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Rapid Note

Large copper isotope effect on the pseudogap in the high-temperature superconductor $HoBa_2Cu_4O_8$

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Abstract. The copper isotope effect (^{63}Cu *vs.* ^{65}Cu) on the relaxation rate of crystal-field excitations in the slightly underdoped high-temperature superconductor $HoBa_2Cu_4O_8$ has been investigated by inelastic neutron scattering. For the ^{63}Cu compound there is clear evidence for the opening of an electronic gap in the normal state at $T^* \approx 160$ K far above $T_c = 79.0$ K. Upon substitution of ^{63}Cu by ^{65}Cu, T_c decreases marginally to 78.6 K, whereas T^* is increased to about 185 K. This large copper isotope shift $\Delta T^*(\mathrm{Cu}) = T^*(^{65}\mathrm{Cu}) - T^*(^{63}\mathrm{Cu}) \approx 25$ K – together with the corresponding oxygen isotope shift $\Delta T^*(\mathrm{O}) = T^*(^{18}\mathrm{O}) - T^*(^{16}\mathrm{O}) \approx 50$ K found in an earlier investigation – suggests that phonons or lattice fluctuations involving both the copper and the oxygen ions are important for the pairing mechanism in high-T_c materials.

PACS. 74.25.-q General properties; correlations between physical properties in normal and superconducting states – 74.72.Bk Y-based cuprates– 76.20.+q General theory of resonances and relaxations

One of the most unusual phenomena observed in high-temperature superconductors is the existence of the so-called pseudogap region in underdoped cuprates, which is characterised by the suppression of low energy spectral weight in the normal state above the superconducting transition temperature T_c. The experimental discovery of the pseudogap gave rise to an impressive number of models for the mechanism that causes the Cooper pairs to form [1]. In the past, measurements of the isotope effect were essential to establish the BCS model of classical superconductors. Likewise, experiments searching for an isotope effect on the pseudogap temperature T^* may be of crucial importance to discriminate between the different pairing scenarios developed for the cuprate superconductors. This was the motivation for our neutron spectroscopic studies of the relaxation rate of crystal-field excitations in the slightly underdoped high-T_c cuprate $HoBa_2Cu_4O_8$. The present experiments gave evidence for a large copper isotope effect on the pseudogap temperature T^*, namely $\Delta T^*(\mathrm{Cu}) = T^*(^{65}\mathrm{Cu}) - T^*(^{63}\mathrm{Cu}) \approx 25$ K. This result – together with the corresponding oxygen isotope shift $\Delta T^*(\mathrm{O}) = T^*(^{18}\mathrm{O}) - T^*(^{16}\mathrm{O}) \approx 50$ K found in an earlier investigation [2] – suggests that phonons or lattice fluctuations involving both the copper and the oxygen ions are important for the pairing mechanism.

The principle of neutron spectroscopic investigations of the crystal-field interaction in rare-earth based high-T_c superconductors was described in recent review articles [3,4]. By this technique transitions between different crystal-field levels associated with the rare-earth ions can be directly measured. In the normal metallic state the excited crystal-field levels interact with phonons, spin fluctuations, and charge carriers (electrons or holes), which limit the lifetime of the excitation, thus the observed crystal-field transitions exhibit line broadening. Lovesey and Staub [5] put forward the idea that the relaxation rate is dominated by phonon interactions. In their calculations they use a truncated crystal-field level scheme, *i.e.*, they neglect all but three of the crystal-field states which for the case of $Ho_{0.1}Y_{0.9}Ba_2Cu_3O_7$ leads to an unreasonably good agreement with the experimental data [6]. The inclusion of the complete set of crystal-field levels, however, produces a drastically different temperature dependence of the linewidth [7], *i.e.*, the phonon damping picture is no longer supported. Moreover, phonon relaxation exhibits a continuous temperature behaviour of the linewidth and cannot reproduce the step-like features observed in several high-T_c cuprates at or above T_c [6,8]. Therefore we describe the linewidth

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$\Gamma_n(T)$ in the normal state by the modified Korringa law [6]

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

where $J_{\rm ex}$ is the exchange integral between the $4f$ electrons of the rare-earth ions and the charge carriers, M_{ij} the matrix element of the crystal-field transition $|i\rangle \rightarrow |j\rangle$ with energy transfer $\hbar\omega_{ij} = \hbar\omega_i - \hbar\omega_j$, and $\chi''(\hbar\omega_{ij}) = \pi N^2(E_{\rm F})\hbar\omega_{ij}$ is the generalised susceptibility of the copper-oxide layers in the normal state with $N(E_{\rm F})$ being the density-of-states of the charge carriers at the Fermi energy $E_{\rm F}$. In superconducting compounds, however, the pairing of the charge carriers creates an energy gap Δ below the superconducting transition temperature $T_{\rm c}$ and thereby suppresses $N(E_{\rm F})$, thus crystal-field excitations with energy $\hbar\omega_{ij} < 2\Delta$ do not have enough energy to span the gap, and consequently there is no interaction with the charge carriers. For an isotropic gap function the intrinsic linewidth in the superconducting state is then given by

$$\Gamma_{\rm s}(T) = \Gamma_n(T)\exp(-\frac{\Delta}{k_{\rm B}T}) \cdot \quad (2)$$

This means that $\Gamma_{\rm s}(T \ll T_{\rm c}) \approx 0$, and line broadening sets in just below $T_{\rm c}$ where the superconducting gap opens. The exponential temperature dependence of $\Gamma_{\rm s}\,(T)$ was nicely demonstrated in the first neutron spectroscopic study on the classical superconductor $La_{1-x}Tb_xAl_2$ [9] as well as for the high-$T_{\rm c}$ compound $HoBa_2Cu_3O_{6.96}$ [8]. On the other hand, neutron experiments performed for $Ho_{0.1}Y_{0.9}Ba_2Cu_3O_7$ [6] revealed an unusual temperature dependence, *i.e.*, $\Gamma_{\rm s}(T)$ does not follow the behavior predicted by equation (2), but increases already far below $T_{\rm c}$. This was ascribed to a high degree of gap anisotropy, since an anisotropic gap function gives rise to certain relaxation channels even at $T \ll T_{\rm c}$, particularly along the directions involving nodes. An anisotropic gap function was also inferred from neutron crystal-field studies on the high-$T_{\rm c}$ compounds $HoBa_2Cu_4O_8$ and $Er_2Ba_4Cu_7O_{15}$ [10].

The present neutron scattering experiments searching for a Cu isotope effect on the pseudogap were performed on the high-resolution time-of-flight spectrometer FOCUS installed at the spallation neutron source SINQ at PSI Villigen. The incident neutron wavelength was 5 Å giving an energy resolution of 0.1 meV at the elastic position. The powder samples were prepared from isotopically pure ^{63}Cu and ^{65}Cu metals. CuO powder was obtained by oxygenation of the metals at 900 °C in an oxygen atmosphere for 20 h with one intermediate grinding. Stoichiometric mixtures of Ho_2O_3, $BaCO_3$ and ^{63}CuO (^{65}CuO) were prereacted at 870, 910 and 915 °C with intermediate grinding, resulting in a mixture of $HoBa_2Cu_3O_7$ and CuO. The polycrystalline $HoBa_2Cu_4O_8$ samples were then obtained by a high-oxygen-pressure solid-state reaction synthesis at 1000 °C and 450 bars oxygen pressure for 60 h. Neutron powder diffraction performed on the high-resolution diffractometer HRPT at SINQ confirmed the single-phase character of the samples. The critical temperatures of the ^{63}Cu and ^{65}Cu compounds were measured by magnetometry to be (79.0 ± 0.1) K and (78.6 ± 0.1) K, respectively, giving a copper isotope shift $\Delta T_{\rm c} = -(0.4 \pm 0.2)$ K which is in agreement with the value $\Delta T_{\rm c} = -(0.25 \pm 0.06)$ K found for $YBa_2Cu_4O_8$ [11].

Figure 1 shows neutron spectra observed for $HoBa_2{}^{65}Cu_4O_8$ at low energy transfers. There are two strong ground-state crystal-field transitions at energies $\hbar\omega_1$=0.6 meV and $\hbar\omega_2$=1.3 meV, *i.e.*, $\hbar\omega_i \ll 2\Delta_{\rm max}$ ($\sim$ 66 meV) [10]. With increasing temperature the crystal-field transitions exhibit line broadening. In addition, further states become increasingly populated giving rise to excited crystal-field transitions. The energy spectra were fitted according to the crystal-field model for $HoBa_2Cu_4O_8$ as described in detail in reference [10]. The only free parameters were an overall scale factor for the intensities and a temperature dependent linewidth $\Gamma(T)$. The results of the fitting procedure are shown by solid lines in Figure 1.

Figure 2 displays the temperature dependence of the intrinsic linewidth (HWHM). The linewidth is zero at the lowest temperatures, then it increases monotonically up to 180 K. A notable enhancement occurs between 180 and 185 K. Above 185 K the linewidth increases almost linearly with temperature as predicted by equation (1). Any deviation of the linewidth from the normal-state behaviour can be attributed to the opening of a gap (or a pseudogap). We therefore identify the temperature where the enhancement occurs with the temperature where the pseudogap opens, *i.e.*, we set $T^* \approx 185$ K. This can be very clearly visualized by plotting the linewidth in reduced units $\Gamma(T)/\Gamma_n(T)$ as shown in Figure 3.

The linewidth observed for the copper isotope substituted compound $HoBa_2{}^{63}Cu_4O_8$ exhibits a similar relaxation behavior (see Fig. 3), but the enhancement occurs at lower temperatures between 150 and 160 K, *i.e.*, we set $T^* \approx 160$ K. These experiments give evidence therefore for a large copper isotope effect $\Delta T^* \approx 25$ K on the pseudogap. In earlier neutron spectroscopic studies [2] on the oxygen isotope substituted compound (*i.e.*, $HoBa_2Cu_4{}^{16}O_8$ *vs.* $HoBa_2Cu_4{}^{18}O_8$) we found an even larger isotope effect $\Delta T^* \approx 50$ K on the pseudogap as shown in Figure 3.

Superconductivity is the result of two distinct quantum phenomena, pairing at a characteristic temperature T^* and long-range phase coherence at the superconducting transition temperature $T_{\rm c}$. In conventional homogeneous superconductors these two phenomena occur simultaneously, *i.e.*, $T^* = T_{\rm c}$. On the other hand, there are numerous indications that an intrinsic inhomogeneity is pertinent to the low temperature state of underdoped cuprates, *i.e.*, two kinds of quasiparticles are present as suggested very early by Gor′kov and Sokol [12]. These may be considered on the one hand as highly mobile fermionic ones in a conventional carrier band, and on the other hand as slow nearly localised ones in a narrow band. A recent analysis of the magnetic susceptibility of $La_{2-x}Sr_xCuO_4$ supported this view and identified the slow carriers to result from bipolarons which condense into cluster or stripe

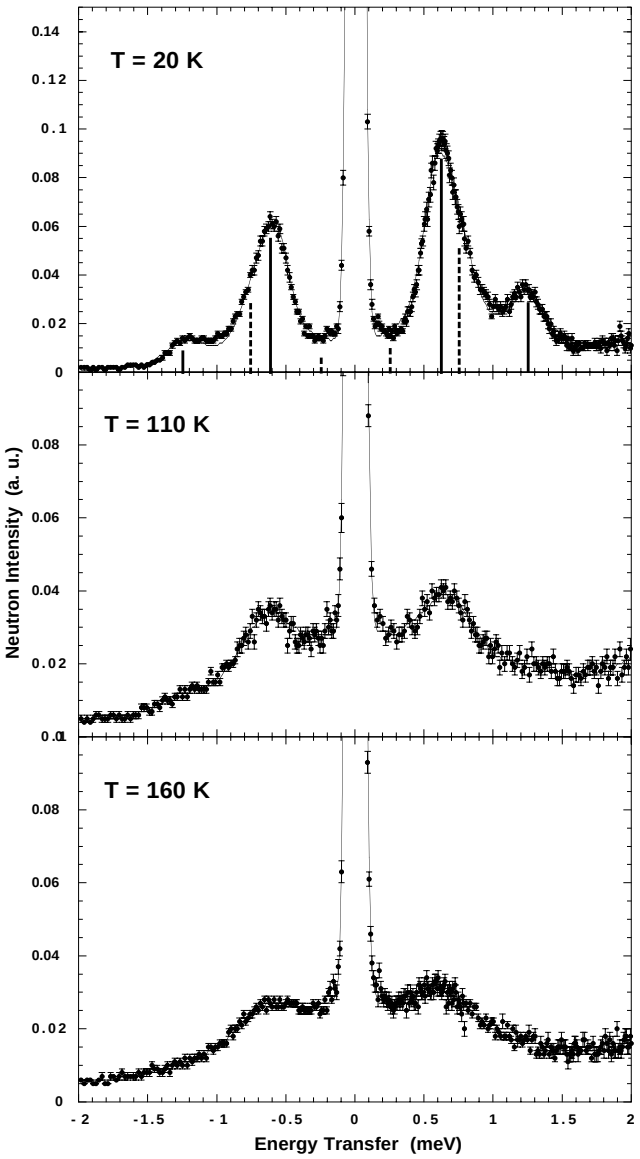

Fig. 1. Energy spectra of neutrons scattered from $HoBa_2{}^{65}Cu_4O_8$ as taken on the time-of-flight spectrometer FOCUS at SINQ (PSI Villigen). The lines are the result of a least-squares fitting procedure as described in the text. The solid and dashed vertical bars denote ground-state and excited-state crystal-field transitions, respectively.

aggregates below T^* [13]. Evidence for the formation of stripes was recently provided by observations of anomalous effects in the phonon spectra of $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_x$ [14,15]. Pairing occurs naturally in such a spatially confined region, since localised states always interact with each other through the lattice deformation. Upon lowering the temperature bulk superconductivity is then achieved at T_c by the onset of global phase coherence.

The present relaxation data clearly support the picture described above. Firstly, we observe a notable reduction of the linewidth below T^* indicating the opening of a pseudogap. However, the line narrowing is not complete. This may be due to the presence of fermionic quasiparticles in the region between the stripes and/or

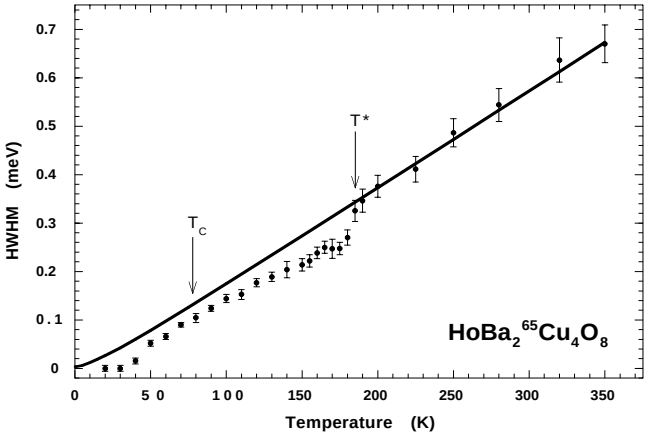

Fig. 2. Temperature dependence of the intrinsic linewidth (HWHM) corresponding to the crystal-field transition at 0.6 meV in $HoBa_2{}^{65}Cu_4O_8$. The line denotes the linewidth in the normal state as calculated from equation (1).

to the unusual anisotropy of the pseudogap which opens up at different temperatures for different points in momentum space as evidenced by angle-resolved photoemission spectroscopy (ARPES) experiments in underdoped $Bi_2Sr_2CaCu_2O_{8+\delta}$ [16]. Secondly, the opening of the pseudogap exhibits pronounced isotope effects. For $^{16}O \rightarrow {}^{18}O$ isotope substitution this is actually expected from the polaron-like mechanism associated with the Jahn-Teller phonon modes, since the bandwidth W depends on the ionic mass M according to $W \propto \exp\{-\gamma\sqrt{M}\}$ and therefore exhibits band narrowing, which results in an enhancement of T^*. For $^{63}Cu \rightarrow {}^{65}Cu$ isotope substitution, on the other hand, the relevant mechanism giving rise to an enhancement of T^* has to be associated with a local copper phonon mode. This could be of a buckling type [17] or umbrella type [18] motion which both involve out-of-plane displacements of the Cu ions. Thirdly, the linewidth is drastically reduced below T_c, but it does not exhibit the exponential behaviour predicted by equation (2) which can again be explained by the anisotropy of the gap function [6,10].

Our observation of large copper and oxygen isotope effects on the pseudogap temperature T^* contrasts with NMR and NQR studies on $YBa_2Cu_4O_8$ which resulted in either an absence or a very small isotope shift ΔT^* for both Cu and O isotope substitutions [11,19,20]. On the other hand, X-ray absorption near-edge spectroscopy (XANES) experiments [21] revealed a huge oxygen isotope effect $\Delta T^* \approx 60$ K associated with the onset of local lattice fluctuations in $La_{2-x}Sr_xCuO_4$. This discrepancy can be explained by the time over which the spectral response is collected. The time scale for lattice fluctuations is 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.

For quite a long time high-temperature superconductivity in cuprates has been widely believed to occur in a homogeneous system through a magnetic interaction, but this assumption is now seriously challenged by recent experimental observations that suggest spatial charge

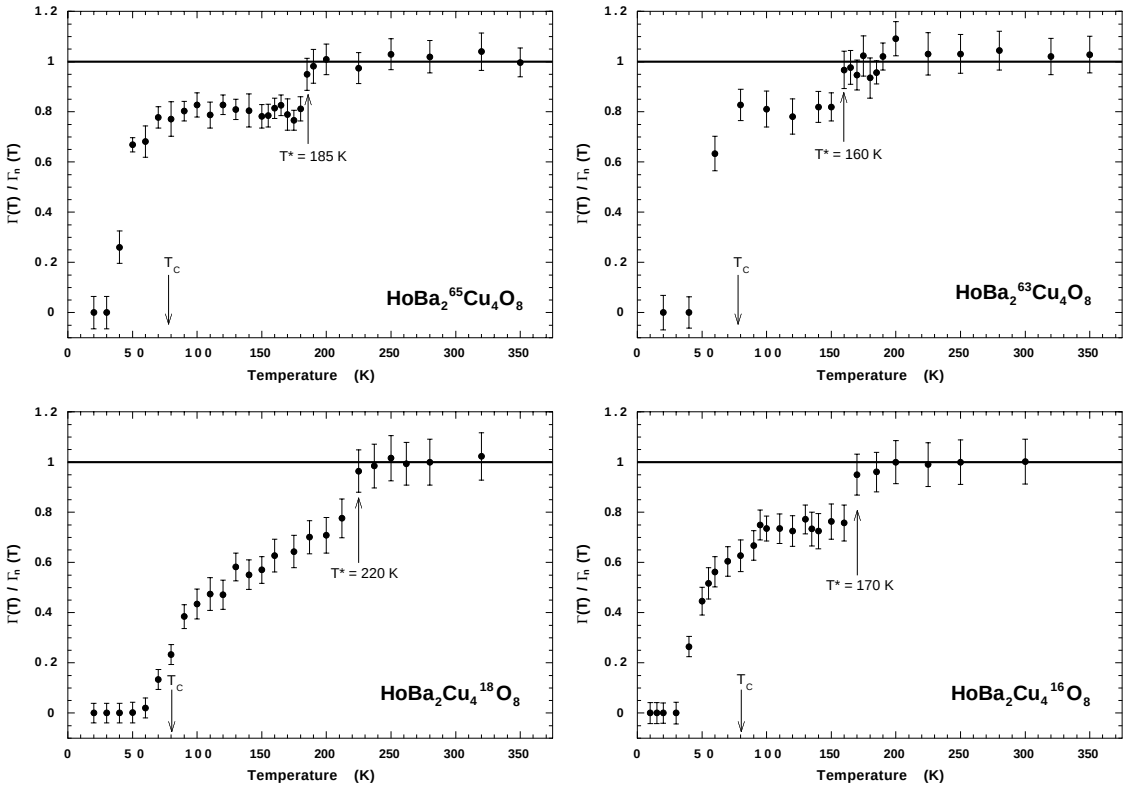

Fig. 3. Temperature dependence of the reduced linewidth observed for both copper and oxygen (Ref. [2]) isotope substituted $HoBa_2Cu_4O_8$. The solid lines represent the normal state linewidth expected by the Korringa law.

inhomogeneity, lattice and isotope effects. Several theoretical attempts have been made to incorporate the new findings into a model describing the interaction of the charge carriers with the relevant phonon modes as well as with the copper spins [22–24]. So far only phonon modes associated with the Jahn-Teller like oxygen vibrations have been considered in the interaction Hamiltonian. The additional observation of a copper isotope effect on T^* as described in the present work clearly requires the inclusion of local phonon modes presumably associated with a buckling or umbrella type motion of the Cu ions. This appears to be important for a proper treatment of the interaction Hamiltonian, since the copper isotope coefficient associated with T^* is $\alpha^*_{\rm Cu} \approx -4.9$, *i.e.*, roughly twice as large as the corresponding oxygen isotope coefficient $\alpha^*_{\rm O} \approx -2.2$ [2].

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