Two resonant magnetic modes in an overdoped high-$T_c$ superconductor

S. Pailhès$^1$, Y. Sidis$^1$, P. Bourges$^{1,*}$, C. Ulrich$^2$, V. Hinkov$^2$, L.P. Regnault$^3$,
A. Ivanov$^4$, B. Liang$^2$, C.T. Lin$^2$, C. Bernhard$^2$, and B. Keimer$^2$

$^1$ Laboratoire Léon Brillouin, CEA-CNRS, CE-Saclay, 91191 Gif sur Yvette, France.
$^2$ Max-Planck-Institut für Festkörperforschung, 70569 Stuttgart, Germany.
$^3$ CEA Grenoble, DRFMC, 38054 Grenoble cedex 9, France.
$^4$ Institut Laue Langevin, 156X, 38042 Grenoble cedex 9, France.

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.

In various high-$T_c$ superconductors with crystal structures comprised of CuO$_2$ monolayer units ($Tl_2Ba_2CuO_{6.5+x}$) and bilayer units (YBa$_2$Cu$_3$O$_7$ (YBCO) $^2$ $^3$ $^4$ $^5$ $^6$ $^7$ and Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ (BSCO) $^8$), the magnetic excitation spectrum in the superconducting (SC) state is dominated by a long-standing puzzle, and the spectral weight ratio of both modes yields an estimate of the onset of particle-hole spin-flip excitations. Differences in the spin dynamics in $o$ and $e$ channels can even lead to inter- and intra-layer pairing states of different symmetry $^9$. 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 $^10$. About 60 single crystals with a total volume of 350 mm$^3$ were co-aligned with a total mosaicity of 1.4$^\circ$ as shown in Fig. $^11$A. Prior to alignment, the Ca content and superconducting transition temperature were determined by energy dispersive x-ray analysis (EDX) 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 < 4K, Fig. $^11$B). To achieve the overdoped state, the samples were annealed in flowing oxygen at 500 $^\circ$C for 150h yielding $x \simeq 1$. The total crystal mosaic has an onset $T_c$ of 85.5 $\pm$ 0.6 K and calcium content of 10 $\pm$ 1% (mean $\pm$ standard deviation).

The measurements were taken at the 2T triple axis spectrometer at the Laboratoire Léon Brillouin (Saclay, France), and at the IN8 triple
vectors indexed in units of the tetragonal reciprocal lattice \( Q \) were accessible. We use a notation in which cuprates reads

\[
\chi_{o,e}(Q, \omega) = \text{Im} \chi_{o,e}(Q, \omega)
\]

where \( \text{Im} \chi_{o,e}(Q, \omega) \) is the imaginary part of the dynamical magnetic susceptibility in the odd and even channels, respectively. \( zc = 3.3 \) \( \AA \) 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 \( Q = (0, 0, 5.2) \) versus excitation energy \( E \). Constant-energy scans at \( E^o = 36 \) meV along the \( L \)-direction perpendicular to the CuO\(_2\) planes at 10 K 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 \( (H, H, L_0) \) 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 \( E = E^o \) and \( Q = Q_{AF} \).

axis spectrometer at the Institut Laue Langevin (Grenoble, France). On 2T, 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 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 \( 2\pi/a = 1.64 \) \( \AA^{-1} \) and \( 2\pi/c = 0.54 \) \( \AA^{-1} \).

As discussed previously \[14, 17, 18\], the cross section for magnetic neutron scattering from bilayer cuprates reads

\[
\frac{\partial^2 \sigma(Q, \omega)}{\partial \Omega \partial \omega} \propto F^2(Q) \left[ \sin^2(\pi z L) \text{Im} \chi_o(Q, \omega) + \cos^2(\pi z L) \text{Im} \chi_e(Q, \omega) \right]
\]

where \( \text{Im} \chi_o,e(Q, \omega) \) is the imaginary part of the

---

**FIG. 1:** (left) Susceptibility of 15 individual \( \text{Y}_{1.9} \text{Ca}_{0.1} \text{Ba}_2 \text{Cu}_3 \text{O}_7 \) 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 co-oriented overdoped single crystals. 60 crystals are glued onto Al plates only one of which is shown for clarity.

**FIG. 2:** 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 \( E^o = 36 \) meV along the \( L \)-direction perpendicular to the CuO\(_2\) planes at 10 K 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 \( (H, H, L_0) \) 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 \( E = E^o \) and \( Q = Q_{AF} \).
ergy for a given temperature difference, because the background is predominantly determined by multphonon 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. 2b and 2c) 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 \(\Delta Q = 0.25 \pm 0.0.05\) Å\(^{-1}\) determined for the resonant mode in YBCO\(_7\). The temperature dependence of the peak intensity (Fig. 2d) shows that the mode vanishes in the normal state, similarly to the optimally doped systems.

While these observations are largely consistent with previous work [2,3,4,5,6,7], some new aspects of the data of Fig. 2 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. 2b). Second, the sinusoidal intensity modulation along \(L\) is not complete as some intensity remains at \(L = 3.6\) and 7.2 (Fig. 2c). 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. 3a) reveals a new mode around an energy of 43 meV, clearly different from the mode energy in the odd channel (open symbols in Fig. 3a). Such an even excitation has not been observed in previous INS 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 [10].

In-plane constant-energy scans performed at maxima of the even structure factor in different Brillouin zones (Figs. 3a and 3b) 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\(^{2+}\) [11] (Fig. 3b). 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. 3c) differs from the \(\cos^2\) dependence expected for the even mode (Eq. 1). As shown by Fig. 3b, the deviation from the expected \(\cos^2\) dependence is probably related to a combined effect of the anomalous lineshapes of both modes and their relative spec-
FIG. 4: Temperature dependence of the neutron intensity at $Q_{AF} = (0.5, 0.5, L)$ at the even mode energy $E^e_o = 45$ meV and $L = 3.5$ (full circles and left scale). The temperature dependence of the odd mode (open circles and right scale) of Fig. 4, has been superposed without the error bars for clarity.

The temperature dependences of the odd and even modes are closely similar (Fig. 4). Moreover, Fig. 4 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. 4). The energy profiles of both modes are identical to within the experimental error. Calculation of the magnetic intensity to that of an optical phonon [6] and integrating over the asymmetric profiles in energy yields spectral weights of $W_o(Q_{AF}) = \int \omega d\omega f m(\omega) = 0.8 \mu_B^2/L$ per formula unit (f.u.) and $W_e(Q_{AF}) = 0.36 \mu_B^2/L$ per odd and even modes, respectively. Averaged over the entire Brillouin zone, this corresponds to $\langle W_o(Q) \rangle = 0.042 \mu_B^2/L$ and $\langle W_e(Q) \rangle = 0.036 \mu_B^2/L$. These values should be compared with $W_o(Q_{AF}) = 1.6 \mu_B^2/L$ and $W_o(Q) = 0.043 \mu_B^2/L$ for the odd mode in YBCO [7]. 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 [17, 18, 20]. The observation that the difference between the mode energies, $E^e_o - E^o_o \approx 7$ meV, is of the order of $J_\perp \sim 10$ meV, the interlayer superexchange coupling determined experimentally in insulating YBCO [19], 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, $\omega_c - E^o_o \approx 18$, so that

$$\frac{W_o(Q_{AF})}{W_e(Q_{AF})} = \frac{\omega_c - E^o_o}{\omega_c - E^e_o} \quad (2)$$

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 $Q_{AF}$. 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 $\omega_c$ 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 $\omega_c$ 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 $\Delta_k$.

*To whom correspondence should be addressed; E-mail: bourges@bali.saclay.cea.fr

[1] H.F. He et al., Science 295, 1045 (2002).
[2] J. Rossat-Mignod et al., Physica C 185-189, 86 (1991).
[3] H.A. Mook et al., Phys. Rev. Lett. 70, 3490 (1993).
[4] H.F. Fong et al., Phys. Rev. Lett. 75, 316 (1995).
[5] P. Bourges, L.P. Regnault, Y. Sidis, C. Vettier, Phys. Rev. B 53, 876 (1996).
[6] H.F. Fong et al., Phys. Rev. B 61, 14773 (2000).
[7] P. Dai et al., Phys. Rev. B 63, 054525 (2001).
[8] H.F. Fong et al., Nature 398, 588 (1999).
[9] H.F. He, et al., Phys. Rev. Lett. 86, 1610 (2001).
[10] Ar Abanov et al., Phys. Rev. Lett. 89, 177002 (2002), and references therein.
[11] M. Eschrig, M.R. Norman, Phys. Rev. B 67, 144503 (2003), and references therein.
[12] J.F. Zasadzinski et al., Phys. Rev. Lett. 87, 067005 (2001), and references therein.
[13] D. Reznik et al., Phys. Rev. B 53, R14741 (1996).
[14] T. Li, Phys. Rev. B 64, 012503 (2001).
[15] C.T. Lin, B. Liang, H.C. Chen, J. Crystal Growth 237-239, 778 (2002).
[16] D.L. Feng et al., Phys. Rev. Lett. 86, 5550 (2001); Y.D. Chuang et al., Phys. Rev. Lett. 87, 117002 (2001); A. Kaminski et al., Phys. Rev. Lett. 90, 207003 (2003).
[17] D.Z. Liu, Y. Zha, K. Levin, Phys. Rev. Lett. 75, 4130 (1995).
[18] A.J. Millis, H. Monien, Phys. Rev. B 54, 16172 (1996).
[19] S. Shamoto et al., Phys. Rev. B 48, 13817 (1993).
[20] F. Onufrieva, P. Pfeuty, Phys. Rev. B 65, 054515 (2002).