

Oxygen and copper isotope effects on the pseudogap in the high-temperature superconductor $\text{La}_{1.81}\text{Ho}_{0.04}\text{Sr}_{0.15}\text{CuO}_4$ studied by neutron crystal-field spectroscopy

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The oxygen and copper isotope effects on the relaxation rate of crystal-field excitations in the optimally doped high-temperature superconductor $\text{La}_{1.81}\text{Ho}_{0.04}\text{Sr}_{0.15}\text{CuO}_4$ have been investigated by means of inelastic neutron scattering. For the ^{16}O compound there is clear evidence for the opening of an electronic pseudogap in the normal state at $T^* \approx 60$ K, far above $T_c \approx 32$ K. Upon substituting ^{16}O by ^{18}O , T^* is shifted to about 70 K. On the other hand, no shift is found for the copper isotope substitution, i.e., $T^*(^{63}\text{Cu}) \approx T^*(^{65}\text{Cu}) \approx 60$ K. These results, together with the large oxygen and copper isotope effects on T^* for $\text{HoBa}_2\text{Cu}_4\text{O}_8$, give evidence that the pseudogap formation in the single-layer LSCO and bilayer YBCO type compounds is governed by an additional local mode in the latter.

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Superconductivity is the result of two distinct quantum phenomena: pairing of the charge carriers at a characteristic temperature T^* and long-range phase coherence at the superconducting transition temperature T_c . In conventional superconductors these two phenomena occur simultaneously, i.e., $T^* = T_c$. In contrast, for high-temperature superconductors we have $T^* > T_c$ over a large doping range; thus the so-called pseudogap region ($T_c < T < T^*$) is clearly the most challenging part of the phase diagram. The experimental discovery of the pseudogap region gave rise to an impressive number of models for the mechanism of high-temperature superconductivity.¹ In the past, measurements of the isotope effect were essential to establish the BCS model of classical superconductors. Likewise, experiments searching for isotope effects on the pseudogap temperature T^* may be of crucial importance to discriminate between the different pairing scenarios developed for the cuprate superconductors.

Recently, we studied the oxygen and copper isotope effects on T^* by neutron scattering measurements of the relaxation rate of crystal-field excitations in the bilayer high- T_c compound $\text{HoBa}_2\text{Cu}_4\text{O}_8$ which gave evidence for large isotope shifts $\Delta T_O^* \approx 50$ K (Ref. 2) and $\Delta T_{Cu}^* \approx 25$ K (Ref. 3). While the observed oxygen isotope shift (^{16}O vs ^{18}O) was quantitatively accounted for by models based on charge ordering⁴ and strong nonlinear electron-phonon effects⁵ associated with Jahn-Teller-like oxygen vibrations and stripe formation,⁶ we are not aware of any theoretical attempts to understand the observed copper isotope shift (^{63}Cu vs ^{65}Cu). Such investigations would be highly desirable, since the copper isotope coefficient associated with T^* is $\alpha^*(\text{Cu}) = -4.9$,³ i.e., roughly twice as large as the corresponding oxygen isotope coefficient $\alpha^*(\text{O}) = -2.2$.² The observed copper isotope effect on T^* in $\text{HoBa}_2\text{Cu}_4\text{O}_8$ clearly indicates the importance of local copper lattice modes which could be either of an in-plane copper-oxygen bond stretching type⁷ or an umbrella-type⁸ motion involving out-of-plane displacements of the Cu ions. The latter mode is absent in the single-

layer high- T_c compound $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ due to the inversion symmetry at the Cu site. Thus a study of the copper isotope effect in this compound would definitely discriminate between the possible copper modes.

In this paper we report on neutron spectroscopic investigations of the oxygen and copper isotope effects on the relaxation rate of crystal-field excitations in the optimally doped high- T_c compound $\text{La}_{1.81}\text{Ho}_{0.04}\text{Sr}_{0.15}\text{CuO}_4$. The data provide clear evidence for an oxygen isotope shift $\Delta T_O^* \approx 10$ K, whereas no shift was observed for copper isotope substitution, i.e., $\Delta T_{Cu}^* \approx 0$ K. These results complement our earlier findings for $\text{HoBa}_2\text{Cu}_4\text{O}_8$,^{2,3} indicating an additional interaction in the origin of the pseudogap in the bilayer high- T_c compounds compared to the single-layer ones. More specifically, the pseudogap formation in both single-layer and bilayer high- T_c compounds is governed by Jahn-Teller-type oxygen vibrations,⁶ but for the bilayer compounds an umbrella-type motion of the Cu ions has to be considered additionally.

The principle of neutron spectroscopic investigations of the crystal-field interaction in high- T_c superconductors was described in review articles.^{9,10} 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.² The corresponding intrinsic linewidth $\Gamma_n(T)$ increases almost linearly with temperature according to the well-known Korringa law.¹¹ In the superconducting state, however, the pairing of 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

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

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. For anisotropic gap functions the situation is more complicated, since certain relaxation channels exist even at the lowest temperature.¹²

For the present experiments four samples of the optimally doped high- T_c compound $\text{La}_{1.81}\text{Ho}_{0.04}\text{Sr}_{0.15}\text{CuO}_4$ were prepared for the isotopes ^{16}O and ^{18}O as well as ^{63}Cu and ^{65}Cu . The Ho^{3+} content has to be kept below $\sim 5\%$ in order to ensure the sample homogeneity and single-phase character.¹³ The samples were synthesized by a conventional solid-state reaction using stoichiometric amounts of dried La_2O_3 (99.9%), Ho_2O_3 (99.9%), SrCO_3 (99.9%), and CuO (99%). The powders were mixed, ground thoroughly, pressed into pellets, and fired in air at 850°C (30 h), 900°C (40 h), and 950°C (50 h) with intermediate grindings. After the neutron scattering experiments, the $\text{La}_{1.81}\text{Ho}_{0.04}\text{Sr}_{0.15}\text{Cu}^{16}\text{O}_4$ sample was subject to ^{18}O diffusion in order to obtain $\text{La}_{1.81}\text{Ho}_{0.04}\text{Sr}_{0.15}\text{Cu}^{18}\text{O}_4$. The process was performed in a closed system at 850°C during 100 h as described in Ref. 14. The ^{18}O concentration was determined by mass spectrometry during the exchange process to be $(81 \pm 1)\%$. The copper-isotope-substituted samples were prepared from very-high-purity ^{63}Cu and ^{65}Cu metals. For this purpose, ^{63}CuO and ^{65}CuO powders were obtained by oxygenation of the metals at 900°C during 20 h with one intermediate grinding. From there on, the solid-state reaction took place as described above. All samples were confirmed by high-resolution neutron-powder diffraction to be single phase (impurity phases less than $\sim 1\%$). The structural parameters and oxygen contents of all samples were found to be the same within experimental uncertainties. The critical temperatures were determined by dc magnetometry to be $T_c \approx 32$ K, and the observed isotope shifts turned out to be $\Delta T_c(\text{O}) = -(0.43 \pm 0.05)$ K and $\Delta T_c(\text{Cu}) = -(0.37 \pm 0.04)$ K, which can be described by the isotope coefficients $\alpha_{\text{O}} = 0.11 \pm 0.01$ and $\alpha_{\text{Cu}} = 0.29 \pm 0.04$, in agreement with literature data.^{15,16}

The inelastic 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. FOCUS and IN5 were operated with incoming neutron wavelengths of 5.75 and 6 Å, giving energy resolutions at the elastic position [full width at half maximum (FWHM)] of 46 and 55 μeV , respectively. The samples were enclosed under He atmosphere in Al cylinders and placed into a cryostat in order to reach temperatures in the range $10 \leq T \leq 100$ K. The raw data were corrected for absorption, detector efficiency, background, and detailed balance effects according to standard procedures.

Figure 1 shows energy spectra of neutrons scattered from $\text{La}_{1.81}\text{Ho}_{0.04}\text{Sr}_{0.15}\text{Cu}^{16}\text{O}_4$. There are strong ground-state crystal-field transitions at $\hbar\omega \approx \pm 0.18$ meV, i.e., $|\hbar\omega| \ll 2\Delta_{\text{max}} [\sim 16$ meV (Ref. 17)]. Further transitions are ex-

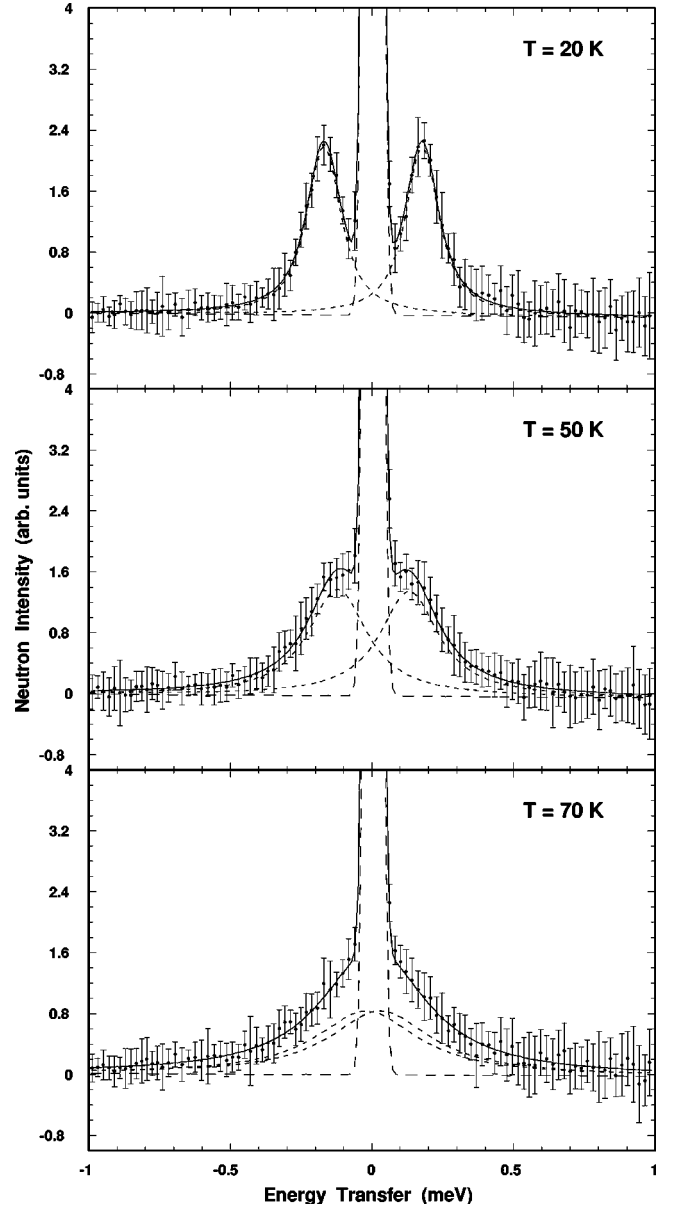


FIG. 1. Energy spectra of neutrons scattered from $\text{La}_{1.81}\text{Ho}_{0.04}\text{Sr}_{0.15}\text{Cu}^{16}\text{O}_4$ as taken on FOCUS. The solid lines are fits to the data which include the relaxation as described in the text. The dashed lines denote the observed crystal-field excitations and the elastic line.

pected to appear above 10 meV and to be at least one order of magnitude less intense,¹⁸ which means that the observed low-energy crystal-field spectrum will not be contaminated by excited-state transitions for temperatures up to 100 K. At $T = 10$ K the width of the crystal-field transitions is considerably broader than the instrumental energy resolution, typically of the order of 140 μeV , which is due to local structural distortions around the Ho^{3+} ions resulting from doping with Sr^{2+} ions. With increasing temperature the crystal-field transitions renormalize due to relaxation effects; i.e., the linewidths increase and the energies decrease. The lines in Fig. 1 show the result of a least-squares fitting procedure in which the crystal-field transitions were described by a con-

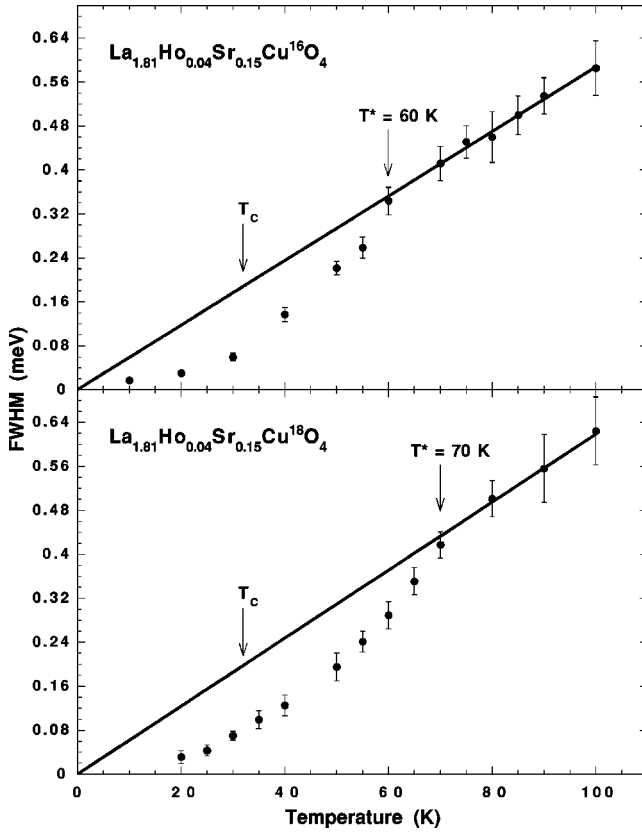


FIG. 2. Temperature dependence of the intrinsic linewidth (FWHM) corresponding to the lowest ground-state transition in $\text{La}_{1.81}\text{Ho}_{0.04}\text{Sr}_{0.15}\text{Cu}^{16}\text{O}_4$ and $\text{La}_{1.81}\text{Ho}_{0.04}\text{Sr}_{0.15}\text{Cu}^{18}\text{O}_4$. The lines denote the linewidth in the normal state calculated from Eq. (2).

volution of a temperature-independent Gaussian function (corresponding to the residual low-temperature width of $140 \mu\text{eV}$ as explained above) with a temperature-dependent Lorentzian function describing the intrinsic linewidth $\Gamma(T)$ due to the interaction with the charge carriers. The fitting parameters were therefore the intrinsic linewidth $\Gamma(T)$, the energy of the crystal-field transition, and an overall scale factor for the intensities. Similar energy spectra were obtained for the isotope-substituted ^{18}O , ^{63}Cu , and ^{65}Cu compounds which all gave evidence for a ground-state crystal-field transition at the same energy ($\pm 0.18 \text{ meV}$ at low temperature) as for the ^{16}O compound within the experimental uncertainties.

Figure 2 (upper panel) shows the temperature dependence of the intrinsic linewidth $\Gamma(T)$ determined for the ^{16}O compound. The linewidth (FWHM) is rather small below 30 K; then it increases monotonically up to 60 K. Above 60 K the linewidth increases linearly as expected for the normal state; i.e., we set $T^*(^{16}\text{O}) \approx 60 \text{ K}$. The solid line denotes the linewidth in the normal state which—considering only the first-excited crystal-field state—is given by the modified Korringa law¹¹

$$\Gamma(T) = 2\pi J_{ex}^2 N^2(E_F) \hbar \omega M^2 \coth\left(\frac{\hbar \omega}{2k_B T}\right), \quad (2)$$

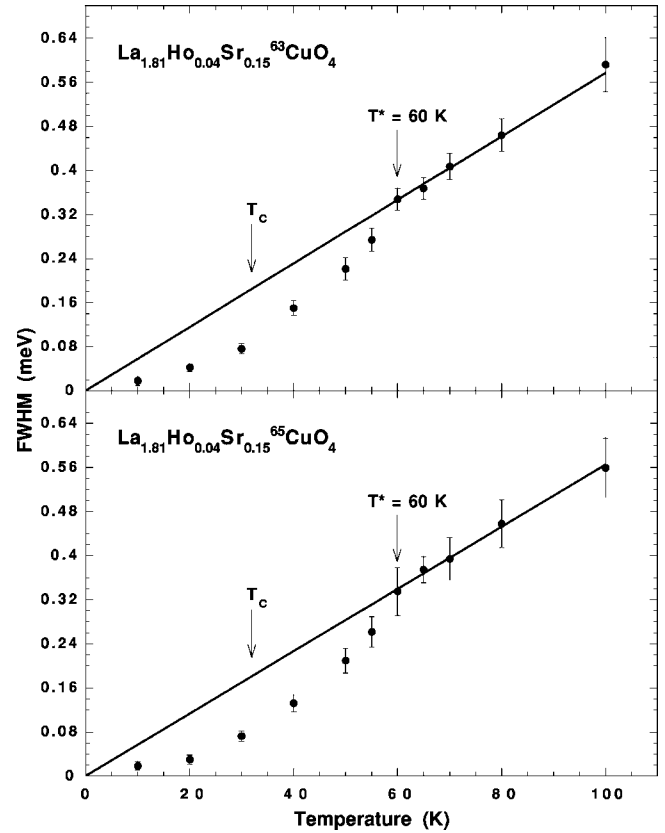


FIG. 3. Temperature dependence of the intrinsic linewidth (FWHM) corresponding to the lowest ground-state transition in $\text{La}_{1.81}\text{Ho}_{0.04}\text{Sr}_{0.15}^{63}\text{CuO}_4$ and $\text{La}_{1.81}\text{Ho}_{0.04}\text{Sr}_{0.15}^{65}\text{CuO}_4$. The lines denote the linewidth in the normal state calculated from Eq. (2).

where J_{ex} is the exchange integral between the $4f$ electrons of the Ho^{3+} ions and the charge carriers, $N(E_F)$ is the density of states at the Fermi level, and M is the transition matrix element of the crystal-field transition with energy $\hbar \omega = \pm 0.18 \text{ meV}$. We took $M^2 = 37.6$ as resulting from the extrapolation procedure described above.¹⁸ From the high-temperature linewidth data ($T > 60 \text{ K}$) we obtain $J_{ex}N(E_F) = 0.0057(2)$.

The temperature evolution of the intrinsic linewidth determined for the ^{18}O compound is shown in Fig. 2 (lower panel) which has a similar shape as for the ^{16}O compound. However, the crossover into normal-state behavior clearly occurs at a higher temperature; i.e., we set $T^*(^{18}\text{O}) \approx 70 \text{ K}$. The slope in the normal state ($T > 70 \text{ K}$) is governed by $J_{ex}N(E_F) = 0.0058(2)$. Our data give evidence for a large oxygen isotope shift of the pseudogap temperature T^* at optimal doping, namely $\Delta T^*(\text{O}) \approx 10 \text{ K}$, which gives rise to an isotope coefficient $\alpha^*(\text{O}) \approx -1.3$.

Figure 3 shows the temperature dependence of the intrinsic linewidth determined for the ^{63}Cu (upper panel) and ^{65}Cu (lower panel) compounds. The relaxation behavior is similar to the ^{16}O compound, and there is practically no difference between the ^{63}Cu and ^{65}Cu data; i.e., we have $T^*(^{63}\text{Cu}) \approx T^*(^{65}\text{Cu}) \approx 60 \text{ K}$. This means that there is no copper isotope effect on T^* , i.e., $\Delta T^*(\text{Cu}) \approx 0 \text{ K}$. From the slope in the normal state ($T > 60 \text{ K}$) we obtain $J_{ex}N(E_F)$

$=0.0057(2)$ and $J_{ex}N(E_F)=0.0056(2)$ for the ^{63}Cu and ^{65}Cu compounds, respectively.

For all isotope-substituted samples the slope parameters $J_{ex}N(E_F)$ of the relaxation data in the normal state turned out to be the same within experimental uncertainties; i.e., there is no ambiguity concerning the “Korringa line” in Figs. 2 and 3. This also proves that all the samples—although separately synthesized—were actually equivalent concerning the doping level, which is important for the reliability of the reported isotope shifts for both T_c and T^* .

The oxygen isotope substitution (^{16}O vs ^{18}O) affects T_c and T^* in a different manner. A small negative shift is found in the former, whereas a large positive shift is found in the latter. This is in agreement with earlier results obtained for $\text{HoBa}_2\text{Cu}_4\text{O}_8$,² in which the large value of $\Delta T^*(\text{O}) \approx 50$ K was interpreted in terms of a polaron-like mechanism²² associated with the oxygen Jahn-Teller modes.⁶ Since a strong Jahn-Teller effect is also present in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, the same mechanism is likely to apply here.

The copper isotope substitution (^{63}Cu vs ^{65}Cu) results in a small negative shift for T_c and in the absence of a shift for T^* . This is in contrast to the case of $\text{HoBa}_2\text{Cu}_4\text{O}_8$,³ for which a large value of $\Delta T^*(\text{Cu}) \approx 25$ K was reported. This large copper isotope shift was associated with a local copper

mode, although the experiment did not provide direct information about the specific type of lattice mode involved. By comparing $\Delta T^*(\text{Cu})$ for both $\text{HoBa}_2\text{Cu}_4\text{O}_8$ and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, it is now possible to assign the copper mode to the umbrella-type mode,⁸ which is present in the former compound but not in the latter. It favors an intersite bipolaron component in the bilayer compounds²³ which have T_c 's twice as large as the single-layer compounds.

In conclusion, the present neutron spectroscopic results of the oxygen and copper isotope effects on the pseudogap temperature T^* in the single-layer compound $\text{La}_{1.81}\text{Ho}_{0.04}\text{Sr}_{0.15}\text{CuO}_4$ —together with earlier results obtained for the bilayer compound $\text{HoBa}_2\text{Cu}_4\text{O}_8$ (Refs. 2 and 3)—give evidence for the prominent role of local oxygen and copper lattice modes which have to be considered in the interaction Hamiltonian describing the superconducting state of high- T_c compounds. Whereas both Jahn-Teller-type oxygen modes and umbrella-type copper modes are relevant for the bilayer compounds, the latter are absent for the single-layer compounds.

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