Existence of low-lying electron spin excitations in the superconducting state of the $Tl_2Ba_2CuO_{6+x}$ system

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The rate of spin-lattice relaxation of ^{205}Tl has been measured for $Tl_2Ba_2CuO_{6+x}$ samples with $T_c = 30$ and 100 K in fields from 0.5 to 7 T. At $T_c < 60$–70 K this rate increases with decreasing field. In a sample with $T_c = 30$ K this increase is observed even in the normal state, so fluctuations of vortices can be ruled out as a possible reason for this increase. It has been established previously that the spin component of the Knight shift is independent of the field and exhibits a gap behavior at $T < T_c$. These facts indicate that the mechanism for the nuclear relaxation probably involves antiferromagnetic fluctuations of electron spins, which persist below the transition temperature in the $Tl_2Ba_2CuO_{6+x}$ system. © *1994 American Institute of Physics.*

1. An important feature of the electron system of the high-T_c superconductors is a strong electron–electron interaction of an antiferromagnetic type. In the normal state, this interaction leads to a significant increase in the imaginary part of the dynamic spin susceptibility, $\chi''(q)$, near the corresponding wave vector q_{AF}. This interaction is manifested as peaks on a plot of the cross section for inelastic magnetic scattering of neutrons versus q (see, for example, Refs. 1–3 and the literature cited there). At the same time, the increase in the component of the spin fluctuations with $q = q_{AF}$ corresponding to the increase in χ'' leads to an increase in the rate of nuclear spin–lattice relaxation, T_1^{-1}, and to a deviation from the Korringa law $T_1^{-1} \propto T$, which holds for the normal state of simple metals (see, for example, the review in Ref. 4 and the literature cited there).

The neutron data on the behavior of spin fluctuations in the superconducting state are slightly contradictory. According to Ref. 1, low-frequency spin excitations freeze as $T \rightarrow 0$, demonstrating the presence of a gap, in YBCO samples with $T_c = 47$, 59, and 91 K. More-recent measurements, in contrast, seem to show that a complete freezing does not occur in YBCO with $T_c = 53$ K (Ref. 5) or in superconducting LSCO samples.[2,3] This result could be explained by zeros of the order parameter, which would be possible in the case of a pairing with a nonzero orbital angular momentum. Another possibility is an effect of paramagnetic impurities which destroy the gap. That such impurities are present in the LSCO samples studied in Ref. 2 was demonstrated by the behavior of the specific heat.

The existence of low-frequency spin excitations at $T \ll T_c$ should also affect the behavior of the rate of nuclear spin–lattice relaxation. Instead of the exponential freezing, T_1^{-1} should fall off as T^3 if the order parameter has a d symmetry, while it should fall off as T if there is a gapless situation. The latter behavior is observed in zinc-doped YBCO samples.[6] A $T_1^{-1} \propto T^3$ law is sometimes seen in the behavior of undoped YBCO (Refs. 7 and 8, for example).

However, we need to bear in mind that the low-temperature behavior of T_1^{-1} may be distorted by other contributions to the nuclear spin–lattice relaxation. Some information regarding the mechanism for this relaxation can be extracted from measurements of the field dependence of T_1^{-1}. This was one of the ideas which stimulated the work reported in Refs. 9–13.

It has been found in YBCO-123 (Refs. 9, 10, and 12), YBCO-124 (Ref. 10), and also LSCO (Ref. 9) that the relaxation rates of ^{63}Cu and ^{17}O increase slightly with increasing field at $T<T_c$. the reason may be an increase in the number of vortices.[14] In contrast, our own measurements[13] of T_1^{-1} for ^{205}Tl nuclei in a $Tl_2Ba_2CuO_6$ with $T_c=100$ K have shown that the field dependence is the opposite in this case—that $^{205}T_1^{-1}$ increases with decreasing field. This fact, along with the $^{205}T_1^{-1} \propto T$ dependence below 20 K, was interpreted in Ref. 13 as evidence of a relaxation caused by thermal fluctuations of the vortex lattice in a layered semiconductor.

In the present letter we are reporting measurements of $^{205}T_1^{-1}$ in Tl-2201 samples with $T_c=100$ and 30 K in fields from 0.5 to 7 T. The new results demonstrate that the interpretation of Ref. 13 is not sufficient. They show that there is apparently one more contribution to the spin–lattice relaxation of Tl nuclei in the Tl-2201 system, and that this contribution falls off with increasing field. Comparing the behavior of $^{205}T_1^{-1}$ with the behavior of the spin component of the Knight shift, $^{205}K_s$, we conclude that this contribution probably stems from antiferromagnetic fluctuations of electron spins. A slightly unexpected result is that these fluctuations are seen most prominently in the superconducting state.

2. The temperature dependence of $^{205}T_1^{-1}$ was measured in oriented polycrystalline samples of $Tl_2Ba_2CuO_6$ with $T_c=100$ K and of $Tl_2\ Ba_2CuO_{6.3}$ with $T_c=30$ K. The samples were prepared by grinding single crystals, whose composition was determined by x-ray diffraction.[15] The measurements were carried out at several field values from 0.5 to 7 T in the orientations $H\|c$ and $H\|ab$ on a Bruker MSL-300 spectrometer by the standard saturation–restoration method. The length of the 90° pulse was typically 1.3–1.7 μs. The measurements below T_c were carried out during cooling in a field. At all temperatures, the time evolution of the intensity of the NMR signal after saturation could be approximated fairly well by a single exponential curve, although the systematic discrepancies increased slightly with decreasing temperature below T_c.

3. Figures 1 and 2 show the temperature dependence of the quantity $1/T_1T$ for two samples, in various fields and orientations. For the sample with $T_c=100$ K (Fig. 1), the field dependence of $1/T_1T$ becomes significant at $T<50$–60 K; this result had been established previously.[13] A new result is that in fields below 3.5 T the quantity $1/T_1T$ is no longer constant at temperatures $T<15$–20 K; it instead increases with decreasing temperature, at a progressively increasing rate as the field is lowered.

In the sample with $T_c=30$ K (Fig. 2) the increase in $1/T_1T$ with decreasing field is seen even in the normal state. The field dependence becomes particularly strong just

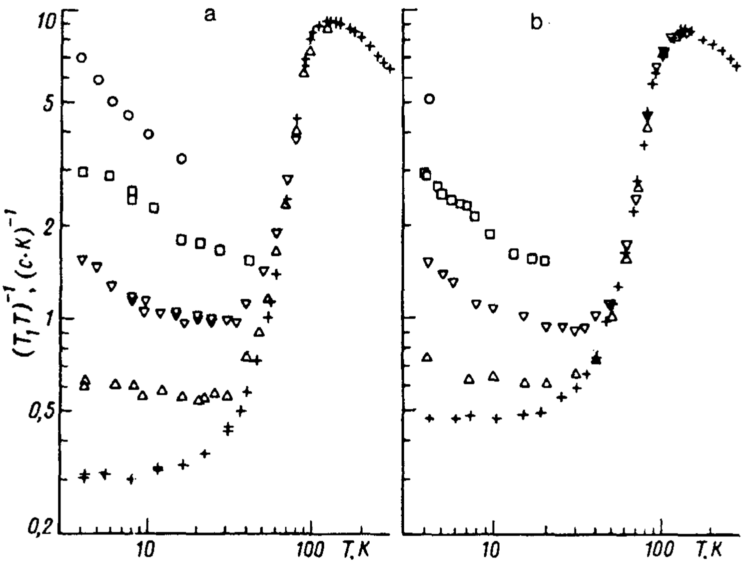

FIG. 1. Plot of $^{205}(T_1T)^{-1}$ versus T for a sample with $T_c = 100$ K. a: $H \| ab$. b: $H \| c$. ○—0.48 T; □—0.9 T; ∇—1.78 T; Δ—3.58 T; +—7.05 T.

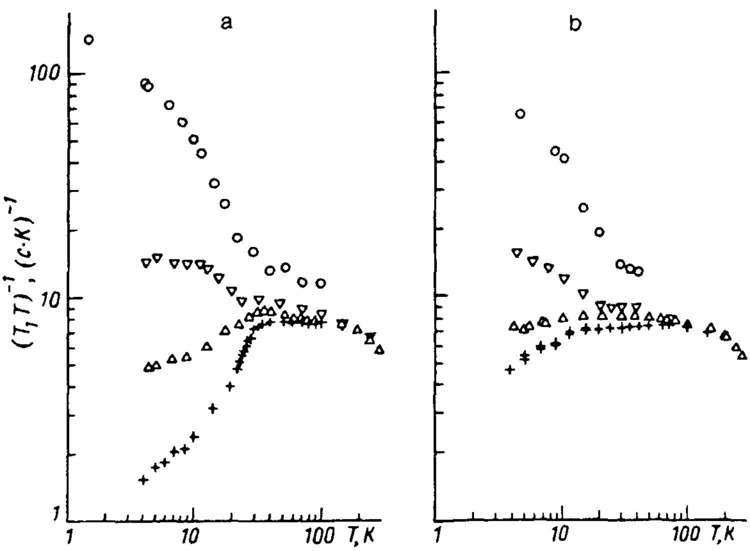

FIG. 2. Plot of $^{205}(T_1T)^{-1}$ versus T for a sample with $T_c = 30$ K. a: $H \| ab$. b: $H \| c$. ○—0.48 T; ∇—1.78 T; Δ—3.58 T; +—7.05 T.

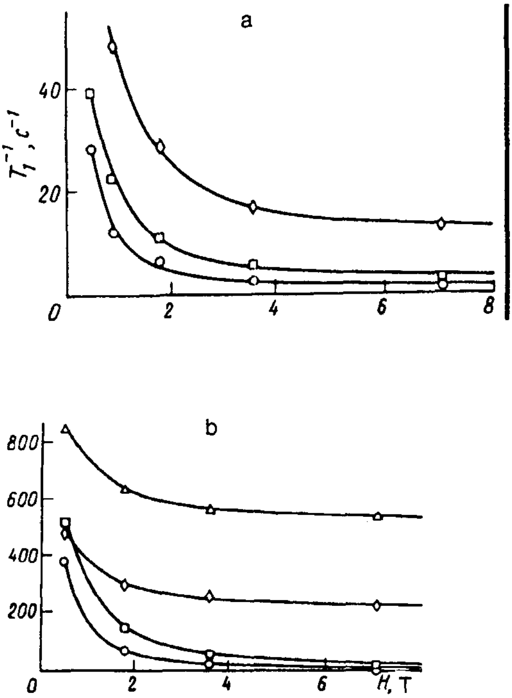

FIG. 3. Field dependence of T_1^{-1} for a sample with $T_c = 100$ K (a) and for one with 30 K (b) at various temperatures. ○—4.2 K; □—10 K; ◇—30 K; Δ—70 K. The solid curves are fits of Eq. (1).

below T_c. In the orientation $H\|ab$ at $T=4.2$ K, the quantity $1/T_1T$ increases by nearly two orders of magnitude as the field is reduced from 7 to 0.5 T.

At a constant temperature, the field dependence of T_1^{-1} is described fairly well for both samples, and for both field orientations, by

$$1/T_1 = A/[1+(H/H_0)^2]+B, \quad (1)$$

as is shown in Fig. 3 for two samples at several temperatures in fields $H\|ab$. The first term in this expression is a Lorentzian with a relaxation time $\tau = 1/\gamma H$, where γ is the nuclear gyromagnetic ratio. This term may reflect the frequency spectrum of spin fluctuations. The second term is associated with relaxation mechanisms which do not depend on the field.

Within the interpolation error, the constant H_0 found from the experimental curves is independent of the field orientation. At a given temperature it is approximately the same for the samples with the different values of T_c, increasing from 0.5 T at 4.2 K to ~1 T at 30–40 K. These results correspond to the value $\tau \approx 10^{-8}$ s. In contrast with this very strong field dependence of $1/T_1T$, we find an absolutely normal behavior of the Knight shift of ^{205}Tl for both samples. In the orientation $H\|ab$, it is independent of the field even in this superconducting state. It freezes exponentially as $T \to 0$, demonstrating the presence of a gap.[16]

4. In summary, the explanation of the low-temperature behavior of $^{205}T_1^{-1}$ offered in Ref. 13 for a sample with $T_c = 100$ K—on the basis of a contribution from fluctuations of the vortex lattice—turns out to be inadequate in fields below 3.5 T. Furthermore, that explanation is completely wrong for a sample with $T_c = 30$ K, for which a field dependence of T_1^{-1} is seen above T_c, while at $T < T_c$ there is no temperature region with $T_1^{-1} \propto T$. We must therefore assume that yet another mechanism comes into play in these cases, and that this other mechanism dominates the relaxation. Since we are talking about TlO planes, we might suspect the presence of magnetic moments on copper ions, which fill about 10% of the Tl sites in a random way.[15] However, the contribution of the Curie type to the susceptibility of crystals with $T_c = 100$ K does not exceed a value corresponding to about 1% of the centers[17] with $S = 1/2$. This conclusion agrees with crystal-chemistry arguments,[15] according to which copper ions should be in a Cu^{+1} state in the TlO planes.

As well as we can judge from the contrast between the anomalous behavior of $1/T_1T$ and the normal behavior of the Knight shift,[16] this unknown relaxation mechanism might involve spin fluctuations of the electron system with an antiferromagnetic interaction, with certain q components of the dynamic susceptibility being significantly greater than the uniform value. The results reported here show that such spin excitations probably persist in the superconducting state of the overdoped $Tl_2Ba_2CuO_{6+x}$ system. Their contribution to the spin dynamics increases markedly as we go from the sample with $T_c = 100$ K to that with $T_c = 30$ K.

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