Magnetic correlations in $YBa_2Cu_3O_{6+x}$ at superconducting concentrations

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Neutron-scattering measurements have been carried out on three large single crystals of $YBa_2Cu_3O_{6+x}$ with superconducting transition temperatures $T_c=25$, 45, and 50 K. Strong two-dimensional magnetic correlations are found in the first two, and the magnetic cross sections at low temperatures are almost as strong as in compounds with smaller x. However, the magnetic intensities at low energies below 10 meV decrease considerably on heating to 300 K. A large decrease of the magnetic inelastic cross section was observed in the third sample ($T_c=50$ K) relative to the first two at these low energies. The implications of these results are discussed.

I. INTRODUCTION

Spin correlations in the high-T_c oxides have been extensively investigated by neutron-scattering techniques.[1] A major unresolved problem concerns the magnetic correlations in $YBa_2Cu_3O_{6+x}$ in the superconducting compositions with $x \geq 0.4$. Two-magnon Raman scattering[2] as well as NMR measurements[3] have indicated strong coupling of Cu^{2+} magnetic moments. On the other hand, neutron-scattering studies[4] reported a nonobservable magnetic cross section at $x=1$. It is important to characterize how the magnetic correlations which are observed in concentrations below $x=0.4$ (see Fig. 1) are transformed when superconductivity sets in at higher values of x. This aspect of the magnetism in the $La_{2-y}Sr_yCuO_4$ system has already been investigated.[5,6] With increasing dopant concentration y, the correlation length becomes shorter but the integrated magnetic cross sections at low energies remain unchanged below 300 K. In the superconducting crystal of $y=0.15$ ($T_c=33$ K) an anomalous intensity decrease around 150 K was observed on cooling.[6]

We have investigated in this paper, by neutron-scattering techniques, three large single crystals with oxygen concentration x in the range of $x=0.4$ to 0.5; these are superconductors, but they are close to the region of magnetic long-range order in the phase diagram. The crystals were grown and treated at the Institute for Molecular Science, and the details have been described elsewhere.[7] The oxygen content was controlled by annealing in an argon or oxygen atmosphere at 470–700 °C. To obtain large crystals it was necessary to start with a mixture rich in Ba and Cu. "Ingot crystals" can contain large crystals of $YBa_2Cu_3O_{6+x}$ as well as polycrystalline $BaCuO_2$ impurities. The best samples (subsequently referred to as Nos. 29 and 30) contain a large fraction of

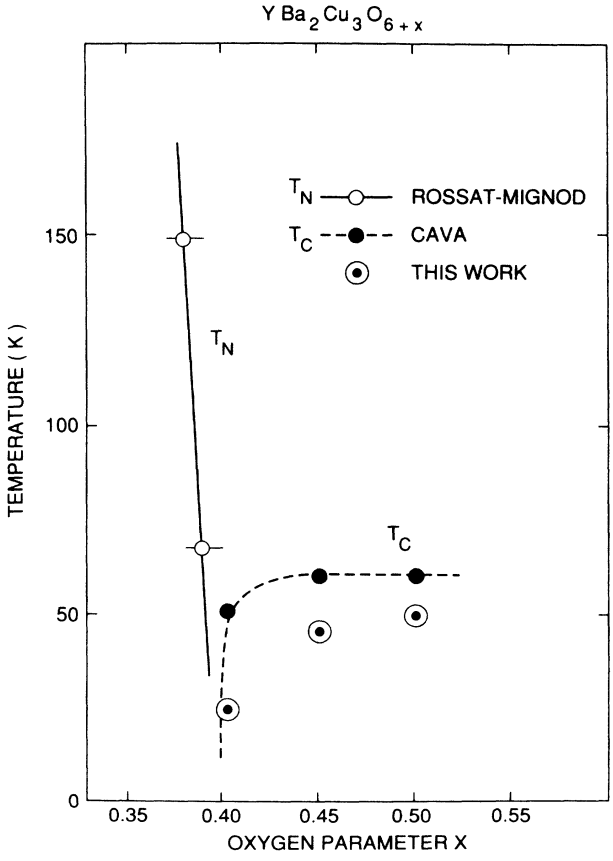

FIG. 1. Phase diagram of $YBa_2Cu_3O_{6+x}$ near the magnetic-superconducting boundary $x=0.4$. Open circles are data for T_N taken from Rossat-Mignod (Ref. 9) and solid circles are data for T_c taken from Cava *et al.* (Ref. 12).

uniquely oriented crystal blocks of nearly 1 cm^3 volume with a mosaic spread less than 2°.

This report follows our previous neutron-scattering studies of single crystals of $YBa_2Cu_3O_{6+x}$.[7,8] Meanwhile Rossat-Mignod *et al.*[9,10] also carried out extensive neutron-scattering experiments on the same system. These previous studies have established the magnetic phase diagram (see Fig. 1) and the two-dimensional correlations in the CuO_2 planes. The present paper reports our first successful attempt to extend the measurements to the superconducting concentrations.

II. SAMPLE CHARACTERIZATION

The overall phase diagram of the $YBa_2Cu_3O_{6+x}$ system is now well established, as shown in Fig. 1. However, not all physical properties are a unique function of the single oxygen parameter x.[11–13] Ordering of oxygen in the chain layers is also important, and different annealing conditions can shift the orthorhombic-tetragonal boundary considerably. For our phase diagram we have decided to adapt the lattice parameters given by Cava *et al.*[12]. This is also consistent with the phase diagram given by Rossat-Mignod *et al.*[9] At present we have no direct way to determine x of the very samples used in neutron scattering except for lattice parameters and superconducting transition temperature T_c. It is very important to measure the properties of the whole crystals, as small pieces chipped off an edge may not be representative of the bulk.

All of the ingot crystals are too big for SQUID measurements of the Meissner effect. Thus, transition temperatures T_c were obtained by a simple measurement of the ac susceptibility. Two coils of 50 turns were wound directly around the sample, and the mutual inductance was monitored as a function of temperature. The frequency was 300 Hz, and the ac magnetic field was less than 0.01 G. As shown in Fig. 2 the single-crystal samples do not show as sharp a drop as a fully oxydized polycrystalline sample does. This broadening effect is probably due to small inhomogeneities in the oxidation level combined with a rapid variation of T_c with x in this region of x. The implication of the inhomogeneities for the interpretation of the diffraction results will be discussed later.

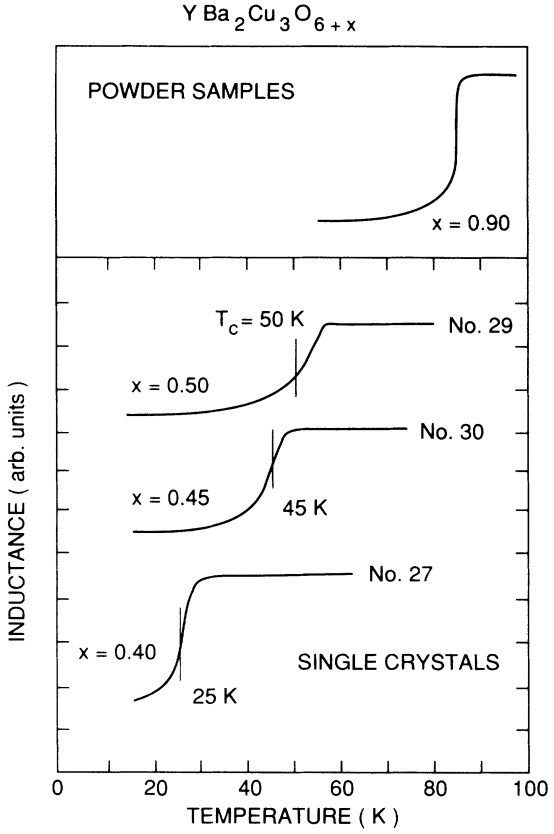

FIG. 2. T_c determination by ac induction method. Top figure shows typical data for powder samples obtained by the identical setup.

The results of high resolution measurements of the lattice constants of these single crystals are listed in Table I. These measurements were done at relatively tight collimations and at two neutron energies, 13.7 and 8.4 meV. Cava *et al.*[11,12] emphasized that the abrupt jump of the c lattice parameter takes place *within* the orthorhombic phase and not at the boundary to the tetragonal phase. Sample No. 27 corresponds precisely to this condition. As shown in Fig. 3 all three lattice parameters consistently identify the three crystals as $x=0.40$, 0.45, and 0.50.

TABLE I. Characterization of $YBa_2Cu_3O_{6+x}$ single crystals. The lattice constants were measured at room temperature. The estimated relative error for lattice constants is 0.06%; the estimated error for absolute values is 0.2%.

Oxygen Parameter, x	0.30	0.40	0.45	0.50
IMS sample No.	21[a]	27	30	29
T_c (K)	(T_N=260)	25	45	50
Volume (cm^3) ~	0.5	0.9	1.0	1.0
Lattice Constant (Å)				
c	11.815	11.796	11.744	11.737
a		3.856	3.855	3.846
b		3.878	3.878	3.884
$(a+b)/2$	3.863	3.867	3.866	3.865

[a]Labelled as crystal 3 in Ref. 8.

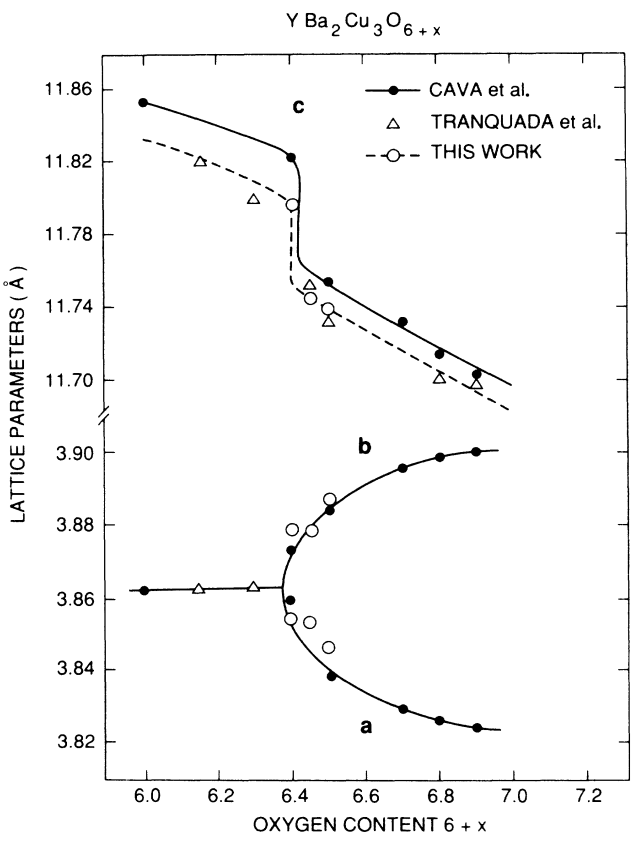

FIG. 3. Lattice constants at room temperature. Solid circles are powder samples of Cava *et al.* (Ref. 12) and triangles are previous single-crystal study of IMS samples by Tranquada *et al.* (Ref. 8).

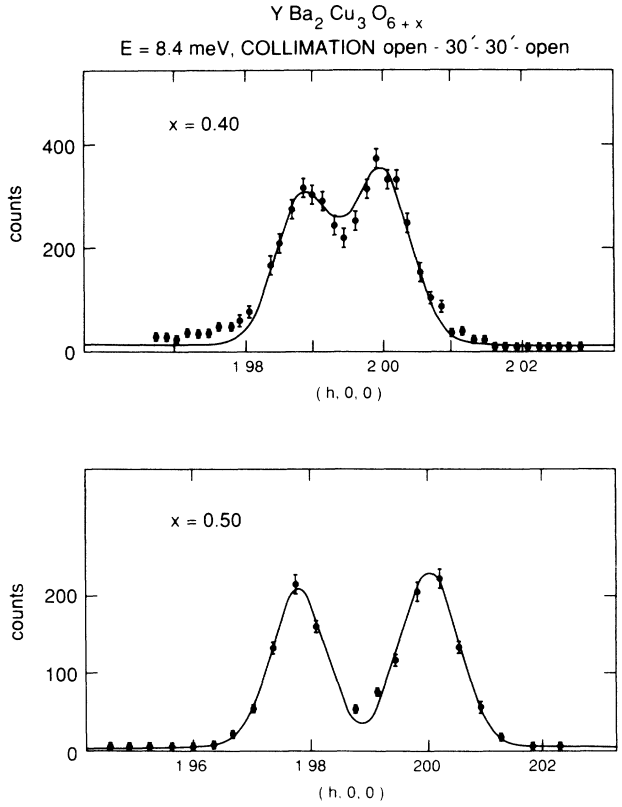

FIG. 4. High-resolution scans of orthorhombic splittings for two single crystals of $YBa_2Cu_3O_{6+x}$. Data are taken with 8.4-meV neutrons from a PG (004) monochromator and 30′ collimation. Solid lines are best Gaussian fits (see text).

The relative sizes of the crystals were estimated from phonon intensities measured around (006).

Figure 4 shows two profiles of orthorhombic splittings taken with a high-resolution spectrometer TAS7 with 8.4 meV neutrons [from a pyrolytic graphite (PG) (004) monochromator]. From the numerical analysis of (200) scans, we conclude that the observed linewidths are 0.010–0.012 rlu compared to the experimental resolution of 0.009 rlu, where rlu stands for reciprocal lattice unit. However, the (200) and (020) peaks (simultaneously present due to twinning) are not completely separated for $x=0.40$ and 0.45 and this makes the estimate of possible tetragonal phase very difficult. In the case of the $x=0.50$ sample we can set a relatively tight limit of 10% for the tetragonal component coexisting in the orthorhombic phase.

III. INELASTIC NEUTRON SCATTERING

The inelastic neutron-scattering measurements were carried out with the triple axis spectrometer TAS6 situated at a cold source beam port in the DR3 reactor at Risϕ. Pyrolytic graphite (002) reflections were used for the monochromator and analyzer. The analyzer energy was kept fixed at 13.7 meV and higher-order contamination was eliminated by a 5-cm pyrolytic graphite filter. Collimations between source, monochromator, sample, analyzer, and detector were rather open (typically 100, 50, 100, 100 min of arc respectively) in order to maximize intensities. Each crystal was wrapped in Al foil and mounted in a thin-walled Al container which in turn was enclosed in an Al can filled with He gas for heat-exchange purposes. The cooling was provided by a Displex closed-cycle refrigerator and the temperatures were measured with either a Ge or a Pt resistor.

The scattering geometry is shown in Fig. 5. The scan across the $(\frac{1}{2}\frac{1}{2}l)$ line (scan A) characterizes two-dimensional (2D) correlation in the CuO_2 layers. Scan B, along the ridge of $(\frac{1}{2}\frac{1}{2}l)$ shows nearly constant magnetic cross sections for La_2CuO_4. However, in the $YBa_2Cu_3O_{6+x}$ system, the cross sections are modulated because of the bilayer nature of the magnetic coupling.[7,8] This modulation is demonstrated for the $x=0.45$ sample at 11 K in Fig. 5(a). Constant-E scans across the ridge (scan A in Fig. 5) are shown in Fig. 6 for all three crystals. Since all samples have nearly the same volume (Table I), this figure shows a sudden decrease of magnetic intensities between $x=0.45$ and 0.50. Further measurements were carried out for $x=0.50$ ($T_c=50$ K) at different excitation energies as shown in Fig. 7. Though

counting statistics are rather poor, these figures indicate nearly the same cross section between 3 and 8 meV. We could not study higher-energy transfer since the spectrometer was located at the cold source.

The temperature dependence of this magnetic scattering for the $x=0.45$ sample is shown in Fig. 8. Note that the intensity drops by about a factor of 5 on increasing the temperature from 100 to 300 K. The temperature dependence of the $x=0.40$ sample is very similar. These results are very unique characteristics of the current samples. It has been demonstrated that, in both $La_{2-y}Sr_yCuO_4$ as well as insulating $YBa_2Cu_3O_{6+x}$, the intensities of magnetic excitations above T_N are nearly temperature independent between 300 and 4 K for the energy range up to 15 meV. We have not attempted similar measurements for the $x=0.50$ sample since the intensities were so low. However, data shown in Fig. 6 suggest that the decrease of magnetic intensities on heating may not be as pronounced as in the other two samples.

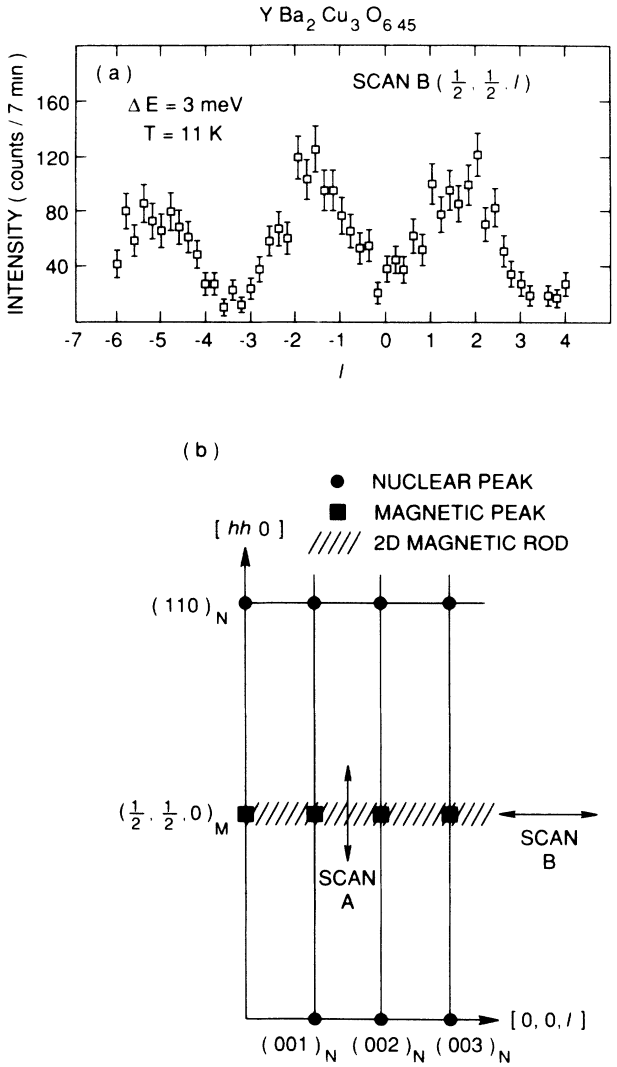

FIG. 5. (a) Example of intensity modulation by the bilayer 2D magnetic correlations. (b) Scattering geometry in reciprocal lattice for $YBa_2Cu_3O_{6+x}$.

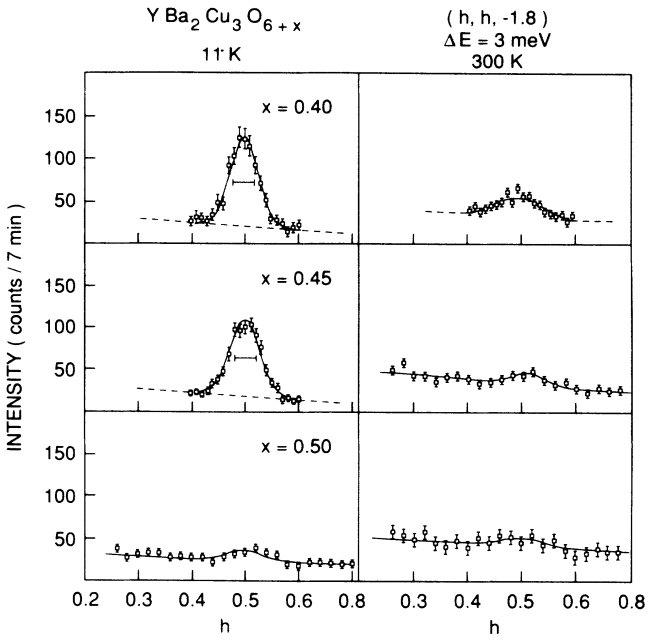

FIG. 6. Comparison of magnetic cross sections of three superconducting crystals of $YBa_2Cu_3O_{6+x}$. Notice the sudden decrease of intensities between $x=0.45$ and $x=0.50$.

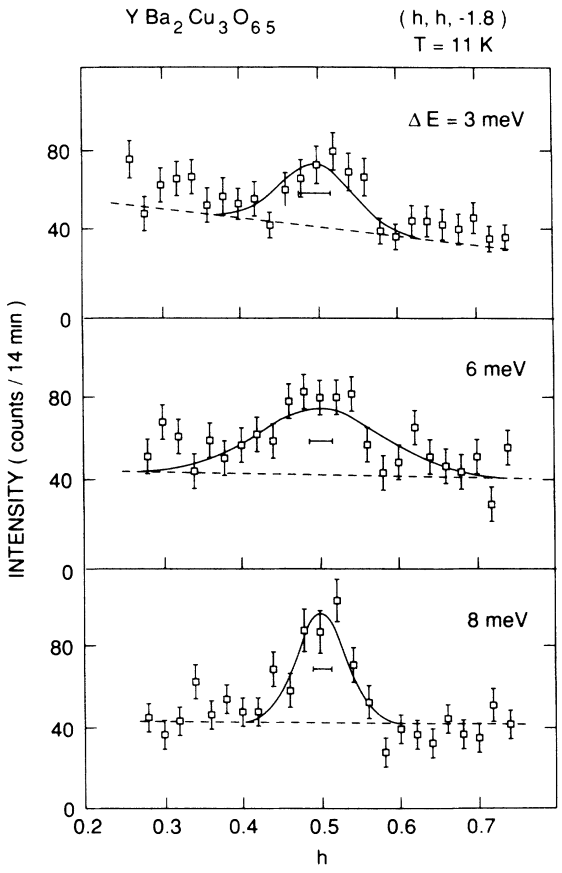

FIG. 7. Magnetic cross sections across the 2D ridge [see A in Fig. 5(b)] for $YBa_2Cu_3O_{6.5}$. Solid lines are best Lorentzian fits.

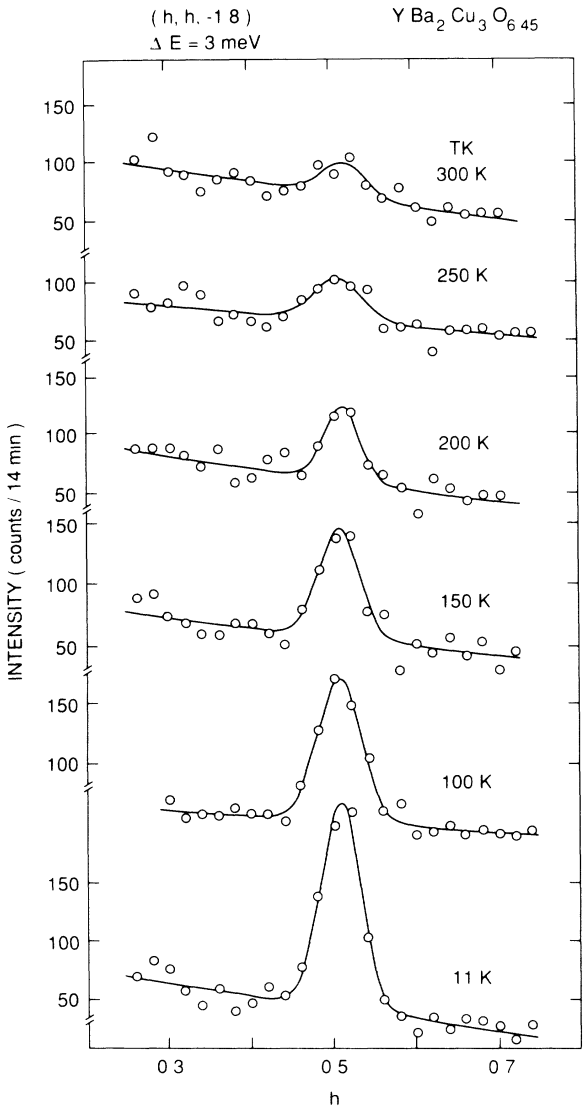

FIG. 8. Temperature dependence of magnetic cross sections of $YBa_2Cu_3O_{6.45}$. Notice that the line widths are nearly temperature independent.

IV. DISCUSSION

Before we assess the findings in the current study, we have to consider once more the uniformity of these crystals. As we discussed in Sec. II, there are noticeable spreads in T_c, and a-b splittings are too small for clear discrimination. Moreover, we do not know yet the Meissner percentage even for $x=0.50$. However, there is one characteristic common to all these crystals which we would like to emphasize. This is the lack of magnetic Bragg peaks at low temperature. As demonstrated carefully by Rossat-Mignod *et al.*,[9] it is very easy to detect them if even a small part of the sample is magnetically ordered.

A. $x=0.40$ and 0.45 crystals

These two superconducting crystals, with T_c's of 25 and 45 K, respectively, exhibit strong inelastic magnetic cross sections at low temperature. Unlike $La_{2-y}Sr_yCuO_4$ (Ref. 5), however, the low-energy signal decreases significantly with increasing temperature (see Fig. 8). The line widths are nearly temperature independent; thus, the decrease of peak intensity cannot result simply from line broadening. The absence of magnetic Bragg peaks implies that the observed magnetic excitations are strongly affected by the presence of holes in the CuO_2 planes, while the intensity modulation shown in Fig. 5(a) clearly indicates that the scattering is coming from antiferromagnetically correlated CuO_2 bilayers. The temperature dependence may indicate that the spin-spin correlation length decreases at higher temperatures. The apparent saturation of magnetic scattering at low temperature might be related to reports of low-temperature spin freezing observed by neutron spin echo[14] and muon spin rotation[15] measurements in superconducting samples with $0.4 \leq x \leq 0.6$.

In the past we have *assumed* that the magnetic cross sections are nearly temperature independent for all high T_c oxides. This was a natural extension of the $La_{2-y}Sr_yCuO_4$ results. Thus we, as well as other researchers in the field, looked for magnetic cross sections mainly at room temperature and at excitation energies below 10 meV. It is now clear that new experimental windows must be found for superconducting compositions with $x > 0.40$.

How far in energy does this unique temperature dependence persist? A preliminary study of magnetic excitations at higher energy (up to 45 meV) was carried out for the $x=0.40$ crystal at Brookhaven before the reactor went into a prolonged shut down. Sketchy data suggest that higher-energy excitations are probably weakly temperature dependent. We are planning to extend these measurements to the $x=0.45$ and 0.50 samples.

B. $x=0.50$ crystal

Finally, we would like to comment on the sudden decrease in the magnetic cross section observed when x increases from 0.45 to 0.50. Even though T_c changes only from 45 to 50 K the orthorhombic splitting showed a large jump at this concentration (see Table I and Fig. 4). There may also be a large increase of Meissner fraction at this x as indicated by Cava *et al.*[10] It is crucial to demonstrate in the future that the $x=0.50$ crystal actually has a large Meissner fraction. This may be achieved by a muon spin rotation measurement, which can probe a large fraction of the crystal. In order to understand the whole picture of magnetic response we definitely need neutron scattering data at higher excitation energies.

One way in which to explain the sudden decrease in magnetic cross section with oxygen content is to assume that the cross section is strongly diminished at all energies when the compound is doped with a sufficient density of mobile holes to make it a superconductor. The results[5] on Sr-doped La_2CuO_4 indicate, to the contrary, that the Q-integrated low-energy magnetic cross section for a CuO_2 plane is not significantly diminished by the presence of holes. Another possibility is that a "pseudogap" is formed in the magnetic excitation spectrum.

Such an apparent behavior has been observed[6] recently in $La_{1.85}Sr_{0.15}CuO_4$. A temperature-dependent gap might be expected if the spin fluctuations are involved in the hole-pairing interaction responsible for the superconductivity. A third alternative is that the low-energy magnetic scattering may be depressed due to strong damping of long-wavelength spin fluctuations. The damping would occur because of the reduction in the magnetic correlation length due to a high density of mobile holes. In the latter two cases, the magnetic scattering intensity should still be reasonably strong at higher excitation energies, corresponding to shorter wavelengths. We are planning to test these hypotheses experimentally in the near future.

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