example, the material variation studies of Cooper et al.,\textsuperscript{9} deduced that 
\( J \approx 1/r^n \) with \( n=4 \pm 2 \), in mild disagreement with 
the apparent dependence derived from our pressure measurements of 
\( n=6.4 \pm 0.8 \). Furthermore, the weak apparent dependence of \( \Delta \) on Cu-O spacing deduced from 
pressure measurements on LazCu\textsubscript{04},\textsuperscript{26} is in dramatic 
contrast to the very strong apparent dependence of \( 1/r^n \) with 
\( n=6 \pm 2 \) found in material variation studies.\textsuperscript{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\textsuperscript{5,6} has found for a large number of high-\( T_c \) materials that the Madelung potential contributions to \( \Delta \) 
depend significantly on the out-of-plane structure.

Measurements of the pressure dependence of \( J \) can be combined with high-pressure neutron-diffraction 
measurements\textsuperscript{12} of \( T_N \) to estimate the dependence of the 
effective interplanar coupling \( J_1 \) 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 \( \xi \), the reduced 
moment \( M^2 \), and \( J \), given self-consistently by

\[
T_N \approx J_1 M^2 \xi^2(T_N).
\]

The temperature dependence of the 2D correlation length \( \xi \) has the form\textsuperscript{28}

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

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

The pressure dependence of \( J_1 \) 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 \( M^2 \),\textsuperscript{28} both measured by neutron scattering on samples of LazCu\textsubscript{04} 
with a somewhat higher oxygen doping level and lower \( T_N \) than our sample. The calculated \( J_1 \) is extraordinarily 
sensitive to pressure, increasing about a factor of 20 in 
100 kbar. While \( J_1 \) 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\textsuperscript{14} which are comparable in magnitude to \( J_1 \). 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 LazCu\textsubscript{04} 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 LazCu\textsubscript{04}. 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\(^3\) recently reported a theoretical analysis of the material dependence of \(J\) and \(\Delta\) 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 \(\Delta\). Instead, we believe, as discussed above, that it arises because either (a) the large value of \(t_{pd}/\Delta\) leads to a reduction in \(\gamma\) from the perturbation theory result that \(\gamma = 4\), where \(J \sim t_{pd}^2\) or (b) \(t_{pd}\) has an anomalously weak dependence on \(t\) Cu-O spacing.

We have benefited from discussions with S. L. Cooper, S. Fahy, D. R. Jennison, R. Merlin, R. M. Metzger, D. S. Schiferl, E. B. Stechel, K. Syassen, and U. Venkateswaran. Part of this work was performed while M.C.A. was at Los Alamos National Laboratory, Los Alamos, New Mexico, and S.B.D. at AT&T Bell Laboratories, Murray Hill, New York. M.C.A. is grateful to the Superconductivity Pilot Center, Los Alamos National Laboratory for travel assistance. Work at Los Alamos was performed under the auspices of the U.S. Department of Energy.

\(^{1}\)P. W. Anderson, Science, 235, 1196 (1987); V. J. Emery, Phys. Rev. Lett. 58, 2794 (1987).
\(^{2}\)M. S. Hybertson, M. Schluter, and N. E. Christenson, Phys. Rev. B 39, 9028 (1989).
\(^{3}\)M. S. Hybertson, E. B. Stechel, M. Schluter, and D. R. Jennison, Phys. Rev. B 41, 11068 (1990); J. F. Annett, R. M. Martin, A. K. McMahan, and S. Satpathy, \textit{ibid.} 40, 2620 (1989).
\(^{4}\)E. B. Stechel and D. R. Jennison, Phys. Rev. B 38, 4632 (1988).
\(^{5}\)J. B. Torrance and R. M. Metzger, Phys. Rev. Lett. 63, 1515 (1989).
\(^{6}\)Y. Ohta, T. Tohyama, and S. Maekawa, Phys. Rev. B 43, 2968 (1991).
\(^{7}\)P. E. Sulewski, P. A. Fleury, K. B. Lyons, S.-W. Cheong, and Z. Fisk, Phys. Rev. B 41, 225 (1990).
\(^{8}\)Y. Tokura, S. Koshihara, T. Arima, H. Takagi, S. Ishibashi, T. Ido, and S. Uchida, Phys. Rev. B 41, 11657 (1990).
\(^{9}\)S. L. Cooper, G. A. Thomas, A. J. Millis, P. E. Sulewski, J. Orenstein, D. H. Rapkine, S.-W. Cheong, and P. L. Trever, Phys. Rev. B 42, 10785 (1990).
\(^{10}\)M. Yoshida, N. Koshizuka, and S. Tanaka, Phys. Rev. B 42, 8760 (1990).
\(^{11}\)R. Griessen, Phys. Rev. B 36, 5284 (1987).
\(^{12}\)S. Katano, N. Mori, H. Takahashi, and H. Takei, J. Phys. Soc. Jpn. 58, 3890 (1989).
\(^{13}\)For a review, see S. Sugai, in \textit{Mechanisms of High Temperature Superconductivity}, edited by H. Kamimura and A. Oshima (Springer-Verlag, Berlin, 1989).
\(^{14}\)A. Jayaraman, Rev. Mod. Phys. 55, 65 (1983).
\(^{15}\)R. J. Hemley, H. K. Mao, P. M. Bell, and B. O. Mysen, Phys. Rev. Lett. 57, 747 (1986).
\(^{16}\)S. B. Dierker, M. C. Aronson, and B. S. Dennis (unpublished).
\(^{17}\)R. R. P. Singh, P. A. Fleury, K. B. Lyons, and P. E. Sulewski, Phys. Rev. Lett. 62, 2736 (1989).
\(^{18}\)M. J. Akhtar, C. R. A. Catlow, S. M. Clark, and W. M. Temmerman, J. Phys. C 21, L917 (1988).
\(^{19}\)H. J. Kim and R. Moret, Physica C 156, 363 (1988).
\(^{20}\)K. C. Johnson, and A. J. Sievers, Phys. Rev. B 10, 1027 (1974).
\(^{21}\)T. Kaneko, H. Yoshida, S. Abe, H. Morita, K. Noto, and H. Fujimori, Jpn. J. Appl. Phys. 26, L1374 (1987), and references therein.
\(^{22}\)M. J. Massey, N. H. Chen, J. W. Allen, and R. Merlin, Phys. Rev. B 42, 8776 (1990).
\(^{23}\)F. C. Zhang and T. M. Rice, Phys. Rev. B 37, 3759 (1988).
\(^{24}\)K. N. Shrivastava and V. Jaccarino, Phys. Rev. B 13, 299 (1976); N. Fuchikami, J. Phys. Soc. Jpn. 28, 871 (1970); L. J. de Jongh and R. Block, Physica 79B, 568 (1975).
\(^{25}\)D. W. Smith, J. Chem. Phys. 50, 2784 (1969).
\(^{26}\)U. Venkateswaran, K. Syassen, H. Mattausch, and E. Schonherr, Phys. Rev. B 38, 7105 (1988); and private communication. The value of \(\Delta\) determined optically is somewhat different from the Hubbard model \(\Delta\) due to excitonic effects, but is expected to have the same pressure dependence.
\(^{27}\)W. Weber, Phys. Rev. Lett. 58, 1371 (1987).
\(^{28}\)S. Chakravarty, B. I. Halperin, and D. R. Nelson, Phys. Rev. B 39, 2344 (1989).
\(^{29}\)Y. Endoh \textit{et al.}, Phys. Rev. B 37, 7443 (1988).
\(^{30}\)Y. Ohta, T. Tohyama, and S. Maekawa, Phys. Rev. Lett. 66, 1228 (1991).