Magnetic Dynamics in Underdoped $YBa_2Cu_3O_{7-x}$: Direct Observation of a Superconducting Gap

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(Received 18 September 1996)

Polarized and unpolarized triple-axis neutron measurements were performed on an underdoped crystal of $YBa_2Cu_3O_{7-x}$ ($x = 0.4 \pm 0.02$, $T_c = 62.7$ K). Our results indicate, contrary to earlier evidence, that the spin excitations in the superconducting state are essentially the same as those in the fully doped material except that the unusual 41 meV resonance is observed at 34.8 meV. The normal state spin excitations are characterized by a weakly energy-dependent continuum whose temperature dependence shows the clear signature of a superconducting gap at T_c. The enhancement at the resonance is accompanied by a suppression of magnetic fluctuations at both higher and lower energies. [S0031-9007(96)02014-5]

PACS numbers: 74.72.Bk, 61.12.Ex

Recently, there has been a great deal of interest in underdoped superconducting copper oxides because these materials display unusual normal state properties [1] that suggest the opening of a pseudogap (a suppression of spectral weight) in the spin or charge excitation spectrum well above T_c [2]. The central issue is whether the physics of underdoped cuprates is fundamentally different from the description of the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity. Although there is ample evidence [3–5] for the existence of a pseudogap in underdoped cuprates, no one has established a direct correlation between the pseudogap and the superconductivity. Furthermore, it is not known whether a superconducting gap opens at T_c.

Magnetic inelastic neutron scattering is a powerful technique for measuring the wave vector dependence of the superconducting gap function [6] because the imaginary part of the dynamic susceptibility, $\chi''(\mathbf{q}, \omega)$, probed by neutrons is directly associated with electron-hole pairs formed by transitions across the Fermi surface. In the BCS theory of superconductivity, such transitions become disallowed for all wave vectors with energy transfer ($\hbar\omega$) below 2Δ ($3.52 k_B T_c$ for the weak-coupling limit) at $T = 0$ K, where Δ is the superconducting gap. Since the availability of large single crystals of $YBa_2Cu_3O_{7-x}$ [denoted as $(123)O_{7-x}$], there have been a large number of neutron scattering experiments on this system across the whole doping range [7–11]. The nature of the scattering at low temperatures in the superconducting state of highly doped $(123)O_{7-x}$ appears established. Early measurements by Rossat-Mignod and co-workers [7] indicated an enhancement of scattering in the superconducting state near 41 meV. Polarized neutron experiments by Mook *et al.* [9] have shown that below about 50 meV the magnetic scattering is dominated by a peak that is sharp in energy, located at 41 meV, and centered at (π, π) in the reciprocal lattice. The peak is generally referred to as a resonance peak and a number of theoretical explanations have been proposed [12]. Since the resonance disappears in the normal state [11], it may be a signature of the superconducting state.

Although there is general agreement about the low temperature spin excitations for highly doped $(123)O_{7-x}$, $\chi''(\mathbf{q}, \omega)$ for underdoped compounds ($0.6 > x \geq 0.35$) has been far from clear. Using unpolarized neutrons, Rossat-Mignod and co-workers [7,10] as well as Tranquada *et al.* [8] have reported two distinctive features in $\chi''(\mathbf{q}, \omega)$ that are not present for highly doped $(123)O_{7-x}$. The first of these is an energy gap in the spin excitation spectrum (below which no magnetic intensity can be found) which is much less than 2Δ. They also reported a complicated temperature dependence of $\chi''(\mathbf{q}, \omega)$, but found no resonance coupled directly to T_c.

We report here the first polarized neutron scattering measurements on an underdoped single crystal of $(123)O_{7-x}$ ($x = 0.4 \pm 0.02$, $T_c = 62.7$ K). These experiments are able to isolate the magnetic scattering from nonmagnetic sources such as phonons and demonstrate that a clear superconducting gap opens in the spin excitation spectra at T_c. This gap, observed at wave vector (π, π), is 28 meV ($5.2 k_B T_c$) at the lowest temperatures which is large compared to that expected in the weak-coupling BCS limit. We also show, contrary to earlier evidence, that the low temperature spin excitations in the superconducting state are very much like those found for the fully doped material except for a change in the energy scale. The unusual resonance, found at 41 meV in the fully doped materials, is thus not unique to materials with high doping. In fact, the resonance energy falls with T_c and is at 34.8 meV for $(123)O_{6.6}$.

The polarized and unpolarized beam experiments have been performed on a twinned disk shaped crystal $(123)O_{6.6}$ (22.9 mm in diameter and 10.8 mm in thickness) that weighs 25.59 g and has a mosaic of 0.9° as measured from the (006) reflection. Similar to other large single crystals of $(123)O_{7-x}$ used in previous neutron scattering experiments [9,11], our sample contains approximately 14 mol% Y_2BaCuO_5 as an impurity [13] determined by neutron powder diffraction and Rietveld analysis on identically prepared samples. Oxygenation of large, dense $(123)O_{7-x}$ samples suitable for neutron scattering experiments is not a trivial matter. For example, although the T_c of $(123)O_{7-x}$ exhibits the well known "60 K plateau" for $x \approx 0.4$ [14], previous neutron scattering samples with the nominal oxygen content of $(123)O_{6.6}$ [8] have had a T_c variation of as much as 7 K. To overcome this difficulty, an improved technique for oxygenating dense $(123)O_{7-x}$ was used. Briefly, the sample was oxygenated in a thermogravimetric apparatus (TGA) by annealing to the equilibrium weight (± 0.1 mg) at T-$p[O_2]$ conditions for $(123)O_{6.6}$ as calculated from the thermodynamic models that were fitted to experimental data [15]. Instead of quenching the sample after annealing, the partial pressure of oxygen (99.999% purity) in the TGA was adjusted continuously throughout the cooling process to maintain a constant sample mass, thus ensuring uniformity in oxygen content and an equilibrium crystal structure [16]. The advantage of such a technique is clearly evident in the ac susceptibility measurement shown in Fig. 1 which gives a superconducting onset temperature of 62.7 K, the highest for any $(123)O_{6.6}$ samples studied by neutron scattering. The room temperature lattice parameters [$a = 3.8316(5)$ Å, $b = 3.8802(6)$ Å, and $c = 11.743(2)$ Å], the orthorhombicity [$200(b-a)/(b+a) = 1.2604$], and the unit cell volume ($V = 174.59$ Å^3) are consistent with the $(123)O_{6.6}$ powder sample oxygenated using the identical methods [17].

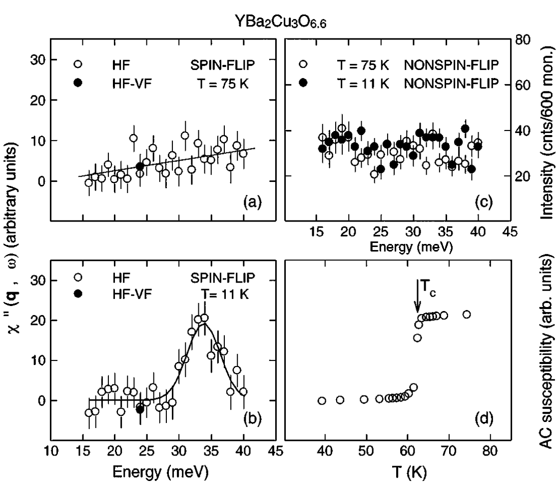

FIG. 1. (a) Polarized beam measurements of $\chi''(\mathbf{q}, \omega)$ for the $(-0.5, -1.5, 1.7)$ r.l.u. position at 75 K and (b) 11 K, obtained by subtracting the background [21], correcting for incomplete polarization, and dividing by the Bose population factor $n(\omega) + 1$. The filled circles represent twice the SF, HF-VF, scattering. The flipping ratio for HF and VF are 15.8 ± 0.25 and 16.5 ± 0.26, respectively. The solid lines are guides to the eye. (c) The phonon scattering normalized to 600 monitor counts. (d) ac susceptibility of the sample, showing the onset T_c of 62.7 K with a transition width that is 3.3 K wide.

Inelastic measurements were made at the High-Flux Isotope Reactor at Oak Ridge National Laboratory using the HB-1 and HB-3 triple-axis spectrometers with a fixed final neutron energy of 30.5 meV and a pyrolytic graphite (PG) filter before the analyzer [9]. To separate magnetic from nuclear scattering in polarized beam experiments, it is often sufficient to measure the spin-flip (SF) scattering and the non-spin-flip (NSF) scattering. In cases where the magnetic signal is on top of a large background, the SF scattering can be measured with neutron polarization first parallel to the momentum transfer (horizontal guide field or HF) and then perpendicular (VF). The difference (HF-VF) gives one-half of the magnetic intensity completely free of background effects [18].

For the experiment we index reciprocal (Q) space by using the orthorhombic unit cell so that momentum transfers (Q_x, Q_y, Q_z) in units of Å^{-1} are at positions $(H, K, L) = (Q_x a/2\pi, Q_y b/2\pi, Q_z c/2\pi)$ reciprocal lattice units (r.l.u.). Most of our measurements were made in the $(H, 3H, L)$ Brillouin zone. For highly doped $(123)O_{7-x}$, this scattering geometry was first used by Fong *et al.* [11] and has the advantage of having less phonon and accidental Bragg scattering.

Since previous investigations on highly doped $(123)O_{7-x}$ showed magnetic scattering that peaked at (π, π) with a sinusoidal modulation along the $(0, 0, L)$ direction, we looked for magnetic signal in the normal and superconducting states at $(-0.5, -1.5, 1.7)$ which corresponds to the maximum intensity of the $(0, 0, L)$ modulation. The results of the measurement are shown in Fig. 1. The dynamic susceptibility is featureless at 75 K, but at 11 K is dominated by a peak at $\sim$34 meV. In addition, the low energy excitations ($\hbar\omega \leq 28$ meV) vanish to within the error of the measurements, consistent with the opening of an energy gap. The NSF data indicate that the phonon scattering is essentially unchanged in this zone between 11 and 75 K. Consequently, our conclusions about the magnetic excitations in underdoped $(123)O_{6.6}$ are different from those of previous unpolarized experiments [7,8,10] which reported a broad peak around 22 meV in the normal state and observed no 34 meV resonance or 28 meV gap in the superconducting state.

Figure 2 summarizes the wave vector dependence of the magnetic excitations. The 24 meV constant-energy scan at 75 K peaks at (π, π) with a full width half maximum of 0.32 Å^{-1} which corresponds to an antiferromagnetic correlation length of $\sim$20 Å. The same scan was taken at 11 K with both HF and VF. To within the error of the measurement, no magnetic intensity is present. Similar scans were made at $\hbar\omega = 34$ meV. The intensity of the resonance peak clearly increases below T_c. The NSF phonon scattering (not shown) for these scans is featureless and changes negligibly between these temperatures.

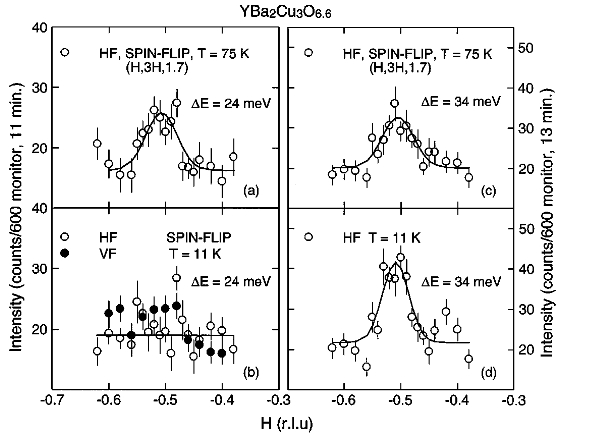

FIG. 2. (a) Polarized SF, $(H, 3H, 1.7)$ scans using HF for $\hbar\omega = 24$ meV at $T = 75$ K, and (b) 11 K. The filled circles in (b) are the SF scattering using VF. HF-VF scattering shows no magnetic signal. (c) SF, HF, $(H, 3H, 1.7)$ scan for $\hbar\omega = 34$ meV at $T = 75$, and (d) 11 K. Solid lines in (a), (c), and (d) are Gaussian fits to the data. The solid line in (b) is a guide to the eye.

Since the phonon scattering does not change between 11 and 75 K in the $(H, 3H, L)$ zone, unpolarized neutrons are used to determine the temperature dependence of the resonance. Comparison of the difference spectra in Fig. 3 reveals that the resonance softens and broadens slightly at high temperatures. The energy threshold below which the scattering is suppressed, indicated by arrows in the figure, moves from 25 meV at 50 K to 28 meV at 11 K, indicating that the gap increases in energy with cooling. In addition, the energy width of the resonance narrows from 6.6 meV at 50 K to 5.5 meV at 11 K, and is resolution limited at 11 K. The negative values in the subtractions of Fig. 3 show the opening of an energy gap in $\chi''(\mathbf{q}, \omega)$, consistent with polarized results of Fig. 1. Furthermore, our data [Fig. 3(c)] suggest that the enhancement at the resonance is accompanied by a suppression of the fluctuations both below and above it. This point is clear from negative values on both sides of the resonance. A detailed comparison between $(123)O_{6.93}$ and $(123)O_{6.6}$ will be reported in a forthcoming paper [19].

One signature of the magnetic fluctuations in $(123)O_{7-x}$ is its sinusoidal intensity modulation along the $(0, 0, L)$ direction. These modulations, seen in all the $(123)O_{7-x}$ neutron scattering experiments [7–11], are the result of the antiferromagnetic CuO_2 bilayer coupling and may have important theoretical consequences [12,20]. Since there are no magnetic fluctuations at low temperatures below 28 meV, the difference spectra between 75 and 11 K should give an accurate account of the normal state magnetic scattering. Figure 3(d) shows such a scan along the L direction at $\hbar\omega = 24$ meV together with a calculated profile for the acoustic mode of the antiferromagnetic bilayer coupling [7,8]. Clearly, the bilayer modulation is present in the normal state, and the acoustic mode adequately describes the data.

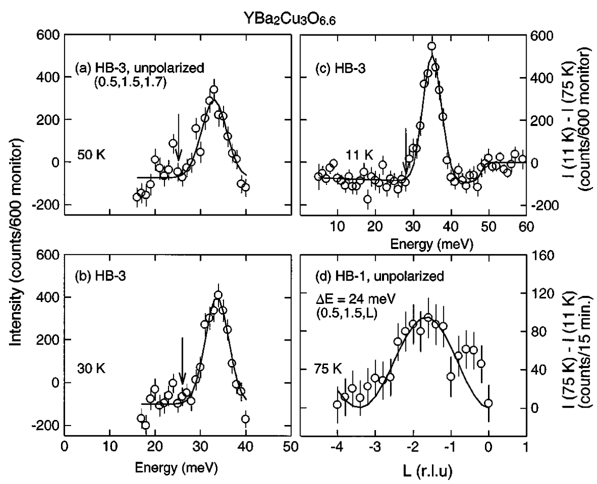

FIG. 3. Unpolarized beam measurements at (0.5,1.5,1.7) r.l.u. in which the data at 7 K are subtracted from (a) 50 K, (b) 30 K, and (c) 11 K data. For energy transfers above 45 meV, the data were taken with neutron final energy of 35 meV. The lines are fits to Gaussians and linear backgrounds. Arrows in the figure indicate points defined arbitrarily at 1% of the resonance intensity. (d) Unpolarized beam constant-energy scan along $(0.5, 1.5, L)$ at $\hbar\omega = 24$ meV using HB-1. The spectrum is obtained by subtracting the signal at 75 K from the $T = 11$ K background. The solid line is the expression $f^2_{\mathrm{Cu}}(\mathbf{Q}) \sin^2(\pi z L)$ normalized to the intensity at $(0.5, 1.5, -1.7)$, where $f_{\mathrm{Cu}}(\mathbf{Q})$ is the Cu magnetic form factor, and $z \times c = 3.342$ is the distance between adjacent copper-oxide planes.

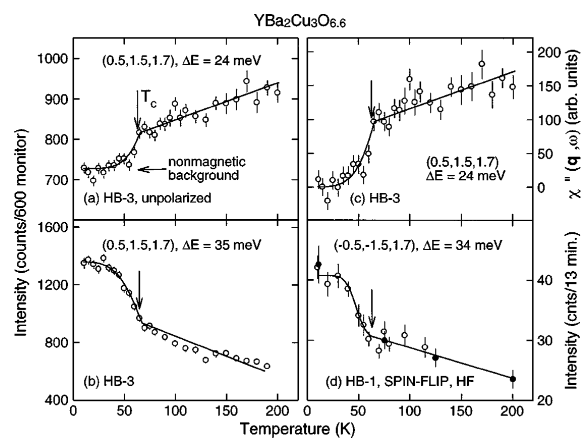

FIG. 4. Temperature dependence of the scattering at (0.5,1.5,1.7) for (a) $\hbar\omega = 24$, and (b) 35 meV. (c) $\chi''(\mathbf{q}, \omega)$ at $\hbar\omega = 24$ meV obtained by subtracting the nonmagnetic scattering and dividing by the Bose population factor $n(\omega) + 1$. (d) Temperature dependence of the polarized SF scattering at $(-0.5, -1.5, 1.7)$ for $\hbar\omega = 34$ meV. The filled circles represent the peak intensity of constant-energy scans and Gaussian fits to the data (Fig. 2) show a temperature independent background of 20 ± 1.5 counts. Arrows in the figure indicate the onset of T_c and solid lines are guides to the eye.

In Fig. 4 we plot the temperature dependence of scattered intensity at 24 and 35 meV which corresponds to frequencies below and above the gap energy, respectively. The intensity for both frequencies changes drastically at T_c, but in opposite directions. Below T_c, the intensity at $\hbar\omega = 24$ meV decreases precipitously, showing the opening of the superconducting gap while the temperature dependence of the resonance at 35 meV parallels that of the 41 meV resonance for highly doped $(123)O_{7-x}$ [9,10]. Since the polarized HF-VF data at 24 meV show no magnetic signal at 11 K, we are able to determine the low temperature background (see Fig. 4). The corresponding $\chi''(\mathbf{q}, \omega)$ can then be calculated via the fluctuation-dissipation theorem and shows a clear suppression at T_c. An unusual feature of the temperature dependence of the resonance is that although a large increase in intensity takes place below T_c, a smaller increase is observed that extends to temperatures well above T_c. No such behavior is observed for ideally doped $(123)O_{6.93}$ [9,10].

In conclusion, we have shown that magnetic excitations for underdoped $(123)O_{6.6}$ are essentially the same as those in the fully doped material except for a change in the energy scale. The normal state scattering is characterized by a weakly energy-dependent continuum whose temperature dependence shows the clear signature of a superconducting gap at T_c.

We thank G. Aeppli, P.W. Anderson, D. Pines, D.J. Scalapino, D.G. Mandrus, G.D. Mahan, B.C. Chakoumakos, R.F. Wood, and J. Zhang for helpful discussions. This research was supported by the U.S. DOE under Contract No. DE-AC05-96OR22464 with Lockheed Martin Energy Research, Inc.

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