Spin Fluctuations in Superconducting $YBa_2Cu_3O_{6.5}$

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Antiferromagnetic spin fluctuations in superconducting $YBa_2Cu_3O_{6+x}$ have been studied using inelastic neutron scattering. In a crystal with $x=0.5$ and $T_c=50$ K, we have observed spin fluctuations at 12 K having a cross section which increases with increasing excitation energy. The data are consistent with highly overdamped spin waves and a very short spin-spin correlation length.

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The existence of spin fluctuations in copper-oxide superconductors is crucial to magnetic models[1] of the superconducting mechanism. Antiferromagnetic spin fluctuations have recently been observed directly by neutron scattering[2] in a single crystal of $La_{1.85}Sr_{0.15}CuO_4$ with $T_c=33$ K, and their presence in metallic $YBa_2Cu_3O_{6+x}$ has been inferred from Cu nuclear relaxation rates.[3] On the other hand, in a neutron-scattering study of polycrystalline $YBa_2Cu_3O_7$ using polarized neutrons,[4] the low-energy inelastic magnetic scattering cross section was found to be negligible, and it was concluded that the Cu atoms have essentially no magnetic moment.

We recently reported[5] an initial study of three large, orthorhombic crystals of $YBa_2Cu_3O_{6+x}$ with $x=0.4$, 0.45, and 0.5 having superconducting transition temperatures $T_c=25$, 45, and 50 K, respectively. Inelastic neutron-scattering measurements performed at Risø National Laboratory revealed strong antiferromagnetic excitations at low temperature in the two crystals with lower oxygen contents; however, at an excitation energy of 3 meV the cross section was strongly diminished in the sample with $T_c=50$ K. A clue to the drastic change in scattering comes from a very recent spin rotation (μSR) study of a series of powder samples.[6] Static magnetic order was observed at $T<0.1$ K for $x\lesssim 0.5$; the magnetic component was absent only in samples with $T_c\gtrsim 50$ K. Thus, we suspect that the $x=0.4$ and 0.45 crystals are magnetically inhomogeneous; the scattering from the $x=0.5$ crystal should be more representative of the metallic phase of $YBa_2Cu_3O_{6+x}$. In order to determine the cross section at higher excitation energies, further measurements have been performed at the NRU reactor at Chalk River Nuclear Laboratories. Here we report new results at excitation energies up to 15 meV measured at a temperature of 12 K for the $x=0.45$ and 0.5 crystals. We find that spin fluctuations are still present in the $x=0.5$ sample. Though small at low energy, the magnetic cross section increases significantly at higher excitation energies to a magnitude roughly comparable with that observed in magnetically ordered crystals.

The measurements were performed at triple-axis spectrometer L3 using a strained Si(111) monochromator crystal and the (002) reflection of pyrolytic graphite for the analyzer. Collimations of 53′ and 60′ were used from monochromator to sample to analyzer, with open collimation from reactor to monochromator and analyzer to detector. All measurements were taken with a final neutron energy of 14.7 meV and with a pyrolytic graphite filter after the sample to eliminate higher-order neutrons. Each sample was held in a small Al box, which was mounted inside an Al can with He exchange gas. The sample container was fastened to the cold finger of a closed-cycle refrigerator. Detailed characterizations of the crystals are given in Ref. 5; the lattice parameters are listed in Table I.

Each crystal was mounted with its $[1\bar{1}0]$ axis vertical, so that we could study scattering in the (hhl) scattering zone. Elastic magnetic scattering from a single Néel ordered CuO_2 plane would occur along the rod $(\frac{1}{2},\frac{1}{2},l)$. For antiferromagnetically coupled bilayers as occur in tetragonal $YBa_2Cu_3O_{6+x}$, the scattered intensity for acoustic spin waves is modulated by a factor $\sin^2(\pi z l)$, where zc is the spacing between two CuO_2 layers along the c axis.[7,8] Despite the fact that no long-range magnetic order could be detected in the orthorhombic crystals, the scattering from spin fluctuations at 3 meV exhibited the same acoustic mode modulation in the $x=0.4$ and 0.45 crystals at 11 K.[5] In order to characterize the spin fluctuations as a function of the two-dimensional

TABLE I. Oxygen content, superconducting transition temperature T_c, and room-temperature lattice parameters for the two $YBa_2Cu_3O_{6+x}$ single crystals studied by neutron scattering (from Ref. 5).

x	T_c (K)	a (Å)	b (Å)	c (Å)
0.45	45	3.855	3.878	11.744
0.5	50	3.846	3.884	11.739

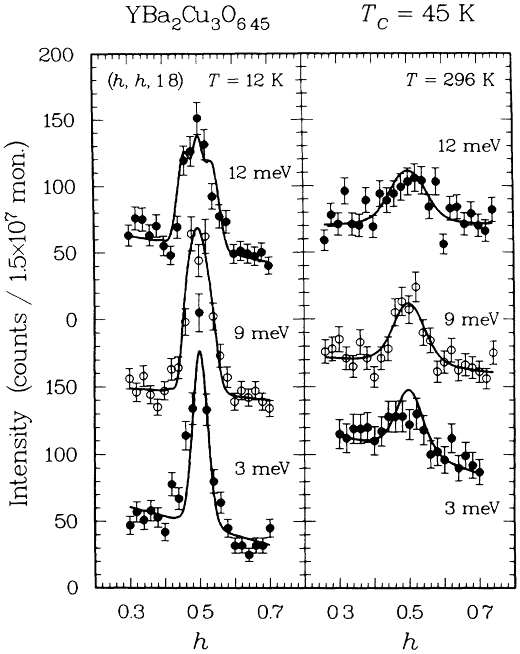

FIG. 1. Constant-E scans across the 2D antiferromagnetic rod at $E=3$, 9, and 12 meV and $T=12$ and 296 K measured on the $YBa_2Cu_3O_{6.45}$ crystal. Solid lines are fits using Eq. (1) as discussed in the text. Counting time varied from 10 min/point at 12 meV to 20 min/point at 3 meV. The higher background at 296 K is probably caused by scattering from N_2 inadvertently present in the sample can.

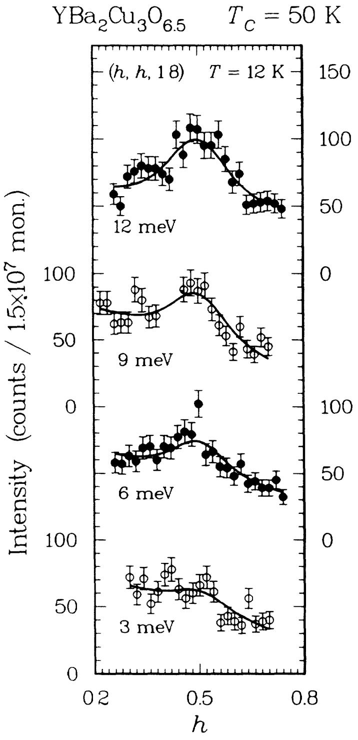

FIG. 2. Constant-E scans across the 2D antiferromagnetic rod at $E=3$, 6, 9, and 12 meV and $T=12$ K measured on the $YBa_2Cu_3O_{6.5}$ crystal. Solid lines are fits using Eq. (1) as discussed in the text.

(2D) wave vector, we have performed scans at a constant-energy transfer (in energy-loss mode) in which the momentum transfer **Q** is scanned perpendicular to the 2D scattering rod [scans of type A in Fig. 1(b) of Ref. 7]. Examples of such constant-E scans measured for the $x=0.45$ and 0.5 crystals at 12 K are shown in Figs. 1 and 2. (The scans were performed at a point l along the rod where the acoustic-mode modulation along the rod is a maximum.) For both samples, the scattering is found to peak on the rod and to have a peak width significantly broader than resolution. Note that for measurements in this energy range on magnetically ordered crystals, spin waves could not be resolved because of the extremely high spin-wave velocity, so that a single resolution-limited peak was observed.[7-9]

The intensity as a function of excitation energy at the point $\mathbf{Q}=(\frac{1}{2},\frac{1}{2},1.8)$ is shown more clearly in Fig. 3. The background signal as determined from the constant-E scans has been subtracted from these data. The scattering volumes for the two crystals, estimated from measurements of longitudinal phonons at (0,0, 6.25), are very similar (~ 1 cm^3),[5] so it is reasonable to compare the scattered intensities on the same absolute scale. For the $x=0.45$ sample, the intensity peaks at low energy and decreases as the energy increases. As observed previously, the signal from the $x=0.5$ crystal is strongly depressed at low energy; however, now we see that the intensity increases with energy until at 15 meV the intensity is similar to that for the $x=0.45$ sample. It is also comparable to that for a magnetically ordered

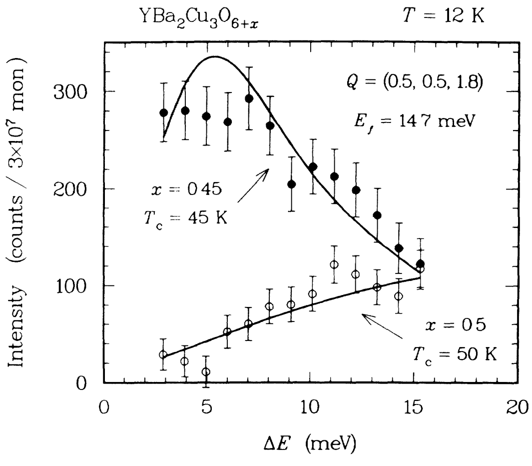

FIG. 3. Constant-**Q** scans measured at $\mathbf{Q}=(\frac{1}{2},\frac{1}{2},1.8)$ and $T=12$ K on the $x=0.45$ (solid circles) and $x=0.5$ (open circles) crystals. A constant background value has been subtracted from each set of data. The solid lines are fits using Eq. (1) as discussed in the text.

crystal[8] with $x=0.3$. The measurements at 296 K on the $x=0.45$ sample (see Fig. 1) show that the scattered intensity has decreased at all energies.

In a study[2] of magnetic excitations in $La_{1.85}Sr_{0.15}CuO_4$ it was suggested that the decrease in the low-energy inelastic cross section below 150 K might occur due to the opening of a gap in the spin excitation spectrum. Motivated by that work, we wanted to test whether the depression of the low-energy cross section for the $x=0.5$ sample could be interpreted *without* invoking a gap. In the absence of specific theoretical predictions, we decided to model the data with the standard formula for paramagnetic scattering from a system of correlated spins:[10]

$$S(\mathbf{Q},\omega)=\frac{\hbar\omega}{1-e^{-\hbar\omega/kT}}\frac{A}{\kappa^2+q^2}\left[\frac{\Gamma}{(\hbar\omega-\hbar\omega_{\mathbf{q}})^2+\Gamma^2}+\frac{\Gamma}{(\hbar\omega+\hbar\omega_{\mathbf{q}})^2+\Gamma^2}\right], \tag{1}$$

where $\mathbf{q}=\mathbf{Q}-\mathbf{Q}_{\text{rod}}$, $\mathbf{Q}_{\text{rod}}=(\frac{1}{2},\frac{1}{2},l)$, and κ is the inverse of the correlation length ξ. The frequencies of the damped spin waves are taken to be $\omega_{\mathbf{q}}=cq$, where c is the spin-wave velocity. Comparing Eq. (1) with the formula used by Tyč, Halperin, and Chakravarty[11] to parametrize their numerical results for the 2D Heisenberg antiferromagnet, the two are quite similar if we set $\Gamma/\hbar\equiv\kappa c$. This condition means that a spin wave with $q<\kappa$ (i.e., $\lambda>\xi$) is overdamped. We assume that essentially all of the magnetic scattering comes from the CuO_2 layers, which seems quite reasonable considering the strong intensity modulation due to bilayer coupling observed in the $x=0.4$ and 0.45 crystals.[5] Note that for $T=0$ and $\mathbf{q}=0$, Eq. (1) reduces to

$$S(\mathbf{q}=0,\omega)\,|_{T=0}=\frac{2A}{\kappa^2\Gamma}\frac{\hbar\omega}{(\hbar\omega/\Gamma)^2+1}, \tag{2}$$

which has a peak at $\hbar\omega=\Gamma$. To compare the model scattering function with the data it is necessary to convolve it with the spectrometer resolution function.

The energy dependence of the cross section at 12 K (see Fig. 3) should be described by Eq. (2). Fitting this data yields Γ values of 2.5 and 30 meV for the $x=0.45$ and 0.5 samples, respectively. Thus, the low-energy depression observed for $x=0.5$ can be explained as a strong damping of the spin fluctuations rather than as evidence for a gap. With $\Gamma/\hbar=\kappa c$, and assuming $\hbar c$ to be the same for the two samples, the increased damping can be explained by a reduced correlation length. A much longer correlation length for the $x=0.45$ sample would be consistent with the recent μSR work.[6]

Can the temperature dependence of the scattering for the $x=0.45$ sample be properly modeled with Eq. (1)? Assuming that the only temperature-dependent parameter is κ, the values of κ, $\hbar c$, and A were adjusted by trial and error (with κc constrained to equal $\Gamma/\hbar$) to obtain a reasonable fit to the data at both temperatures. (A linear background was also included.) The results are the solid curves in Fig. 1, which were calculated using the parameters shown in Table II. The curves in Fig. 2 for $x=0.5$ were calculated using the same $\hbar c$ and with $\kappa=\Gamma/\hbar c$ (see Table II).

One problem with the present analysis is that the widths of the peaks in Fig. 1, which appear to be more or less independent of energy, are poorly described. This deficiency could be remedied by allowing the overdamped spin waves to disperse out of incommensurate $\mathbf{q}$ rods, rather than $\mathbf{q}=0$ (at the expense of introducing a new parameter). There is experimental evidence[2,12] for such incommensurate behavior in $La_{2-x}Sr_xCuO_4$. Furthermore, several theoretical analyses predict spin canting[13] about holes or domain-wall formation[14] which might lead to incommensurate inelastic scattering. Inclusion of such effects would lead to quite different absolute values of κ and c, but Γ would change relatively little.

The present experimental results provide clear evidence for significant antiferromagnetic spin fluctuations in superconducting $YBa_2Cu_3O_{6+x}$. In their study of $YBa_2Cu_3O_7$, Brückel *et al.*[4] assumed that the total magnetic scattering for any Cu spins present would be distributed over a very small energy range. Integrating only over low energies ($\hbar\,|\omega|<12$ meV at 110 K), they observed a negligible magnetic cross section and concluded that no spins are present. We have shown for an $x=0.5$ sample that while the magnetic cross section is strongly damped at low energies, it becomes quite significant at higher energies. Determination of the net spin density would require integration over a much larger energy scale. Also, the strong damping of the spin fluctuations provides a useful signature—the observed scattering for $x=0.5$ cannot be explained by a magnetic impurity with a long correlation length.

Although we have not demonstrated a direct connection between spin fluctuations and superconductivity, it is of interest to consider what such a connection might imply in different models.[15] Suppose that Cu and hole spins combine to form quasiparticles which, in turn, pair up in a BCS superconducting state. In that case, one might expect a gap to form in the spin fluctuation spec-

TABLE II. Parameters for the model scattering function, Eq. (1), which were adjusted by trial and error to obtain a reasonable fit to the experimental data.

x	T (K)	A	$\hbar c$ (meV Å)	κ ($Å^{-1}$)
0.45	12	9	100	0.025
0.45	296	9	100	0.13
0.5	12	200	100	0.3

trum below T_c, with a minimum value at $T \ll T_c$ of $2\Delta = 3.5kT_c \approx 15$ meV for $T_c = 50$ K. Suppose, on the other hand, that the holes pair by interacting with the Cu spins, but that the hole and Cu spins retain their individual identities. In that case, as for phonons in a superconductor where electron-phonon coupling causes pairing, the damping of the spin waves should decrease below T_c, but not gap should appear. Although we lack adequate measurements of the temperature dependence, the observation of strong spin fluctuation scattering below the BCS gap energy tends to favor the latter picture.

Very recently we were informed by Rossat-Mignod of his group's current neutron-scattering study[16] of an $x = 0.45$ crystal with $T_c = 35$ K. While the magnetic cross section they have observed at 5 K is similar to the data for our $x = 0.5$ crystal shown in Fig. 3, they suggest that a magnetic gap might exist for $\hbar\omega \lesssim 2$ meV. We have argued here that our results can be modeled without invoking any gaps. Further experimental and theoretical work is required to establish a better understanding of the magnetic correlations in these superconducting samples. Nevertheless, the observation of magnetic correlations drastically modified by a high concentration of holes in superconducting $YBa_2Cu_3O_{6.5}$ seems to provide further support for magnetic pairing theories.

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[1] For examples, see the following reviews: T. M. Rice, Z. Phys. B **67**, 141 (1987); V. J. Emery, MRS Bull. **14**, 67 (1989).

[2] G. Shirane *et al.*, Phys. Rev. Lett. **63**, 330 (1989).

[3] M. Horvatić *et al.*, Phys. Rev. B **39**, 7332 (1989); C. H. Pennington *et al.*, *ibid.* **39**, 274 (1989); W. W. Warren, Jr., *et al.*, Phys. Rev. Lett. **62**, 1193 (1989).

[4] T. Brückel *et al.*, Europhys. Lett. **4**, 1189 (1987).

[5] G. Shirane *et al.*, Phys. Rev. B (to be published).

[6] R. F. Kiefl *et al.*, Phys. Rev. Lett. **63**, 2136 (1989).

[7] M. Sato *et al.*, Phys. Rev. Lett. **61**, 1317 (1988).

[8] J. M. Tranquada *et al.*, Phys. Rev. B **40**, 4503 (1989).

[9] C. Vettier *et al.*, Phys. Scr. **T29**, 110 (1989).

[10] W. Marshall and R. D. Lowde, Rep. Prog. Phys. **31**, 705 (1968).

[11] S. Tyč, B. I. Halperin, and S. Chakravarty, Phys. Rev. Lett. **62**, 835 (1989).

[12] T. R. Thurston *et al.*, Phys. Rev. B **40**, 4585 (1989).

[13] A. Aharony *et al.*, Phys. Rev. Lett. **60**, 1330 (1988); B. I. Shraiman and E. D. Siggia, Phys. Rev. Lett. **62**, 1564 (1989); A. Mauger and D. L. Mills, Phys. Rev. B **40**, 4913 (1989).

[14] N. Bulut, D. Hone, D. J. Scalapino, and N. E. Bickers (to be published); H. J. Schulz (to be published).

[15] T. M. Rice, Phys. Scr. **T29**, 72 (1989).

[16] J. Rossat-Mignod *et al.*, in Proceedings of the International Conference on the Physics of Highly Correlated Electron Systems, Sante Fe, New Mexico, 11-15 September 1989 [Physica B (to be published)]; J. Rossat-Mignod (private communication).