Spin Fluctuations and Superconductivity in $Ba_2YCu_3O_{6+\delta}$

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We report observation of spin-pair excitations in $Ba_2YCu_3O_{6+\delta}$, with δ in the range 0.0–0.9. The frequency of the excitations, and hence the value of the exchange constant, $J=950$ cm^{-1}, is similar to that reported recently for (nonsuperconducting) La_2CuO_4. The present observation of magnetic excitations in a superconducting material, and of their evolution as a function of δ, demonstrates a large influence of carrier concentration on the spin-fluctuation dynamics.

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The recently discovered high-temperature superconductors fall into two classes[1,2]: the 30–40-K materials derived from the La_2CuO_4 parent ternary compound, and the 90–95-K materials based on the quaternary $Ba_2YCu_3O_7$. Among their similarities is the presence of CuO_2 planes with a nearly square lattice. It is now largely accepted that a BCS mechanism based upon phonon-induced pairing cannot account for the high superconducting transition temperatures. Alternative theoretical approaches have been suggested,[3] invoking nonphonon pairing mediators of relatively high energy. These mechanisms include excitons, polarons, plasmons, spin fluctuations, and others. A lack of experimental evidence has prevented the testing of these theoretical ideas. Very recently, neutron-scattering experiments[4] in (nonsuperconducting) La_2CuO_4 revealed strongly correlated spin fluctuations of a two-dimensional nature, but could not determine their dynamics. Our inelastic light-scattering studies of this system[5] have demonstrated that the spin fluctuations in $La_{2-x}CuO_{4+\delta}$ are characterized by an extremely large exchange energy with $J\simeq 1100$ cm^{-1}$=137$ meV. These results all pertain to a nonsuperconducting system. Until now no experimental evidence has been reported on such excitations in the superconductors themselves.

In this Letter we report the first spectroscopic observation of highly energetic spin excitations in a high-temperature superconductor. We find that their behavior is correlated with carrier concentration. In particular, as detailed below, we have observed inelastic light-scattering spectra due to spin-pair excitations in single crystals of $Ba_2YCu_3O_{6+\delta}$ for several values of δ in the range 0.0–0.9. The energies of these spin pairs, as well as the spectral line shapes, depend strongly on δ and weakly on temperature over the interval studied. The typical spin-pair energies of 1000–2700 cm^{-1} are large enough to give rise to carrier pairing energies sufficient to permit the high-temperature superconductivity.

Spectra reported here were excited with 4579, 4880, and 5145 Å from a cw argon-ion laser, with an incident power of roughly 100 mW, focused to a line 0.1×2 mm^2 in size on the unpolished surface of the single-crystal samples. A prism monochromator was utilized to remove plasma fluorescence from the incident beam and the scattered light was analyzed by a double-grating spectrometer, with photon-counting electronics. Spectra were not corrected for the spectral response of the detection equipment. The samples for this study were oriented by x-ray diffraction. Since the crystals were microtwinned in the basal plane, we could not distinguish x from y in the crystallographic sense. As an extension of the notation used previously,[5] we define $y=(100)$ or $y'=(110)$ to lie in the scattering plane, with x (x') perpendicular to it. We use the conventional notation for the $Ba_2YCu_3O_7$ system, where the Cu—O bonds in the planes lie along (100).

The crystals of $Ba_2YCu_3O_{6+\delta}$ were grown from a partially melting mixture of barium oxide, copper oxide, and yttrium oxide in alumina or zirconia crucibles.[6] Slow cooling in an air atmosphere produced single-crystal platelets of $\simeq 80$ μm thickness (in the c direction) and several millimeters lateral extent. The as-grown crystals are superconducting with onset (at the surface) typically 60 K, indicating the nominal value $\delta\simeq 0.6$–0.7 at the surface and lower in the crystal interior. Several samples were annealed in oxygen, air, or nitrogen atmospheres to modify δ in a controlled fashion from this as-grown condition. Oxygen annealing produced $\delta\rightarrow 1$ with a superconducting T_c near 90 K, while nitrogen annealing reduced T_c and after 2 h annealing at 700 °C rendered samples fully nonsuperconducting. Conditions established for the control of oxygen stoichiometries in ceramic samples[7] were utilized to produce single-crystal samples with intermediate δ values. Raman scattering in zz (edge) geometry, with use of a microprobe, was used to probe oxygen stoichiometry[8,9] in some of the samples.

None of our samples show magnetic susceptibility peaks between 4 K and room temperature, indicating an absence of magnetic ordering transition in this range. However, we cannot exclude a value of T_N above room temperature.

Figure 1 shows inelastic light-scattering spectra at room temperature for nonsuperconducting crystals, excited with several different laser wavelengths. The

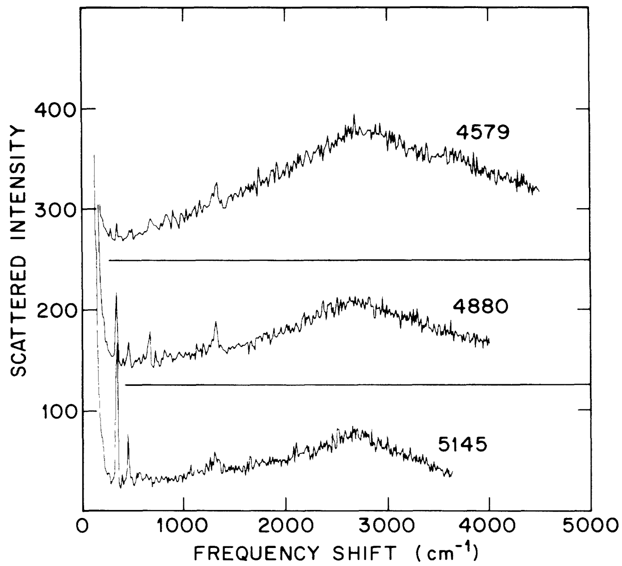

FIG. 1. Three spectra obtained at 20 K in *yy* geometry on a $Ba_2YCu_3O_{6+\delta}$ sample annealed at 700 °C for 2 h in N_2 to provide $\delta \cong 0.0$. The three traces are obtained at the indicated incident laser wavelengths. The base lines for all three traces are shown individually. The laser power for the run at 4579 Å is half that of the other two.

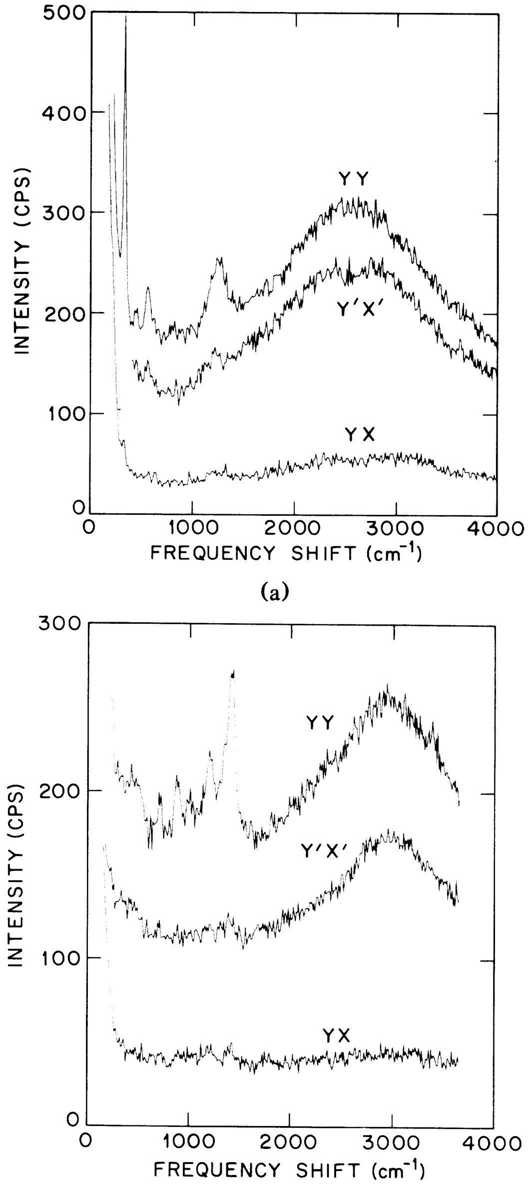

FIG. 2. (a) Spectra obtained for $Ba_2YCu_3O_{6+\delta}$ with $\delta = 0.0$ (nonsuperconducting) in three geometries relative to the basal plane. The *yy* trace is shifted 50 cps upward for display, otherwise the scales are identical. Incident wavelength is 4880 Å. (b) A similar set of spectra for $La_{2-x}CuO_{4+\delta}$.

feature of primary interest here is the broad peak centered at 2600 cm^{-1} frequency shift. Although no prior experimental evidence exists[10] for spin correlations in $Ba_2YCu_3O_{6+\delta}$, we interpret this feature as a spin-pair excitation by virtue of the similarities to the $La_{2-x}CuO_{4+\delta}$ spectra.[5] The polarization selection rules are identical to those for $La_{2-x}CuO_{4+\delta}$. As seen in Fig. 2, the peak is observed in *yy* and *y'x'* geometries, but not in *yx*, in both materials. Here the first and second indices refer to the polarization directions of the incident and scattered electric fields, respectively. The directions *x* and *y* are those which connect the Cu nearest neighbors in the planes. Attempts to verify the predicted absence of *zz* scattering[5] in $Ba_2YCu_3O_{6+\delta}$ have thus far failed because of technical difficulties in achieving fluorescence-free spectra from the edges of the $\simeq$80-μm-thick plates.

Not only are the observed selection rules in $Ba_2YCu_3O_{6+\delta}$ the same as those of $La_{2-x}CuO_{4+\delta}$, but the frequencies and line shapes observed are similar as well. In the latter material, long-range antiferromagnetic order is known to develop between 50 and 300 K for a range of x and δ values.[11] Neutron scattering has verified the development of antiferromagnetic order and the existence of antiferromagnetic spin fluctuations of 2D character with long-range instantaneous correlations.[4,11] Although analogous neutron experiments have not yet been performed for the $Ba_2YCu_3O_{6+\delta}$ system, the similarity in the Cu-O planar structure to that of La_2CuO_4 strongly suggests that they should sustain similar excitations and dynamics.[10] Our spectra represent direct experimental evidence for this expectation.

As Fig. 2 demonstrates strikingly, the magnetic scattering exhibits distinctive selection rules. Parkinson[12] has provided a theory which describes in quantitative detail the B_{1g} spectra observed[13] in K_2NiF_4. An instructive way of obtaining the weighting factors as a function of $\mathbf{k}$ was explicated by Fleury and Loudon.[14] Their technique may be applied to the scattering Hamiltonian given by Parkinson[12] for the K_2NiF_4 structure:

$$\sum_{\sigma_{ij}}(\mathbf{E}\cdot\boldsymbol{\sigma}_{ij})(\mathbf{E}'\cdot\boldsymbol{\sigma}_{ij})\mathbf{S}_i\cdot\mathbf{S}_j \tag{1}$$

where $\mathbf{E}$ and $\mathbf{E}'$ are the incident and scattered electric fields and the sum is carried out over all nearest-neighbor vectors $\boldsymbol{\sigma}_{ij}$. To understand the contribution from magnons at any given $\mathbf{k}$, we first expand the spin operators in terms of magnon operators. The contribution of the magnon pair at $\mathbf{k},-\mathbf{k}$ is proportional to $[F_{EE'}(\mathbf{k})]^2$, where $F_{EE'}(k)$ is a trigonometric factor which depends on the orientations of $\mathbf{E}$ and $\mathbf{E}'$. Choosing axes as above, we have $\sigma_1=\pm(100)$ and $\sigma_2=\pm(010)$, from which we obtain

$$F_{yy}=\cos k_y a,\quad F_{y'y'}=\tfrac{1}{2}[\cos k_y a+\cos k_x a],$$
$$F_{y'x'}=\tfrac{1}{2}[\cos k_x a-\cos k_y a], \tag{2}$$
$$F_{yx}=F_{zz}=F_{yz}=F_{xz}=0.$$

Hence, we expect scattering only in $y'x'$, yy, and $y'y'$ geometries. Note that these selection rules (for a single pair of magnon modes) do not correspond to any single symmetry type in the tetragonal point group. This property, a signature of a pair-excitation process, stems from the fact that a pure symmetry state involves a superposition of all eight elements in the *star* of $\mathbf{k}$, not just the two at $\mathbf{k}$ and $-\mathbf{k}$. In the actual point group, C_2, symmetry considerations do little to restrict the selection rules. However, using the fact that the structure is nearly tetragonal (D_{2d}), we find that the representation spanned by the magnon-pair states in the star of a general $\mathbf{k}$ in the xy plane spans a representation which includes both A_{1g} and B_{1g} symmetries. B_{2g} is also included, but is prohibited by the coefficient of $\mathbf{S}_i\cdot\mathbf{S}_j$ in the Hamiltonian (1). Thus, if we ignore the deviation from tetragonality, the only in-plane symmetry prohibited in this case is pure xy. The only spectral feature that fits this description is the one centered at 2600 cm^{-1}. We note, in particular, that the feature near 1200 cm^{-1} in $Ba_2YCu_3O_7$ (near 1500 cm^{-1} in La_2CuO_4) is absent in $y'x'$, and thus cannot be due to two-magnon scattering. Its energy in both cases appears appropriate for defect-induced scattering from a *single* spin flip next to a vacancy, but it is not clear that such a mechanism would yield the observed selection rules.

From Eqs. (2) it is evident that the A_{1g} and B_{1g} components in the pseudotetragonal symmetry correspond to different averages over the Brillouin zone. The B_{1g} component ($F_{y'x'}$) emphasizes the zone boundary while the A_{1g} ($F_{y'y'}$) excludes it. (An analogous difference occurs[15] in $RbMnF_3$.) Although it is not displayed here, for lack of space, we have measured the $y'y'$ spectrum and confirmed this qualitative prediction.

In the $y'x'$ geometry the B_{1g} spin-pair mode dominates the spectrum of the N_2-annealed sample. Using this geometry, we have carried out experiments on sam-

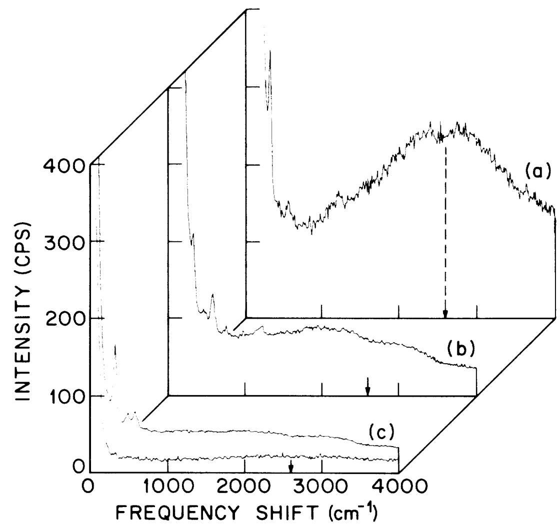

FIG. 3. Room-temperature $y'x'$ spectra of $Ba_2YCu_3O_{6+\delta}$ platelets for various values of δ. Sample (a) is annealed 2 h at 700 °C in N_2 to remove the superconducting behavior entirely ($\delta\cong 0.0$). Spectrum is averaged 6 s per point. The arrow and dashed line indicates the center of the peak, for reference. Sample (b) is annealed at 600 °C in air for 30 h to equilibrate δ at about 0.6, giving a measured superconducting transition temperature of 60 K. Spectrum averaged 66 s per point. Sample (c) is annealed in oxygen to obtain $\delta\cong 0.9$ with a measured bulk superconducting transition at 88 K. Incident wavelength is 4880 Å. The upper and lower traces displayed in (c) are for the $y'x'$ and yx geometries, respectively, averaged for 96 and 24 s per point. All spectra are displayed with the same vertical gain, with scales displaced as indicated. The arrows in parts (b) and (c) indicate the peak position shown in part (a).

ples annealed to provide a range of δ values. A comparison of three of these is shown in Fig. 3. The semiconducting ($\delta\simeq 0.0$) sample exhibits a well-defined peak at 2600 cm^{-1}. If we assume that this feature arises from magnon pairs, as in K_2NiF_4 and La_2CuO_4, and that the system may be approximated as a square-lattice, 2D, spin-$\frac{1}{2}$ Heisenberg system, with only nearest-neighbor interactions, we expect the peak spectral response to lie at $\omega_{2m}=2.7J$.[12,16] Thus, we obtain $J\approx 950$ cm^{-1} for $\delta\simeq 0.0$.

The line shape is not well reproduced by that calculated for magnon-pair scattering in a planar antiferromagnet. Applying the results of Parkinson[12] for spin $\frac{1}{2}$ we obtain a zero-temperature width (FWHM) of $\simeq 0.32J$, far smaller than that observed ($\sim J$). In La_2CuO_4 the width observed is $\sim 0.7J$. The origin of the additional broadening is not yet understood, even in the semiconducting samples of $YBa_2Cu_3O_6$. Contributions could arise from finite temperature, the presence of mobile holes, the nonlinear influence of fluctuations, or the possibility that the ground state of the system is not a simple Néel state. With regard to the latter possibility, we note that our quantitative result for J is model dependent. It is probably not seriously in error, since the interaction is short range and the B_{1g} component depends mainly on short-range correlation. However, a truly quantitative result must await development of a theory which reproduces the details of the line shapes observed. Our experiments should provide guidance for the development of such a theory.

In the semiconducting sample the observed temperature dependence of the line shape is slight, as was observed in La_2CuO_4 as well.[5] Preliminary observations indicate the same for $\delta > 0$. More extensive temperature experiments are not underway.

The main effect of increasing δ, in addition to raising T_c, is a broadening and weakening of the spin-pair peak, while its center of gravity moves to lower-frequency shift. This behavior is qualitatively similar to that observed[17] for magnon-pair spectra in diluted antiferromagnetic insulators. It suggests then that the spin system in the planes is diluted (that is, spins are removed) as the oxygen concentration is increased. We note, though, that other factors may have an influence. For example, the increase of the a and c lattice constants known to accompany oxygen removal in $Ba_2YCu_3O_{6+\delta}$ may provide an additional modifying effect on the exchange energy as δ is varied.

In summary we have presented measurements of spin dynamics in the high-temperature oxide superconductors. The high energy of the observed spin-pair excitations corresponds to an antiferromagnetic exchange energy of $J \cong 950\ cm^{-1}$, within a Heisenberg spin-$\frac{1}{2}$ model for the CuO_2 planes. Importantly, on the one hand, the spin fluctuations are shown to persist into the superconducting composition while, on the other hand, the spin dynamics are shown to be influenced by the carrier concentration δ, thereby demonstrating that the spins and carriers are coupled. Although spin-mediated carrier pairing has not been confirmed, the large value of J suggests that such pairing could occur at quite high temperatures ($\simeq 1000$ K). It is clear from these results that any theory of superconductivity in the copper oxides must account explicitly for these highly energetic spin fluctuations.

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[1]K. Kishio, K. Kitizawa, S. Kanabe, I. Yasuda, N. Sugii, H. Takagi, S.-I. Uchida, K. Fueki, and S. Tanaka, Chem. Lett. No. 2, 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 *Proceedings of the International Workshop on Novel Mechanisms of Superconductivity, Berkeley, California, 1987,* edited by S. A. Wolf and V. Z. Kresin (Plenum, New York, 1987).

[4]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).

[5]K. B. Lyons, P. A. Fleury, J. P. Remeika, T. J. Negran, Phys. Rev. B **37**, 2353 (1988).

[6]L. F. Schneemeyer, J. V. Waszczak, T. Siegrist, R. B. van Dover, L. W. Rupp, B. Batlogg, R. J. Cava, and D. W. Murphy, Nature (London) **328**, 601 (1987).

[7]P. K. Gallagher, Adv. Ceram. Mater. **2**, 632 (1987).

[8]M. Stavola, D. M. Krol, W. Weber, S. A. Sunshine, A. Jayaraman, G. A. Kourouklis, R. J. Cava, and E. A. Reitman, Phys. Rev. B **36**, 850 (1987).

[9]D. M. Krol, M. Stavola, W. Weber, L. F. Schneemeyer, J. V. Waszczak, S. Zahurak, and S. Kosinski, Phys. Rev. B **36**, 8325 (1987).

[10]After submission of this work, reports have appeared of a magnetic ordering above room temperature for small δ. See N. Nishida *et al.*, Jpn. J. Appl. Phys. Pt. 1 **26**, L1856 (1987).

[11]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, Phys. Rev. Lett. **59**, 1045 (1987).

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

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

[14]P. A. Fleury and R. Loudon, Phys. Rev. **166**, 514 (1968).

[15]R. J. Elliott and M. F. Thorpe, J. Phys. C **2**, 1630 (1969).

[16]D. Huse, private communication.

[17]P. A. Fleury, W. Hayes, and H. J. Guggenheim, J. Phys. C **8**, 2183 (1975).