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Light scattering from quantum spin fluctuations in $R_2\text{CuO}_4$ ($R = \text{La}, \text{Nd}, \text{Sm}$)

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Raman spectra reveal spin fluctuation scattering over the energy range $0–8000$ cm$^{-1}$ (0–1 eV) in single crystal $\text{La}_2\text{CuO}_4$ ($T$ phase), $\text{Nd}_2\text{CuO}_4$, and $\text{Sm}_2\text{CuO}_4$ ($T'$ phase). From the $B_{1g}$ symmetry spectra, values of the exchange parameter $J$ for these crystals are determined to be $1030\pm50$, $871\pm50$, and $888\pm50$ cm$^{-1}$, respectively. All three materials also exhibit broad spectral features of $A_{1g}$ and $B_{2g}$ symmetry, which are forbidden within the classical spin-pair excitation model, but allowed by quantum fluctuations. The line shapes for spectra of all three symmetries agree with recent model calculations for the planar calculations for the planar quantum antiferromagnet. While the spectra for crystals with the $T'$ structure are nearly identical, subtle differences from the spectra of $\text{La}_2\text{CuO}_4$ ($T$ structure) indicate a sensitivity to the structure outside of the $\text{CuO}_2$ planes.

I. INTRODUCTION

Recently, a comparison of our inelastic-light-scattering spectra with a theoretical calculation$^1$ of nearest neighbor spin-pair scattering for the spin-$\frac{1}{2}$ planar Heisenberg antiferromagnet has dramatically demonstrated that quantum fluctuations are responsible for the anomalously large linewidth observed$^2$ for $B_{1g}$ symmetry in $\text{La}_2\text{CuO}_4$. In addition, it was argued that the quantum fluctuations could permit next-nearest-neighbor scattering processes, forbidden in the pure Néel (classical) ground state, of $A_{1g}$ and $B_{2g}$ symmetry. The observation of this $A_{1g}$ scattering intensity in $\text{La}_2\text{CuO}_4$ was previously noted.$^{1,3}$

In $\text{La}_2\text{CuO}_4$ the observed spectral weight in the $A_{1g}$ feature is of the same order of magnitude as the $B_{1g}$ feature, contrary to naive expectations. Contributions to the spin-pair scattering cross section involving the influence of the atoms outside of the $\text{CuO}_2$ planes might explain the observed magnitude of the $A_{1g}$ feature. In such a case, one may argue that the spectra might be sensitive to the out-of-plane structure. In this paper, we present spectra from three single crystals: $\text{La}_2\text{CuO}_4$, $\text{Nd}_2\text{CuO}_4$, and $\text{Sm}_2\text{CuO}_4$, which have a different out-of-plane structure. For $\text{La}_2\text{CuO}_4$ ($T$), the Cu has octahedral coordination to the oxygen, while in $\text{Nd}_2\text{CuO}_4$ and $\text{Sm}_2\text{CuO}_4$ ($T'$) the coordination is square planar$^4$ (see Fig. 1).

II. EXPERIMENTAL DETAILS

The $\text{La}_2\text{CuO}_4$ crystal, grown from a pure CuO flux, is the same crystal used in previous works$^1,3$ and has a measured Néel temperature of 265 K. The $\text{Nd}_2\text{CuO}_4$ and $\text{Sm}_2\text{CuO}_4$ single crystals were grown from a CuO flux, as has been previously described.$^5$ For the $\text{Nd}_2\text{CuO}_4$, $T_N \sim 245$ K. Susceptibility and neutron scattering determinations of $T_N$ for $\text{Sm}_2\text{CuO}_4$ are precluded by its large temperature-dependent paramagnetism and the large neutron absorption cross section of Sm. Since each of the as-grown crystals exhibited at least one highly reflecting face, free of residual flux, no polishing was necessary, and all spectra were taken from as-grown surfaces. The basal plane dimensions of the $\text{La}_2\text{CuO}_4$, $\text{Nd}_2\text{CuO}_4$, and $\text{Sm}_2\text{CuO}_4$ crystals were $8 \times 10$, $3 \times 2$, and $4 \times 6.5$ mm$^2$, respectively.

The spectra were obtained with 20 mW from an Ar ion laser focused to a line $0.1 \times 1.5$ mm$^2$ on the samples at room temperature. Three excitation wavelengths—5145, 4880, and 4579 Å—were used to probe the resonance behavior of the features of interest. The laser power was determined with a Coherent Model 210 power meter.

FIG. 1. Comparison of the $T$ and $T'$ crystal structures. For the $T$ structure, the Cu ions are surrounded by oxygen octahedra, while for the $T'$ structure, the Cu ions are fourfold coordinated to the oxygen ions in the plane.
The scattered light was collected at right angles to the incident beam with f/4 optics and passed through a Spex Triplemate spectrometer to a liquid-nitrogen-cooled charge-coupled-device (CCD) camera. The spectra have all been calibrated to a standard lamp to correct for the response of the spectrometer and detector, so that the spectra at different excitation frequencies may be directly compared.

The crystal structures for the T and T' phases, shown in Fig. 1, both exhibit two-dimensional (2D) CuO₂ sheets. In the T phase, the Cu ions are sixfold coordinated to the surrounding oxygens, which enclose the Cu ions in an octahedral cage, as shown in Fig. 1. The La ion is ninefold coordinated to the surrounding oxygens, four of which lie in the CuO₂ plane below the La, four of which are the apical oxygens from the four surrounding octahedra, and the apical oxygen is located in the octahedron directly above it.

In the T' phase the rare-earth ions remain above (and below) the centers of the CuO₂ squares. However, the coordination of the oxygens to the rare-earth ions becomes eightfold by moving the apical oxygens further from the plane, to lie midway between the two nearest CuO₂ sheets and directly above and below the in-plane oxygens. This displacement of the apical oxygens destroys the octahedral coordination at the Cu sites, resulting in a square planar coordination. The rare-earth ion thus sits in the center of a tetragonal cage of oxygens.

In order to discuss the various symmetry components of the Raman tensor, the axes along the planar Cu—O bonds are defined as x and y. The x' and y' axes are defined by a 45° rotation from the xy axes. With the incident and scattered light both polarized along the y axis (yy), the spectrum contains the A₁g and B₁g symmetry components. The xy spectrum reveals the B₂g component. After a simple 45° rotation of the crystal, the polarized scattering (y'y') gives the sum of the A₁g and B₂g scattering, while the depolarized scattering (y'x') gives the B₁g component. Any contribution from surface fluorescence will appear in all of these symmetry combinations. In the case of Nd₂CuO₄ and Sm₂CuO₄, this contribution appears to be less than 5% of the B₁g peak value, while it is somewhat larger for La₂CuO₄. The fluorescence background may be removed from the A₁g by subtracting the xy spectrum from the y'y' spectrum, to obtain the pure A₁g component. The background cannot be so unambiguously removed from the B₁g and B₂g components, however, and the spectra presented here include this contribution to the intensity, which therefore contributes to the uncertainty in the scattering cross section.

III. DATA AND DISCUSSION
A. B₁g features
The most prominent feature in the Raman spectra of the insulating cuprates is the B₁g spin pair mode, which is shown in Figs. 2(a)–2(c). This B₁g scattering is well-described by the effective interaction Hamiltonian:

\[ H_R = C \sum_{ij} (E_{inc} \cdot \sigma_{ij})(E_{sc} \cdot \sigma_{ij})S_i \cdot S_j, \]  

where \(E_{inc}\) and \(E_{sc}\) are electric field vectors for the incident and scattered photons, and \(\sigma_{ij}\) is a unit vector connecting spin sites \(i\) and \(j\). The matrix elements and other details of the excited-state exchange determining \(H_R\) are contained in the prefactor \(C\).

The spectra shown in Figs. 2(a)–2(c) all peak near 3000 cm⁻¹ and exhibit widths [full width at half maximum (FWHM)] of about 1200 cm⁻¹. In addition, the curves have similar asymmetries, with greater spectral weight appearing on the high-frequency side of the peaks. Since the theoretical calculation can provide only values for the frequency moments, or equivalently the cumulants, of the lineshape \(I(\omega)\), the cumulants of the curves in Figs. 2(a)–2(c) have been extracted using

\[ M_1 = \int \omega I(\omega) d\omega / I_T, \]  
\[ (M_n)^\prime = \int (\omega - M_1)^n I(\omega) d\omega / I_T, \]

for \(n > 1\), where

\[ I_T = \int I(\omega) d\omega. \]

![FIG. 2. Raman spectra of various symmetries for different incident laser wavelengths. The baselines are indicated at the right for the upper two spectra in each figure part, which are shifted upward for clarity. The curves are ordered according to their laser excitation wavelength, \(\lambda_L\): 5145 Å (top), 4880 Å (middle), and 4579 Å (bottom, unshifted). Spectra have been separated according to their symmetry: (a)–(c) \(B_{1g}\), (d)–(f) \(A_{1g}\), and (g)–(i) \(B_{2g}\). For each symmetry, spectra are shown for each of the three compounds: (a), (d), (g) La₂CuO₄; (b), (e), (h) Nd₂CuO₄; (c), (f), (i) Sm₂CuO₄. The \(A_{1g}\) and \(B_{1g}\) spectra are plotted on the same scale, for ease of comparison, while the \(B_{2g}\) spectra are multiplied by a factor of 2. Note also that the low frequency portion of the 5145 Å spectrum in (d) is reduced by a factor of 2.](image-url)
The values of peak position and the various cumulants are tabulated in Table I. In calculating the cumulants, the fluorescence background is subtracted by assuming a linear form and setting the spectral intensity to zero at the high- and low-frequency limits of the mode. For any particular sample, the variations among the peak and cumulant values for different laser wavelengths found in Table I provide limits on the influence of this background subtraction.

From the cumulants in Table I, values for the exchange parameter $J$ may be extracted, given the theoretical prediction$^1$ that $M_1 / J = 3.58 \pm 0.06$. Averaging the values obtained for different laser wavelengths, we find $J$ to be $1030 \pm 50$ cm$^{-1}$, $871 \pm 50$ cm$^{-1}$, and $888 \pm 50$ cm$^{-1}$ for La$_2$CuO$_4$, Nd$_2$CuO$_4$, and Sm$_2$CuO$_4$, respectively. The value of $J$ for La$_2$CuO$_4$ compares well with the value of $J = 1080 \pm 40$ cm$^{-1}$ obtained from recent inelastic neutron scattering experiments.$^{10}$

The value of the second cumulant, $M_2$, provides a dramatic verification of the dominant role of quantum fluctuations, and supports the validity of Ising series expansion methods.$^1$ In particular, the observed ratios of $M_2 / M_1$, as given in the last column of Table I, are close to the theoretical value of 0.23 $\pm$ 0.02. Conventional spin-wave theory,$^8$ which ignores quantum fluctuations, predicts the much smaller ratio $M_2 / M_1 = 0.11$. The narrower width predicted by spin wave theory is indeed observed in the isomorphic K$_2$NiF$_4$ spin-ladder system.$^7$ The third cumulant, although more sensitive to the experimental background subtraction procedure, is in quite reasonable agreement with the theoretical prediction of $M_3 / M_1 = 0.27$, for all three samples. Spin wave theory predicts $M_3 / M_1 = 0.06$.

Returning to the exchange parameter $J$, Table II compares $J$ values derived from Fig. 2 with the Cu-O distances of La$_2$CuO$_4$,$^{11}$ Nd$_2$CuO$_4$,$^{12}$ Sm$_2$CuO$_4$, and Ba$_2$YCu$_3$O$_6$.$^{13}$ Within the three-band Hubbard model, the dependence of $J$ on the Cu-O distance can be qualitatively understood. For weak exchange, with $t_0 \ll U$, $\varepsilon_p$, the exchange is determined by the Cu-O hopping $t_0$ and the on-site oxygen on-site energy, and $U$ is the on-site Coulomb repulsion at the Cu ion. Although the accepted values$^{15}$ of $t_0 \approx 1.3$ eV and $\varepsilon_p \approx 3.6$ eV for La$_2$CuO$_4$ violate the assumptions under which Eq. (5) is valid, qualitatively at least, it predicts that as the Cu-O distance is reduced, $t_0$ increases, leading to an increase in $J$, as observed (see Table II). Comparing the $J$ values derived for La$_2$CuO$_4$, Ba$_2$YCu$_3$O$_6$, and Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$Cu$_3$O$_{6+y}$ also yields an increasing $J$ with decreasing Cu-O distance,$^{16}$ although the variation of $\varepsilon_p$ due to crystal-field effects for the very different structures may play an important role. More realistic calculations are needed to provide a more reliable estimate of the dependence of $J$ on the Cu-O distance.

Examining superexchange antiferromagnets with weak exchange,$^{17}$ specifically $\text{X}_2\text{MF}_4$ (X=K, Rb, Tl; $\text{M} = \text{Mn}, \text{Co}, \text{Ni}$), shows that the Hubbard model provides an adequate description of the dependence of $J$ on the M-F separation, when $J$ is in the range of applicability of Eq. (5). Approximating the distance dependence of the $p-d$ overlap by a power law,$^{18}$ and ignoring any change in $U$ or $\varepsilon_p$, leads to $J \sim d^{-n}$ with $n = 14$. This compares favorably with the experimental values$^{17}$ $n \approx 12$. For the cuprates, we find $0 \leq n \leq 4$. We attribute this disagreement to the fact that the exchange is too strong for Eq. (5) to apply to the cuprates. However, the success of the Hubbard model for the fluorides suggests that calculations in a limit more appropriate to the cuprates might yield a useful description in that case as well.

**B. $A_{1g}$ and $B_{2g}$ features**

As mentioned, classical theory$^8$ predicts only $B_{1g}$ scattering intensity for the planar nearest-neighbor

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu-O distance ($\text{Å}$)</th>
<th>$J$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$_2$CuO$_4$</td>
<td>1.907</td>
<td>1030</td>
</tr>
<tr>
<td>Nd$_2$CuO$_4$</td>
<td>1.970</td>
<td>871</td>
</tr>
<tr>
<td>Sm$_2$CuO$_4$</td>
<td>1.955</td>
<td>888</td>
</tr>
<tr>
<td>Ba$_2$YCu$_3$O$_6$</td>
<td>1.941</td>
<td>792</td>
</tr>
</tbody>
</table>

### Table I. Values of the cumulants of the $B_{1g}$ spin-pair mode for La$_2$CuO$_4$, Nd$_2$CuO$_4$, and Sm$_2$CuO$_4$

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lambda_c$ (Å)</th>
<th>$\omega_p$ (cm$^{-1}$)</th>
<th>$M_1$ (cm$^{-1}$)</th>
<th>$M_2$ (cm$^{-1}$)</th>
<th>$M_3$ (cm$^{-1}$)</th>
<th>$M_2 / M_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$_2$CuO$_4$</td>
<td>5145</td>
<td>3210 ± 10</td>
<td>3760 ± 50</td>
<td>850 ± 50</td>
<td>840 ± 100</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>4880</td>
<td>3130</td>
<td>3650</td>
<td>940</td>
<td>830</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>4579</td>
<td>3133</td>
<td>3700</td>
<td>1050</td>
<td>990</td>
<td>0.28</td>
</tr>
<tr>
<td>Nd$_2$CuO$_4$</td>
<td>5145</td>
<td>2806</td>
<td>3014</td>
<td>722</td>
<td>460</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>4880</td>
<td>2760</td>
<td>3110</td>
<td>860</td>
<td>675</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>4579</td>
<td>2800</td>
<td>3240</td>
<td>910</td>
<td>780</td>
<td>0.28</td>
</tr>
<tr>
<td>Sm$_2$CuO$_4$</td>
<td>5145</td>
<td>2858</td>
<td>3044</td>
<td>693</td>
<td>460</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>4880</td>
<td>2859</td>
<td>3167</td>
<td>794</td>
<td>633</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>4579</td>
<td>2897</td>
<td>3330</td>
<td>920</td>
<td>820</td>
<td>0.28</td>
</tr>
</tbody>
</table>

### Table II. Comparison of the exchange parameter $J$, derived from the spectra for various compounds, with the Cu-O distance.

- $J = \frac{4t_0^6}{\varepsilon_p^2 U} + \frac{4t_0^4}{2\varepsilon_p^3 U}$, $t_0$ is the Cu to O hopping rate, $\varepsilon_p$ is the one-electron oxygen on-site energy, and $U$ is the on-site Coulomb repulsion at the Cu ion.
Heisenberg antiferromagnet. Accounting for quantum fluctuations in the ground state leads to additional allowed scattering in the $A_{1g}$ and $B_{2g}$ symmetries. The spectra observed in these symmetries are shown in Figs. 2 (d)–2(i), for the three compounds. Both features are much broader than the $B_{1g}$ modes of Figs. 2(a)–2(c). The much sharper structure in the $A_{1g}$ spectra near 1500 cm$^{-1}$ has been attributed to two-phonon scattering$^{19}$ and will not be discussed further here. For the purposes of the discussion that follows, these phonons are subtracted off by extrapolating the intensity at a frequency above the phonons linearly to zero at zero frequency. By varying the frequency at which the extrapolation begins, an estimate of the error incurred may be obtained. The fluorescence background that is present in the $B_{2g}$ data is estimated and subtracted in the same manner as in the $B_{1g}$ case. The resulting error estimates are larger in the $B_{2g}$ case, however, since the spectral weight is much smaller in these features than in the $B_{1g}$ mode.

In the classical Néel ground state, the spins on nearest-neighbor (NN) Cu sites are aligned antiparallel. The diagonal-next-neighbor (DNN) sites are on the same sublattice, and therefore have aligned spins. In the spin$^{\frac{1}{2}}$ case, quantum fluctuations lead to a 30% probability that DNN spins will be antiparallel, which allows a spin-pair excitation by Eq. (1), with $\sigma_{ij}$ being a unit vector connecting a given site to a DNN site. This new DNN term gives rise to both $A_{1g}$ and $B_{2g}$ scattering. Ising series-expansion calculations predict$^{1}$ that these features are broader than the $B_{1g}$ scattering with $M_1 \approx 3.5J$, $M_2 \approx 1.2J$ for $A_{1g}$, and $M_1 \approx 3.9J$, $M_2 \approx 1.1J$ for $B_{2g}$. Within the same model, the ratio of the $B_{2g}$ to $A_{1g}$ integrated intensities is calculated to be $\sim 0.4$. The cumulants calculated from the $A_{1g}$ and $B_{2g}$ data are displayed in Table III, as ratios to the $J$, which is obtained from the $B_{1g}$ spectrum at each laser frequency. In addition, the ratios of the total integrated intensities of $B_{1g}$ to $A_{1g}$ and $B_{2g}$ to $A_{1g}$ are indicated. From the table, the cumulants predicted by the Ising series-expansion are seen to agree to within $\sim 20\%$ with the experimental. The ratios of the $B_{2g}$ to $A_{1g}$ integrated intensities lie somewhat below the expected value of $\sim 0.4$. However, since the integrated intensity of the fluorescence background may be comparable to that of the $B_{2g}$ feature, the experimental uncertainties in this ratio are large.

Although the Ising series-expansion calculation$^{1}$ gives a reasonable agreement with the observed $A_{1g}$ and $B_{2g}$ moments, it makes no predictions regarding the relative magnitude of the conventional nearest-neighbor ($B_{1g}$) and the quantum-fluctuation-allowed DNN ($A_{1g}$ and $B_{2g}$) processes. We may, however, estimate these relative magnitudes as follows. Because Eq. (1) has the formal appearance of an exchange term, it might seem that the simplest way to produce the DNN coupling required for the $A_{1g}$ process is to perform the NN spin exchange twice. From this viewpoint, one expects this higher-order process to have a cross section orders of magnitude smaller than the NN one. However, Fig. 2(a) and 2(d) show that experimentally the two are comparable in La$_2$CuO$_4$, with a ratio of the $B_{1g}$ to $A_{1g}$ spectral intensities varying from 0.4 to 1.5, depending on excitation wavelength. Thus, either the $A_{1g}$ and $B_{2g}$ spectra are not due to spin-pair excitations, or this expectation is overly simplistic. It has been suggested that the $A_{1g}$ and $B_{2g}$ features may arise from charge transfer rather than spin-pair excitations.$^{20}$ We expect the relevant electronic energies, and therefore the spectral peak positions, to change substantially among the three compounds. However, the observed frequencies for the $A_{1g}$ and $B_{2g}$ features remain approximately the same for all three materials. That is, they scale very well with $J$, as determined from the $B_{1g}$ feature, which provides strong evidence of their magnetic rather than charge transfer origin.

The Raman cross sections for the NN and DNN processes are calculated from matrix elements of the exchange operator, $V_{ss} = e^2/r_{ij}$. These same matrix elements determine the ground-state exchange $J$. The small DNN ground-state exchange thus appears to imply a small DNN to NN intensity ratio. In calculating the Raman cross sections, however, the exchange matrix elements are weighted by dipole matrix elements and energy denominators which may emphasize intermediate states coupling equally well to NN and DNN sites. Obvious

### Table III: Ratios of the cumulants and integrated intensities of the $A_{1g}$, $B_{1g}$, and $B_{2g}$ scattering for La$_2$CuO$_4$, Nd$_2$CuO$_4$, and Sm$_2$CuO$_4$ at several laser excitation wavelengths.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lambda$ (Å)</th>
<th>$M_1/J$</th>
<th>$M_2/M_1$</th>
<th>$B_{2g}/M_1$</th>
<th>$B_{1g}/A_{1g}$</th>
<th>$I_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$_2$CuO$_4$</td>
<td>5145</td>
<td>3.7</td>
<td>0.38</td>
<td>4.1</td>
<td>0.22</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>4880</td>
<td>3.6</td>
<td>0.39</td>
<td>4.7</td>
<td>0.25</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td>4579</td>
<td>4.2</td>
<td>0.39</td>
<td>5.1</td>
<td>0.23</td>
<td>1.5</td>
</tr>
<tr>
<td>Nd$_2$CuO$_4$</td>
<td>5145</td>
<td>3.7</td>
<td>0.34</td>
<td>3.9</td>
<td>0.21</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>4880</td>
<td>3.8</td>
<td>0.38</td>
<td>4.0</td>
<td>0.25</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>4579</td>
<td>3.9</td>
<td>0.37</td>
<td>4.6</td>
<td>0.30</td>
<td>2.8</td>
</tr>
<tr>
<td>Sm$_2$CuO$_4$</td>
<td>5145</td>
<td>3.6</td>
<td>0.33</td>
<td>4.1</td>
<td>0.23</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>4880</td>
<td>3.9</td>
<td>0.35</td>
<td>4.1</td>
<td>0.24</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>4579</td>
<td>4.2</td>
<td>0.35</td>
<td>4.6</td>
<td>0.29</td>
<td>3.1</td>
</tr>
</tbody>
</table>

Theory | 3.5 | 0.34 | 3.9 | 0.28 | ~0.4 |
candidates considered for these intermediate states are
electronic excitations (i) of the La (Nd,Sm) ions, (ii) of the
out-of-plane oxygens, and (iii) within the CuO$_2$ plane.
The evidence presented indicates that (iii) and possibly (ii)
are realized.

Although some variation is observed in comparing
spectra of the $T$ and $T'$ structure samples, it is far less
than expected for a mechanism involving (ii). The spectra
in Fig. 2 show that while the ratio of $B_{1g}$ to $A_{1g}$ integrat-
ed intensities for La$_2$CuO$_4$ varies from 0.4 to 1.5, this ra-
tio varies between 2.3 and 2.8 for Nd$_2$CuO$_4$ and 2.6 and
3.1 for Sm$_2$CuO$_4$. In addition, the resonance behavior of the $A_{1g}$
mode changes, as seen in Figs. 2(d)–2(f). While for La$_2$CuO$_4$ the $A_{1g}$ features weaken as the laser excitation
frequency increases, these features remain relatively
constant for Nd$_2$CuO$_4$ and Sm$_2$CuO$_4$. Although the reso-
nant enhancements in La$_2$CuO$_4$ appear consistent with
electronic structure calculations,$^{21}$ which indicate the
presence of unoccupied bands of La character 2 eV above
the Fermi energy, similar calculations$^{22}$ for Nd$_2$CuO$_4$ find
that the Nd bands are shifted upward by 2 eV relative to the
position of the La bands in La$_2$CuO$_4$. Such a large change
in the electronic energies would result in much
weaker spin-fluctuation scattering in Nd$_2$CuO$_4$, contrary
to the observations.

Within the CuO$_2$ plane, the $E_u$ charge transfer mode,$^{20}$
which places a hole on the four oxygens not surrounding a
Cu site, couples equally to the NN and DNN Cu ions.
Changes in the charge transfer gap$^{23}$ between La$_2$CuO$_4$
and Nd$_2$CuO$_4$, which appear at approximately 1.5 eV,
may provide an explanation of the decreased DNN cou-
pling in the $T'$ materials. While La$_2$CuO$_4$ evidences a
"soft gap," the leading edge of the Nd$_2$CuO$_4$ gap exhibits
a very sharp structure, perhaps signaling the formation of a
Cu-O exciton. The formation of an exciton, binding the
hole more strongly to the Cu ion in the $T'$ structure,
could explain why the DNN coupling is weaker than the
NN coupling for these materials. Although the in-plane oxygen $E_u$
charge transfer thus seems a likely candidate for the
dominant resonant state, contributions from other
states might account for the differences among the three
samples. For example, the similarities between Nd$_2$CuO$_4$
and Sm$_2$CuO$_4$ spectra argue for some involvement of
mechanism (ii).

Whatever the microscopic details of the intermediate
state, two general facts can be invoked to explain the ob-
served discrepant ratios of the NN to DNN coupling in
the ground state and in the Raman cross section: (1) The
different symmetries of the interaction Hamiltonian $V$ for
the Raman matrix element and the superexchange imply
that the virtual transitions will couple to different inter-
mediate states. (2) The presence of the incident photon
energy in the energy denominators may enhance the con-
tribution of the various intermediate states to the Raman
cross section compared with their appearance in the
ground-state superexchange calculation. Encouraged by
the success of cluster calculations$^{24}$ in describing the
La$_2$CuO$_4$ system, we believe that the identification of the
relevant intermediate states and a calculation of the reso-
nance behavior of the various symmetry Raman cross
sections lie within the grasp of theory.

IV. CONCLUSIONS

Inelastic-light-scattering spectra from La$_2$CuO$_4$,
Nd$_2$CuO$_4$, and Sm$_2$CuO$_4$ all exhibit pronounced spin-
fluctuation scattering of the expected $B_{1g}$ symmetry,
from which values of the microscopic Cu-Cu exchange
parameter $J$ have been determined. The values lie in the
1000 cm$^{-1}$ range and show a weak decrease with in-
creasing Cu-O distance. The line shapes, absolute intens-
ities, and resonance behavior of the $B_{1g}$ modes for all
three compounds are quite similar.

The classically forbidden, but quantum allowed, $A_{1g}$
and $B_{2g}$ diagonal spin-pair spectra for the three materials
exhibit subtle differences in absolute intensities and reso-
nance enhancement which correlate with structural
differences between the $T$ and $T'$ phases. These changes
reflect the sensitivity of the Raman cross section for these
modes to the details of the out-of-plane structure. It is
hoped that a microscopic understanding of these Raman
cross sections will aid in constructing a fuller picture of
charge transfer and doping behavior as the antiferromag-
netic systems are moved toward the superconducting
regime.

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