Direct measurement of the electron spin-lattice relaxation time of paramagnetic centers in a high-T_c superconductor

V. A. Atsarkin, A. A. Bush,* and G. A. Vasneva
Institute of Radio Engineering and Electronics, 103907 Moscow, Russia
**Moscow Institute of Radio Engineering, Electronics, and Automation, 117454 Moscow, Russia*

(Submitted 16 June 1993)
Pis'ma Zh. Eksp. Teor. Fiz. **58**, No. 2, 103–106 (25 July 1993)

The electron spin-lattice relaxation time T_1 in a high-T_c superconductor has been measured directly by a method of modulated ESR saturation in which the longitudinal magnetization is detected. The temperature dependence of T_1 for paramagnetic Cu^{2+} centers has been found for a $YBa_2Cu_3O_{7-\delta}$ sample. The relaxation accelerates just below T_c, possibly because of the opening of the superconducting gap.

The spin-lattice relaxation time T_1 is one of the most important magnetic-resonance characteristics. It embodies extensive information on the dynamics of internal fields and on the electronic states of solids, as can be seen from the numerous corresponding studies carried out to measure T_1 of nuclear spins in high-T_c superconductors. Data on the electron spin-lattice relaxation of paramagnetic probes might also be of much assistance, especially since in this case the time T_1 depends on the spectral density of the fluctuating internal fields at the ESR frequency, which is three orders of magnitude higher than in the case of nuclear spins. Still, there have been no direct measurements of T_1 of unpaired electron spins in high-T_c superconductors (except in the case of the very fast relaxation, with $T_1 \sim 10^{-9}$ s, which is manifested by a broadening of ESR lines;[1,2] however, that method is still indirect, and it cannot be used in the case of nonuniform broadening).

The reason for this situation is that it is technically impossible to cause any significant saturation of ESR lines in a high-T_c superconductor by means of a resonant microwave field. For the typical linewidths $\Delta H \sim 200$–400 Oe and times $T_1 \sim 10^{-7}$–10^{-9} s, a power on the order of a kilowatt would be required to reach a saturation factor $s=(\gamma H_1)^2 T_1 T_2 \sim 1$. Such a power level is absolutely unacceptable because of the heating of the sample [here γ is the gyromagnetic ratio, H_1 is the peak value of the microwave field, and $T_2 \sim 1/(\gamma \Delta H) \sim 10^{-9}$ s is the transverse relaxation time].

In this letter we are reporting the first direct measurement of T_1 for electron spins in a high-T_c superconductor. The measurement was based on an ESR line of Cu^{2+} ions. We used a modified version of the procedure of Refs. 3 and 4, which made it possible to obtain reliable data at very low saturation factors, $s \sim 10^{-3}$–10^{-2}.

Here is the experimental procedure. A high-T_c superconductor sample, ground

into a powder with a grain size of about 10 μm, was potted in paraffin and placed in a microwave cavity (with $Q=200$). The special design of the cavity allowed the penetration of rf fields in the megahertz range through the cavity (more on this below). The cavity was fed a microwave power $P\sim 200$ mW at a frequency of 9.4 GHz, tuned to the ESR line of interest in the external magnetic field H. Before being applied to the cavity, the microwave power was modulated deeply at a frequency $\Omega\sim 10^6$–10^8 s^{-1}, in the range of the expected values of T_1^{-1}. As a result, the magnetic-resonance transition underwent a weak ($s\ll 1$) periodic saturation at the frequency Ω, which gave rise to an oscillatory longitudinal magnetization:

$$M_z(t)=(u+iv)\exp(i\Omega t), \tag{1}$$

where u and v are the amplitudes of the components oscillating, respectively, in phase ($\phi=0$) and in quadrature ($\phi=\pi/2$) with respect to the modulating voltage. These amplitudes are proportional to the real part and the imaginary part of the dynamic magnetic susceptibility at the frequency Ω.

The signals were received by an inductance coil oriented along H and tuned to Ω; then they were amplified and identified by lock-in detectors. The real signals from the samples of the high-T_c superconductor, with a volume on the order of 10 mm^3, were very weak: less than 0.1 μV at the coil. Detecting them was thus not a trivial matter. To improve the sensitivity we used multichannel accumulation and bridge methods for canceling stray pickup.

It is not difficult to show that in the case of interest here ($1/\gamma\Delta H\ll T_1$; $s\ll 1$) the signals U and V at the outputs of the detectors are

$$U=ANPg(H-H_0)T_1\Omega\frac{1}{1+\Omega^2T_1^2}, \tag{2}$$

$$V=ANPg(H-H_0)T_1\Omega\frac{\Omega T_1}{1+\Omega^2T_1^2}, \tag{3}$$

where A is an instrumental factor, $g(H-H_0)$ is the form factor of the unsaturated ESR line, H_0 is the resonance field, and N is the number of spins in the sample. The voltage across the receiving coil, we might note, is $\pi/2$ out of phase with $M_z(t)$, so the signal U is detected by a quadrature detector, and V by an in-phase detector.

From the ratio $V/U=\Omega T_1$ we can thus determine the time T_1 directly, while measurements at various frequencies Ω make it possible to monitor the validity of the results. Furthermore, the magnitudes of U and V are proportional to the saturation factor [the factor containing $Pg(H-H_0)T_1$]. We thus have an additional opportunity to measure T_1, by comparing the amplitudes of the signals from the test sample and from a reference sample with a known relaxation time. It is thus possible to measure very short times T_1 when we are unable to measure the signal V.

Figure 1 illustrates the method. We studied a $YBa_2Cu_3O_{6.87}$ sample synthesized by the standard solid-phase procedure. Its superconducting transition temperature was $T_c=91$ K. At temperatures in the range 60–300 K the measured ESR spectrum contained a relatively weak line (representing about 0.5% of the total amount of

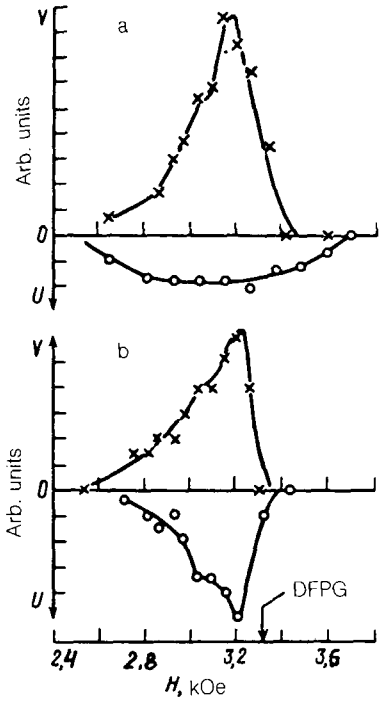

FIG. 1. The relaxation signals U and V from a $YBa_2Cu_3O_{6.87}$ sample at $T=78$ K at the frequencies $\Omega/2\pi=1.3$ MHz (a) and 290 kHz (b). For clarity, the signals have been plotted on different sides of the abscissa.

copper) which is typical of Cu^{2+} ions and which has been described in the literature repeatedly (e.g., Refs. 1 and 5–7). The nature of this line is still being debated. Some investigators attribute it to the nonmetallic "green" phase Y_2BaCuO_5 (Ref. 6), while others attribute it to various structural defects involving oxygen vacancies.[1,7] Superimposed on this signal for our sample was a far broader ($\Delta H\approx 400$ Oe) strong line (which may have formed during the grinding of the powder[8]).

Figure 1a shows the signals U and V detected at $T=78$ K and $\Omega/2\pi=1.3$ MHz versus the field H near resonance. The relatively narrow ($\Delta H\approx 200$ Oe) and asymmetric line typical of Cu^{2+} ions in $YBa_2Cu_3O_{7-\delta}$ is seen only in V; the weak U signal has the form of the broad line mentioned above in this case. Therefore, the time T_1, for the "main" spectrum of Cu^{2+}, satisfies the condition $\Omega T_1 \gg 1$, while the time T_1', for the "parasitic" signal, satisfies the condition $\Omega T_1' \ll 1$. Comparison with the reference sample (the free radical DPPH, for which the time is $T_1''=6\times 10^{-8}$ s) yields the estimates $T_1\approx 5\times 10^{-7}$ and $T_1'\approx 5\times 10^{-9}$ s. This example shows how overlapping ESR spectra with different relaxation rates can be separated.

To improve the accuracy of the T_1 measurements, we used a lower modulation frequency, $\Omega/2\pi=290$ kHz. In this case, U and V are comparable in magnitude (Fig. 1b), and the broad parasitic signal is not seen. The measurement time is $T_1=6.8\times 10^{-7}$ s.

Figure 2 shows the temperature dependence of T_1 in the range 60–140 K. We note the following.

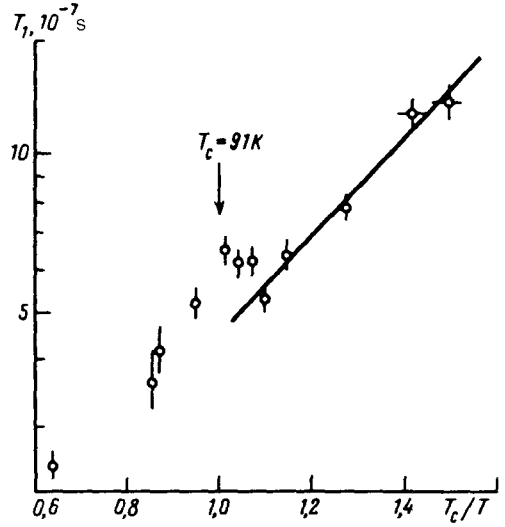

FIG. 2. Temperature dependence of the spin-lattice relaxation time of Cu^{2+} ions in $YBa_2Cu_3O_{6.87}$. The solid line is a plot of $\exp(2.3T_c/T)$, where T_c=91 K.

1. In the normal state, the temperature dependence of the relaxation rate is significantly stronger than the linear dependence predicted by the Korringa law. The absolute values of T_1 are larger by nearly two orders of magnitude than those measured from the broadening of the ESR lines of impurity Gd^{3+} ions in the same material.[1,2] This result suggests that the Cu^{2+} ions which provide the ESR spectrum are not in a metallic phase.

2. There is a structural feature: an acceleration of the relaxation just below T_c, which is known to be predicted by the BCS theory.[9] The results below T_c conform fairly well to an $\exp(\Delta/T)$ law with $\Delta=2.3T_c$, again in agreement with the BCS theory. However, we do not rule out the possibility that this is merely coincidence, since the temperature dependence is almost identical on the two sides of T_c.

One might suggest that the combination of a "nonmetallic" $T_1(T)$ dependence and a "superconducting" one stems from the particular type of small-scale phase stratification in[10,11] $YBa_2Cu_3O_{7-\delta}$, such that the paramagnetic Cu^{2+} centers in regions of nonmetallic phase nevertheless sense the conduction electrons in neighboring regions. Something along this line was also suggested in Refs. 1 and 6. These arguments are of course preliminary and must be tested in future research.

Finally, we wish to express our belief that direct measurements of the electron spin-lattice relaxation time open up some very extensive opportunities for obtaining new information on the electronic structure and magnetic fluctuations in high-T_c superconductors. We believe that essentially all ESR studies of the high-T_c superconductors can now be repeated and supplemented with measurements of T_1.

We wish to thank V. V. Demidov for many useful discussions and assistance in this study, A. E. Mefed and E. R. Gin for their cooperation in the development of the apparatus, and K. K. Abenov for participation in the measurements of the ESR

spectra. This study was carried out as part of Project 90004 of the State Program on High Temperature Superconductivity.

[1]N. E. Alekseevskii, A. V. Mitin, V. I. Nizhankovskiĭ *et al.*, J. Low Temp. Phys. **77**, 87 (1989).
[2]V. E. Kataev, Yu. S. Greznev, E. F. Kukovitskiĭ *et al.*, JETP Lett. **56**, 385 (1992).
[3]J. Herve and J. Pescia, C. R. Acad. Sci. **251**, 665 (1960).
[4]A. I. Polyakov and Yu. A. Ryabikin, Izv. Akad. Nauk Kaz. SSR, No. 2, 60 (1973).
[5]F. Mehran, S. E. Barnes, T. R. McGuire *et al.*, Phys. Rev. **B36**, 740 (1987).
[6]J. Genossar, D. Shaltiel, V. Zevin *et al.*, J. Phys. Cond. Matt. **1**, 9471 (1989).
[7]J. Stankowski, W. Kempinski, and Z. Trybula, Acta Phys. Pol. Ser. **A80**, 571 (1991).
[8]J. Stankowski, W. Hilczer, J. Baszyński *et al.*, Solid State Commun. **77**, 125 (1991).
[9]J. Winter, *Magnetic Resonance in Metals*, Oxford Univ. Press, 1971.
[10]S. Pekkar, A. Jánossy, and A. Rockenbauer, Physica C**181**, 11 (1991).
[11]I. N. Kurkin, I. Kh. Salikhov, L. L. Sedov *et al.*, Zh. Eksp. Teor. Fiz. **103**, 1342 (1993) [Sov. Phys. JETP **76**, 657 (1993)].

Translated by D. Parsons