Magnetic Excitations and their energy change available to Superconducting Condensation in Optimally Doped YBa$_2$Cu$_3$O$_{6.95}$

Hyungje Woo$^{1,2}$ Pengcheng Dai$^{1,2}$ S. M. Hayden$^3$ H. A. Mook$^2$
T. Dahn$^4$, D. J. Scalapino$^5$, T. G. Perring$^6$, and F. Doğan$^7$

$^1$ Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee 37996-1200, USA
$^2$ Center for Neutron Scattering, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA
$^3$ H. H. Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL, UK
$^4$ Institut für Theoretische Physik, Universität Tübingen, Auf der Morgenstelle 14, D-72076 Tübingen, Germany
$^5$ Department of Physics, University of California, Santa Barbara, California 93106, USA
$^6$ ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon, OX11 0QX, UK
$^7$ Department of Ceramic Engineering, University of Missouri-Rolla, Rolla, Missouri 65409-0330, USA

Understanding the magnetic excitations in high-transition temperature (high-$T_c$) copper oxides is important because they may mediate the electron pairing for superconductivity [1, 2]. By determining the wavevector ($Q$) and energy ($h\omega$) dependence of the magnetic excitations, one can calculate the change in the energy available to the superconducting condensation energy $\Delta E_{ex}$ for the high-$T_c$ superconductor YBa$_2$Cu$_3$O$_6$$+\delta$, the most prominent feature in the magnetic excitations is the resonance $[6, 7, 8, 9, 10, 11, 12]$. Although the resonance has been suggested to contribute a major part of the superconducting condensation $[4, 13]$, the accuracy of such an estimation has been in doubt because the resonance is only a small portion of the total magnetic scattering $[12, 13, 14]$. Here we report an extensive mapping of magnetic excitations for YBa$_2$Cu$_3$O$_{6.95}$ ($T_c \approx 93$ K). Using the absolute intensity measurements of the full spectra, we estimate the change in the magnetic exchange energy between the normal and superconducting states and find it to be about 15 times larger than the superconducting condensation energy $[15, 16]$. Our results thus indicate that the change in the magnetic exchange energy is large enough to provide the driving force for high-$T_c$ superconductivity in YBa$_2$Cu$_3$O$_{6.95}$.

If magnetic excitations are mediating electron pairing in the high-$T_c$ copper oxides, one expects that the change in magnetic exchange energy provides enough energy for superconducting condensation. The condensation energy is known experimentally from specific heat measurements for YBa$_2$Cu$_3$O$_6$$+\delta$ (YBCO) to be $\sim 3$ K/formula unit (f.u.) $[12, 13]$. Within the $t$-$J$ model the change in magnetic exchange energy can be calculated from the nearest neighbor spin correlations $[2, 4, 5]$:

$$\Delta E_{ex} = 2J \left( \left\langle \vec{S}_i \cdot \vec{S}_j \right\rangle_S - \left\langle \vec{S}_i \cdot \vec{S}_j \right\rangle_N \right)$$

where $J$ is the exchange interaction, $\vec{S}_i$ and $\vec{S}_j$ are the electron spin operators at nearest-neighbor Cu sites $i$ and $j$ in the CuO$_2$ plane, respectively. Instead of estimating the magnetic resonance’s contribution to the superconducting condensation $[12, 13]$, we seek here to calculate $\Delta E_{ex}$ from the entire observable magnetic excitation spectrum. In general, a complete determination of the magnetic excitation spectrum is difficult as spin fluctuations can spread over a large wavevector and energy range. YBCO has two CuO$_2$ planes per unit cell (bilayer) and therefore the magnetic excitations have odd (acoustic) or even (optical) symmetry with respect to the neighboring planes (Fig. 1). For optimally doped YBCO, the magnetic excitation spectrum is dominated by a resonance mode centered at 41 meV in the acoustic channel $[3, 4]$, and a mapping of the acoustic and optical magnetic excitations should allow an estimation of $\Delta E_{ex}$.

Figure 1 summarizes the key conclusions of our work. The optical and acoustic spin fluctuations can be separated by their differences in $q_z$-dependence (Fig. 1b). The total magnetic response $\chi''(Q, \omega)$ can then be written as:

$$\chi''(q_x, q_y, \omega) = \chi''_{ac}(q_x, q_y, \omega) \sin^2(q_z d/2) + \chi''_{oa}(q_x, q_y, \omega) \cos^2(q_z d/2),$$

where $d = 3.342$ Å is the spacing between the nearest neighbor CuO$_2$ planes along the $c$-axis. To probe the entire magnetic spectra in optical and acoustic channels of YBCO, we used the MAPS spectrometer at ISIS Facility $[12, 17]$ and chose incident beam energies of $E_i = 30, 40, 62.5, 75, 90, 110, 130, 138, 160, 210, 280, 360,$ and 450 meV with the incident beam along the $c$-axis. The position sensitive detectors on MAPS allow a complete determination on the $Q$-structure of incommensurate spin fluctuations for YBCO in one experimental setting $[12]$. This avoids the complication of de-convoluting the instrumental resolution necessary for structure determination of incommensurate peaks using triple-axis spectroscopy $[18]$. The temperatures probed were $T = 15, 100,$ and 290 K. The intensity difference between 15 K and 100 K is almost entirely magnetic because of the small value of $Q^2$ probed by the experiment and small change in the Bose factor for $h\omega > 30$ meV $[7, 10, 16]$.

Figures 2(a)-(c) summarize the temperature depen-
On warming to 100 K, the resonance disappears and the scattering shows a sharp resonance centered at 41 meV obtained by using reciprocal lattice units (r.l.u.), where \( a = 3.82, b = 3.88 \) and \( c = 11.68 \) Å are lattice parameters of the scattering around the 41 meV acoustic resonance \( \omega \). (a) Schematic diagram for YBCO. (b) The \( T \)-dependence of acoustic and optical spin fluctuations for \( E_i = 200 \) meV. (c) Dispersion of constant energy peaks in \( \chi''(Q, \omega) \). The orientation of incommensurate peaks is shown in the inset. (d) Dispersion constant energy peaks in \( \chi''(Q, \omega) \). The solid line shows spin-wave dispersion from undoped YBa\(_2\)Cu\(_3\)O\(_6\) \( \approx 15 \) K in (d) while (a) shows incommensurate scattering. The intensity of phonons increases with increasing temperature and wavevector \( \omega \).

### FIG. 1: Summary of \( Q \) and \( \omega \)-dependence of dynamic susceptibility for YBCO. Our experiments were carried out on the \( \sim \)117-g YBCO single crystal \( (T_c = 92.5 \) K) used in previous work. We specify the momentum transfer \( (q_h, q_k, q_l) \) (in units of \( \AA^{-1} \)) as \( (h, k, l) = (q_h a/2\pi, q_k b/2\pi, q_l c/2\pi) \) in reciprocal lattice units (r.l.u.), where \( a = 3.82, b = 3.88 \) and \( c = 11.68 \) Å are lattice parameters. The red circles and black squares are obtained from undoped YBa\(_2\)Cu\(_3\)O\(_6\) \( \approx 15 \) K for optical (d)-(f), and acoustic (a)-(c), \( E_i = 210 \) meV. A clear commensurate magnetic scattering is seen at \( \sim 40 \) meV at 15 K in (d) while (a) shows incommensurate scattering. The intensity of phonons increases with increasing temperature and wavevector (Fig. 2(e)). Further warming to 290 K does not change the scattering significantly (Fig. 2(f)).

Figure 3 summarizes the optical spin fluctuations for \( 31 \leq \hbar \omega \leq 75 \) meV. For \( 31 \leq \hbar \omega \leq 34 \) meV, the scattering shows no difference between normal and superconducting states (Figs. 3(a) and 3(e)). Since there is little normal state magnetic scattering, there must be an optical spin gap around 34 meV. On increasing the energy transfer to \( \hbar \omega = 39 \pm 5 \) meV, where the acoustic channel has a commensurate resonance, spin fluctuations in the optical channel form a broad incommensurate structure away from \( (1/2, 1/2) \) (Fig. 3(b)). Figure 4f confirms the incommensurate nature of the scattering and shows that the \( (h, h) \) and \( (h, 0.5) \) cut directions are inequivalent. For \( \hbar \omega = 52 \pm 5 \) meV, again we find incommensurate peaks but this time the scattering is more box-like with enhanced corners (Figs. 3(c) and 3(g)). The orientation of the scattering is rotated 45° from that in Fig. 4(b), similar to acoustic high-energy spin excitations in YBa\(_2\)Cu\(_3\)O\(_6\) \( \approx 15 \) K reveals no observable magnetic scattering (Fig. 3(h)).

Figures 4(a)-(e) show the intensity difference spectra between 15 K and 100 K at various energies in the acoustic channel. For \( 20 \leq \hbar \omega \leq 27 \) meV, the temperature difference has negative intensity, possibly due to a reduction in the magnetic response on entering the superconducting channel. For \( 31 \leq \hbar \omega \leq 75 \) meV, the scattering shows a sharp resonance centered at \( (1/2, 1/2) \) \( \approx 15 \) K for optical (d)-(f), \( E_i = 90 \) meV, and acoustic (a)-(c), \( E_i = 210 \) meV. A clear commensurate magnetic scattering is seen at \( \sim 40 \) meV at 15 K in (d) while (a) shows incommensurate scattering.
FIG. 3: Temperature difference (15 K−100 K) at various energies for optical mode defined as scattering with $\cos^2(qzd/2) > 0.8$. Images (a)-(d) are obtained with $E_i = 75, 90, 130, 210$ meV, respectively. The image at $\bar{h}\omega = 45.5 \pm 1.5$ meV does not have enough statistics to determine the $Q$-structure. Panels (e)-(h) are cuts with $h \omega = 32.5 \pm 1.5, 5, 5.2 \pm 5.6, 6 \pm 9$ meV, respectively. The upper panel of (h) shows a cut through the unsubtracted data of (h) at 15 K. The vertical error bars in (e-h) are statistical uncertainties ($1\sigma$).

FIG. 4: Temperature difference spectra (15 K−100 K) at various energies for acoustic mode defined as any scattering with $\sin^2(qzd/2) > 0.8$ (see Fig. 1d). Images (a)-(e) are obtained with $E_i = 90, 210, 210, 90, 110$ meV, respectively. Cuts in (f)-(j) are obtained with $h \omega = 41 \pm 5, 31 \pm 4, 40 \pm 5, 55.5 \pm 3.5, 64.5 \pm 4.5$ meV, respectively. The upper panel of (j) shows a cut through the unsubtracted data of (e) at 15 K. The instrumental $Q$-resolutions are marked by white circles in (a)-(e). The vertical error bars in (f-j) are statistical uncertainties ($1\sigma$).
magnetic spectral weight gradually increases from above the spin-gap value of ~30 meV \cite{10}, peaks at 46 meV, and finally diminishes for energies above ~70 meV. The acoustic channel behaves similarly although it peaks at the expected resonance position of 40 meV \cite{11}. The magnitude of the total spectral weight in the optical channel \(\langle m^2\rangle_{op} = 0.078 \pm 0.02 \mu_B^2\) and in the acoustic channel is \(\langle m^2\rangle_{ac} = 0.102 \pm 0.02 \mu_B^2\) per f.u. respectively. This value is similar to that for YBa\(_2\)Cu\(_3\)O\(_{6.6}\) around the acoustic resonance energy \(\langle m^2\rangle_{ac} = 0.12 \pm 0.02 \mu_B^2/f.u.\) for \(24 < h\omega < 44 \text{ meV}\) \cite{12}. Since the high-energy response in underdoped YBa\(_2\)Cu\(_3\)O\(_{6+x}\) \((x = 0.5, 0.6)\) takes up much more spectral weight than the resonance \cite{11, 12}, it is surprising that there is essentially no observed magnetic response for energies above 60 meV in YBCO (Fig. 1f). Compared to undoped YBa\(_2\)Cu\(_3\)O\(_{6.15}\) \cite{20, 21}, which has a total integrated moment of ~0.4 \(\mu_B^2/\text{f.u.}\) when integrated up to 120 meV, the total integrated moment in optimally doped YBCO has only about 26\% of the spectral weight in the same energy range in the acoustic channel only.

Using the spin excitation spectra in Figs. 3 and 4, we have calculated the changes in the magnetic excitations from the normal to the superconducting state and estimated \(\delta \langle \vec{S}_i \cdot \vec{S}_j \rangle = -0.020 \pm 0.008/\text{f.u.},\) where \(\langle \vec{S}_i \cdot \vec{S}_j \rangle\) is the spin-spin correlation function for nearest neighbour copper atoms (see supplementary information). This estimate neglects contributions from energies below 24 meV and above 70 meV, where magnetic scattering is difficult to resolve. Also, in Eq. 11 the difference between normal and superconducting state is meant to be determined at the same temperature, while here we had to take normal state data at 100 K and superconducting state data at 15 K neglecting a possible temperature dependence of the normal state magnetic excitations. In order to assess the error introduced by these neglects, we have fitted an RPA-BCS model calculation of the spin excitation spectrum \cite{22} to our data and calculated the missing contributions within this model. This calculation indicates that our value for \(\Delta E_{xx}\) could be of order 30\% too large due to these neglects (see supplementary information).

Assuming an exchange coupling of \(J = 100 \text{ meV}\), the change in exchange energy would be \(\Delta E_{xx} = 2J \delta \langle \vec{S}_i \cdot \vec{S}_j \rangle = -4.1 \text{ meV/f.u.} = -24 \text{ K/planar Cu}\). This value is a factor of 1.3 times larger than the 18 K/Cu estimated from the acoustic resonance alone in previous work \cite{8}. Even if we consider that our estimation may be too large by 30\%, the change in the exchange energy is still much larger than the \(U_0 \approx 25(J/\text{mole}) \approx 0.26 \text{ meV/f.u.} = 3 \text{ K/planar Cu}\). This value indicates that our value for \(\Delta E_{xx}\) is actually incommensurate and this naturally explains the large Q-widths previously reported. Second, our determination of the dynamical susceptibility in absolute units allows an estimation of the change of the magnetic excitation energy available to the superconducting condensation energy \(\Delta E \approx 4\) \cite{4, 14, 20}. We find that the magnetic exchange energy is about 15 times larger than that of the superconducting condensation energy, thus indicating magnetism can be the driving force for electron pairing and superconductivity.

\begin{thebibliography}
1. Scalapino, D. J. The case for \(d_{x^2-y^2}\) pairing in the cuprate superconductors. Phys. Reports 250, 330-365 (1995).
2. Chubukov, A., Pines, D., & Schmalian, J., in The Physics of Superconductors, Vol I, Conventional and High-\(T_c\) Superconductors (ed. by Bennemann, K.H. & Ketterson, J.B.) 495-590 (Springer, Berlin, 2003).
3. Scalapino, D. J. & White, S. R. Superconducting condensation energy and an antiferromagnetic exchange-based pairing mechanism. Phys. Rev. B 58, 8222-8224 (1998).
4. Demler, E. & Zhang, S-C. Quantitative test of a microscopic mechanism of high-temperature superconductivity. Nature 396, 733-735 (1998).
5. Maier, Th. A. On the nature of pairing in the two-dimensional \(t-J\) model. Physica B 359-361, 512-514 (2005).
6. Rossat-Mignod, J. et al. Neutron scattering study of the YBa\(_2\)Cu\(_3\)O\(_{6+x}\) system. Physica C 185, 86-92 (1991).
7. Mook, H. A. et al. Polarized neutron determination of the magnetic excitations in YBa\(_2\)Cu\(_3\)O\(_7\). Phys. Rev. Lett. 70, 3490-3493 (1993).
8. Mook, H. A. et al. Spin fluctuations in YBa\(_2\)Cu\(_3\)O\(_{6.6}\). Nature 395, 580-582 (1998).
9. Fong, H. F. et al. Spin susceptibility in underdoped YBa\(_2\)Cu\(_3\)O\(_{6+x}\). Phys. Rev. B 61, 14773-14786 (2000).
10. Dai, P., Mook, H. A., Hunt, R. D., & Doğan, F. Evolution of the resonance and incommensurate spin fluctuations in superconducting YBa\(_2\)Cu\(_3\)O\(_{6+x}\). Phys. Rev. B 63, 054525 (2001).
11. Stock, C. et al. From incommensurate to dispersive spin fluctuations: The high-energy inelastic spectrum in superconducting YBa\(_2\)Cu\(_3\)O\(_{6.5}\). Phys. Rev. B 71, 024522 (2005).
12. Hayden, S. M., Mook, H. A., Dai, P., Perring, T. G., & Doğan, F. The structure of the high-energy spin excitations in a high-transition-temperature superconductor. Nature 429, 531-534 (2004).
13. Dai, P. et al. The magnetic excitation spectrum and thermodynamics of high-\(T_c\) superconductors. Science 284, 1344-1347 (1999).
14. Kee, H-Y., Kivelson, S. A. & Aeppli, G. Spin-1 Neutron Resonance Peak Cannot Account for Electronic Anomalies in the Cuprate Superconductors. Phys. Rev. Lett. 88, 257002 (2002).
15. Loram, J. W., Mirza, K. A., Cooper, J. R. & Tullon, J. L. Specific heat evidence on the normal state pseudogap, J. Phys. Chem. Solids. 59, 2091-2094 (1998).
16. Lortz, R. et al. Evolution of the specific-heat anomaly
\end{thebibliography}
of the high-temperature superconductor in YBa$_2$Cu$_3$O$_7$
under the influence of doping through application of pressure
up to 10 GPa. J. Phys.: Condens. Matter 17, 4135-4145 (2005).

[17] Woo, H. et al. Mapping spin-wave dispersions in stripe-
ordered La$_{2-x}$Sr$_x$NiO$_4$ ($x = 0.275, 0.333$). Phys. Rev. B 72, 064437 (2005).

[18] Reznik, D. et al. Dispersion of Magnetic Excitations in
Optimally Doped Superconducting YBa$_2$Cu$_3$O$_{6.95}$. Phys.
Rev. Lett. 93, 207003 (2004).

[19] Regnault, L. P. et al. Spin dynamics in the high-$T_c$
superconducting system YBa$_2$Cu$_3$O$_{6+x}$. Physica B 213 &
214, 48-53 (1995).

[20] Hayden, S. M. et al. High-frequency spin waves in
YBa$_2$Cu$_3$O$_{6.15}$. Phys. Rev. B 54, R6905-R6908 (1996).

[21] Reznik, D. et al. Direct observation of optical magnons in
YBa$_2$Cu$_3$O$_{6.2}$. Phys. Rev. B 53, R14741-R14744 (1996).

[22] Dahm, T. et al., Nodal quasiparticle lifetimes in cuprate
superconductors. Phys. Rev. B 72, 214512 (2005).

[23] Pailhes, S. et al. Resonant Magnetic Excitations at High
Energy in Superconducting YBa$_2$Cu$_3$O$_{6.85}$. Phys. Rev.
Lett. 93, 167001 (2004).

[24] Pailhes, S. et al. Two Resonant Magnetic Modes in an
Overdoped High $T_c$ Superconductor. Phys. Rev. Lett. 91,
237002 (2003).

[25] Chen, W. Q. & Weng, Z. Y. Spin dynamics in a doped-
Mott-insulator superconductor. Phys. Rev. B 71, 134516
(2005).

[26] Chakravarty, S. & Kee, H-Y. Measuring condensate
fraction in superconductors. Phys. Rev. B 61, 14821-14824
(2000).

 Correspondence and requests for materials should
be addressed to P.D. (daip@ornl.gov) or H.A.M.
(ham@ornl.gov).

Acknowledgments We thank Elbio Dagotto, Z. Y.
Wen, and F. C. Zhang for helpful discussions. This work
is supported by the US DOE Office of Science, Division of
Materials Science, Basic Energy Sciences under contract
No. DE-FG02-05ER46202 (H.W. and P.D.). Oak Ridge
National Laboratory is supported by the US DOE under
contract No. DE-AC05-00OR22725 with UT/Battelle
LLC. SMH is supported by the UK EPSRC. DJS would
like to acknowledge the Center for Nanophase Material
Science at Oak Ridge National Laboratory for their sup-
port. Supplementary Information accompanies this pa-
per on www.nature.com/naturephysics.

Competing financial interests
The authors declare that they have no competing fi-
nancial interests.