

Absence of an isotope effect in the magnetic resonance in high- T_c superconductors

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An inelastic neutron-scattering experiment has been performed in the high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{6.89}$ to search for an oxygen-isotope shift of the well-known magnetic-resonance mode at 41 meV. Contrary to a recent prediction [I. Eremin *et al.*, Phys. Rev. B **69**, 094517 (2004)], a negligible shift (at best $\leq +0.2$ meV) of the resonance energy is observed upon oxygen isotope substitution ($^{16}\text{O} \rightarrow ^{18}\text{O}$). This suggests a negligible spin-phonon interaction in the high- T_c cuprates at optimal doping.

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In conventional superconductors, pairing between electrons is mediated by lattice vibrations.¹ This has been demonstrated by an isotope effect on the superconducting (SC) transition temperature, T_c . In high- T_c copper oxide superconductors, T_c exhibits a weak shift at optimal doping upon isotope substitution,² which increases at lower doping. In particular, the oxygen-isotope shift ($^{16}\text{O} \rightarrow ^{18}\text{O}$) has been extensively studied.³⁻⁵ At optimal doping, a small isotope-effect exponent is deduced $\alpha_{T_c} = -d \ln T_c / d \ln M \approx 0.05$ much lower than the $\frac{1}{2}$ value expected from pure electron-phonon interaction, casting some doubt on a superconducting mechanism mediated by phonons. Further, the proximity of the antiferromagnetic (AF) insulating state and the unconventional d -wave symmetry of the SC gap favored mechanisms for high- T_c superconductivity where electron-electron (el-el) interactions predominate. However, there has been a revival of interest in electron-phonon coupling as several experiments point towards a non-negligible electron-phonon interaction.⁶⁻⁸ In particular, the “kink” change of slope of electronic dispersion observed around ~ 70 meV by angle-resolved photoemission spectroscopy (ARPES) along the nodal direction in various cuprates could be interpreted as an electronic coupling to a phonon mode.⁶ As a matter of fact, various physical properties, such as penetration depth⁷ or ARPES spectra,⁸ display relatively large isotope effects thus highlighting the open question: What can be the role of phonons in determining the superconducting properties of cuprates?

On the other hand, the spin excitation spectrum of the copper oxide superconductors is particularly rich. Above T_c , magnetic fluctuations are mainly observed around the planar wave vector $\mathbf{Q}_{\text{AF}} \equiv (\pi/a, \pi/a)$, characteristic of antiferromagnetism (AF) in the undoped parent compounds.⁹⁻¹² Below T_c , a collective magnetic mode, referred to as the “resonance peak,” appears at a well-defined energy⁹⁻¹⁴ at $(\pi/a, \pi/a)$ and exhibits strong dispersions for wave vectors around \mathbf{Q}_{AF} (Refs. 15–17). This mode is now observed in all high- T_c superconductor systems studied by inelastic neutron-scattering (INS) experiments^{9,18,19} whose maximum T_c reaches 90 K. Recently, an analogous feature has even been reported in the single-layer material $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ as well.²⁰

Depending on whether or not the magnetic fluctuations are observed in the normal state, the resonance peak either corresponds to a modification of magnetic spectrum in both momentum and energy (in underdoped cuprates)¹⁰⁻¹² or simply emerges from the magnetic electron-hole continuum (in optimally doped and overdoped cuprates).^{14,17,21}

This mode is typically assigned to an excitonic bound state in the superconductivity induced gap in the spectrum of electron-hole spin-flip Stoner excitations.²²⁻³⁰ Within that framework, the resonant mode is a direct consequence of unconventional superconductivity of d -wave symmetry occurring in the high- T_c copper oxides. This approach is particularly suited for optimally doped superconductors where normal-state magnetic fluctuations are consistent with a broad magnetic electron-hole continuum. Further, the most recent neutron developments¹⁶ allow “silent bands” (where the magnetic collective mode is overdamped) to be related to the detailed momentum shape of the Stoner continuum expected from the Fermi surface topology and the d -wave superconducting order parameter. This connection has been explicitly assigned in Ref. 30. This spin exciton mode can be derived from an effective t - J Hamiltonian.^{26,29} Within that model, an interesting proposal has been made²⁹ that magnetic properties could display significant isotopic effects if both the hopping integral, t , and the superexchange interaction between neighboring spins, J , are renormalized by phonons. By changing the oxygen isotope ^{16}O by ^{18}O , they predict a change of the resonance peak position of a few meV, mostly due to a renormalization of the hopping integral.

Thus, by measuring the isotope dependence of the position of the resonance peak, INS could provide direct evidence for the presence of the electron-phonon coupling in cuprates. In contrast, we here report the probable absence of an isotope effect in the magnetic-resonance peak in $\text{YBa}_2\text{Cu}_3\text{O}_{6.89}$ (YBCO).

The inelastic neutron experiment was performed on the 1T spectrometer at Laboratoire Léon Brillouin (LLB) in Saclay. The spectrometer used a vertically and horizontally focusing monochromator and analyzer, comprising Cu (111) crystals and pyrolytic graphite (PG002) crystals, respec-

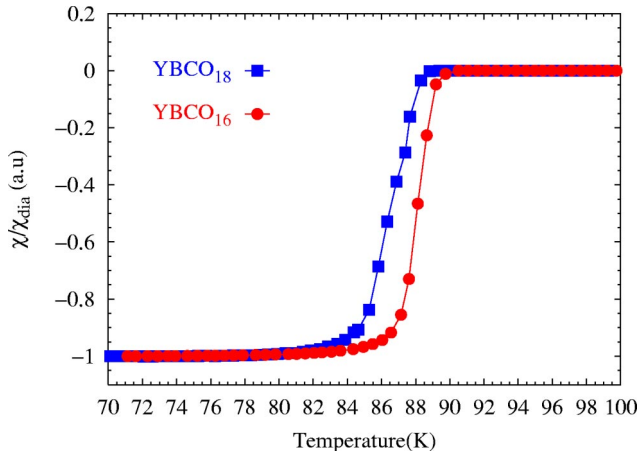


FIG. 1. (Color online) Magnetic susceptibility of both sample arrays used in this experiment. Onset superconducting temperatures occur at 88.8 K for samples with ^{18}O and 90 K for ^{16}O . The curve of each mounting has been obtained by weighting the susceptibility curve of each individual single crystal by their mass. The dispersion of T_c for the samples of each array is less than 0.3 K.

tively. The measurements were performed with a fixed final neutron energy of 30.5 meV. A filter was inserted into the scattered beam in order to eliminate higher-order contamination. The crystals were oriented such that momentum transfers \mathbf{Q} of the form $\mathbf{Q}=(H,H,L)$ were accessible. We use a notation in which \mathbf{Q} is indexed in units of the tetragonal reciprocal lattice vectors $2\pi/a=1.63 \text{ \AA}^{-1}$ and $2\pi/c=0.54 \text{ \AA}^{-1}$.

High-quality single crystals of $\text{YBa}_2\text{Cu}_3^{16}\text{O}_{7-\delta}$ of typical mass $\sim 0.1\text{--}0.2$ g, were prepared. They have been separated in two distinct sets of similar total mass (~ 0.6 g). The two batches of samples were mounted in a furnace in separate quartz tubes side by side to ensure identical thermal history. One tube was charged with high-purity ^{16}O oxygen gas while the other was charged with 99% ^{18}O enriched oxygen. After annealing for 24 h at 830 °C the pair of tubes was removed, evacuated, recharged, and reannealed for a total of 10 exchanges to ensure maximal isotope exchange. Both sample sets were then slow cooled over 48 h to 550 °C then annealed there for 10 days to ensure the same uniform oxygenation of the chains. The samples were lightly underdoped as confirmed by thermoelectric power measurements.³¹ Based on previous annealing experience for YBCO ceramics and crystals³⁴ we expect the samples to have an oxygen content of ≈ 6.89 and an underdoped hole concentration of $n_h \approx 0.145$. The magnetic susceptibility for each individual sample has been measured by a superconducting quantum interference device (SQUID) magnetometer. The crystals for each individual sample were then aligned on two distinct arrays (referred hereafter as S_{16} and S_{18}) of similar volume, each array being made of about four single crystals. The magnetic susceptibility measurements of each sample mounting are shown on Fig. 1: one can identify the onset of the superconducting transition at 90 K for S_{16} and 88.8 K for S_{18} . A difference in T_c of ~ 1.2 K is then observed between both samples. It is actually larger than the reduction expected from the usual isotope effect which is about -0.77 ± 0.2 K for

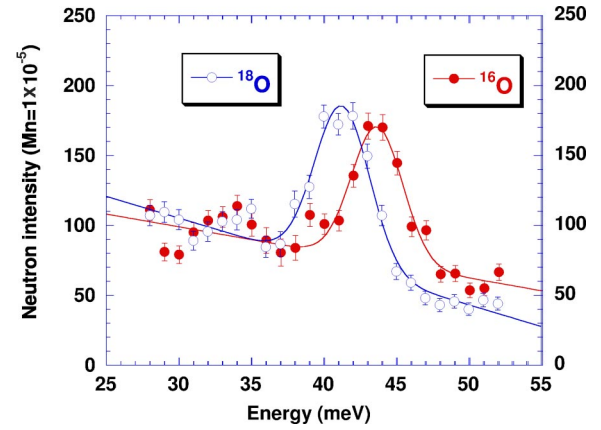


FIG. 2. (Color online) Neutron intensity measured at $\mathbf{Q} = (-0.5, -0.5, 10.3)$ and at $T = 100$ K showing an oxygen phonon mode in both the ^{16}O and ^{18}O samples.

similarly doped YBCO (Ref. 4). The slight excess in isotopic shift in T_c is possibly significant and may suggest a slightly lower oxygen content and doping state for the ^{18}O sample, despite the attempt to ensure identical thermal histories. To address this issue, we further determined the c -lattice parameter of both samples. Accurate measurements using the triple axis 4F1 spectrometer installed on a cold source at LLB yield $c = 11.674 \text{ \AA} \pm 0.004$ for S_{16} and $c = 11.678 \text{ \AA} \pm 0.004$ for S_{18} . These c -lattice parameters are consistent with an oxygen content of about $x = 0.89$ (Refs. 32 and 33), and given the slope $\partial c / \partial x = -0.11 \text{ \AA}$ (Refs. 32 and 33), indicates that the ^{18}O sample has a possible lower oxygen content by $\Delta x = 0.02 \pm 0.03$. Thus, it is in agreement with the possibility that part of the difference in T_c for each sample is related to a slight difference in doping. Using the relationship between oxygen content and the hole doping,³⁴ this would correspond to a difference of $\sim \delta n_h = 0.004 \pm 0.006$ in doping.

In order to check the isotope exchange process, we performed Raman scattering at room temperature as well as INS measurements of a particular oxygen phonon mode. The three oxygen modes observed in Raman scattering, namely the c -axis vibration of the apical oxygen and the in-phase and out-of-phase oxygen vibrations in the CuO_2 plane, revealed isotopic shifts to lower energy in the ^{18}O sample with respect to the ^{16}O sample. Assuming that they are pure oxygen modes, the fraction of exchanged oxygen is $y \approx 0.95 \pm 0.05$. Being a surface-sensitive technique, Raman scattering does not indicate if the isotope exchange occurred within the bulk of the samples. This might be problematic as oxygen diffusion is very slow. We then measured with inelastic neutron scattering a particular phonon mode whose eigenvector is predominantly related to a vibration along the c axis of the oxygens of the CuO_2 plane.¹³ This phonon mode, measured at $\mathbf{Q} = (-0.5, -0.5, 10.3)$ where its structure factor is larger, is found at 43.6 ± 0.1 meV in S_{16} and 41.3 ± 0.1 meV in S_{18} (Fig. 2). Again, assuming that the phonon is a pure oxygen mode, this corresponds to an isotope exchange of $y = 0.92 \pm 0.08$. In fact, the eigenvector for that specific mode corresponds to about 90% weighting by the oxygen atoms. Therefore, the energy shift of the phonon measured in INS is fully consistent with the nearly full oxygen exchange de-

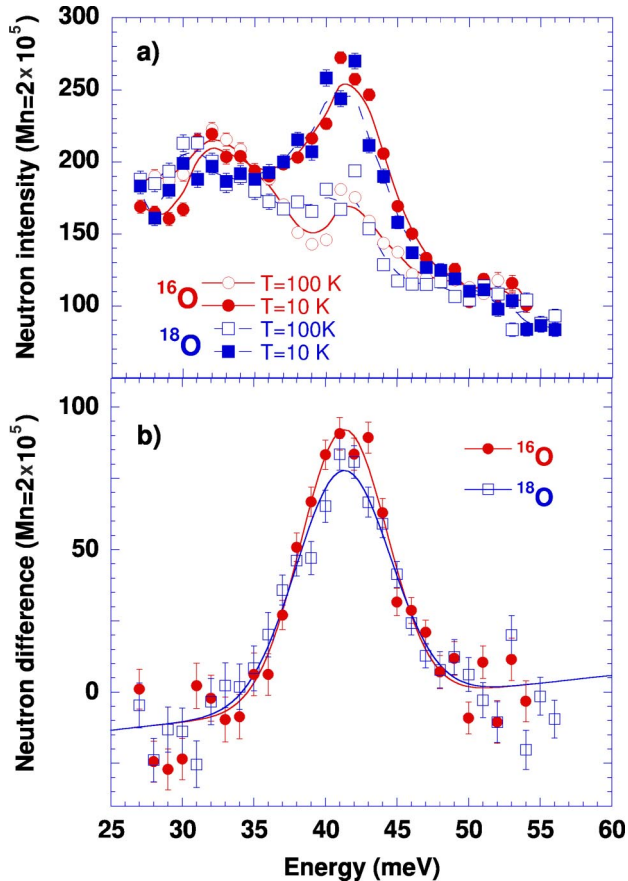


FIG. 3. (Color online) Resonant magnetic peak intensity in both the ^{16}O and ^{18}O samples: (a) Raw neutron intensity at 12 and 100 K for both samples; (b) Difference of the neutron intensity 12–100 K for each sample. The total counting time reached 1.5 h per point at each temperature to reduce the error bar on the energy of the resonance to 0.12 meV. The curves are not normalized by samples mass.

duced from the Raman data. The oxygen exchange thus occurred throughout the bulk of the material, thus confirming the sample homogeneity.

We now turn to the central result of this report. Following previous studies,^{10,13,16,17} we identify the resonant magnetic mode by constructing, for each sample, the difference between constant- \mathbf{Q} scans measured at 12 K ($<T_c$) and 100 K ($>T_c$) and at the wave vector $\mathbf{Q}=(-0.5, -0.5, 5.1)$. The magnetic-resonant mode in both samples is shown in Fig. 3(b) as well as the raw energy scans for both samples in Fig. 3(a). At $T=100$ K, the background, which displays the same phonon mode as the mode shown in Fig. 2 but with much weaker intensity,¹³ is also shifted upon the isotope substitution. This phonon is known to exhibit no temperature dependence across T_c . Further, the phonon-scattering structure factor for the chosen wave vector with $L=5.1$ is reduced enough that the background subtraction procedure in the determination of the resonance peak energy, its broadening, and its amplitude does not affect significantly the observed difference of Fig. 3(b). The resonance peak energy is found at $\omega_R=41.26\pm 0.12$ meV in S_{16} and $\omega_R=41.31\pm 0.12$ meV in S_{18} . The two energies are therefore not distinguishable within errors. The two peaks exhibit a slight difference in amplitude

as well as in width (7.1 ± 0.3 meV for S_{16} and 7.8 ± 0.3 meV for S_{18}). In principle, the observed width is not intrinsic but is controlled by the convolution product of dispersive excitations around (π, π) with the spectrometer resolution.^{15,16} The product of the peak amplitude by its width in Fig. 3(b), representing the magnetic-resonant spectral weight at (π, π) , is similar in both samples within errors. Using the spectral weight of the phonon presented in Fig. 2, one can calibrate the absolute magnetic intensity of the resonance peak.^{11,13} For both samples, we deduce an energy-integrated magnetic spectral weight of $2.6\pm 0.4\mu_B^2$ at the (π, π) wave vector, or $0.06\pm 0.01\mu_B^2$ for energy- and q -integrated magnetic spectral weight in agreement with a previous report for a similar doping level.¹¹

We then basically observe no isotope effect of the magnetic-resonance peak: $\alpha_{\omega_R} = -d \ln \omega_R / d \ln M \approx 0$. To be complete, there is, however, the possibility of a slight difference in doping between the two samples which might induce a slight change in the resonance energy if the resonance energy is proportional to T_c , as it is typically observed.^{10,11} (To what accuracy this proportionality strictly applies is still an open question.) According to this empiric relation, the resonance peak energy could be renormalized by about 0.5% in the ^{18}O sample as compared with the ^{16}O sample, i.e., an energy shift of ~ -0.18 meV. In such a case, an isotope effect can be estimated of $\delta\omega_R \approx +0.23$, yielding an isotope exponent of $\alpha_{res} = -0.05$. Therefore, the isotope shift of the resonance peak energy can be at most $\delta\omega_R \leq 0.23$ meV ± 0.2 meV. The deduced isotope effect on the resonance peak is then very small and actually similar in magnitude to the small isotope effect of the superconducting transition for optimally doped cuprates, $\alpha_{T_c} = 0.05$ (Ref. 2), although with an opposite sign. It should be noticed that the overall effect might be simply overshoot by the difference in doping between both samples.

The absence of an isotope effect on the resonance energy is actually quite surprising as, in the spin exciton model, the bound-state energy is very sensitive to both band structure, via the hopping integrals t, t', \dots , and the interactions, g . Within a random-phase approximation (RPA) scheme, the resonance energy at the AF wave vector is usually defined as the pole of the interacting susceptibility, $1 - g/2 \text{Re} \chi_0(Q_{AF}, \omega_R) = 0$ (Refs. 23–30), where $\chi_0(Q, \omega) \propto 1/t$ is the bare spin susceptibility of a d -wave superconductor. The interaction g can be either the superexchange interactions,^{23,24,26,28,29} $4J_{AF}$ at (π, π) , or some spin-fermion coupling.^{25,27,30} Looking in more detail at the pole condition, one clearly sees that a shift in g and t have opposite effects on the resonance energy ω_R : if the interaction is reduced, the resonance energy will increase, whereas if the band hopping integral is reduced the resonance energy will decrease. Using such a model, Eremin *et al.*²⁹ expected a shift of about -2 meV of the resonance peak from ^{16}O to ^{18}O , corresponding to $\alpha_{\omega_R} = 0.4$. That was because the band-structure hopping integral t is thought to be the quantity strongly dependent on the electron-phonon coupling. As the observed δ_{ω_R} has an opposite sign (if any) of the theoretical prediction,²⁹ it

is doubtful that the electron-phonon coupling is renormalizing the band-structure hopping integral. Within that model, one can nevertheless explain the observed positive sign of $\delta\omega_R$ by a small renormalization of the interaction g rather than t . Our maximum estimate of $\delta\omega_R \leq 0.23$ meV would typically yield $\delta g/g \leq -0.4\%$, in agreement with the expected impact of the interactions term.²⁹ More specifically, if the interaction is assigned to the AF superexchange, we obtained an isotopic change of J_{AF} compatible with the one, $\delta J/J \sim -0.6\%$ (Ref. 3), deduced from the Néel temperature in undoped cuprates. Finally, this simple analysis of the tiny shift (if any) of the resonance peak energy in terms of the spin-exciton model shows that the various microscopic terms entering in its expression do not exhibit a strong isotope effect, thus placing a severe limit on the role of electron-phonon coupling in high- T_c cuprates.

In conclusion, using inelastic neutron-scattering experiments, we observe no significant shift of the magnetic-resonance peak energy in YBCO upon substitution of oxygen ^{16}O by its isotope ^{18}O . In contrast to previous claims, this suggests that the spin-phonon coupling is negligible in high- T_c cuprates near optimal doping. The absence of a measurable effect on the INS resonance mode does not, however, exclude the possibility that isotope substitution can have a noticeable effect on the magnetic properties at much lower doping.

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