Large Isotope Effect on the Pseudogap in the High-Temperature Superconductor $HoBa_2Cu_4O_8$

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The oxygen isotope effect on the relaxation rate of crystal-field excitations in the slightly underdoped high-temperature superconductor $HoBa_2Cu_4O_8$ has been investigated by means of inelastic neutron scattering. For the ^{16}O compound there is clear evidence for the opening of an electronic gap in the normal state at $T^* \approx 170$ K far above $T_c = 79$ K. Upon oxygen isotope substitution (^{16}O vs ^{18}O) T_c decreases marginally to 78.5 K, whereas T^* is shifted to about 220 K. This huge isotope shift observed for T^* 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.

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The existence of a pseudogap in the electronic excitation spectra of underdoped high-T_c superconductors is considered to be among the most important features of cuprates. The pseudogap phenomena mean the suppression of low frequency spectral weight above the superconducting temperature T_c. They are universal phenomena in various compounds of underdoped cuprates. Evidence for gaplike structures in the normal state at $T^* > T_c$ has been provided by a variety of experimental methods, particularly by heat capacity experiments in $YBa_2Cu_3O_{6+x}$ [1], angle-resolved photoemission spectroscopy measurements in $Bi_2Sr_2CaCu_2O_{8+x}$ [2], nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) results in $YBa_2Cu_4O_8$ [3,4], as well as neutron spectroscopic measurements in $HoBa_2Cu_4O_8$ and $Er_2Ba_4Cu_7O_{15}$ [5]. Existing models for the pseudogap involve several mechanisms such as a precursor pairing due to enhanced fluctuations [6], a spin gap due to antiferromagnetic correlations [7], a gap due to a periodic modulation of the charge density [8], and a gap due to strong electron-lattice (bi)polaronic interactions [9]. Experiments searching for an isotope effect (i.e., exchange of ^{16}O vs ^{18}O) on the pseudogap temperature T^* are therefore crucial to discriminate between the different models. Such measurements were performed for $YBa_2Cu_4O_8$ by NMR and NQR techniques [3,4] which resulted in either an absence or a very small isotope shift ΔT^*. However, x-ray absorption near-edge spectroscopy (XANES) experiments [10] revealed a huge isotope effect associated with the onset of local lattice fluctuations in $La_{2-x}Sr_xCuO_4$, whose characteristic temperature T^* increases from 110 to 170 K upon replacing ^{16}O by ^{18}O.

Here we report on neutron spectroscopic investigations of the isotope effect on the relaxation rate of crystal-field excitations in $HoBa_2Cu_4O_8$. Earlier data gave clear evidence for the opening of a pseudogap at $T^* \approx 170$ K for the ^{16}O sample [5]. We will show that upon replacing ^{16}O by ^{18}O the characteristic temperature increases to $T^* \approx 220$ K. This large isotope shift $\Delta T^* \approx 50$ K implies that the isotope effect on the pseudogap is driven by interactions on a time scale $10^{-8} \gg \tau > 10^{-13}$ s which cannot be resolved by NMR and NQR experiments.

The principle of neutron spectroscopic investigations of the crystal-field interaction in high-T_c superconductors was described in recent review articles [11,12]. By this technique transitions between different crystal-field levels can be directly measured. In the normal metallic state the excited crystal-field levels interact with phonons, Cu spin fluctuations, and charge carriers (electrons or holes). These interactions 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. The corresponding intrinsic linewidth $\Gamma_n(T)$ increases almost linearly with temperature according to the well-known Korringa law [13]. In the superconducting state, however, the pairing of the charge carriers creates an energy gap $\Delta(\mathbf{k})$, thus crystal-field excitations with energy $\hbar\omega < 2\Delta(\mathbf{k})$ do not have enough energy to span the gap, and consequently there is no interaction with the charge carriers. For an isotropic gap function $\Delta(\mathbf{k}) = \Delta$ the intrinsic linewidth in the superconducting state is then given by

$$\Gamma_s(T) = \Gamma_n(T) \exp\left(-\frac{\Delta}{k_B T}\right). \tag{1}$$

This means that $\Gamma_s(T \ll T_c) \approx 0$, and line broadening sets in just below T_c where the superconducting gap opens. The exponential temperature dependence of $\Gamma_s(T)$ was nicely demonstrated in the first neutron spectroscopic study on the classical superconductor $La_{1-x}Tb_xAl_2$ [14]. On the other hand, neutron experiments on the optimally doped high-T_c compound $Ho_{0.1}Y_{0.9}Ba_2Cu_3O_7$ [15] revealed an unusual temperature dependence, i.e., $\Gamma_s(T)$ does not follow the behavior predicted by Eq. (1), but increases already far below T_c. This was ascribed to a high degree of gap anisotropy, since an anisotropic gap function gives rise to certain relaxation channels even at the lowest temperature, particularly along the directions of **k** involving nodes. An anisotropic gap function was also inferred from neutron crystal-field studies on the slightly underdoped high-T_c compounds $HoBa_2Cu_4O_8$ and $Er_2Ba_4Cu_7O_{15}$. However, in these measurements the normal-state behavior is fully recovered only far above T_c at $T^* \approx 170$ K [5] which clearly supports the existence of a pseudogap.

We have performed new inelastic neutron scattering experiments to study the isotope effect on the relaxation rate of crystal-field excitations in $HoBa_2Cu_4O_8$ by substituting ^{16}O vs ^{18}O. The ^{16}O sample was prepared by a high-oxygen-pressure solid-state reaction synthesis as described elsewhere [16]. After completion of the neutron experiments [5] the sample was subjected to ^{18}O diffusion, which was performed in a closed system at 725 °C during 100 h. During this procedure, the reaction chamber was partly evacuated (0.2 bars) and filled again with ^{18}O (1.3 bars) every 12 h, as the volume of the chamber (200 cm^3) was not sufficient to obtain a reasonably large ^{18}O fraction in a one-step process. The ^{18}O concentration was determined from the weight difference of the isotope-enriched sample to be $(75 \pm 5)\%$. The neutron experiments were then repeated for the ^{18}O substituted sample under exactly the same instrumental conditions. Afterwards the sample was back exchanged from ^{18}O to ^{16}O. Additional neutron experiments were then performed for the ^{16}O compound in order 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 $^{16}O \rightarrow {}^{18}O$ and $^{18}O \rightarrow {}^{16}O$ substitution as well as with aging (the time span between all the experiments was about two years).

The critical temperatures T_c of the ^{16}O and ^{18}O compounds were determined by magnetometry to be 79 and 78.5 K, respectively. The observed oxygen isotope shift on T_c, i.e., $\Delta T_c \approx -0.5$ K can be described by the isotope coefficient α defined by the relation $T_c \propto M^{-\alpha}$, where M is the mass of the oxygen ion. For the above compounds we derive $\alpha = 0.05 \pm 0.02$, in agreement with literature data [3,4].

The neutron scattering experiments were performed on the high resolution time-of-flight spectrometers IN5 and FOCUS installed at the Institute Laue-Langevin (Grenoble) and at the Paul Scherrer Institute (Villigen), respectively. In both experiments 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.

Figure 1 shows energy spectra for $HoBa_2Cu_4{}^{18}O_8$. There are two strong ground-state crystal-field transitions at $\hbar\omega_1 = 0.6$ meV and $\hbar\omega_2 = 1.3$ meV [17], i.e., $\hbar\omega_i \ll 2\Delta_{\max}$ (~66 meV [5]). With increasing temperature the crystal-field transitions exhibit line broadening. In addition, excited crystal-field states become increasingly populated giving rise to excited crystal-field transitions. The corresponding energies did not change within the experimental error with respect to the ^{16}O compound [5]. The energy spectra were fitted according to the neutron cross section for crystal-field transitions which is given in the dipole approximation by [18]

$$\frac{d^2\sigma}{d\Omega\, d\omega} \propto \sum_{i,j} M_{ij}^2 \exp\left(-\frac{\hbar\omega_i}{k_B T}\right) \Big/ Z\delta(\hbar\omega_{ij} \pm \hbar\omega), \qquad (2)$$

where M_{ij} is the transition matrix element of the crystal-field transition $|i\rangle \rightarrow |j\rangle$, Z is the partition function, and

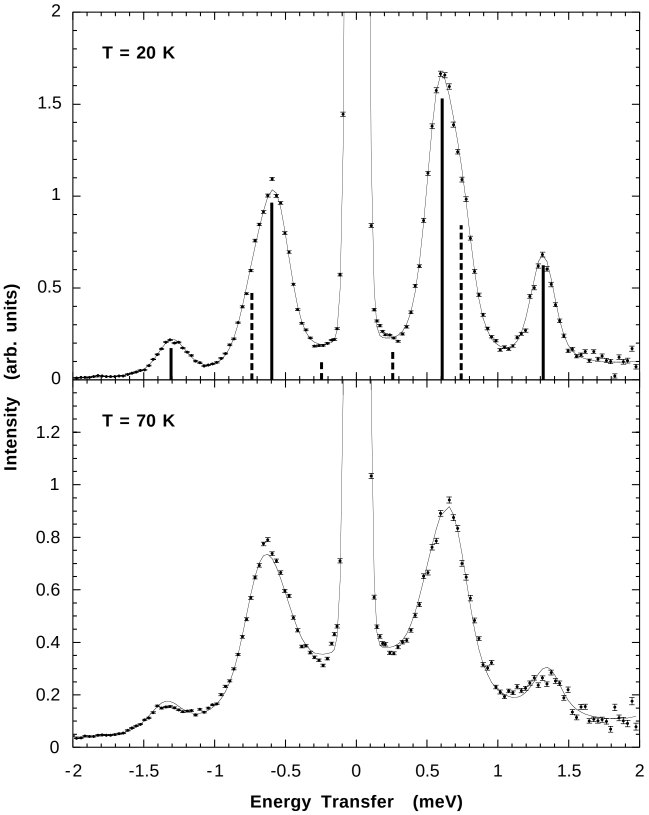

FIG. 1. Energy spectra of the neutrons scattered from $HoBa_2Cu_4{}^{18}O_8$ as taken on IN5. The solid lines are fits to the data which include the relaxation as described in the text. The solid and dashed vertical bars indicate the energy and intensity of the ground-state and excited-state crystal-field transitions, respectively, in the low-energy part of the spectra.

$\hbar\omega_{ij} = \hbar\omega_j - \hbar\omega_i$. M_{ij} and $\hbar\omega_{ij}$ were kept fixed at the values obtained for the ^{16}O compound [5]. The final spectra were obtained by convoluting the instrumental resolution function with the crystal-field intrinsic Lorentzian function, whose linewidth is given in the normal state by the modified Korringa law [15]

$$\Gamma_n^{ij}(T) = 2J_{\mathrm{ex}}^2\left[M_{ij}^2 \coth\left(\frac{\hbar\omega_{ij}}{2k_BT}\right)\chi''(\hbar\omega_{ij}) + \sum_{n\neq i} M_{\mathrm{in}}^2 \frac{\chi''(\hbar\omega_{\mathrm{in}})}{\exp(\frac{\hbar\omega_{\mathrm{in}}}{k_BT}) - 1} + \sum_{n\neq j} M_{nj}^2 \frac{\chi''(\hbar\omega_{nj})}{\exp(\frac{\hbar\omega_{nj}}{k_BT}) - 1}\right], \quad (3)$$

where J_{ex} is the exchange integral between the $4f$ electrons of the Ho^{3+} ions and the charge carriers, and $\chi''(\hbar\omega_{ij})$ is the local susceptibility. For the normal-state susceptibility we used $\pi N^2(E_F)\hbar\omega_{ij}$, where $N(E_F)$ is the electronic density of states at the Fermi energy. Equation (3) was also used to correlate the relaxation widths of the different crystal-field transitions, so that the only free parameters in the fitting procedure were then an overall scale factor for the intensities and a temperature-dependent linewidth $\Gamma(T) \sim [J_{\mathrm{ex}}N(E_F)]^2$. The results of the fitting procedure are shown by solid lines in Fig. 1.

Figure 2 (upper panel) shows the temperature dependence of the intrinsic linewidth (HWHM) corresponding to the $\Gamma_3^{(1)} \rightarrow \Gamma_4^{(1)}$ transition from the ground state to the first excited state at $\hbar\omega = 0.6$ meV, derived for the ^{18}O compound. The two data sets (IN5 and FOCUS) are rather consistent. The linewidth is zero below 60 K, then it increases almost linearly up to 210 K. The linewidth is steplike enhanced between 210 and 220 K. Above 220 K it increases again linearly as expected for the normal state. We therefore identify the temperature where the steplike enhancement occurs with the temperature where the pseudogap opens, i.e., we set $T^* \approx 220$ K. From the high-temperature data ($T \geq 220$ K) we obtained $J_{\mathrm{ex}}N(E_F) = 0.0063 \pm 0.0007$, which is somehow larger than the value 0.0036 derived for $\mathrm{Ho}_{0.1}\mathrm{Y}_{0.9}\mathrm{Ba}_2\mathrm{Cu}_3\mathrm{O}_7$ [15].

Figure 2 (lower panel) shows the temperature dependence of the intrinsic linewidth derived for the same crystal-field transition in the ^{16}O compound. The figure includes earlier data taken on IN5 [5] as well as the data obtained on FOCUS for the back-exchanged compound. The nice consistency of the two data sets confirms the stability of the "1248" structure against oxygen isotope substitution. 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 enhancement of the linewidth occurs at much lower temperatures between 160 and 170 K, i.e., $T^* \approx 170$ K [5]. From the high-temperature data ($T \geq 170$ K) we derived $J_{\mathrm{ex}}N(E_F) = 0.0060 \pm 0.0007$ which agrees within the experimental error with the value determined for the ^{18}O compound. Our experiments give evidence therefore for a large isotope shift $\Delta T^* \approx 50$ K which is in complete disagreement with the results of NMR and NQR experiments [3,4], but of the same order as observed in [10]. In analogy to the isotope effect on T_c, we can define the isotope effect on T^* by an isotope coefficient $\alpha^* = -2.2 \pm 0.6$.

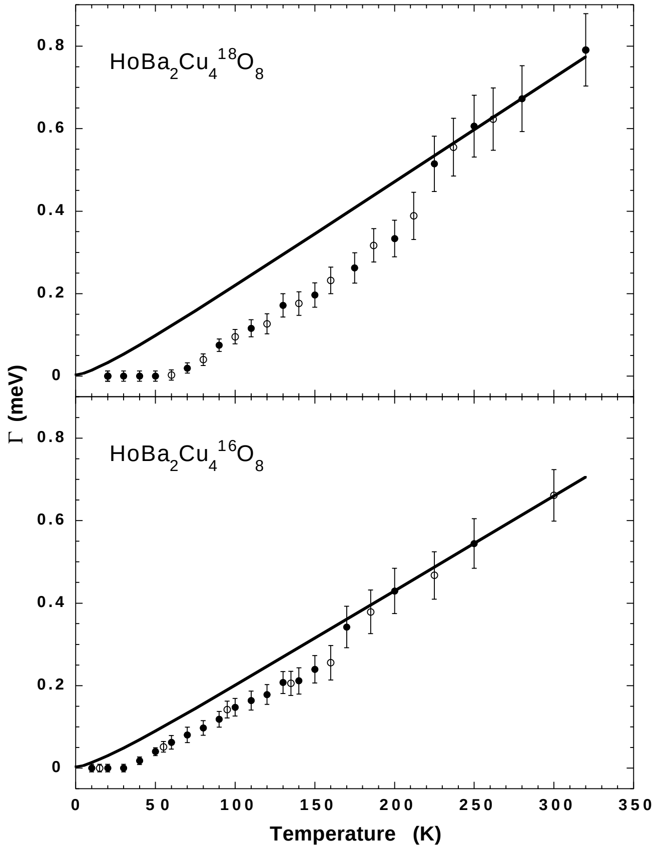

FIG. 2. Temperature dependence of the intrinsic linewidth $\Gamma(T)$ (HWHM) corresponding to the $\Gamma_3^{(1)} \rightarrow \Gamma_4^{(1)}$ ground-state transition in $\mathrm{HoBa}_2\mathrm{Cu}_4{}^{18}\mathrm{O}_8$ and $\mathrm{HoBa}_2\mathrm{Cu}_4{}^{16}\mathrm{O}_8$. The lines denote the linewidth in the normal state calculated from Eq. (3). The full and open circles correspond to the data taken on IN5 and FOCUS, respectively. The FOCUS data for $\mathrm{HoBa}_2\mathrm{Cu}_4{}^{16}\mathrm{O}_8$ refer to the back-exchanged compound.

Let us comment on the discrepancies in ΔT^* resulting from the different experimental techniques mentioned above. All methods are local probes with an interaction range of a few Å. The major difference, however, is the time over which the spectral response is collected. NMR and NQR techniques work at 10–100 MHz frequencies, thus they are insensitive to any mechanisms which are faster than about 10^{-8} s. Neutron spectroscopy as applied in the present work, on the other hand, involves energies of some meV and is therefore susceptible to dynamical effects of the order of 10^{-13} s. XANES spectroscopy is an even faster method with a time scale of 10^{-15} s. The time scale associated with each experimental method is essential for the detection of dynamical correlations. For example, the time scales for spin and lattice fluctuations are of the order of 10^{-12} s, thus they can easily be resolved by XANES and neutron spectroscopy, but not by NMR and NQR experiments. We can therefore immediately conclude that the mechanism giving rise to the isotope effect on the pseudogap has to involve a time scale $10^{-8} \gg \tau > 10^{-13}$ s.

The XANES experiments [10] were discussed along the lines of recent theories [9] and experiments [19] for underdoped $La_{2-x}Sr_xCuO_4$ which concluded that (bi)polaron formation takes place below a critical temperature. This leads to a coexistence of small (bi)polaronic and Fermi-liquid charge carriers, consistent with the inhomogeneous nature of the superconducting state in cuprates which was theoretically predicted and established by a variety of local techniques [20]. The comparable size of the isotope shift ΔT^* in the underdoped high-T_c superconductors $La_{2-x}Sr_xCuO_4$ [10] and $HoBa_2Cu_4O_8$ (present work) suggests that the same effects are present.

We point to the striking similarity between isotope substitution and underdoping with respect to both T_c and T^*. Underdoping produces a slight decrease of T_c, but a large increase of T^*, i.e.,

$$\left| \frac{\Delta T_c}{\Delta n} \right| \Big/ \left| \frac{\Delta T^*}{\Delta n} \right| \ll 1 \,, \tag{4}$$

where n is the carrier density. This ratio has the same sign and is similar in size to the ratio of the isotope coefficients

$$\frac{\alpha}{\alpha^*} \propto \frac{\Delta T_c}{\Delta M} \Big/ \frac{\Delta T^*}{\Delta M} \tag{5}$$

determined in the present work. Indeed, a relation involving the term $\Delta T_c/\Delta n$ was recently derived for the nonadiabatic contribution of α [21].

Our findings strongly support the fact that electron-phonon induced effects have to be incorporated in any model for high-T_c superconductivity. A recent theoretical investigation [22] 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 oxygen isotope effect on T^* is limited to methods like XANES [10] and neutron scattering (present work).

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