Isotope Dependence of the Spin Gap in $YBa_2Cu_4O_8$ as Determined by Cu NQR Relaxation

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We performed high accuracy ^{63}Cu NQR spin-lattice relaxation and SQUID magnetization measurements on ^{16}O and ^{18}O exchanged $YBa_2Cu_4O_8$ to determine the isotope shift of the temperature of the opening of the spin gap, T^*, and the superconducting transition temperature, T_c. The corresponding isotope exponents are $\alpha_{T^*} = 0.061(8)$ and $\alpha_{T_c} = 0.056(12)$ which are the same within the error bars and suggest a common origin for the superconducting and the spin gap. [S0031-9007(98)08085-5]

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One of the central and heavily debated questions in high-temperature superconductivity research concerns the origin of the so-called pseudogap occurring in the normal state of underdoped superconductors [1]. The pseudogap refers to the transfer to higher energy of the density of low-energy excited states. One may ask whether the pseudogap is caused by superconducting correlations, which develop above T_c, or whether it is an independent phenomenon. In nuclear magnetic resonance (NMR) and neutron scattering experiments, the pseudogap reveals itself as a spin gap. For instance, the Cu spin-lattice "relaxation rate per temperature unit," $(T_1T)^{-1}$, increases with falling temperature and reaches a maximum at T^*, which is a proper scale for the temperature dependence of the spin gap. For $YBa_2Cu_4O_8$ (Y124), the corresponding values are $T_c = 81$ K and $T^* \approx 150$ K.

Recently [2], we detected anomalies in the temperature dependence of several NMR and NQR (nuclear quadrupole resonance) quantities measured in the normal state of Y124, for instance in NQR frequencies, Knight shifts, line widths, and relaxation times. These anomalies, which occur around $T^\dagger = 180$ K, are the signature of an electronic crossover which involves enhanced charge fluctuations in planes and chains. Because of the proximity of $T^\dagger$ and T^*, we have argued that the spin gap effect in Y124 is caused by a transition due to a charge density wave (CDW) instability [3]. Using the *t-J* model and including electron-phonon interaction, we could, among others, explain the strong temperature dependence of the magnetic shift of the planar Cu nuclei, which we had measured previously [4], and we predicted a dependence of T^* on the isotope mass. Thus, corresponding measurements allow one to check the consistency of the CDW model.

NMR/NQR are techniques that can determine the pseudogap with a precision allowing one to establish whether an isotope effect is present or not. Y124, because of its well-defined oxygen stoichiometry and its negligible oxygen diffusion, is the ideal compound for such a study that requires experimental results not hampered by reproducibility problems. Therefore, the NQR study of the isotope effect on the spin gap in Y124 and its comparison with the superconducting gap is a unique experiment to explore the relation between the two gaps.

In this Letter, we report a high-accuracy NQR study of the planar ^{63}Cu nuclei, supplemented by susceptibility measurements, on ^{16}O and ^{18}O exchanged Y124 samples which revealed the presence of an isotope effect on both T_c and T^*. Both isotope exponents, defined as $\alpha = -\Delta \ln(T^*)/\Delta \ln(m)$ and correspondingly for T_c, are finite and have, within the experimental error, the same value. This result is contrary to a recent study [5] which reported the absence of an isotope effect in the pseudogap of Y124 as determined by ^{89}Y NMR.

In our ^{63}Cu NQR experiments, we measured the temperature dependence of three NQR parameters: the ^{63}Cu NQR frequency, the spin-lattice relaxation (characterized by the time constant T_1), and the Gaussian component of the spin-spin relaxation (time constant T_{2G}), and this for ^{16}O and ^{18}O enriched samples. The ^{63}Cu nuclei yield a single NQR signal at the frequency

$$\nu_Q = \frac{eQV_{zz}}{2h}\sqrt{1 + \frac{1}{3}\eta^2}, \tag{1}$$

where eQ is the Cu quadrupole moment, V_{zz} is the largest principle component of the electric field gradient (EFG) tensor present at Cu site, and η is the EFG's asymmetry parameter, which is nearly zero in our case.

The spin-lattice "relaxation rate per temperature unit," $(T_1T)^{-1}$, is given by the Moriya formula [6]:

$$(T_1T)^{-1} = k_B(\gamma^2/2\mu_B^2)\sum_{\mathbf{q}} |A^2(\mathbf{q})|\chi''(\mathbf{q}, \omega_Q)/\omega_Q\,, \tag{2}$$

where $A(\mathbf{q})$ is the Fourier-transformed hyperfine coupling constant, and $\chi''(\mathbf{q}, \omega_Q)$ is the imaginary part of the dynamic electronic spin susceptibility. The rate $1/T_{2G}$ follows from

$$(1/T_{2G})^2 \propto \int d^2\mathbf{q}\, A^4(\mathbf{q})\chi^2(\mathbf{q})\,, \tag{3}$$

where $\chi(\mathbf{q})$ is the static spin susceptibility [7].

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$\chi''(\mathbf{q},\omega)$, $\chi(\mathbf{q})$, and $A(\mathbf{q})$ for the planar Cu are strongly enhanced at the antiferromagnetic (AF) wave vector $\mathbf{Q}_{\mathrm{AF}} = (\pi/a, \pi/a)$. Therefore, $(T_1T)^{-1} \propto \chi''(\mathbf{Q}_{\mathrm{AF}}, \omega_Q)$, and $1/T_{2G} \propto \chi(\mathbf{Q}_{\mathrm{AF}}) = 2/\pi \int_0^\infty d\omega \times \chi''(\mathbf{Q}_{\mathrm{AF}}, \omega)/\omega$. If the ω dependence of $\chi''(\mathbf{Q}_{\mathrm{AF}}, \omega)$ is not affected by its temperature variation, except for a scaling factor, $(T_1T)^{-1}$ and $1/T_{2G}$ have the same temperature dependence. However, a redistribution of the spectral density from low to high energies in the excitation spectrum, i.e., the opening of a pseudogap, induces a reduction of $(T_1T)^{-1}$ without affecting sensibly $1/T_{2G}$. Thus, if present, a reduction of the spin gap induced by the isotope substitution shows up as an increase in the $(T_1T)^{-1}$ values without a detectable effect on $1/T_{2G}$.

We took great care in sample preparation and handling and in performing the NQR measurements which yielded high-precision data. A Y124 polycrystalline sample was synthesized by the solid-state reaction technique which is described in detail elsewhere [8]. X-ray investigations showed that 98% of the sample was phase pure Y124. The sample was divided in three parts. One part received no additional treatment; the second and third part were annealed in ^{18}O and ^{16}O, respectively, under exactly the same conditions. The annealing process was performed in a sealed ampoule at 725 °C and in an oxygen atmosphere of 1.3 bar with heating and cooling rates of 10 and 5 °C/min, respectively. During the exchange process, the oxygen atmosphere in the ampoule was refreshed four times. By measuring the weight loss of the ^{18}O exchanged sample after back exchange of ^{18}O with ^{16}O, we found that the ^{18}O content was 88%.

Room temperature x-ray measurements revealed a small difference in the lattice parameters of the two oxygen exchanged samples. The lattice parameters, given in Å, are 3.8411(1), 3.8717(1), 27.2372(8) for the ^{16}O and 3.8408(1), 3.8718(1), 27.2366(8) for the ^{18}O samples.

The NQR measurements were carried out by using a standard pulse spectrometer. The two oxygen exchanged samples were inserted into a probe head with two radio frequency coils which allowed an automatic switchover of the electronics from one sample to the other. This procedure minimizes the effect of possible slow drifts of the characteristics of the electronic apparatus or of the temperature. Both resonant circuits were damped to ensure three things: a homogeneous inversion of the NQR line, a nearly identical performance of both circuits, and the independence from temperature of the characteristics of these circuits. For each temperature, T_1 was measured by the inversion recovery sequence several times (typically 20 times) to reduce the statistical error and to estimate the error through the distribution of the T_1 results.

To determine the sample temperatures, we inserted $KClO_3$ powder into the two oxygen substituted samples and measured the ^{35}Cl NQR frequency whose temperature dependence is precisely tabulated for thermometric use [9]. This procedure also monitors the heating effects of the radio frequency pulses. The absolute temperatures of the two samples have an uncertainty of at most 0.03 K and the temperatures of the two samples differ by less than 0.1 K. From the observation of the ^{35}Cl NQR line width, it was also possible to exclude, within each sample, the presence of temperature gradients larger than 0.1 K. Because of "slow drifts" during the long measuring times, the error in temperature is less than 0.2 K for the final T_1 result.

We will now present our experimental results and their analysis. The magnetization curves of the three samples were measured by field-cooled magnetization measurements using a SQUID magnetometer and an applied field of 10 G. The resultant magnetization curves (see insert of Fig. 2) show sharp transitions from normal to superconducting state which is a signature of the good homogeneity of the samples. The curves yield a T_c shift of $T_c(18) - T_c(16) = -0.47(10)$ K, and an isotope exponent of $\alpha_{T_c} = 0.056(12)$, in agreement with $\alpha_{T_c} = 0.076(10)$, the only result available in the literature [5]. The magnetization curves of the ^{16}O exchanged and the untreated sample coincide.

According to Eq. (1), width and shape of an NQR line depend on the EFG distribution, induced by crystal inhomogeneity and imperfections, in the sample. The NQR lines of all three samples have the same shape and width which has a low value of 120 to 130 kHz depending on temperature. These facts prove again the high quality and homogeneity of the samples and demonstrate that the degree of disorder of the samples has not been altered by the oxygen substitution process. This latter fact is confirmed by the identity of the magnetization curves of the ^{16}O exchanged and the untreated sample.

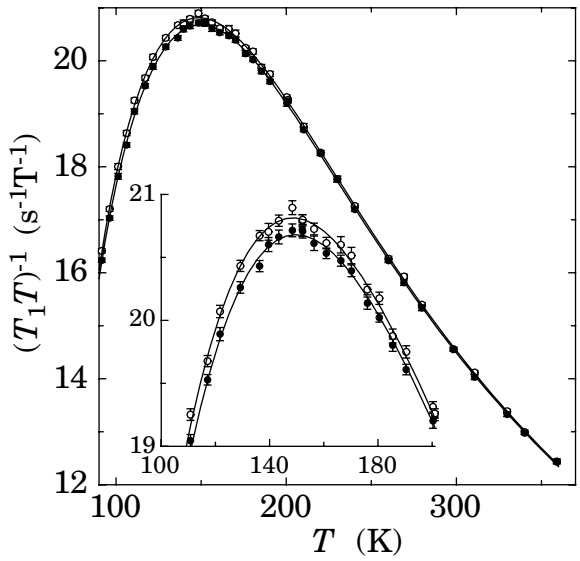

FIG. 1. ^{63}Cu spin-lattice "relaxation rate per temperature unit," $(T_1T)^{-1}$, of ^{16}O (•) and ^{18}O (∘) exchanged Y124 samples. The data are fitted using a modified version of Eq. (4) as described in the text. Inset: Zoom of the $(T_1T)^{-1}$ data around T^*.

The Cu NQR frequency of the ^{18}O sample, $\nu_Q(18)$, is shifted with respect to the frequencies of the ^{16}O and the untreated sample. At 300 K, the values are $\nu_Q(18) = 29.7350(20)$ MHz and $\nu_Q(16) = 29.7455(20)$ MHz. The shift is caused by an isotope effect on the lattice parameters whose differences, in isotopic variants, are attributed to the quantum mechanical zero-point displacement and to the thermal lattice expansion. We will discuss the ν_Q shift and its temperature dependence elsewhere.

In Fig. 1, we present the $(T_1T)^{-1}$ results whose general behavior is consistent with the measurements of Refs. [10,11]. However, we were able to reduce the errors on the $(T_1T)^{-1}$ data to the extremely low values of approximately 0.3%; thus, these data have, to our knowledge, the highest accuracy of all measurements of this type. The maximum of the $(T_1T)^{-1}$ data of the ^{18}O sample is higher than that of the ^{16}O sample and it is shifted to lower temperature. The effect is more evident in Fig. 2 where the difference of the $(T_1T)^{-1}$ data of the two oxygen exchanged samples is plotted. The fit curve will be discussed below. For control, we also measured $(T_1T)^{-1}$ of the untreated sample at four temperatures. As expected, the results are, within the error bars, the same as those for the ^{16}O exchanged sample (Fig. 2). This measurement once again confirms that all the changes in the physical properties induced by the oxygen annealing process, have to be considered as due to the isotope exchange only. Finally, we measured, at 100 K, T_{2G} for both oxygen exchanged samples and obtained $T_{2G}(18) = 39.00\ \mu$s and $T_{2G}(16) = 39.02\ \mu$s, which are the same values within 0.1%.

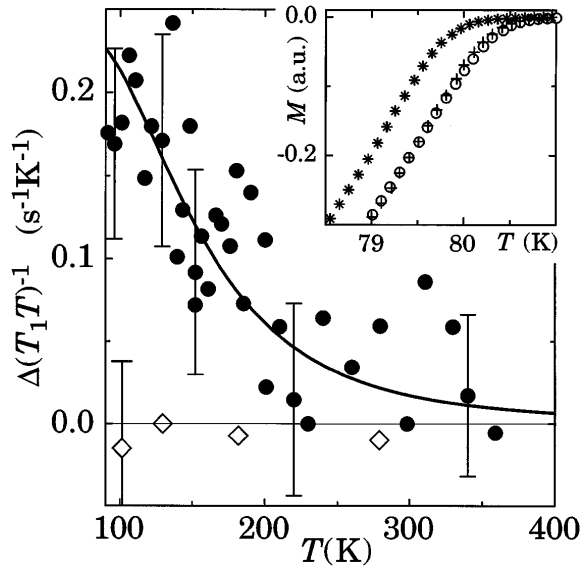

FIG. 2. The difference of the values for the relaxation rate per temperature unit (taken from Fig. 1), $\Delta(T_1T)^{-1}$, plotted against temperature (•). The data are fitted by the modified Eq. (4). The ◇ symbols present the corresponding difference for the untreated and the ^{16}O exchanged samples. Inset: Magnetization plotted against temperature for the untreated (∘), the ^{16}O (+), and the ^{18}O (∗) exchanged Y124 samples.

The fact that the $(T_1T)^{-1}$ curve for the ^{18}O exchanged sample lies higher than the corresponding curve for the ^{16}O exchanged sample, while both samples have the same T_{2G}, implies that from the two samples the ^{18}O exchanged one has a lower value spin gap. The fit of the $(T_1T)^{-1}$ data allows one to extract quantitative informations on the isotope effect.

Since at present no theoretical derivation of T_1 exists which takes into account the presence of the spin gap and its isotope effect, one must analyze the $(T_1T)^{-1}$ data with the help of a phenomenological function. We use the relation

$$(T_1T)^{-1} = CT^{-a}\left[1 - \tanh^2\left(\frac{\Delta}{2T}\right)\right], \qquad (4)$$

which is frequently used in describing T_1 data [12] and which is based on a function used by Tranquada *et al.* [13] to describe properly the dynamic susceptibility data in the presence of a spin gap, as determined by neutron scattering measurements. The factor CT^{-a}, with $a \simeq 1$, takes into account the high-temperature Curie-like divergence of $(T_1T)^{-1}$, and the hyperbolic tangent describes the temperature dependent gap. Δ is a measure for the gap and it is the only parameter allowed to differ for the two sets of data. It is important to stress that T^*, defined as the maximum of Eq. (4), and Δ are strictly proportional, so that also T^* can be used as a proper parameter for the temperature scale of the gap.

Equation (4) describes reasonably well the two sets of $(T_1T)^{-1}$ data. In particular, the function successfully predicts a higher maximum for the sample with a lower T^*. A simultaneous fit of Eq. (4) to the two data sets yields the parameters $a = 1.157$, $\Delta(16) = 246.9$ K, and $\delta = \Delta(18) - \Delta(16) = -1.31(13)$ K. The resulting "spin gap isotope exponent" is $\alpha_{T^*} = \alpha_\Delta = 0.052(7)$. However, the statistical analysis for the fit involving Eq. (4) reaches a χ^2 value of only 237 for 68 degrees of freedom which corresponds to an unacceptably low confidence level. Thus, Eq. (4) does not describe the data within the statistical accuracy of the measurements.

Therefore, we have modified Eq. (4) by replacing the temperature T by the expression $T' = T + a_0 + a_1/T + a_2/T^2$ where each of the three new parameters is required to have the same value for the two data sets, i.e., Δ is again the only parameter allowed to differ for the two sets. The fit now yields a χ^2 value of 52.4 for 65 degrees of freedom, which results in a confidence level of 0.85. The partial χ^2 for the ^{16}O and ^{18}O data are 25.9 and 26.5, respectively, which are also statistically reasonable values. Thus, the modified Eq. (4) is a good description of the temperature dependence of $(T_1T)^{-1}$ in the normal phase of underdoped cuprates. The best value of the T^* shift is 0.96 K resulting in an isotope exponent $\alpha_{T^*} = 0.061(8)$. We also tried a second and a third degree polynomial

fitting function which yielded isotope exponents in good agreement with $\alpha_{T^*} = 0.061(8)$.

The presence of an oxygen isotope effect on T^* indicates that the lattice is also involved in the opening of the spin gap, and thus places strong constraints on theories that describe its microscopic origin. Theories that consider only spin correlations responsible for the origin of the spin gap [14,15], need the introduction of a coupling between the spin and the lattice degrees of freedom in order to describe correctly our experimental results. The evidence of an isotope effect on the spin gap is consistent with the supposition, made by Suter *et al.* [2], of a relation between the electronic crossover mentioned above and the spin gap opening. Such a relation is naturally explained by theories that relate the spin gap to a CDW instability [3,16].

Though there exists a large variety of theoretical scenarios and models of high-temperature superconductivity in which the appearance of the pseudogap is an essential ingredient [14,15,17], most of the authors do not explicitly discuss a possible isotope effect on the pseudogap. This is partly understandable in view of the scarcity of experimental results on this aspect.

To our knowledge, the only quantitative prediction of an isotope dependence of the pseudogap had been made within the CDW scenario mentioned above [3]. Assuming $T_{\mathrm{CDW}} = 180$ K as the temperature of the CDW transition, the model predicts $\alpha_{T_{\mathrm{CDW}}} \approx 0.17$ which is larger than the experimental value for α_{T^*}. Recently, Varlamov *et al.* [18] have improved the original CDW scenario and have calculated [19] $\alpha_{T_{\mathrm{CDW}}} = 0.028$ which is roughly a factor of 2 smaller than the experimental value. It is important to stress that according to this model, $\alpha_{T_{\mathrm{CDW}}}$ and α_{T^*} do not need to be identical. However, the result that both parameters are of the same order, is consistent with a possible relation between a CDW transition and the opening of the spin gap.

Our experimental result for α_{T^*} is different from the one obtained in the recent work of Williams *et al.* [5], who found no evidence of an isotope effect on the spin gap as measured by ^{89}Y NMR Knight shift, that probes the uniform spin susceptibility. This fact confirms that a distinction has to be made between the behavior of the spin susceptibility at $\mathbf{q} = 0$ and at $\mathbf{q} = \mathbf{Q}_{\mathrm{AF}}$ [12,20,21].

In summary, we have shown by high-precision ^{63}Cu NQR spin-lattice relaxation experiments that the spin gap as characterized by the temperature T^*, is isotope dependent with an isotope exponent $\alpha_{T^*} = 0.061(8)$ which agrees quite well with the corresponding exponent $\alpha_{T_c} = 0.056(12)$ for T_c as determined by SQUID magnetization measurements. This fact seems to confirm the growing evidence for a common origin of the superconductivity and the pseudogaps [20,22]. Finally, a possible relation between the opening of the spin gap and a CDW transition has been discussed.

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