Doping and Isotope Dependence of the Pseudogap in High- T_c Cuprates Observed by Neutron Crystal-Field Spectroscopy: A Fast Local Probe

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The temperature dependence of the relaxation rate of crystal-field excitations in the high- T_c superconductors $\text{HoBa}_2\text{Cu}_4\text{O}_8$ and $\text{HoBa}_2\text{Cu}_3\text{O}_x$ ($6.4 < x < 7$) was investigated by inelastic neutron scattering techniques. The data show clear evidence for the opening of an electronic gap in the normal state at $T^* > T_c$ in the underdoped regime as well as for slightly overdoped samples. For $\text{HoBa}_2\text{Cu}_4\text{O}_8$ T^* increases from 170 to 220 K upon oxygen isotope substitution (^{16}O vs ^{18}O). This huge isotope shift (which is absent in NMR and NQR experiments) suggests that the mechanism leading to an isotope effect on the pseudogap has to involve a time scale in the range $10^{-8} \gg \tau > 10^{-13}$ s.

KEY WORDS: Doping; isotope effect; pseudogap; high- T_c cuprates; crystal-field spectroscopy.

1. INTRODUCTION

The existence of a pseudogap in the normal state of underdoped high-temperature superconductors is considered to be among the most important features of cuprates. Evidence for gaplike structures in the normal state at $T^* > T_c$ was provided by a variety of experimental methods, particularly by angle-resolved photoemission spectroscopy (ARPES) measurements in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ [1], nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) results in $\text{YBa}_2\text{Cu}_4\text{O}_8$ [2,3], and neutron spectroscopic measurements in $\text{Tm}_{0.1}\text{Y}_{0.9}\text{Ba}_2\text{Cu}_3\text{O}_{6.9}$ [4], $\text{HoBa}_2\text{Cu}_4\text{O}_8$, and $\text{Er}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ [5,6]. Experiments searching for an isotope effect (i.e., exchange of ^{16}O vs ^{18}O) on the pseudogap temperature T^* are crucial to discriminate between the different models for the pseudogap. Such measurements were performed for $\text{YBa}_2\text{Cu}_4\text{O}_8$ by NMR and NQR techniques [2,3], which resulted in either an absence or a very small isotope shift ΔT^* . Our recent neutron spectroscopic investigations on $\text{HoBa}_2\text{Cu}_4\text{O}_8$ [6], however, showed

that the pseudogap temperature T^* increases from 170 to 220 K upon replacing ^{16}O by ^{18}O . This large oxygen isotope shift $\Delta T^* \approx 50$ K implies that the formation of the pseudogap is driven by interactions on a time scale $10^{-8} \text{ s} \gg \tau > 10^{-13} \text{ s}$ which cannot be resolved by NMR and NQR experiments.

Here we report on further neutron spectroscopic measurements performed for $\text{HoBa}_2\text{Cu}_3\text{O}_x$ in the strongly underdoped ($x = 6.46, 6.56$) and in the slightly overdoped ($x = 6.96$) regimes to establish a phase diagram for the 123-type compounds.

2. NEUTRON CRYSTAL-FIELD SPECTROSCOPY

In neutron spectroscopic investigations transitions between different crystal-field levels associated with the rare-earth ions can be directly measured. The thereby excited crystal-field states are subject to interactions with phonons, Cu spin fluctuations, and charge carriers, which limit the lifetime of the excitation; thus the observed crystal-field transitions exhibit line broadening. The interaction with the charge carriers is by far the dominating relaxation mechanism. In the normal metallic state the corresponding line-

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width increases almost linearly with temperature according to the well-known Korringa law [7]. In the superconducting state, however, the pairing of the charge carriers creates an energy gap Δ , thus crystal-field excitations with energy $\hbar\omega < 2\Delta$ do not have enough energy to span the gap, and consequently there is no interaction with the charge carriers. Any deviation of the linewidth from the Korringa behavior can therefore be attributed to the opening of a gap (or a pseudogap). For more detailed information on this technique we refer to recent review articles [8].

The present neutron scattering experiments were performed on the high-resolution time-of-flight spectrometers FOCUS and IN5 installed at the Paul Scherrer Institute (Villigen) and at the Institute Laue-Langevin (Grenoble), respectively. For both spectrometers the incident neutron wavelength was 5 Å, giving an energy resolution of 0.1 meV at the elastic position. The raw data were corrected for absorption, detector efficiency, background, and detailed balance effects according to standard procedures.

First, we present the data obtained for the slightly overdoped compound $\text{HoBa}_2\text{Cu}_3\text{O}_{6.96}$ for which the superconducting ordering temperature was determined by magnetic susceptibility measurements to be $T_c \approx 92$ K. The crystal-field level scheme was established by neutron spectroscopy [9], which yields 17 singlet states up to an energy of 73 meV. Figure 1 shows selected low-energy spectra observed for both Stokes (energy transfer $\hbar\omega > 0$) and anti-Stokes ($\hbar\omega < 0$) processes which exhibit ground-state and excited-state crystal-field transitions at energy transfers $|\hbar\omega| \ll 2\Delta$ (≈ 66 meV [5]). With increasing temperature the crystal-field transitions exhibit line broadening. The energy spectra were fitted as described in detail in Refs. 5 and 6. The results of the fitting procedure are shown by solid lines.

Figure 2 shows the temperature dependence of the resulting intrinsic linewidth (HWHM) corresponding to the strongest crystal-field transition at $|\hbar\omega| \approx 0.5$ meV. The linewidth is zero up to 90 K, then it raises exponentially up to 105 K. Above 105 K it increases linearly according to the Korringa law as expected for the normal state, which is indicated by the solid line. We therefore identify the temperature where the deviation from the Korringa law occurs with the temperature where the pseudogap opens, i.e., we set $T^* \approx 105$ K.

Similar spectra were obtained for the strongly underdoped compounds $\text{HoBa}_2\text{Cu}_3\text{O}_{6.46}$ ($T_c \approx 30$ K)

Fig. 1. Energy spectra of neutrons scattered from $\text{HoBa}_2\text{Cu}_3\text{O}_{6.96}$ as taken on FOCUS. The lines are profile fits to the data. The solid and dashed vertical bars indicate the energy and intensity of the observed ground-state and excited-state crystal-field transitions, respectively.

and $\text{HoBa}_2\text{Cu}_3\text{O}_{6.56}$ ($T_c \approx 60$ K), however, the cross-over into the normal state behavior occurred at much higher temperatures, $T^* \approx 250$ and 230 K, respectively.

Very detailed experiments were performed to

Fig. 2. Temperature dependence of the intrinsic linewidth (HWHM) corresponding to the lowest crystal-field transition in $\text{HoBa}_2\text{Cu}_3\text{O}_{6.96}$. The line denotes the linewidth expected from the Korringa law.

study the oxygen isotope effect in $\text{HoBa}_2\text{Cu}_4\text{O}_8$ [6]. After completion of the experiments for the ^{16}O compound, the sample was subjected to ^{18}O diffusion resulting in an ^{18}O concentration of $(75 \pm 5)\%$. The neutron experiments were then repeated for the ^{18}O substituted sample under exactly the same instrumental conditions. Afterward the sample was back-exchanged from ^{18}O to ^{16}O . Additional neutron experiments were then performed for the ^{16}O compound to exclude effects due to deterioration of the sample which could possibly occur in the oxygenation process. However, neutron diffraction experiments confirmed that the “1248” compounds are very stable from the structural point of view, i.e., their stoichiometry and single-phase character as well as their structural parameters did not change upon both $^{16}\text{O} \rightarrow ^{18}\text{O}$ and $^{18}\text{O} \rightarrow ^{16}\text{O}$ substitution. Figure 3 shows the temperature dependence of the intrinsic linewidth (HWHM) corresponding to the lowest crystal-field transition at $|\hbar\omega| \approx 0.6$ meV. We recognize that the relaxation behavior of the ^{16}O sample has a similar shape as for the isotope substituted ^{18}O compound,

but the steplike crossover to the Korringa law occurs at drastically different temperatures, namely, at $T^* \approx 170$ and 220 K for the ^{16}O and ^{18}O compounds, respectively, corresponding to an oxygen isotope shift $\Delta T^* \approx 50$ K. In analogy to the isotope effect on T_c , we can define the isotope effect on T^* by an isotope coefficient $\alpha^* \approx -2.2 \pm 0.6$.

3. DISCUSSION

The results obtained in the present work are summarized in the phase diagram for “123”-type high- T_c superconductors in Fig. 4. It also includes the data obtained for $\text{HoBa}_2\text{Cu}_4\text{O}_8$ [5,6], which, concerning the doping level, is equivalent to a “123” compound with $x = 6.78$ [8]. The values of T^* as a function of doping obtained from neutron crystal-field spectroscopy are in good agreement with the values obtained from ARPES measurements on Bi2212 [1]. This agreement is noteworthy, since neutron spectroscopy is probing the bulk properties, whereas ARPES measurements are rather sensitive to the surface of the sample. For all the doping levels considered the pseudogap temperature T^* is always above the superconducting ordering temperature T_c , even in the slightly overdoped regime. Our data suggest a linear increase of the value of T^* with increasing underdoping. A striking result is the large oxygen isotope shift $\Delta T^* \approx 50$ K observed for $\text{HoBa}_2\text{Cu}_4\text{O}_8$ [6]. A similar effect was found in X-ray absorption near-edge spectroscopy (XANES) experiments on

Fig. 3. Temperature dependence of the intrinsic linewidth (HWHM) corresponding to the lowest crystal-field transition in $\text{HoBa}_2\text{Cu}_4\text{O}_8$. The lines denote the linewidth expected from the Korringa law. The full and open circles correspond to the data taken on IN5 and FOCUS, respectively. The FOCUS data for $\text{HoBa}_2\text{Cu}_4^{16}\text{O}_8$ refer to the back-exchanged compound.

Fig. 4. Phase diagram of “123”-type high- T_c superconductors. The circles refer to the present work. The data for $x = 6.9$ (squares) are taken from Ref. 4. The lines defining the antiferromagnetic ordering temperature T_N as well as the superconducting transition temperature T_c are taken from Ref. 12.

$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ associated with the onset of local lattice fluctuations [10]. These large isotope effects suggest that electron–phonon-induced effects are important for the understanding of the pseudogap. Indeed, a recent theoretical investigation [11] demonstrated that a model involving strong nonlinear electron–phonon effects is able to explain quantitatively the oxygen isotope effect on the pseudogap as well as the occurrence of stripe formation and charge ordering at T^* . Moreover, the underlying time scale was found to be rather fast, so that the detection of an isotope effect on T^* is limited to methods such as ARPES, XANES, and neutron scattering.

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