Two Resonant Magnetic Modes in an Overdoped High T_c Superconductor

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A detailed inelastic neutron scattering study of the overdoped high temperature copper oxide superconductor $Y_{0.9}Ca_{0.1}Ba_2Cu_3O_7$ reveals two-distinct magnetic resonant modes in the superconducting state. The modes differ in their symmetry with respect to exchange between adjacent copper oxide layers. Counterparts of the mode with odd symmetry, but not the one with even symmetry, had been observed before at lower doping levels. The observation of the even mode resolves a long-standing puzzle, and the spectral weight ratio of both modes yields an estimate of the onset of particle-hole spin-flip excitations.

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In various high T_c superconductors with crystal structures comprised of CuO_2 monolayer units ($Tl_2Ba_2CuO_{6+\delta}$ [1]) and bilayer units [$YBa_2Cu_3O_7$ (YBCO) [2–7] and $Bi_2Sr_2CaCu_2O_{8+\delta}$ (BSCO) [8]], the magnetic excitation spectrum in the superconducting state is dominated by a resonant mode. For a given compound, the excitation vanishes at T_c without any marked change of the excitation energy E_r. A comparison of different compounds has uncovered the scaling relation $E_r \sim 5k_BT_c$ [9]. Signatures of a strong interaction of the mode with charged quasiparticles [10] have been observed in various spectroscopic data including angle-resolved photoemission spectroscopy [11] and tunneling [12].

The resonant mode occurs around the planar wave vector $Q_{AF} = (\pi/a, \pi/a)$ characteristic of antiferromagnetic (AF) fluctuations in both monolayer and bilayer systems. (a stands for the Cu-Cu distance in the CuO_2 planes.) Because of the interlayer exchange coupling, bilayer systems are additionally expected to exhibit nondegenerate magnetic excitations with odd (o) and even (e) symmetry with respect to exchange of the layers. While this has been confirmed in insulating YBCO [13] by the observation of acoustic and optical spin waves (whose symmetry is o and e, respectively), one of the most puzzling features of the resonant mode in superconducting bilayer systems is that it appears exclusively in the odd channel. On general grounds, both odd and even parts of the spin susceptibility are required as input for theories of a superconducting pairing mechanism based on magnetism. Differences in the spin dynamics in o and e channels can even lead to interlayer and intralayer pairing states of different symmetry [14]. Despite various attempts in underdoped and optimally doped samples, the even resonant mode has thus far not been observed, presumably due to a much weaker intensity. Here we report, for the first time, the observation of odd and even modes in a superconducting YBCO sample in which the CuO_2 planes are overdoped through partial substitution of Ca^{2+} for Y^{3+}.

$Y_{0.9}Ca_{0.1}Ba_2Cu_3O_{6+x}$ single crystals were prepared by a top-seeded solution growth method described previously [15]. About 60 single crystals with a total volume of 350 mm^3 were coaligned with a total mosaicity of 1.4°

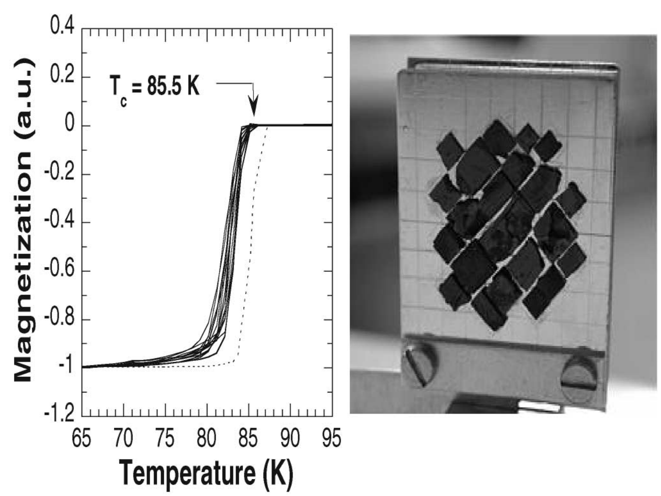

FIG. 1. (left) Susceptibility of 15 individual $Y_{0.9}Ca_{0.1}Ba_2Cu_3O_7$ crystals (full curves). For comparison, the dashed line represents the susceptibility curve taken for one crystal after heat treatment to reduce the oxygen content. Its higher T_c demonstrates that the samples used in the neutron experiments are slightly overdoped. (right) Photograph of the array of cooriented overdoped single crystals. Sixty crystals are glued onto Al plates, only one of which is shown for clarity.

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as shown in Fig. 1 (left panel). Prior to alignment, the Ca content and superconducting transition temperature were determined by energy dispersive x-ray (EDX) analysis and magnetometry, respectively, for each crystal individually. The EDX measurements revealed an excellent homogeneity of the Ca content both parallel and perpendicular to the CuO_2 layers, and the superconducting transitions measured by magnetometry were sharp [full width < 4 K, Fig. 1 (right panel)]. To achieve the overdoped state, the samples were annealed in flowing oxygen at 500 °C for 150 h yielding $x \simeq 1$. The total crystal mosaic has an onset T_c of 85.5 ± 0.6 K and calcium content of $10\% \pm 1\%$ (mean $\pm$ standard deviation).

The measurements were taken at the 2 T triple axis spectrometer at the Laboratoire Léon Brillouin (Saclay, France), and at the IN8 triple axis spectrometer at the Institut Laue Langevin (Grenoble, France). On 2 T, a focusing pyrolytic graphite (PG) (002) monochromator and analyzer were used, with a PG filter inserted into the beam in order to eliminate higher order contamination. The IN8 beam optics includes a vertically and a horizontally focusing Si (111) crystal as monochromator, and a PG (002) analyzer. No filter was required on IN8 because the Si (222) Bragg reflection is forbidden. The crystal was oriented such that momentum transfers Q of the form $Q = (H, H, L)$ were accessible. We use a notation in which Q is indexed in units of the tetragonal reciprocal lattice vectors $2\pi/a = 1.64$ Å^{-1} and $2\pi/c = 0.54$ Å^{-1}.

As discussed previously [6,16,17], the cross section for magnetic neutron scattering from bilayer cuprates reads

$$\frac{\partial^2\sigma(Q,\omega)}{\partial\Omega\partial\omega} \propto F^2(Q)\{\sin^2(\pi z L)\mathrm{Im}[\chi_o(Q,\omega)] + \cos^2(\pi z L)\mathrm{Im}[\chi_e(Q,\omega)]\}, \quad (1)$$

where $\mathrm{Im}[\chi_{o,e}(Q,\omega)]$ is the imaginary part of the dynamical magnetic susceptibility in the odd and even channels, respectively, $zc = 3.3$ Å is the distance between CuO_2 planes within a bilayer unit, and $F(Q)$ is the magnetic form factor of Cu^{2+}. In order to determine the energy of the magnetic resonant mode, we first followed previous work [6] and performed constant-Q scans at $Q = (0.5, 0.5, 5.2)$ where the structure factor for odd excitations is maximum. As previously found in $YBCO_7$ [4,5], antiferromagnetic spin correlations are not observable above the background level in the normal state, so that the normal-state intensity can serve as a reference level. Figure 2(a) shows that the intensity increases in the superconducting state and that the difference between scans taken in the superconducting and normal states exhibits the same prominent peak that heralds the resonant mode in other copper oxides. (Note that the reference level is negative and increases with increasing energy for a given temperature difference, because the background is predominantly determined by multiphonon scattering events.) The peak energy, 36 meV, is lower than the mode energy in optimally doped YBCO, but consistent with observations in slightly overdoped BSCO [9] and with the scaling relation $E_r \sim 5k_BT_c$. Constant-energy scans at 36 meV along $(0.5, 0, 5, L)$ [Figs. 2(b) and 2(c)] exhibit a sinusoidal intensity modulation that confirms the previously observed odd symmetry of the resonant mode [Eq. (1)]. In-plane constant-energy scans along $(H, H, 5.2)$ (not shown) exhibit a peak with an intrinsic full width at half maximum of $\Delta Q = 0.36 \pm 0.05$ Å^{-1}, somewhat larger than $\Delta Q = 0.25 \pm 0.05$ Å^{-1} determined for the resonant mode in $YBCO_7$. The temperature dependence of the peak intensity [Fig. 2(d)] shows that the mode vanishes in the normal state, similarly to the optimally doped systems.

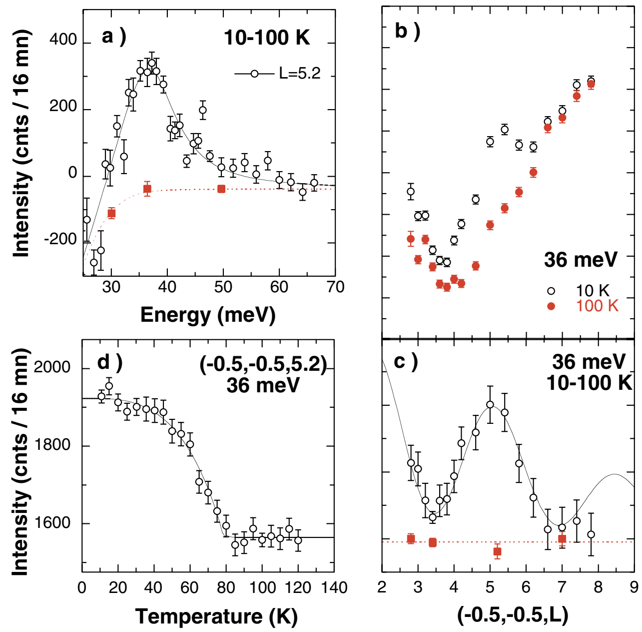

FIG. 2 (color online). (a) Difference of the neutron intensities measured at $T = 10$ K ($< T_c$) and $T = 100$ K ($> T_c$) in the odd channel at $Q = (0.5, 0.5, 5.2)$ versus excitation energy E. (b) Constant-energy scans at $E_r^o = 36$ meV along the L direction perpendicular to the CuO_2 planes at 10 and 100 K. (c) Difference between the two scans shown in (b). The full symbols in (a) and (c) are determined by the difference of constant-energy scans along the (H, H, L_0) direction for different L_0 values. Dotted lines connecting these full symbols then correspond to the reference level of magnetic scattering. (d) Temperature dependence of the neutron intensity at the resonance energy $E = E_r^o$ and $Q = Q_{AF}$.

While these observations are largely consistent with previous work [2–7], some new aspects of the data of Fig. 2(a) are noteworthy. First, in contrast to the resolution-limited energy profile in pure YBCO, the resonant peak in the overdoped material exhibits a broader, asymmetric line shape with a tail above E_r [Fig. 2(a)]. Second, the sinusoidal intensity modulation along L is not complete as some intensity remains at $L = 3.6$ and 7.2 [Fig. 2(c)]. Similar L scans for $YBCO_{6.97}$ show the full modulation [5]. In order to check for a possible admixture of a second mode with even symmetry, we performed constant-Q scans at $Q = (0.5, 0.5, 7)$ where the structure factor for even excitations [Eq. (1)] is near its maximum. The difference of the intensities below and above T_c [closed symbols in Fig. 3(a)] reveals a new mode around an energy of 43 meV, clearly different from the mode energy in the odd channel [open symbols in Fig. 3(a)]. Such an even excitation has not been observed in previous inelastic neutron scattering studies of YBCO and BSCO, most likely because its intensity is smaller at lower doping levels and hence indistinguishable from the background. Further, the overdoped regime could be particularly suited to detect such an even mode because electronic transport between closely spaced CuO_2 layers becomes coherent, as demonstrated by recent experiments showing well-defined bonding and antibonding bands [18].

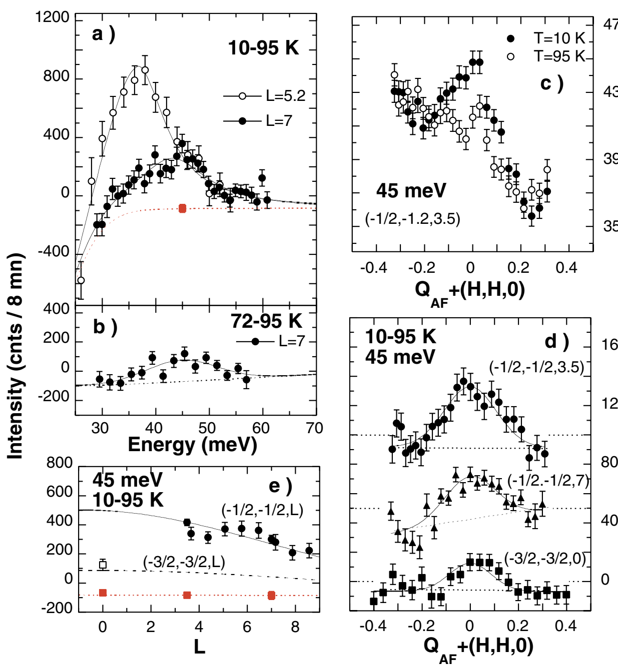

FIG. 3 (color online). (a),(b) Constant-Q scans, (c),(d) constant-energy scans evidencing a second magnetic mode in the even channel around $E_r^e \sim 43$ meV. Panel (c) shows raw neutron scans at two different temperatures, whereas (a), (b), and (d) display the differences of the neutron intensities at $T = 10$ K ($< T_c$) and $T = 100$ K ($> T_c$). The two upper scans in (d) were shifted by 300 counts from the lower one for clarity, and the dotted line represents the background level. (e) Difference between constant-energy scans at $E = 45$ meV obtained at $T = 10$ K and $T = 95$ K along the L direction (open circles). The open square shows the magnetic intensity measured by constant-energy scans at $E = 45$ meV along $Q = (H, H, 0)$ for H around 3/2. The full symbols, connected by the lower dotted line, correspond to the measured reference level of the magnetic scattering determined by constant-energy scans ar $E = 45$ meV along $Q = (H, H, L_0)$ for different L_0 values.

In-plane constant-energy scans performed at maxima of the even structure factor in different Brillouin zones [Figs. 3(c) and 3(d)] show that the intensity is peaked at Q_{AF}. The intensity decreases with increasing total wave vector Q, following the anisotropic magnetic form factor of Cu^{2+} [19] [Fig. 3(e)]. This excludes phonons (whose intensity generally increases with increasing Q) and demonstrates the magnetic origin of the second mode. However, the observed L dependence at $E = 45$ meV [Fig. 3(e)] differs from the $\cos^2$ dependence expected for the even mode [Eq. (1)]. As shown by Fig. 3(a), the deviation from the expected $\cos^2$ dependence is probably related to a combined effect of the anomalous line shapes of both modes and their relative spectral weights.

The temperature dependences of the odd and even modes are closely similar (Fig. 4). Moreover, Fig. 3(b) demonstrates that the even mode remains peaked at 43 meV up to 72 K ($= T_c - 13$ K). The peak amplitude of the even mode thus vanishes at T_c without renormalization of the mode energy, as it does for the odd mode. The findings underline the common origin of both modes. The in-plane Q width of the even mode, measured along the (110) direction, is 0.45 ± 0.05 Å^{-1}, somewhat larger than that of the odd mode [Fig. 3(d)]. The energy profiles of both modes are identical to within the experimental error. Calibration of the magnetic intensity to that of an optical phonon [6] and integrating over the asymmetric profiles in energy yields spectral weights of $W_o(Q_{\mathrm{AF}}) = \int d\omega \mathrm{Im}\chi(Q_{\mathrm{AF}}, \omega) = 0.8\mu_B^2$ per formula unit (f.u.) and $W_e(Q_{\mathrm{AF}}) = 0.36\mu_B^2$/f.u. for odd and even modes, respectively. Averaged over the entire Brillouin zone, this corresponds to $\langle W_o(Q)\rangle = 0.042\mu_B^2$/f.u. and $\langle W_e(Q)\rangle = 0.036\mu_B^2$/f.u. These values should be compared with $W_o(Q_{\mathrm{AF}}) = 1.6\mu_B^2$/f.u. and $\langle W_o(Q)\rangle = 0.043\mu_B^2$/f.u. for the odd mode in $YBCO_7$ [6]. The total magnetic spectral weight observed by neutron scattering is thus preserved in the overdoped regime, but it is spread out over a wider range of energy and momentum.

Two distinct magnetic modes of odd and even symmetry are thus observed by spin-flip neutron scattering in the superconducting state of overdoped YBCO, as predicted by mean-field theories of d-wave superconductors in the presence of antiferromagnetic interactions [16,17,20]. The observation that the difference between the mode energies, $E_r^e - E_r^o \simeq 7$ meV, is of the order of $J_\perp \sim 10$ meV, the interlayer superexchange coupling determined experimentally in insulating YBCO [13], is also consistent with these models. Under the assumption that both modes are bound states in the superconducting energy gap, their spectral weights are predicted to be approximately proportional to their binding energies, $\omega_c - E_r^{o,e}$ [17], so that

$$\frac{W_o(Q_{\mathrm{AF}})}{W_e(Q_{\mathrm{AF}})} = \frac{\omega_c - E_r^o}{\omega_c - E_r^e}. \tag{2}$$

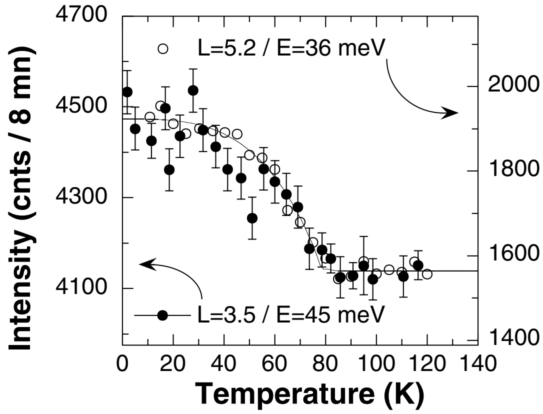

FIG. 4. Temperature dependence of the neutron intensity at $Q_{\rm AF} = (0.5, 0.5, L)$ at the even mode energy $E_r^e = 45$ meV and $L = 3.5$ (full circles and left scale). The temperature dependence of the odd mode (open circles and right scale) of Fig. 2(d) has been superposed without the error bars for clarity.

This yields an estimate of $\omega_c = 49$ meV for the threshold of the continuum of particle-hole spin-flip excitations at the wave vector $Q_{\rm AF}$. The large spectral weight difference thus implies a small binding energy of the even resonant mode. In the limit of small binding energy, one further expects that the normal-state spectral weight below ω_c is only partially redistributed into the bound state below T_c, with the remainder accumulating above the particle-hole threshold. This could provide an explanation for the asymmetric line shape of the mode. A larger distance of the resonant mode to ω_c would also explain why this asymmetry is not observed at optimum doping.

In any case, both the existence of two distinct odd and even excitations and their relative spectral weights put new constraints on the various models to account for the magnetic dynamics in the superconducting cuprates. Notably, our experiments provide an estimate of the locus of the particle-hole spin-flip excitations in the high T_c cuprates, a direct measure of the bulk superconducting energy gap Δ_k.

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