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Spin dynamics in the Cu(2)-O planes of tetragonal and orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ as probed by ^{89}Y NMR

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The ^{89}Y -nuclear relaxation rate is found to be almost similar in the orthorhombic and tetragonal modifications of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. This result is seen as evidence for the unchanged spin dynamics in the Cu(2)-O planes in both compounds and as support for those theories that decouple charge and spin carriers.

The use of microscopic probes such as ESR and NMR gives direct information about the static and dynamic properties of spin and spin-carrying charges in a material. By the absence of an observable ESR signal in single crystals of the 90-K superconductor,^{1,2} the applicability of this technique is limited. Returning to NMR, both Cu and Y nuclei are accessible, the latter being the subject of this Rapid Communication.

We will present data on ^{89}Y nuclear spin lattice relaxation rates in $\text{YBa}_2\text{Cu}_3\text{O}_7$, Y-Ba-Cu-O, both in the 90-K superconductor as well as in its tetragonal modification. In previous ^{89}Y -NMR studies in orthorhombic^{3,4} YBa-CuO, O-Y-Ba-Cu-O, both the temperature dependence of the nuclear relaxation rate (T_{1n}^{-1}) and the observed line shift were interpreted in terms of a Korringa mechanism. The increased linewidth below T_c (Ref. 3) was explained in terms of field gradients caused by vortex formation, while the decrease of Knight shift upon entering the mixed state³ and the line splitting observed already above T_c (Ref. 4) were connected to a charge redistribution in the nearby Cu(2)-O plane. Both the Y relaxation and line broadening are dominated by the Cu-Y electronic spin-nuclear-spin interaction, and similar relaxation behavior for the Y and Cu(2) nuclei has been observed.⁵ We will come back on this point at the end of this communication.

The samples used were prepared as described by van den Berg *et al.*⁶ The O-Y-Ba-Cu-O had a transition of 90 K with a width of 2 K, as determined by ac susceptibility. No superconductivity was observed in the tetragonal sample T-Y-Ba-Cu-O. For the NMR measurements the particles were sealed to prevent deterioration due to contact with water vapor and results were reproducible during the duration of the experiment.

Relaxation times were measured at 9.8 MHz by using a comb of $\pi/2$ pulses followed by a reading pulse of $\pi/2$. A delay time of 200–300 μs was allowed to suppress the effect of "electronic noise" in the signal without too severe a loss of sensitivity; for T-Y-Ba-Cu-O a decay time of about 0.4 ms was typical. Because of the shorter decay time in T-Y-Ba-Cu-O than in O-Y-Ba-Cu-O we were not able to do accurate measurements below 90 K. A flow cryostat provided the variable temperatures, which were measured with a Pt-resistor and a Au-chromel thermocouple.

The Y-NMR data for O-Y-Ba-Cu-O and T-Y-Ba-

Cu-O are given in Fig. 1. For O-Y-Ba-Cu-O the data points of Markert³ are shown, which are similar to ours but cover a larger temperature regime.

In discussion of the T_{1n} data the similarity of the Y data in both modifications of the Y-Ba-Cu-O compounds is the most prominent feature. It has to be realized that the earlier given interpretation in terms of a Korringa process was straightforward in view of the dc electrical resistivity of about $5 \times 10^{-4} \Omega \text{ cm}$, as measured in the *ab* plane,⁷ a factor of 25 times lower than that for YH_2 ; the low Korringa constant agrees with that. For that reason the data in T-Y-Ba-Cu-O are a surprise; the electrical resistivity was found to be a factor of 10^4 higher than the O-Y-Ba-Cu-O (see also Ref. 8).

A similar surprising result has been observed in the low temperature specific heat *C* of these ceramics. In both O-Y-Ba-Cu-O as well as T-Y-Ba-Cu-O a linear term $C \propto \gamma T$ has been measured. The superconducting gap in the orthorhombic phase and the semiconducting gap in the tetragonal compound make such a contribution not likely. A possible reason is the presence of (de)localized electrons close to the Fermi surface.⁹ Such a picture supports a Korringa process due to the presence of "normal" conduction electrons.

FIG. 1. The product of the ^{89}Y relaxation time (T_{1n}) and temperature (T) vs T . The crosses indicate the result of Markert *et al.* (Ref. 3) in O-Y-Ba-Cu-O, circles are our results for T-Y-Ba-Cu-O. In the same figure the line shift, normalized on the "free" Y Larmor frequency is given (triangles); the scale is on the right.

It has to be remembered that the basis of the connection between nuclear relaxation rate and line shift is not the presence of charges but the presence of spin-carrying excitations with Fermi-Dirac statistics¹⁰ having interaction with the nuclear spins. If such excitations are present with almost equal strength in the Cu(2)-O planes of both *T*-Y-Ba-Cu-O or *O*-Y-Ba-Cu-O, similar spin dynamics will be probed by the ⁸⁹Y nuclei. The absence of a correlation between charge transport and nuclear relaxation rate can then be seen as support for those models that decouple charge transport and spin dynamics and especially that assign to the spins a (pseudo-) Fermi surface. It is in the resonant-valence-bond¹¹ (RVB) model that this is done explicitly: the spinons seem to be capable of giving the required relaxation process without directly leading to charge transport. Also with respect to the γT term in the specific heat the spinons in the RVB model can account for it.

As regards the more familiar two-dimensional magnetic excitations, using $A^2/\hbar J$ as an order-of-magnitude estimate for the nuclear relaxation rate, a rate constant of about 10^{-2} s^{-1} is calculated. A denotes the electron-nuclear spin-spin interaction term and J is the Cu(2) exchange constant. Although the calculated value is of the right order of magnitude, we are not aware of a spin-excitation theory (other than the RVB model) which predicts the observed linear temperature dependence of T_{1n} .

It is unlikely that these results can be explained in terms of localized impurities, which will relax nearby nuclear spins while other similar nuclei will reach thermal equilibrium via spin diffusion. Depending on concentration, diffusion barrier, etc., quite a number of cases have to be considered, none of which is expected to give a linear T dependence around room temperature.

For the previous and present Knight-shift data we used a gyromagnetic ratio $\gamma/2\pi = 2085.6 \text{ Hz/mT}$ for the unshifted ⁸⁹Y position. Although this value is quite often used^{3,12,13} a more accurate value is $(\gamma/2\pi) = 2086.27 \text{ Hz/mT}$.¹⁴ More accurate Knight-shift data than ours are then required for a meaningful analysis.¹⁵

We now like to discuss briefly the assignment of the nu-

clear quadrupole resonance (NQR) lines of the Cu nuclei. There is general agreement that there are ⁶³Cu lines at 22 and 31 MHz. Because of the observed intensity ratios the common assignment is of the 31 MHz line to the Cu(2) sites. Dynamic arguments led Warren and co-workers^{5,16} originally to the opposite conclusion, e.g., the "22 MHz" relaxation rate is hardly affected by oxygen deficiency and closely resembles the Y data. Our present results agree with this. The recent finding¹⁷ that Gd replacement on the Y site has a much larger effect on the 31-MHz relaxation rate than on the 22 MHz, seems a convincing result for the identification of the Cu(2) sites and the 22-MHz line. Still, it has to be realized that not only dipolar interactions of the Gd electronic spins with the nearby Cu(2) nuclei are present. There is also an indirect exchange interaction between the Cu(2)O planes via the d_{z^2} orbitals, otherwise the three-dimensional antiferromagnetic ordering at 2.1 K would not occur. This interaction will affect the Cu(1) nuclei. To estimate the change in relaxation rate the dipolar [for Cu(2)] and the exchange [for Cu(1)] mechanisms have to be compared to the strength of the already existing relaxation process.

In summary, the Y relaxation rate is found to slow down only slightly while the electrical conductance changes a few orders of magnitude, if one goes from the 90-K superconducting compound to the tetragonal nonsuperconducting material. From this we conclude that the Cu(2)O spin excitations, which are probed on the Y site, are not directly correlated to the electronic transport properties in the YBa₂Cu₃O_{7- δ} compounds.

A preliminary account of these data was presented at the international conference on high-temperature superconductors and materials and mechanisms of superconductivity in Interlaken.

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