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^{205}Tl NMR in $Tl_2Ba_2CuO_6$ and the t-J model

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The ^{205}Tl nuclear-spin–lattice relaxation rate in $Tl_2Ba_2CuO_{6+\delta}$ has been measured as a function of temperature and oxygen content δ. With a slight increase in oxygen content, T_c decreases from 80 to 0 K; samples with lower T_c's have higher conductivities but slower Tl relaxation rates. The relaxation data closely resemble those for Cu(2) in $YBa_2Cu_3O_7$. Only 0.2% of Cu d spins in the Tl 6s orbital is needed to explain this result. In a simple model calculation we show that such an admixture is quite plausible. An asymmetric location of the Tl^{3+} ions in the crystal lattice is essential. The Cu-spin-dominated relaxation process (which is not inconsistent with a two-band model) and the decrease in the relaxation rate with increasing conductivity are in agreement with the t-J model.

$YBa_2Cu_3O_7$ has been the subject of much of the nuclear-magnetic-resonance (NMR) research on high-T_c superconductors. The recently observed asymmetry in the Cu and O relaxation rates above 120 K (Ref. 1) and the apparent link between the two rates below 120 K are strong criteria for a proper description of the spin dynamics in the normal state and for theories of the superconducting pairing mechanism. At first sight, an extended Hubbard Hamiltonian with holes on the oxygen sites and spins on Cu sites appears to be the most flexible approach and is hard to invalidate.[2] Further simplification into a one-band Hubbard model with only t and J as parameters[3,4] limits the degrees of freedom for fitting the experimental data. In the t-J model, the spins of the holes on the oxygen sites (due to doping) are strongly coupled to those at the Cu sites (already present in the undoped material) forming singlet states. The remaining unpaired Cu spins are the origin of the spectral density. The asymmetry between Cu and O relaxation rates might well be understood in both models[1] on the basis of the q dependence of the imaginary part of the susceptibility. The symmetry of the oxygen sites between the Cu(2) sites cancels the influence of the antiferromagnetically coupled Cu spins. The correlation between the Y Knight shift K and the magnetic susceptibility[5] favors the single-band description.[6] Although an explanation of the Korringa relaxation rate of the oxygen and yttrium spins is still lacking within the t-J model,[6] more phenomenological models with only one spin degree of freedom have been formulated[1,7,8] that give a quantitative agreement with the relaxation data.

In this Rapid Communication we report on Tl-NMR data in $Tl_2Ba_2CuO_{6+\delta}$. The consistency of these results with a one-band model will be addressed especially in the analysis.

The compound $Tl_2Ba_2CuO_{6+\delta}$ might be considered as an ideal NMR system for high-T_c research. Its superconducting transition temperature T_c can be varied from 80 to 0 K by a small increase in the oxygen content, which causes an elongation of the c axis.[9,10] Samples with higher T_c's have lower normal-state conductivities. The oxygen content (and hence T_c) was varied by quenching from different anneal temperatures, e.g., the 80-K sample was obtained by quenching from an anneal temperature of 900 K. The transition temperature of all samples was determined by conductivity measurements in a superconducting quantum interference device magnetometer. The transition in the 80-K sample showed an onset temperature of 82 K and a width of 3 K.[10]

The ^{205}Tl nucleus is a good probe for the spin dynamics. It has a nuclear spin $I=\frac{1}{2}$ with a magnetic moment half that of a proton. Viewing the crystal along the c axis, the Tl site is located almost directly above a Cu site, separated by an oxygen atom.

The NMR experiments were carried out with a standard home-built pulsed spectrometer. ^{205}Tl NMR spectra were obtained by integrating the spin-echo intensity while sweeping the frequency. The sample was prepared from a sintered pellet of $Tl_2Ba_2CuO_{6+\delta}$, which was ground into a fine powder. This powder, being mixed with Stycast 1266, was then sealed in a glass tube. During hardening of the epoxy, the sample was placed in a magnetic field of 4.7 T in order to orient it.[11]

In Fig. 1 we show the temperature dependence of the Tl relaxation rate for the 80-K sample. The data were taken in a field of 4.7 T (about 114.5 MHz). (Oriented) powder spectra were taken at various temperatures. The line is asymmetric with a total width of about 400 kHz.[10] Below T_c there is an angular dependent diamagnetic shift. At $T=10$ K this amounts to 100 kHz for a magnetic-field orientation parallel to the c axis, and about half that value for a perpendicular field. The linewidth and its asymmetry may be due to chemical shift anisotropy[12] and to modulation of the crystal structure.[10,13] For a more detailed analysis, measurements on single crystals[14] are in progress. Within the line, there is a single relaxation rate.

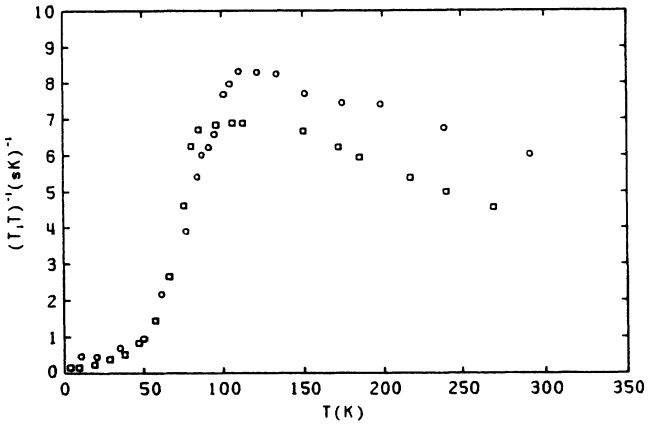

FIG. 1. Temperature-dependence of $(T_1T)^{-1}$ for Tl in $Tl_2Ba_2CuO_6$ and Cu(2) in $YBa_2Cu_3O_7$. The Tl data are denoted by circles, the Cu data of Hammel *et al.* by squares.

Relaxation data from the lower-T_c samples show qualitatively similar temperature dependence, but for the nonsuperconducting sample, the room-temperature relaxation rate is a factor of 1.35 lower than that of the less-conducting 80-K sample.

Figure 1 shows that the relaxation rate of the Tl nuclei is very fast (of the order of 1 ms^{-1}), and its temperature dependence in the normal state is less than linear. Similar observations of the Cu(2) spins in $YBa_2Cu_3O_7$ are given for comparison.[1] We have not yet been able to measure the Cu relaxation rate in the Tl compound, but will assume in the following analysis that the planar Cu relaxation rates for both compounds will only show a minor difference. Figure 1 shows that above 110 K the two relaxation rates are proportional to each other, with a ratio of about 1.2. Furthermore, below 110 K an increase in (T_1T) is already visible, while the same sample showed diamagnetic shielding only below 82 K. This might indicate the opening of a gap in the spin-excitation spectrum around 110 K. Similar observations were made in $Tl_2Ba_2CaCu_2O_{6+\delta}$.[12,15]

The proportionality of the two relaxation rates suggests an admixture of the Cu spins in the Tl 6*s* orbitals. As a consequence of this admixture, and the location of the Tl site with respect to the Cu ions, the antiferromagnetic correlations with $q=(\pi,\pi)$ will enhance the Cu and the Tl relaxation rate in the same way. This effect is canceled at the oxygen or yttrium sites in $YBa_2Cu_3O_7$. If we only consider the isotropic hyperfine interaction, the ratio between the Tl and Cu relaxation rates is determined by the Knight shifts (K) and nuclear gyromagnetic ratio's (γ),

$$T_1(\mathrm{Tl})^{-1}/T_1(\mathrm{Cu})^{-1} = K^2(\mathrm{Tl})\gamma^2(\mathrm{Tl})/K^2(\mathrm{Cu})\gamma^2(\mathrm{Cu}). \quad (1)$$

Taking $\gamma^2(\mathrm{Tl})/\gamma^2(\mathrm{Cu})\simeq 5$ and a hyperfine constant for the 6*s* function at the Tl nucleus of 56534 MHz,[16] compared to 3540 MHz for Cu 4*s*, Eq. (1) predicts an isotropic Tl Knight shift (K) of about 0.2%. For the isotropic Cu Knight shift, the value for Cu(2) in $YBa_2Cu_3O_7$ has been used, which is estimated to be 0.36%. This value corresponds to a probability of 6.8% of finding a Cu spin in a Cu *s* orbital.[17] This result shows that, to explain the relaxation rate on the Tl site, the presence of only 0.2% of Cu spins in the Tl 6*s* orbital is needed. As is true for the Cu(2) isotropic Knight shift in $YBa_2Cu_3O_7$, the isotropic Tl Knight shift can easily be masked by anisotropic contributions.

For a quantitative analysis, we will follow the Mila and Rice quantum chemical analysis of the Cu data in $YBa_2Cu_3O_7$.[17] In Fig. 2 we have sketched the Cu-O-Tl cluster used in the calculation. If the location of the Tl sites were exactly above the Cu sites, no net Cu spin contribution to the Tl orbitals would occur. It will be assumed that the modulation in the structure can be accounted for by a shift of about 0.17 Å in the Tl position.[14] This lowering of the local symmetry by the Tl shift is sufficient to cause the required amount of Cu spin density on the Tl site.

Our basis set contains three orbitals of the central copper atom (s_0, $d_{x^2-y^2}$, and d_{z^2}), a combined orbital of the planar oxygen atoms $[p=\frac{1}{2}(p_{1x}-p_{2y}-p_{3x}+p_{4y})]$, the *s* orbital of the nearest-neighbor planar copper atoms $[s_1=\frac{1}{2}(s_1-s_2+s_3-s_4)]$, the *p* orbitals of the two apex oxygen atoms (p_z^1 and p_z^2), and the two Tl orbitals (s_{Tl}^1 and s_{Tl}^2). Only Tl *s* orbitals are considered because of their large extension and large contact hyperfine term. So the wave function for the Cu spins becomes

$$\psi=\alpha_1 d_{x^2-y^2}+\alpha_2 d_z^2+\alpha_3 s_0+\beta p_1+\gamma s_1 +\delta_1 p_z^1+\delta_2 p_z^2+\varepsilon_1 s_{\mathrm{Tl}}^1+\varepsilon_2 s_{\mathrm{Tl}}^2. \quad (2)$$

As input parameters[18,19] we will use the following es-

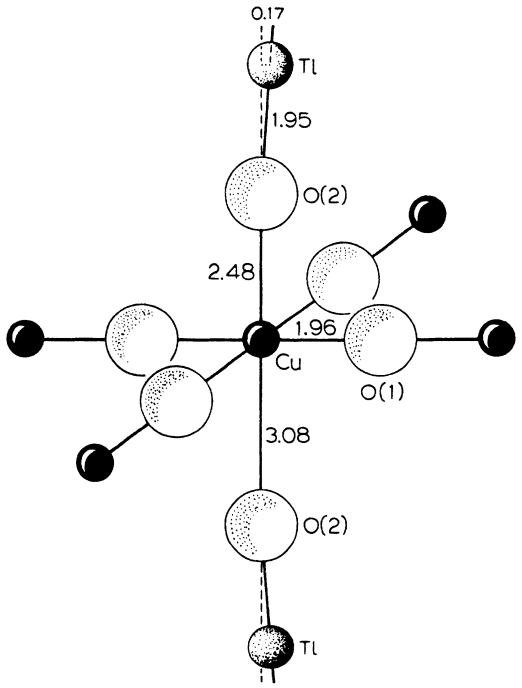

FIG. 2. The Cu-O-Tl cluster as used in the calculation of the Cu-spin admixture in the Tl 6*s* orbital.

timated values (in eV) for the transfer integrals:

$$t^0(d_{x^2-y^2}^{Cu}p^O) = -1.37,\ t^1(d_{z^2}^{Cu}p^O) = 0.89,$$
$$t^2(d_{z^2}^{Cu}p^O) = 0.42,\ t^1(s^{Cu}p^O) = -2.28,$$
$$t^2(s^{Cu}p^O) = -1.48,\ t^0(s^{Cu}p^O) = -3.7,$$
$$t^1(s^{Tl}p^O) = -3.7,\ t^1(d_{x^2-y^2}^{Cu}s^{Tl}) = 0.02,$$
$$t^2(d_{x^2-y^2}^{Cu}s^{Tl}) = 0.01,\ t^1(s^{Cu}s^{Tl}) = -0.42,$$
$$t^2(s^{Cu}s^{Tl}) = -0.25.$$

The relevant energies are taken as follows: $e_d^1 = 0$, $e_d^2 = 1$, $e_s^{Cu} = -6$, $e_p = 4$, $e_s^{Tl} = 0.85$. (The Tl s orbital energy has to remain below 1 eV to ensure that the relevant hole is in the Cu-$3d_{x^2-y^2}$ orbital.) In our notation, t^0 denotes the transfer integrals in the plane, t^1 those above the plane (i.e., the side of the closest oxygen), and t^2 those on the other side. Based on this parameter set there is a 0.4% probability that a Cu spin resides in the Tl s orbital.

The calculation shows that the Cu spin admixture into the Tl orbital to explain the Tl relaxation can be accounted for. The present experiment only sees electronic Cu spins, as expected in the t-J model (in a somewhat broader sense, because in our calculation there is also a small Cu spin density of 0.06% in the d_{z^2} orbital). It should be remarked that the presence of other relaxation paths is not excluded, but the path sketched above is by far the most effective. The increase in conductivity and the decrease in the relaxation rate fit the picture of the number of singlet states increasing or the number of "free" Cu spins decreasing under doping.

In summary we have shown that the proportionality between the Tl and Cu relaxation rates is in agreement with the t-J model, and that the Tl spin is an excellent probe for the Cu spin dynamics in the CuO plane.

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