Phonon and Magnetic Neutron Scattering at 41 meV in $YBa_2Cu_3O_7$

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We report inelastic neutron scattering measurements at excitation energies $\hbar\omega \sim 41$ meV in $YBa_2Cu_3O_7$. We separate magnetic and phonon contributions to the scattering cross section by a detailed analysis of the momentum dependence of the scattered intensity. The previously reported broad peak around $\mathbf{q} = (\pi/a, \pi/a)$ in the normal state can be entirely accounted for by a phonon which primarily involves vibrations of the in-plane oxygen. Magnetic scattering centered around 41 meV and $\mathbf{q} = (\pi/a, \pi/a)$ appears in the superconducting state *only*. Theoretical implications of these findings are discussed.

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An important experimental constraint on microscopic models of the normal and superconducting states of the copper oxide superconductors is the generalized magnetic susceptibility whose imaginary part $\chi''(\mathbf{q}, \omega)$ is measurable by neutron scattering. Below the superconducting transition temperature of fully oxygenated $YBa_2Cu_3O_{6+x}$ ($x \sim 1, T_c \sim 90$ K), a sharp peak in $\chi''(\mathbf{q}, \omega)$ at $\hbar\omega =$ 41 meV and $\mathbf{q}_{2D} = (\frac{1}{2}, \frac{1}{2})$ was discvoered by Rossat-Mignod *et al.* [1] and later confirmed to be of magnetic origin in polarized neutron scattering experiments by Mook *et al.* [2]. (We quote the in-plane momentum $\mathbf{q}_{2D}$ in units of $2\pi/a \sim 1.63$ Å^{-1} and the momentum L perpendicular to the layers in the units of $2\pi/c \sim$ 0.54 Å^{-1}). Because of the extremely time consuming nature of neutron polarization analysis, the presently available polarized-neutron data are very limited, and the normal state data thus far reported are inconclusive. A detailed characterization of the energy, momentum, and temperature dependence of $\chi''(\mathbf{q}, \omega)$ can only be achieved by unpolarized-neutron scattering. Using unpolarized neutron scattering, both Rossat-Mignod *et al.* [1] and Mook *et al.* [2] reported a broad peak around $\mathbf{q}_{2D} = (\frac{1}{2}, \frac{1}{2})$ in the normal state, which they interpreted as arising from magnetic excitations. We exploit the different dependence of phonon and magnetic scattering on the magnitude and direction of the momentum transfer to show that this peak is due to phonon scattering, in particular, scattering from a c-axis vibration of the in-plane oxygen which has been studied extensively by Raman scattering [3]. We agree with previous conclusions [1,2] about the magnetic origin of the sharp peak below T_c. Since there is no evidence for magnetic scattering centered around 41 meV in the normal state, this excitation can be understood as arising from quasiparticle creation by magnetic neutron scattering. An analysis of the coherence factors for this process is given.

Our measurements were made possible by the synthesis of a very large $YBa_2Cu_3O_{6+x}$ crystal of volume $\sim$10 cm^3 and mosaicity $\sim$2°. Careful measurements of the lattice constants show that the crystal is very close to full stoichiometry ($x \geq 0.95$). Susceptibility measurements on crystals prepared under identical conditions revealed superconducting transitions of width 0.25 K at $T_c = 93.0$ K, and Meissner fractions near 100%. Even more stringent tests of sample quality and oxygen content and homogeneity are measurements of the superconductivity-induced softening of certain phonons, as is briefly indicated below.

The neutron experiments were performed on the H7 and H8 triple-axis spectrometers at the High Flux Beam Reactor at the Brookhaven National Laboratory. The (002) reflection of pyrolytic graphite (PG) was used as the analyzer, the beam collimations were 40′-40′-80′-80′, and the final neutron energy was kept fixed at 30.5 meV. We used two different monochromators, the (002) reflection of beryllium yielding an energy resolution of $\Delta E =$ 5.4 meV (full width at half maximum) and the (002) reflection of PG yielding $\Delta E = 8.3$ meV. A PG filter was placed behind the sample in order to eliminate higher order contamination of the scattered beam.

The goal of our experiment was to obtain detailed information about the spatial character of phonon and magnetic excitations which can be extracted from the momentum dependence of the neutron cross section. The cross section for coherent scattering from a phonon mode is proportional to

$$\left(\frac{d^2\sigma}{d\Omega\, dE}\right)_{\text{phonon}} \sim \frac{1}{\omega(\mathbf{q})}\left(\sum_{\mathbf{d}} e^{-i\mathbf{q}\cdot\mathbf{d}}\frac{[\mathbf{Q}\cdot\hat{\eta}_{\mathbf{d}}(\mathbf{q})]e^{-W_{\mathbf{d}}(\mathbf{Q})}b_{\mathbf{d}}}{\sqrt{M_{\mathbf{d}}}}\right)^2, \tag{1}$$

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where $\mathbf{Q}$ is the momentum transferred to the neutron, and $\mathbf{q} = \mathbf{Q} - \tau$ for any reciprocal lattice vector τ. $b_{\mathbf{d}}$, $M_{\mathbf{d}}$, and $\hat{\eta}_{\mathbf{d}}(\mathbf{q})$ are the scattering length, mass, and displacement of the atom at basis site $\mathbf{d}$ in the unit cell, respectively. $W_{\mathbf{d}}$ is the weakly $\mathbf{Q}$-dependent Debye-Waller factor, and $\omega(\mathbf{q})$ is the phonon energy.

Low-energy spin waves in antiferromagnetic $YBa_2Cu_3O_{6+x}$ $(0 \lesssim x \lesssim 0.45)$ give rise to inelastic magnetic scattering around the antiferromagnetic zone center $\mathbf{q}_{2D} = (\frac{1}{2}, \frac{1}{2})$. Because of the strong coupling of Cu spins within one bilayer the cross section for inelastic magnetic neutron depends on L as follows [4]:

$$\left(\frac{d^2\sigma}{d\Omega\, dE}\right)_{\text{magnon}} \sim \frac{f^2(\mathbf{Q}) \sin^2(\pi z_{\text{Cu}} L)}{\omega(\mathbf{q})}, \qquad (2)$$

where $f(\mathbf{Q})$ is the Cu magnetic form factor, and $z_{\text{Cu}} = 0.291$ is the distance between nearest-neighbor Cu spins within one bilayer (for $x = 1$), expressed as a fraction of the lattice constant c. $\omega(\mathbf{q})$ is the spin wave energy. Magnetic excitations similar in character to acoustic spin waves in insulating $YBa_2Cu_3O_{6+x}$, albeit with shorter correlation lengths and reduced low-energy weight, have also been observed in the 60 K superconductors $(0.45 \lesssim x \lesssim 0.7)$ [5].

While the magnetic inelastic scattering intensity generally decreases with Q due to the presence of the magnetic form factor, the phonon intensity increases because of the $\mathbf{Q} \cdot \hat{\eta}$ polarization factor in Eq. (1). In order to distinguish both sources of scattering, a survey of the scattering intensity over a wide range of Q is therefore essential. For a given sample orientation a triple-axis spectrometer allows scans in a two-dimensional section of reciprocal space. We first mounted our sample in the standard orientation for magnetic scattering experiments for which reciprocal space points of the form (H, H, L) are accessible. Figure 1(a) shows a scan in the normal state at $T = 100$ K for which the energy and in-plane momentum transfers are held fixed at 41 meV and $\mathbf{Q}_{2D} = (\frac{1}{2}, \frac{1}{2})$, respectively, and L is scanned over the maximum range allowed by the spectrometer configuration. The scan reveals a sinusoidal modulation of the scattering intensity with L, reminiscent of Eq. (2). Scans for fixed L [Fig. 1(b)] show a broad peak around $\mathbf{Q}_{2D} = (\frac{1}{2}, \frac{1}{2})$. Scans taken for small L in the normal state have therefore been interpreted as evidence for antiferromagnetic spin excitations characterized by short in-plane correlation lengths and strong bilayer coupling [1,2].

However, inspection of Fig. 1 shows that this interpretation is untenable. First and most importantly, the scattering intensity increases with Q, inconsistent with magnetic inelastic scattering, Second, as indicated in the figure, the periodicity of the modulation along L is longer than predicted by Eq. (2). In fact, replacing z_{Cu} by $z_{\text{O}} = 0.244$, the reduced distance between nearest-neighbor oxygens within one bilayer, produces the correct periodicity. (z_{Cu} and z_{O} are different because of a slight buckling of the CuO_2 layers.)

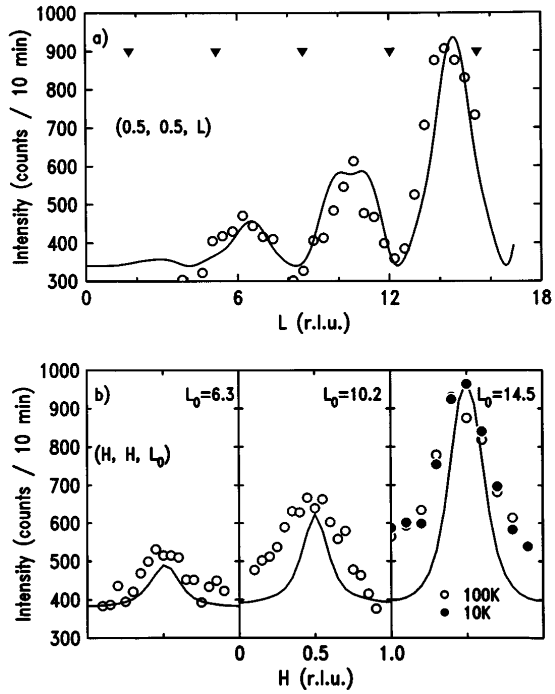

FIG. 1. Constant-energy scans with $\hbar\omega = 41$ meV along (a) $\mathbf{Q} = (\frac{1}{2}, \frac{1}{2}, L)$ and (b) $\mathbf{Q} = (H, H, L)$ with fixed L. The solid lines are predictions of a lattice dynamical calculation for scattering from the 42.7 meV oxygen vibration. Only the background and the overall scale were adjusted. The arrows in (a) indicate the maxima of $\sin^2(\pi z_{\text{Cu}} L)$ [Eq. (2) in the text].

A phonon mode of energy 42.7 meV which involves, primarily, vibrations of the in-plane oxygen is observed by Raman scattering at $\mathbf{q} = 0$ [3]. In neutron scattering experiments with high-energy resolution we have experimentally established that the phonon dispersion is less than 0.2 meV throughout the entire Brillouin zone. (The same measurements also show a superconductivity-induced softening of about 1 meV for $\mathbf{q} = 0$ [6]. Raman [3] and neutron [7] scattering measurements indicate that such large effects only occur in the highest-quality, fully oxygenated samples.) Because of the broad energy resolution used in all magnetic neutron scattering experiments, this phonon therefore contributes to the scattering intensity measured at $\hbar\omega = 41$ meV, $\mathbf{Q}_{2D} = (\frac{1}{2}, \frac{1}{2})$ unless the dynamical structure factor, Eq. (1), vanishes. Since Eq. (1) contains the phonon eigenvector, we have carried out a lattice dynamical calculation of the eigenvectors of this and other phonons for nonzero $\mathbf{q}$. For simplicity we adopted a nearest-neighbor force constant model, taking the force constants of Bates and Eldridge [8] as starting values and adjusting them until good agreement with present knowledge of the $\mathbf{q} = 0$ eigenvectors [9] was reached. The eigenvectors of the 42.7 meV oxygen vibration at $\mathbf{q} = 0$ and $\mathbf{q}_{2D} = (\frac{1}{2}, \frac{1}{2})$ are shown in Fig. 2. The predictions of this model obtained by inserting the calculated eigenvector into Eq. (1) are in excellent agreement with our data, as shown in Fig. 1. In particular, the model explicitly predicts a broad peak at $\mathbf{Q}_{2D} = (\frac{1}{2}, \frac{1}{2})$ which is

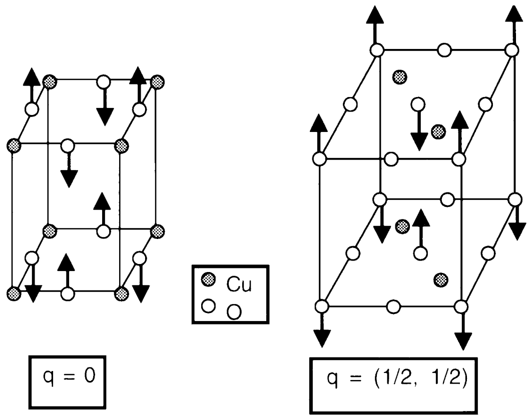

FIG. 2. Calculated eigenvectors of the 42.7 meV phonon for $\mathbf{q} = 0$ and $\mathbf{q} = (\frac{1}{2}, \frac{1}{2}, 0)$. Only one CuO_2 bilayer is shown. The arrows indicate the displacements of the in-plane oxygen ions. For clarity, smaller displacements of the Cu and Y ions are not indicated. In order to display the full symmetry of the mode, a $\sqrt{2}a \times \sqrt{2}a$ cell is shown for $\mathbf{q} = (\frac{1}{2}, \frac{1}{2}, 0)$.

robust against substantial variations of the relevant force constants. We stress that the predictions of the model involve no fits to the data, and by implementing the model of Chaplot [10] we have checked that its qualitative features are unaltered when long-range Coulomb forces are included in the calculation.

Since this phonon is polarized predominately in the c-axis direction, the factor $\mathbf{Q} \cdot \hat{\eta}$ in Eq. (1) suppresses the cross section for small L. On the other hand, the magnetic form factor increases for small L. In order to isolate magnetic excitations contributing to the neutron cross section at 41 meV, it would therefore seem preferable to conduct experiments at $\mathbf{Q} = (\frac{1}{2}, \frac{1}{2}, 1.7)$, where our model predicts the phonon scattering intensity to be very small (Fig. 1). Unfortunately, this point is inaccessible due to kinematic constraints. We therefore reoriented the sample such that reciprocal space points of the form $(3H, H, L)$ were in the scattering plane, which allowed us to reach the equivalent $\mathbf{Q} = (\frac{3}{2}, \frac{1}{2}, 1.7)$ point. $(\frac{3}{2}, \frac{1}{2}, L)$ scans at $\hbar\omega = 41$ meV above and below T_c are shown in Fig. 3. Above T_c the second peak of the sinusoidal L dependence of the phonon dynamical structure factor is clearly discernible, while the first peak is suppressed by the polarization factor, as predicted by the model calculation.

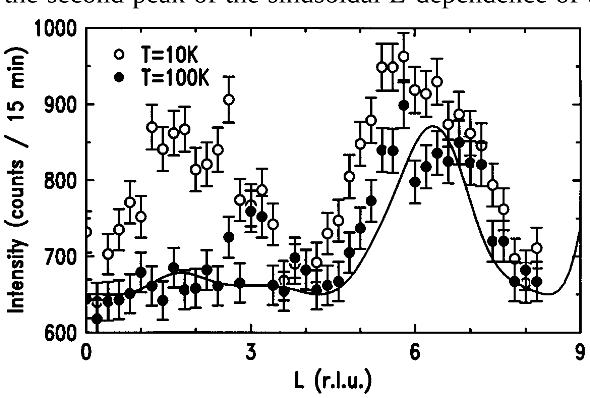

FIG. 3. Constant-energy scans with $\hbar\omega = 41$ meV along $\mathbf{Q} = (\frac{3}{2}, \frac{1}{2}, L)$ in the normal and superconducting states. The solid line is the prediction of the lattice dynamical calculation for scattering from the 42.7 meV phonon.

A new contribution to the neutron cross section appears below T_c. This additional intensity is modulated along L with a smaller periodicity consistent with z_{Cu}^{-1} (or a weighted average of z_{Cu}^{-1} and z_{O}^{-1}), and the peak intensity decreases with increasing L, as expected for magnetic scattering. Our measurements therefore confirm the magnetic origin of the additional scattering at $\hbar\omega = 41$ meV below T_c. Because of the near-absence of one-phonon scattering at $\mathbf{Q} = (\frac{3}{2}, \frac{1}{2}, 1.7)$, we can now study the momentum and energy dependence of the magnetic scattering in detail without polarization analysis. (Because of the extremely large size of our sample, a sizable multiphonon background is present. However, this background is featureless in both energy and momentum and can be readily subtracted from the data.) Figure 4 shows constant-$\mathbf{Q}$ and constant-energy scans through this position. The energy width of the peak is resolution limited even in a high resolution configuration ($\Delta E = 5.4$ meV), which implies an intrinsic width of at most about 3 meV. A deconvolution of the line shape in momentum space yields an intrinsic width of ~ 0.37 Å^{-1} (full width at half maximum).

We thus refute previous evidence for an enhancement of the magnetic cross section at $\hbar\omega = 41$ meV and $\mathbf{q}_{2D} = (\frac{1}{2}, \frac{1}{2})$ in the normal state. Of course, our data do not imply the complete absence of magnetic scattering in the normal state, especially scattering that is either very weak or distributed broadly in both energy and momentum. However, the fact that the 41 meV excitation appears in the superconducting state *only* has important implications for its theoretical interpretation. For high excitation energies and low temperatures, creation of quasi-

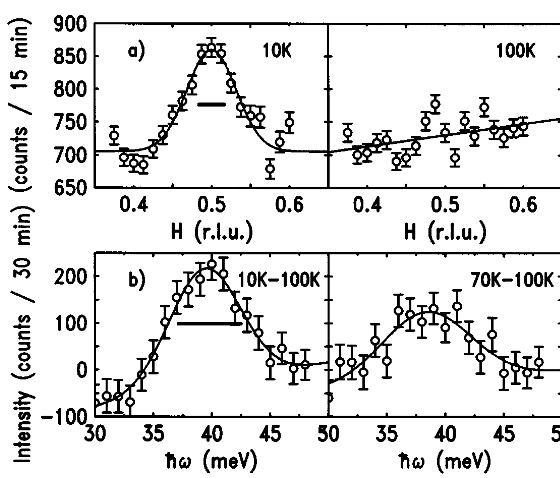

FIG. 4. (a) Constant-energy scans with $\hbar\omega = 41$ meV along $(3H, H, 1.7)$ and (b) constant-$\mathbf{Q}$ scans with $\mathbf{Q} = (\frac{3}{2}, \frac{1}{2}, 1.7)$. In (b) the difference between 10 K (70 K) and 100 K is plotted. The raw data also show a contribution of a phonon centered at $\hbar\omega \sim 30$ meV. The instrumental momentum and energy resolutions are indicated by bars. The solid lines are guides to the eye.

electron/quasihole pairs gives the dominant contribution to $\chi(\mathbf{q},\omega)$. The coherence factor for this process is [11]

$$1 - \frac{\epsilon(\mathbf{k})\epsilon(\mathbf{k}+\mathbf{q}) + \Delta(\mathbf{k})\Delta(\mathbf{k}+\mathbf{q})}{E(\mathbf{k})E(\mathbf{k}+\mathbf{q})}. \quad (3)$$

Here, $\mathbf{k}$ and $\mathbf{k}+\mathbf{q}$ are two-dimensional momenta, $\Delta(\mathbf{k})$ is the energy gap, $\epsilon(\mathbf{k})$ is the single-particle energy measured from the Fermi surface, and $E(\mathbf{k}) = \sqrt{\epsilon(\mathbf{k})^2 + \Delta(\mathbf{k})^2}$ is the quasiparticle energy. The minus sign reflects the fact that the magnetic neutron scattering cross section is odd under time reversal symmetry. The coherence factor is appreciable only if the energy gap has opposite sign at the points at which the two quasiparticles are created. In particular, d-wave symmetry of the energy gap (or a generalization appropriate for orthorhombic structures [12]) would explain why magnetic scattering is enhanced in the superconducting state for scattering between adjacent lobes of the gap [$\mathbf{q} = (k_F, k_F)$], but not for $\mathbf{q} = 0$ [13]. The overall intrinsic momentum width of the 41 meV peak is consistent with four unresolved equivalent peaks at the positions expected in this scenario. (k_F determined by photoemission experiments [14] is close to π/a on the scale of our vertical and in-plane momentum resolutions [5].) Theoretical calculations which include band structure effects and/or final-state interactions between quasiparticles are necessary to explain the experimental observations in detail, especially the sharpness of the peaks in both momentum and energy [15]. Other gap functions with sign reversals between different bands [16] may also be consistent with our data. Further experiments are necessary to elucidate the behavior of the excitation close to T_c.

The sinusoidal dependence of the measured $\chi''(\mathbf{q},\omega)$ on L indicates a strong coupling between adjacent CuO_2 layers. A tight binding model of a Cu_2O_4 bilayer predicts two bands formed by symmetric and antisymmetric combinations of wave functions centered on each of the layers. Intraband and interband transitions have dynamical susceptibilities with different L dependences [5]. The behavior observed in our experiment is the one expected for an interband transition. However, the simple band picture cannot explain why intraband excitations are not observed. Moreover, recent photoemission experiments on bilayer cuprates [17] give no evidence for splitting of the two bands in momentum space or energy, which seems to suggest that the two planes establish their energy gaps structure independently. The L dependence of the neutron scattering signal reported here, on the other hand, shows that the final state is coherent between the planes, requiring interlayer tunneling to play a role.

In conclusion, we have demonstrated experimentally that the 41 meV magnetic excitation in $YBa_2Cu_3O_7$ occurs in the superconducting state only. This observation allows us to identify its origin as quasiparticle pair creation by magnetic neutron scattering, which in turn necessitates a sign reversal of the superconducting gap on the Fermi surface. Neutron spectroscopy is thus an important probe of the microscopic nature of the superconducting state of $YBa_2Cu_3O_7$, and possibly a direct probe of the magnitude and phase of the superconducting energy gap. Detailed calculations are necessary to elucidate the role of band structure, final-state interactions, and interlayer hopping.

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