RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 37, NUMBER 4 1 FEBRUARY 1988

Dynamics of spin fluctuations in lanthanum cuprate

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(Received 19 October 1987)

Raman scattering studies of La_2CuO_4 have revealed a high-frequency component ($\sim$3000 cm^{-1}) which we interpret as due to scattering by spin pairs. Comparison of the spectra with those of K_2NiF_4 leads to a value of $J \sim 1100$ cm^{-1} for the exchange interaction. The two-dimensional nature of the fluctuations suggested by earlier neutron scattering work is indicated here by the insensitivity of the spectra to temperature as well as to departures from stoichiometry which strongly influence the three-dimensional ordering temperature T_N.

A common feature of the high-temperature (30–100 K) superconducting oxides is the appearance of copper-oxygen complexes[1,2] in the form of planes or chains involving average effective copper valences between 2+ and 3+. There are theoretical reasons to believe that Cu–O sheets may exhibit substantial two-dimensional correlation[3] in both the "2:1:4" and the "1:2:3" compounds. In the case of the "2:1:4" compounds such as La_2CuO_4, experimental evidence has recently been forthcoming to support this idea.[4] It has been conjectured[3] that this tendency may provide key insights into high-T_c superconductivity in the related, deliberately doped compounds.[5–7]

The many proposed microscopic sources for superconductivity in the copper oxides include magnetic or spin fluctuations, although detailed calculations have yet to appear. Particularly intriguing observations which set limits on the energy scales for nominally two-dimensional (2D) spin fluctuations in La_2CuO_4 have emerged recently from quasielastic and energy integrated neutron scattering experiments.[8] These results have suggested that the spin fluctuations above T_N (the temperature of onset for long-range antiferromagnetic order in *three dimensions)* are strongly two dimensional in nature, with an unusually high dispersion at low wave vector. The limits of spectroscopic resolution for the neutron experiments[8] suggest that near the Brillouin-zone center, the 2D antiferromagnetic spin fluctuations exhibit a dispersion slope greater than 0.4 eV Å. These fluctuations exhibit instantaneous long-range correlation even well above T_N, leading the authors of Ref. 9 to describe the state as a quantum spin fluid.[9] Such high-energy excitations would provide tempting grist for the theorist's mill relative to high superconducting transition temperatures. However, even discounting the possible connection with superconductivity, La_2CuO_4 represents a challenging embodiment of the spin-$\frac{1}{2}$ Heisenberg antiferromagnetic system in two dimensions, whose dynamics still represents an unsolved theoretical problem.

In this paper we present the first direct determination of spin fluctuation energies in La_2CuO_4 by means of second-order (or spin pair) inelastic light scattering. To a first approximation, the results are easily interpreted by analogy with previous[10] studies of the insulating isomorph, K_2NiF_4.

Single crystals grown from oxide flux, of nominal composition La_2CuO_4, were examined by inelastic light scattering with laser excitation wavelengths between 4579 and 5145 Å. The flux-grown crystals were (001) platelets with an extent of 6–8 mm, and a thickness of 1–2 mm. (In our notation, z is perpendicular to the Cu–O planes.) Both as-grown and annealed samples were examined. In most cases as-grown (001) faces were used, with and without acid etching, and in one case a broken face nearly parallel to (001) was employed for comparison of the xx and zz geometries. The symbols x and y in what follows denote two arbitrary, but mutually perpendicular, directions in the plane perpendicular to (001), with x perpendicular to the scattering plane. Mechanically polishing the samples substantially weakened and broadened the features above 1100 cm^{-1}; hence, none of the samples discussed here was polished. Although a variety of annealing conditions was employed in an attempt to influence T_N, magnetic-susceptibility measurements showed no significant anomalies between 4 and 300 K, indicating that T_N lies outside this range for all our samples.

Laser-plasma fluorescence lines were removed from the incident beam using an Anaspec prism monochromator, and the scattered light was collected at right angles to the incident beam using an $f/3$ lens and sufficient magnification to match the $f/6$ optics of the Spex 1402 spectrometer employed. A spectral slit width of $\sim$10 cm^{-1} was employed, with a step size of 10–13 cm^{-1}.

Typical room-temperature scattering spectra are shown in Fig. 1. The broad peak near 3000 cm^{-1} is identified as resulting from two-magnon scattering, while the sharp peaks in the range 750–1500 cm^{-1} are apparently of a different origin. Possible alternate explanations may lie in localized spin-flip excitations or phonon overtones, perhaps related to impurity or defect structures. Further experiments are necessary to determine their origin.

The focus of the present report is the magnon scattering, primarily manifested in the broad high-energy feature evident in the spectra in Fig. 1. The detailed shape of the high-frequency tail is distorted by the combined grating, spectrometer, and photodetector response as well as by weak fluorescence components. The latter may be responsible for a significant fraction of the intensity observed beyond 4000 cm^{-1} where the Raman feature is becoming weak. Nevertheless, it is clear from the two spectra shown, excited at 5145 and 4880 Å, that the main feature

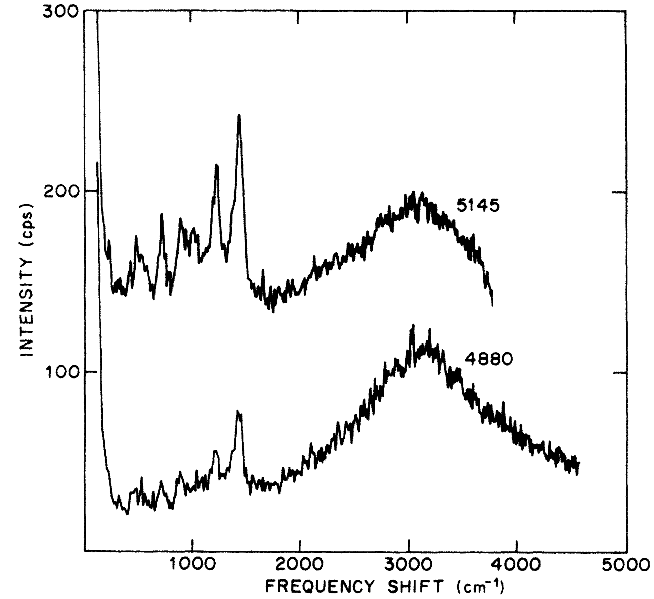

FIG. 1. Two spectra obtained in yy (Brewster) geometry in La_2CuO_4, excited by laser wavelengths of 5145 Å (upper trace) and 4880 Å (lower trace). Laser power was 150 mW, focused to a line 0.2×3 mm, with the sample cooled by flowing He gas. The sample was etched to remove flux and annealed at 346 °C. Traces are offset 90 cps for clarity.

is in fact due to an inelastic scattering process.

Figure 2 shows the polarization selection rules for the 3000-cm^{-1} peak. The yy and xy components are similar in size, and are far larger than the zz. Figure 3 compares spectra obtained at 40 and 300 K, showing a slight broadening and downward shift in the peak at higher temperatures. As we now discuss, all of these attributes support our interpretation of the 3000 cm^{-1} feature as arising from magnon pairs.

In principle, magnon-pair light scattering can provide a quantitative determination of the entire magnon dispersion curve, since pair excitation spectra include contributions from the entire Brillouin zone. In particular, K_2NiF_4 (a prototypical 2D Heisenberg antiferromagnet) has been thoroughly understood on these grounds and provides a useful framework for a quantitative interpretation of our La_2CuO_4 results. The zero-temperature magnon energies are[11]

$$E_{\mathbf{k}}^2 = (SJZ + g\mu H_A)^2 - (SJZ\gamma_{\mathbf{k}})^2 , \tag{1}$$

where $\gamma_{\mathbf{k}} = \frac{1}{2}[\cos(k_x a) + \cos(k_y a)]$, $Z = 4$ is the number of nearest neighbors, $S = \frac{1}{2}$, and J is the exchange interaction constant. For both K_2NiF_4 and La_2CuO_4 the anisotropy field H_A is negligible. We can also ignore the departure from tetragonality[8] (i.e., $a \cong c = 3.79$ Å) in La_2CuO_4.

The scattering of an incident field $\mathbf{E}_1$ into a scattered field $\mathbf{E}_2$ by magnon pairs is described[11] by

$$H^{II} = A \sum_{\langle ij \rangle} [(\mathbf{E}_1 \cdot \boldsymbol{\sigma}_{ij})(\mathbf{E}_2 \cdot \boldsymbol{\sigma}_{ij})(\mathbf{S}_i \cdot \mathbf{S}_j)] , \tag{2}$$

where $\boldsymbol{\sigma}_{ij}$ is the unit vector connecting nearest-neighbor spin sites i and j.

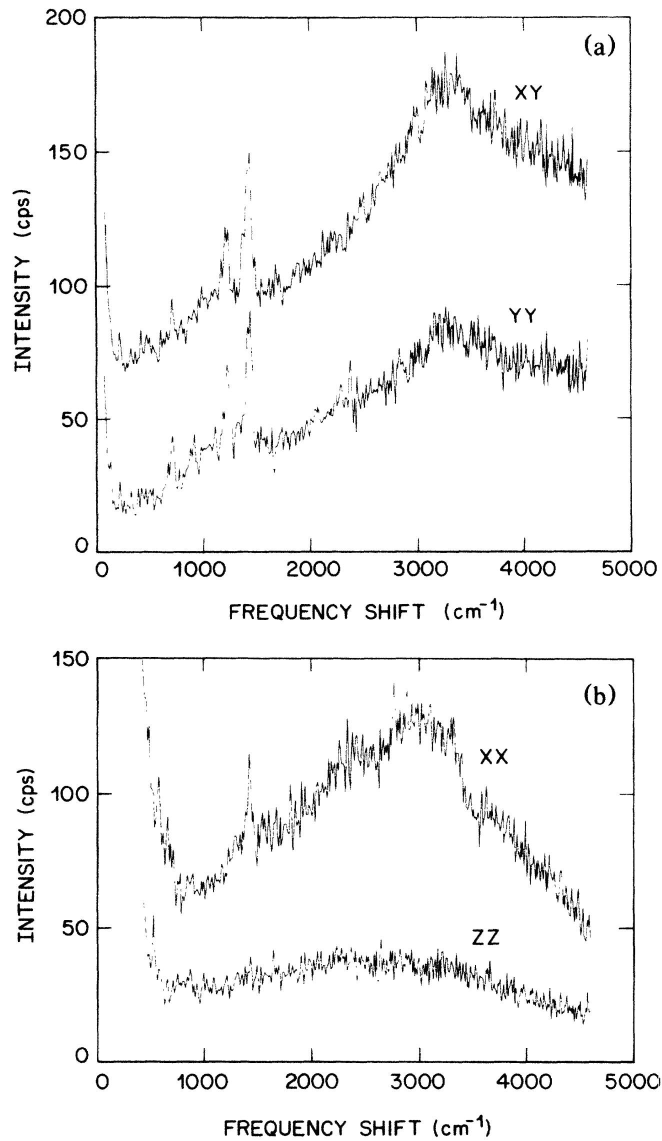

FIG. 2. Polarization selection rules for Raman scattering in La_2CuO_4. (a) Two spectra obtained on an as-grown etched facet in yy and xy geometries. Temperature is 12 K. Upper trace is offset 60 cps. (b) Two spectra obtained on a smooth broken etched face parallel to z in xx and zz (Brewster) geometries. Sample is at room temperature.

Since for La_2CuO_4 the vectors σ_{ij} lie in the xy plane,[4] Eq. (2) predicts[10] that the nonzero Raman tensor elements are α_{xx}, α_{yy}, and α_{xy}. The components α_{xx}, α_{zy}, and α_{zz} should be forbidden. On the other hand, scattering from longitudinal fluctuations such as plasmons,[12] which might have similar energies, should exhibit $\alpha_{xx} \sim \alpha_{yy} \sim \alpha_{zz} \gg \alpha_{xy}, \alpha_{xz}, \alpha_{yz}$, contrary to our observations. The polarization selection we observe is thus consistent with that expected for magnon-pair scattering.

Equation (1) predicts that the energy of a pair of zone-boundary magnons is $2SJZ$. Magnon-magnon interaction

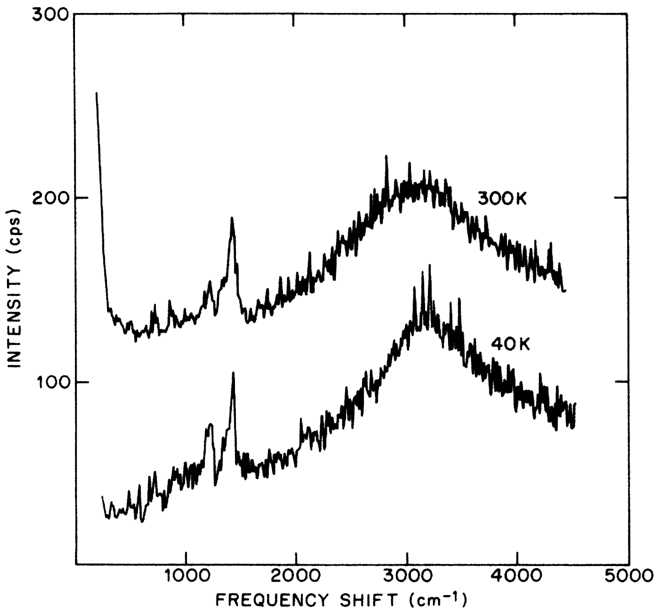

FIG. 3. Raman spectra obtained at two widely separated temperatures in an $La_{2-x}CuO_{4+\delta}$ sample grown with a 10% excess of La to reduce the value of x. Spectra are obtained at 300 and 40 K, on an etched as-grown face, in yy geometry, excited by 4880 Å radiation. Upper trace is offset 90 cps for clarity.

effects[13] reduce the energy of the peak in the magnon-pair light scattering by approximately $2JS$. Accurate account of the spin-$\frac{1}{2}$ system[14] gives a peak position of $\omega_{2m} \cong 2.7J$. Thus, our peak position of ~ 3000 cm^{-1} yields the value $J = 1100$ cm^{-1}. The dispersion relation (1) then gives a zone boundary value of 2200 cm^{-1} and a slope near the zone center of $SJZa/\sqrt{2} = 5900$ cm^{-1} Å $= 0.74$ eV Å. This value is thus consistent with, but considerably greater than, the lower limit of ~ 0.4 eV Å imposed by the neutron scattering study.[8] The larger slope may indicate that our samples in fact have a different oxygen content from those used in the neutron work and may be antiferromagnetic at room temperature, a possibility that is not excluded by the susceptibility measurements.

The renormalization of magnon-pair energies with temperature is very slight in comparison with long-wavelength single-magnon excitations because of the dominance of short-wavelength (near zone boundary) magnons to the former.[10,15] Typically, the magnon-pair spectral weight shifts downward in energy between $T = 0$ and $T = T_N$ by only $\sim 25\%$ in 3D,[16] and by less than 5% in 2D systems.[10] Although $La_{2-x}CuO_{4+\delta}$ has been shown to sustain high-energy spin fluctuations of 2D character, long-range antiferromagnetic order develops in three dimensions at temperatures which depend strongly on x and δ in a manner not yet understood quantitatively. Even so, the magnon-pair spectrum should exhibit only slight modification between $T = 0$ and $T \gg T_N$. Again this behavior is consistent with the observations reported here.

These light-scattering experiments thus provide the first quantitative determination of spin-fluctuation dynamics in the La_2CuO_4 system. The results are consistent with but go well beyond earlier neutron scattering results. Nevertheless, as encouraging as these new results appear, several additional concerns must be mentioned.

The numerical estimate given above assumes that our observation temperature is small compared to the spin-wave energies, a condition that is certainly satisfied. The 3D T_N value for $La_{2-x}CuO_{4+\delta}$ is sensitive to the value of δ, which may be modified by heat treatment subsequent to growth. In addition, wet chemical analysis of the flux-grown crystals shows that for these large (several mm) crystals x ranges from 0.1 to 0.2. The effect of x on T_N is not known. Although we have employed crystals of $La_{2-x}CuO_{4+\delta}$ prepared at varying stoichiometry and under a variety of annealing conditions to influence δ, none of our samples thus far has shown clear evidence of an antiferromagnetic transition between 4 and 300 K in the magnetic susceptibility. Nevertheless, we do not believe that the 2D spin fluctuations are affected substantially by the presence or absence of long-range order, as discussed above.

It is also true that without further experiments we cannot completely reject the possibility that this scattering is due to an exciton. We regard this possibility as rather remote, given the agreement we find with polarization selection rules and peak shape and the numerical consistency between our results and those of the neutron scattering study. It would require an unlikely coincidence for all of these observations to relate to a process other than magnon pairs.

Finally, it is probable that nonzero x and/or δ affects the average Cu valence value, and hence its spin, which in effect means that $La_{2-x}CuO_{4+\delta}$ may behave more like a somewhat diluted 2D antiferromagnet than as a pure one. The detailed effects of variations in x and δ on the antiferromagnetism as well as on the superconductivity in these materials clearly require further study. We do note, however, that we have observed similar scattering features, less completely studied, in $Ba_2YCu_3O_6$, the nonsuperconducting close relative of the "1:2:3" superconductor. We do not yet know whether the existence of highly energetic magnetic excitations in these "precursor" materials may be related to the high value of T_c in the closely related superconductors. Even so, these systems, and La_2CuO_4 in particular, surely represent most interesting 2D magnetic materials in their own right.

Note added. Subsequent to the above work, experiments in samples oriented in the basal plane have revealed a crucial difference between the selection rule behavior of the sharp modes in the range 1200–1500 cm^{-1} and that of the broad magnon feature near 3000 cm^{-1}. Namely, for yx polarization, when x is parallel to (110), both features are absent. [Here (110) is the Cu-O-Cu nearest-neighbor direction.] However, when it is parallel to (100) only the 1200–1500 features are absent. Since the magnon feature is predicted to have intensity in the latter case (and not in the former), this provides a definitive basis for *rejection* of a magnon-pair interpretation of the 1200–1500-cm^{-1} peaks, and in support of our interpretation given above.

We are indebted to B. Batlogg for carrying out the susceptibility measurements on our samples and also to G. Aeppli and B. Batlogg for helpful discussions.

[1]K. Kishio, K. Kitazawa, S. Kanbe, I. Yasuda, N. Sugii, H. Takagi, S.-I. Uchida, K. Fueki, and S. Tanaka, Chem. Lett. 429 (1987).

[2]R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika, E. A. Rietman, S. Zahurak, and g. P. Espinosa, Phys. Rev. Lett. **58**, 1676 (1987).

[3]See, for example, P. W. Anderson *et al.*, Phys. Rev. Lett. **58**, 2790 (1987); V. Emery, *ibid.* **58**, 2794 (1987); J. E. Hirsch, *ibid.* **59**, 228 (1987); B. Shraiman and E. Siggia (unpublished); S. A. Kivelson *et al.*, Phys. Rev. B **35**, 8865 (1987); Y. Hasegawa and H. Fukayama, Jpn. J. Appl. Phys. **26**, L322 (1987).

[4]D. Vaknin, S. K. Sinha, D. E. Moncton, D. C. Johnston, J. M. Newsam, C. R. Safinya, and H. E. King, Phys. Rev. Lett. **58**, 2802 (1987); Y. J. Uemura, W. J. Kossler, X. H. Yu, J. R. Kempton, H. E. Schone, D. Opie, C. E. Stronach, D. C. Johnston, M. S. Alvarez, and D. P. Goshorn, *ibid.* **59**, 1045 (1987).

[5]J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[6]R. J. Cava, R. B. van Dover, B. Batlogg, and E. A. Rietman, Phys. Rev. Lett. **58**, 408 (1987).

[7]H. Takagi, S. Uchida, K. Kitazawa, and S. Tanaka, Jpn. J. Appl. Phys. **26**, L123 (1987).

[8]G. Shirane, Y. Endoh, R. J. Birgeneau, M. A. Kastner, Y. Hidaka, M. Oda, M. Suzuki, and T. Murakami, Phys. Rev. Lett. **59**, 1613 (1987).

[9]Very similar behavior has been observed in $La_2NiO_{4+\delta}$ by G. Aeppli and D. J. Buttrey (private communication).

[10]P. A. Fleury and H. J. Guggenheim, Phys. Rev. Lett. **24**, 1346 (1970).

[11]J. B. Parkinson, J. Phys. C **2**, 2012 (1969).

[12]J. M. Bassat *et al.* Phys. Rev. **35**, 7126 (1987).

[13]W. Hayes and R. Loudon, *Scattering of Light by Crystals,* (Wiley, New York, 1978), p. 273.

[14]D. Huse (private communication).

[15]P. A. Fleury and H. J. Guggenheim, Phys. Rev. B **12**, 987 (1975).

[16]P. A. Fleury, J. Appl. Phys. **41**, 886 (1970); S. R. Chinn, H. J. Zeiger, and J. R. O'Connor, Phys. Rev. B **3**, 1709 (1971).