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A neutron crystal-field study of the copper isotope effect on the pseudogap in the high-T_c cuprate $HoBa_2Cu_4O_8$

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Abstract

The copper isotope effect on the relaxation rate of crystal-field transitions in the slightly underdoped high-temperature superconductor $HoBa_2Cu_4O_8$ has been investigated by means of inelastic neutron scattering. The measurements give clear evidence for the opening of a normal state pseudogap at T^* far above T_c, but it is shifted from $T^*=160(10)$ K for the $HoBa_2{}^{63}Cu_4O_8$ compound to $T^*=185(5)$ K for the $HoBa_2{}^{65}Cu_4O_8$ compound, giving rise to an isotope effect of $\Delta T^*=25(15)$ K.

1. Introduction

The existence of a normal state pseudogap in high-temperature superconductors is considered to be among their most important features, since the pseudogap is widely regarded as being linked to the pairing mechanism. Among others, inelastic neutron scattering has proven to be an ideal technique for studying the opening of the pseudogap at T^*, which is evidenced by a decrease of the electronic density of states $N(E_F)$. By means of this technique, we have recently established a phase diagram for the 123-type compounds, from the strongly underdoped to the slightly overdoped regimes [1]. Moreover, we have measured the oxygen isotope effect on the pseudogap on $HoBa_2Cu_4O_8$ to be $\Delta T^*=50(20)$ K [2]. Here, we report on further neutron spectroscopic measurements to study the copper isotope effect on the pseudogap also on $HoBa_2Cu_4O_8$.

2. Crystal-field spectroscopy

The principle of neutron spectroscopic investigations of the crystal-field interaction in high-T_c superconductors was described in recent review articles [3,4]. 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 [5]. 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

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

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 first observation of crystal-field linewidth changes due to superconductivity was made on the BCS-like superconductor $La_{1-x}Tb_xAl_2$ [6] with $\hbar\omega = 0.68$ meV $< 2\Delta(0) = 0.93$ meV. Subsequent investigations performed on superconducting cuprates showed anomalies consistent with the

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formation of an energy gap at temperatures slightly higher than T_c, for $Ho_{0.1}Y_{0.9}Ba_2Cu_3O_7$ ($\hbar\omega = 0.5$ meV) [7] and $Tm_{0.1}Y_{0.9}Ba_2Cu_3O_7$ ($\hbar\omega = 11.8$ meV) [8]. The results obtained for the Ho compound revealed an unusual temperature dependence of $\Gamma_s(T)$ and of the peak position, which 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 compounds $HoBa_2Cu_4O_8$ and $Er_2Ba_4Cu_7O_{15}$ [9].

3. Experimental

We have performed new inelastic neutron-scattering experiments to study the copper isotope effect on the relaxation rate of crystal-field excitations in $HoBa_2Cu_4O_8$. 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. The $HoBa_2Cu_4O_8$ polycrystalline samples were prepared 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 (SINQ) confirmed the single phase character of the samples.

The critical temperatures were determined through the zero-field-cooled temperature dependence of the DC susceptibility by means of a Quantum Design PPMS 6000 system. They were found to be $T_c = 79.0(0.1)$ K for the $HoBa_2{}^{63}Cu_4O_8$ compound and $T_c = 78.6(0.1)$ K for the $HoBa_2{}^{65}Cu_4O_8$ compound. The observed copper isotope shift on T_c, i.e. $\Delta T_c \approx 0.4 \pm 0.2$ K gives rise to an isotope coefficient of $\alpha_{T_c} = 0.16 \pm 0.08$, which is, within the error bars, comparable to previously reported values [10].

The inelastic neutron scattering experiments were performed on the high resolution time-of-flight spectrometer FOCUS, installed at the SINQ spallation source of the Paul Scherrer Institute (Villigen). The incident neutron wavelength was set to 4.8 Å, giving rise to an energy resolution of 90 μeV at the elastic position. The samples were enclosed into cylindrical aluminum containers of 10 mm diameter and 50 mm height, which were mounted in a closed-cycle refrigerator in order to achieve temperatures in the range 15 K $\leq T \leq$ 350 K. The raw data were corrected for absorption, detector efficiency, background and detailed balance effects according to standard procedures.

4. Results

Fig. 1 shows energy spectra for $HoBa_2{}^{63}Cu_4O_8$. There are two strong ground-state crystal-field transitions at $\hbar\omega_1 = 0.6$ meV and $\hbar\omega_2 = 1.3$ meV (solid vertical lines), i.e. $\hbar\omega_i \ll 2\Delta_{max}$ (~ 66 meV [9]). With increasing temperature, the crystal-field transitions exhibit line broadening. In addition, excited crystal-field states (dashed lines) become increasingly populated giving rise to excited crystal-field transitions. The energy spectra were fitted according to the neutron cross-section for crystal-field transitions, which is given by:

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

where M_{ij} is the transition matrix element of the crystal-field transition $|i\rangle \rightarrow |j\rangle$, Z is the partition function, and $\hbar\omega_{ij} = \hbar\omega_j - \hbar\omega_i$. M_{ij} and $\hbar\omega_{ij}$ were kept fixed at the values obtained for the natural $HoBa_2Cu_4O_8$ compound [9]. 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 [7]

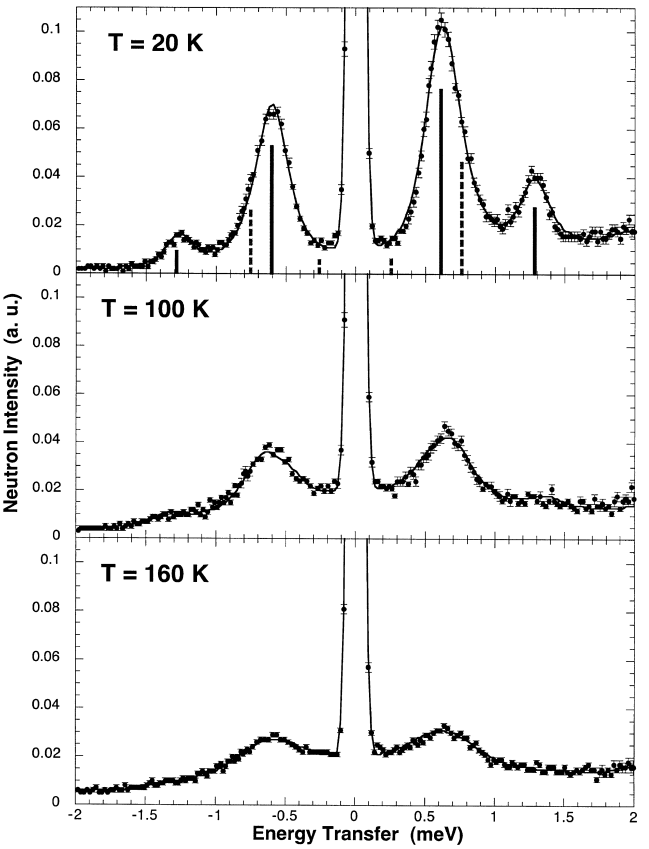

Fig. 1. Energy spectra of neutrons scattered from $HoBa_2{}^{63}Cu_4O_8$ as taken on FOCUS. The solid line is the fit to the data as described in the text.

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

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. Eq. (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 $\Gamma(T) \sim [J_{ex}N(E_F)]^2$. The results of the fitting procedure are shown by solid lines in Fig. 1.

Fig. 2 shows the temperature dependence of the linewidth factor $J_{ex}N(E_F)$ obtained for both $HoBa_2{}^{63}Cu_4O_8$ and $HoBa_2{}^{65}Cu_4O_8$. The data sets for the two samples exhibit similar features. The plots can be divided into three regions:

(i) $T < T_c$: the linewidth is zero at low temperatures and then increases abruptly from $T \approx 40$ K up to T_c.

(ii) $T_c \leq T < T^*$: the linewidth is constant within the error bars until there is a step-like enhancement at T^*.

(iii) $T \geq T^*$: the linewidth is again constant but typically 10% higher than in region (ii).

In the high-temperature limit, the modified Korringa law (3) predicts a linear relationship between the linewidth, Γ, and the temperature, T:

$$\Gamma(T) \propto [J_{ex}N(E_F)]^2 \cdot T \quad (4)$$

which clearly applies for region (iii). For this region, we obtained $[J_{ex}N(E_F)]_{63} = 0.00554(21)$ and $[J_{ex}N(E_F)]_{65} = 0.00559(24)$, which are in agreement with the values found for the ^{16}O- and ^{18}O-substituted $HoBa_2Cu_4O_8$ compounds [2]. In region (ii), the density of states $N(E_F)$ is reduced by typically 10% compared with region (iii). This may be taken as evidence for a 'pseudogap phase', i.e. part of the charge carriers undergo local pairing and thereby create an energy gap, Δ, so that they cannot interact any longer with the crystalline-electric field (CEF) excitations. Our data, displayed in Fig. 2 show a clear isotope effect for the opening of the pseudogap: $T^*_{63} = 160(10)$ K and $T^*_{65} = 185(5)$ K. Finally, in region (i), the density of states $N(E_F)$ becomes completely suppressed, leading to global phase coherence and bulk superconductivity.

The present results can be introduced into the phase diagram for the 123-type compounds as shown in Fig. 3, since $HoBa_2Cu_4O_8$ is, concerning the doping level, equivalent to a 123 compound with $x \approx 6.78$ [3,4]. A detailed discussion about the phase diagram can be found in Ref. [1].

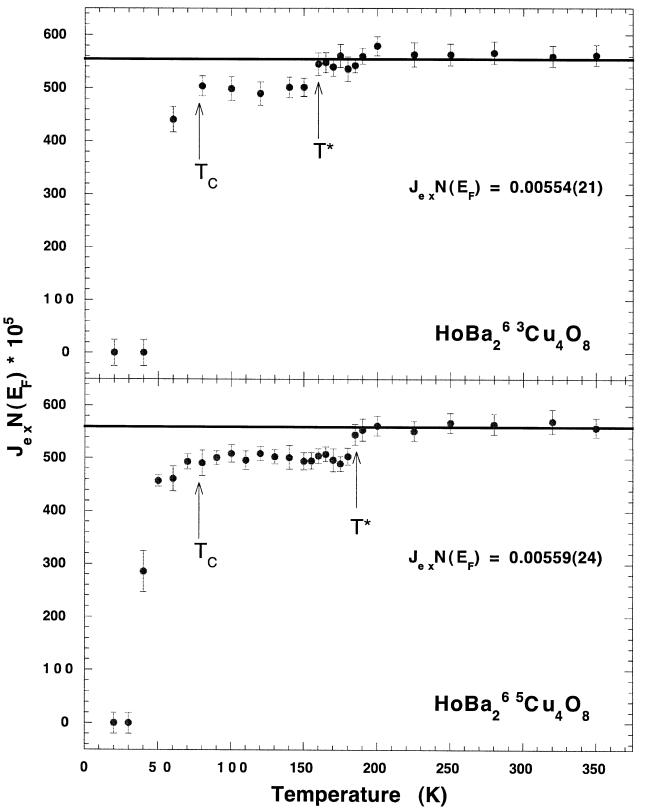

Fig. 2. Temperature dependence of the linewidth factor $J_{ex}N(E_F)$ obtained for $HoBa_2{}^{63}Cu_4O_8$ and $HoBa_2{}^{65}Cu_4O_8$. The solid lines represent the normal state linewidth expected by the Korringa law.

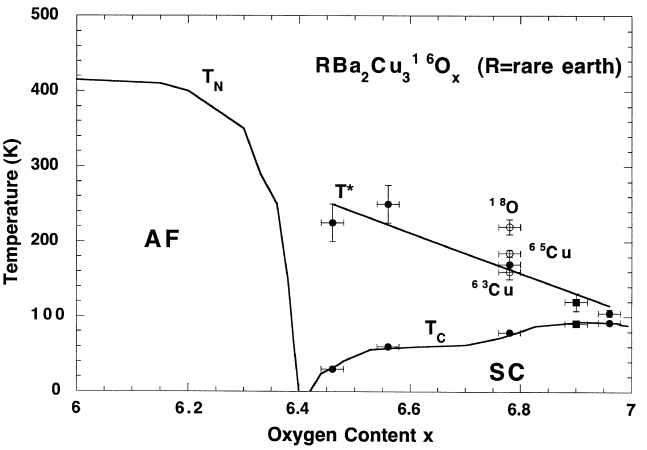

Fig. 3. Phase diagram of 123-type high-temperature superconductors as obtained by inelastic neutron scattering.

5. Conclusion

Our measurements give evidence for a copper isotope effect on the pseudogap of $\Delta T^* = 25(15)$ K. This result, together with the large oxygen isotope effect that we have recently found on the pseudogap temperature [2], as well as similar effects found by XANES on $La_{2-x}Sr_xCuO_4$ [11], suggest that electron–phonon-induced effects may be important for the understanding of the pseudogap, and both the O and Cu ions are involved in this mechanism. Indeed, a recent theoretical investigation [12] demonstrated that a model involving strong nonlinear electron–phonon effects is able to explain quantitatively both the copper and the oxygen isotope effects on the pseudogap. Moreover, the underlying time scale was found to be rather fast, so that the detection of an isotope effect on T^* is limited to fast methods like ARPES, XANES and inelastic neutron scattering.

Acknowledgements

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