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Electron-spin-lattice relaxation in $GdBa_2Cu_3O_{6+x}$

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A method of directly measuring electron-spin-lattice relaxation times T_1 as short as 10^{-9}–10^{-10} s is developed. The technique is based on the relation between the EPR absorption magnitude and the response of longitudinal spin magnetization to a radio-frequency modulation of microwave power. By means of this method, the electron-spin-lattice relaxation of Gd^{3+} ions was studied in high-T_c superconductor $GdBa_2Cu_3O_{6+x}$ at $0.4 \le x \le 0.84$ in the temperature range 77–300 K. It was found that spin-spin interactions between Gd^{3+} ions have no influence on the T_1 value, so Gd^{3+} can be used as a spin probe even in concentrated substances. The relaxation rate $W=(TT_1)^{-1}$ is shown to consist of two parts, W_0 and W_{AF}, resulting from the quasiparticle contribution and the antiferromagnetic fluctuations, respectively. Both contributions reveal a spin gap opening with $\Delta/k_B=200$ K. The temperature variation of W_0 is in agreement with published ^{89}Y NMR data in $YB_2Cu_3O_{6+x}$, the W_0 values being proportional to the ^{89}Y Knight shifts. The ratio W_{AF}/W_0 shows Curie-Weiss behavior and increases strongly as x decreases. This implies incomplete filtering of the antiferromagnetic fluctuations over the finite-sized Gd^{3+} $4f$ orbitals and symmetry breaking due to oxygen vacancies.

I. INTRODUCTION

It is well known that valuable information can be obtained on internal fields and electronic states in high-T_c superconductors (HTSC) by means of measuring nuclear-spin-lattice relaxation time T_1 (see, for example, Refs. 1 and 2 and references therein). Similar information (but at much higher frequencies) might be provided, in principle, but studying the electron-spin-lattice relaxation of paramagnetic centers, either impurities or belonging to the host lattice. However, only little is known about the electron T_1 values in HTSC's. The reason is rather clear: it is very difficult to measure relaxation times as short as 10^{-8}–10^{-10} s at typical EPR linewidths $\Delta B \sim 10^{-2}$–10^{-1} T. In such a case, to achieve saturation factor $s \sim 1$, it is necessary to use microwave power more than kW. This is quite unrealistic because of huge heating of the sample. So the standard techniques of measuring T_1 are inapplicable in this case, and up to now the electronic T_1 values could be extracted only from temperature variation of the EPR linewidth.[3–6] Note, however, that the contribution of T_1^{-1} to the linewidth is often masked by other sources, such as inhomogeneous and dipolar broadening. On the other hand, by measuring the linewidth only the transversal relaxation time T_2, which is not always equal to T_1, can be determined.

In this paper a direct method of measuring electronic T_1 is presented, which enables one to work at extremely low saturation factors $s \sim 10^{-4}$–10^{-3} and to measure T_1 values as short as 10^{-9}–10^{-10} s. This technique is described in Sec. II. In Sec. III we shall present the experimental data obtained by means of our method on the $GdBa_2Cu_3O_{6+x}$ high-T_c system. Finally, in Sec. IV, an interpretation will be suggested based on the assumption of simultaneous contributions of quasiparticles and antiferromagnetic (AF) fluctuations to the relaxation rate.

One of the aims of this work was to test the possibility of using Gd^{3+} as a precise probe of local fields and spin dynamics in HTSC. Recently, a similar work has been made by Jánossy *et al.*[5,6] on $Gd_{0.01}Y_{0.99}Ba_2Cu_3O_{6+x}$; in these papers, the Gd^{3+} T_1 value was extracted from the temperature-dependent part of the EPR linewidth in oriented powders. Jánossy *et al.* found that the temperature variation of Gd^{3+} T_1 was in agreement with the data on T_1 and the Knight shift for ^{89}Y NMR in $YBa_2Cu_3O_{6+x}$ published by Alloul, Ohno, and Mendels.[7] However, the comparison could be made only in a rather narrow temperature range (80–160 K), since there were no data on ^{89}Y T_1 at $T<80$ K,[7] as well as on Gd^{3+} at $T>160$ K (Refs. 5 and 6) (in the latter case, the linewidth became too large so the components of the fine structure could not be resolved).

Our technique enables us to remove the latter restriction and to obtain a deeper insight into spin dynamics in the "123" HTSC system. At the same time, it is interesting to clear up whether this picture may be influenced by dipole-dipole and exchange interactions between the Gd^{3+} spins when their concentration is 100 times increased as compared with Refs. 5 and 6.

II. THE METHOD OF MEASURING T_1

The method used in this work can be considered as a modified version of the modulation technique suggested by Herve and Pescia as early as 1960.[8] A sample under study is prepared as fine powder embedded in paraffin or epoxy. It is placed into a specially designed microwave cavity with its walls transparent to rf magnetic field in the MHz range. Microwave power at the frequency $\omega/2\pi=9.3$ GHz (fitted to EPR in the external magnetic field $B_0 \approx 0.34$ T), before entering the cavity, is subjected to a deep amplitude modulation at the modulation fre-

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quency $\Omega/2\pi \sim 10^6$ Hz. As a result, the EPR saturation factor $s=(\gamma B_1)^2 g(\omega) T_1$ [where γ is the gyromagnetic ratio, B_1 is the half-amplitude of the microwave magnetic field, and $g(\omega)$ is the form factor of the EPR line] is modulated as well, and the oscillating component of the longitudinal spin magnetization $M_z(t)$ arises:

$$M_z(t)=U\cos\Omega t+V\sin\Omega t \ . \tag{1}$$

Here U and V are, respectively, the in-phase and out-of-phase parts of $M_z(t)$ relative to the modulation wave form.

The oscillating magnetization, Eq. (1), induces the in-phase (u) and out-of-phase (v) parts of the ac voltage in a pickup coil wound on the cavity and having its axis parallel to the external field $\mathbf{B}_0$. Then this signal is amplified, lock-in detected, accumulated, and processed.

It is easy to show that under conditions of

$$s \ll 1; \quad (\gamma \Delta B)^{-1} \ll T_1 \ , \tag{2}$$

the following equations hold:[8]

$$u=AM_0(\gamma B_1)^2 g(\omega)\Omega T_1 \frac{1}{1+(\Omega T_1)^2} \ , \tag{3a}$$

$$v=AM_0(\gamma B_1)^2 g(\omega)\Omega T_1 \frac{\Omega T_1}{1+(\Omega T_1)^2} \ , \tag{3b}$$

where A is an instrumental factor and M_0 is the static magnetization of the spins under study.

It is clear from Eqs. (3a) and (3b) that the ratio

$$\frac{v}{u}=\Omega T_1 \tag{4}$$

enables one to determine readily the value of T_1. In practice, the first inequality in Eq. (2) can be ensured by the proper choice of microwave power. As to the second inequality, it is not so essential: the method can also work at $T_1 \sim T_2$, though in such a case Eqs. (3) and (4) must be replaced by more complicated ones.[8]

Although this technique was suggested many years ago, it had never been applied, as far as we know, to studying metals and, particularly, superconductors. It may appear that the obvious obstacle would be an additional phase shift of the registered rf signal when it penetrates the conducting medium. It should be noted, however, that the u and v magnitudes are proportional to the saturation factor s and hence they sample only the limited volume within the microwave skin depth. In normal metals this depth is much less than that at the modulation frequency, so the additional phase shift at Ω is negligible. It can be shown that this remains valid under typical conditions of the EPR registration ($B_0 \sim 0.3$ T) in HTSC at $T<T_c$; in this case, the penetration depths at both microwaves and rf are determined by dissipation on magnetic vortices.[9]

Another, more serious difficulty arises when T_1 value is shorter than 10^{-8} s. The point is that the modulation frequency is limited by $\Omega_{\max} \sim 3\times10^7$ s $^{-1}$ because of a finite quality factor of the microwave cavity, $Q \geq 10^2$. So, at $T_1<10^{-8}$ s we have

$$\Omega T_1 \ll 1 \ , \tag{5}$$

and the v/u ratio, Eq. (4), can hardly be measured with proper accuracy: the method breaks down.

To overcome this difficulty, we have developed a version of the modulation technique which combines measuring the longitudinal magnetization Eq. (1) with registering the EPR absorption at microwaves. This absorption measured at $s \ll 1$ reads

$$P=CM_0(\gamma B_1)^2 g(\omega) \ , \tag{6}$$

where C is another instrumental factor. So under the condition of Eq. (5) one has

$$\frac{u}{P}=\frac{A}{C}\Omega T_1 \ . \tag{7}$$

Equation (7) allows us to determine T_1 provided the A/C ratio is known. This ratio, in its turn, can be easily obtained from the comparison of P and u signals measured on a calibrated EPR probe with a known T_1 value [for instance, diphenylpicrylhydrazyl (DPPH)]. Certainly, all measurements must be carried out at the same conditions.

The described method enables one to measure relaxation rates T_1^{-1} up to 3×10^{10} s^{-1} (the only restriction is the EPR frequency ω). Of course, as seen from Eq. (3), the shorter T_1 the lower the sensitivity. However, by using accumulation and proper processing, this problem has been resolved.

III. RESULTS

A. The samples and the EPR spectrum

The study was performed on $GdBa_2Cu_3O_{6+x}$ samples with $x=0.84$, 0.78, 0.49, and 0.40. Their parameters are presented in Table I. Critical temperatures T_c were measured by ac susceptibility (the middle points of the superconductive transitions). The samples were fabricated by the standard solid-state reaction technique in the Monokristall Institute of the Ukrainian Academy of Sciences (Kharkov, Ukraine). The oxygen content was determined by iodine titration.

EPR spectra were registered using a standard X-band spectrometer (Bruker ER-200). The spectra of all samples were found to be nearly identical. They consisted of a single line with $g=2.0$ and the width (peak-to-peak) $\Delta B_{pp}=0.27$ T. The shape of the line was close to Lorentzian, though there were some deviations on the low-field side.

TABLE I. Characteristics of the samples and fit parameters of Eqs. (9)–(12) for the Gd^{3+} relaxation rate.

x	T_c (K)	Δ/k_B (K)	θ (K)	r	W^0 (10^6 s^{-1}K^{-1})	W' (10^6 s^{-1}K^{-1})
0.84	85	200	20	2.5	8.6	0
0.78	79	200	20	0.5	12.4	0
0.49	48	200	20	0	7.8	0
0.40	25	200	20	0	2.9	1.9

Similar spectra were observed previously in Refs. 10–12. In these papers, the shape and the width of the line were assigned to the exchange narrowing of the multicomponent, dipolar broadened EPR spectrum of Gd^{3+} ions (spin $S=\frac{7}{2}$). The exchange integral was estimated as $J/k_B \approx 0.1$ K, in reasonable agreement with the Curie-Weiss temperature $\theta=-5$ K as known for this substance [recall that $\theta \approx 2zJS(S+1)/(3k_B)$, where $z=4$ is the number of nearest neighbors].[13]

On the other hand, in some earlier papers,[14,3] a narrower EPR spectrum of $GdBa_2Cu_3O_{6+x}$ was reported with $\Delta B_{pp} \approx 0.11$ T. In that case, the linewidth was found to increase slightly with temperature. This temperature-dependent broadening was attributed by the authors of Ref. 3 to the Korringa-like spin-lattice relaxation. The reasons for such a discrepancy between the earlier results[14,3] and the more recent ones[10–12] (as well as ours) are not clear. It is not improbable that structural defects, clusters, and impurity phases (such as, for example, Gd_2BaCuO_5) took an essential part in the formation of the EPR spectrum observed in Refs. 14 and 3.

B. Gd^{3+} spin-lattice relaxation

The Gd^{3+} spin-lattice relaxation time T_1 was measured by the method described in Sec. II. The inequality $\Omega T_1 \ll 1$ was found to be valid within the temperature range $T=77$–300 K for all samples, so that only the u component of the longitudinal magnetization was detectable at the modulation frequency $\Omega/2\pi \approx 1$–2 MHz. Hence the "combined version" was applied; see Eq. (7). In the beginning, DPPH was used as a calibrated probe, its T_1 value (6.5×10^{-8} s) being measured by means of v/u ratio. However, the so-called "green phase" Y_2BaCuO_5 turned out to be more convenient as a reference sample. This substance reveals a strong EPR spectrum of Cu^{2+} ions, the shape and the width of the line being independent on temperature within the range under study.[15] We measured the corresponding T_1 value by means of our combined version. It was found that the spin-lattice relaxation time of Cu^{2+} in Y_2BaCuO_5 is also temperature independent and equal to $(9\pm1)\times10^{-10}$ s at 77–300 K. In the subsequent work, the green phase prepared as fine powder was mixed with the $GdBa_2Cu_3O_{6+x}$ powder and served as a reference for comparing the P and u signals.

A typical example of experimental recording is shown in Fig. 1. The external field B_0 was changed point by point. The same figure shows the standard EPR signals (the derivatives dP/dB_0) taken on the same mixture at the same conditions. The integration of the EPR spectra provides the P values needed for determining T_1 from Eq. (7). It is easy to see that the shape of $u(B_0)$ agrees well with the form factors of the EPR lines (both for Cu^{2+} and Gd^{3+}), just as predicted by Eq. (3).

The accuracy of determining T_1 from such pictures is limited primarily by the integration of very broad Gd^{3+} EPR spectra; this can lead to a systematic error of about ±20%. Relative variations of T_1 with T and x can be measured, however, more exactly (±5%).

The main results of our work are shown in Fig. 2. There are the temperature variations of the Gd^{3+} spin-lattice relaxation rate presented as "the relaxation rate per degree Kelvin," $W=(T_1T)^{-1}$ versus T. The most important features of these data are as follows.

(i) The magnitude of the relaxation rate T_1^{-1} falls within the range 10^8–10^9 s^{-1}. Obviously, these values have nothing to do with the EPR linewidth [$T_2^{-1} \sim (\sqrt{3}/2)\gamma\Delta B_{pp} \sim 3\times10^{10}$ s^{-1}].

(ii) At the highest oxygen content ($x=0.84$), the W value increases sharply in temperature from 77 to 140 K. At higher temperatures, the curve becomes flattened and tends to the Korringa law $W=$const. Similar variations are characteristic of nuclear-spin-lattice relaxation of ^{17}O and ^{89}Y in the underdoped $YBa_2Cu_3O_{6+x}$ system (at $x<1$).[16,7] In both cases, there is no pronounced peculiarity in the vicinity of the superconducting transition. For comparison, the data on ^{89}Y spin-lattice relaxation in $YBa_2Cu_3O_{6.75}$ (Ref. 7) are also plotted in the same figure.

(iii) Decreasing the oxygen index x results in two consequences. First, an overall slowing down of the relaxation rate occurs. It is natural to attribute this to decreasing hole concentration in the conduction band. A similar effect was observed previously in nuclear relaxa-

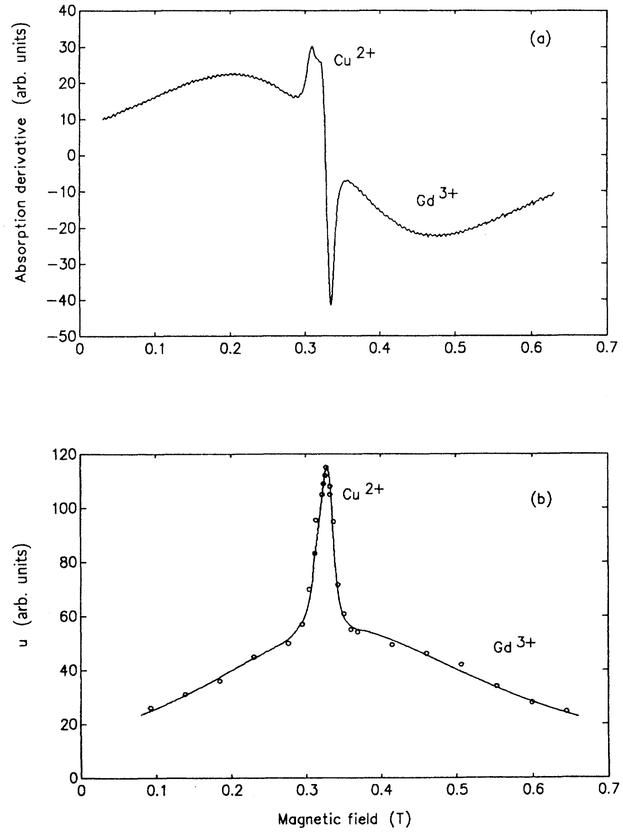

FIG. 1. (a) Gd^{3+} and Cu^{2+} EPR spectra and (b) longitudinal magnetization signals for the mixture $GdBa_2Cu_3O_{6.78}+Y_2BaCuO_5$ at $T=128$ K; $\Omega/2\pi=1.62$ MHz.

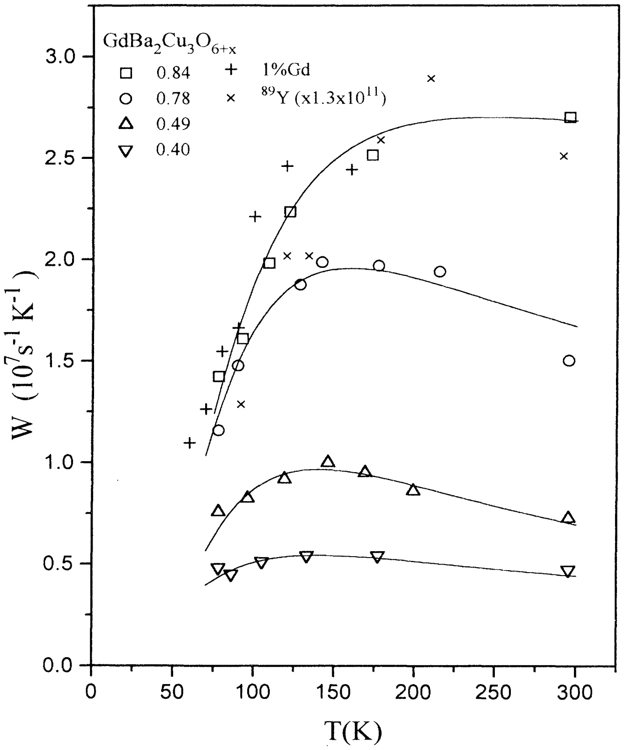

FIG. 2. Gd^{3+} spin-lattice relaxation rate per degree Kelvin $W=(T_1T)^{-1}$ versus T in $GdBa_2Cu_3O_{6+x}$ compared with those in $Gd_{0.01}Y_{0.99}Ba_2Cu_3O_{6.76}$ (Ref. 5) and with ^{89}Y NMR data (Ref. 7) (multiplied by 1.3×10^{11}). Solid curves are calculated according to Eqs. (9)–(12) with the fit parameters shown in Table I.

tion.[7]

Second, the shape of the temperature dependence $W(T)$ is also changed: the curves become more gentle, with a pronounced decay at higher temperatures, so a maximum arises near $T\approx150$ K. Such behavior is typical of NMR relaxation of the planar ^{63,65}Cu(2) nuclei in $YBa_2Cu_3O_{6+x}$;[16] usually it is attributed to the effect of antiferromagnetic fluctuations. This item will be discussed in detail in Sec. IV. At the lowest oxygen content ($x=0.4$), the curve $W(T)$ becomes nearly flat and close to the Korringa law.

(iv) It is worthwhile to compare our data with those obtained on $Gd_{0.01}Y_{0.99}Ba_2Cu_3O_{6.76}$ in Refs. 5 and 6, where the Gd^{3+} relaxation rate was determined from the EPR line broadening. The points shown in Fig. 2 are calculated using the data of Ref. 5 by means of the relation

$$T_1^{-1}=\frac{\sqrt{3}}{2}\gamma(\Delta B_{pp}-\Delta B_{pp}^0)\ , \tag{8}$$

where $\Delta B_{pp}^0=5.5$ mT is a residual width at $T\rightarrow0$. As seen from Fig. 2, in the temperature range available for comparison (77–160 K), the data of Ref. 5 fall very close to our curve ($x=0.78$), apart from an unessential factor of about 1.25. Such a good agreement is even surprising, taking into account that the two samples are far from being identical: in our case, the concentration of the Gd^{3+} ions is 100 times higher.

IV. DISCUSSION

To interpret the experimental data, we make use of the existing concept on spin dynamics in HTSC materials.[17–21] According to this, nuclear-spin-lattice relaxation occurs via fluctuating internal fields caused by a single spin fluid formed by strongly hybridized O $2p$ and Cu d holes. Along the lines of the Mila-Rice model,[17] the fluctuating spins have maximum density on the Cu(2) sites (in the CuO_2 planes), and their coupling with the localized nuclear spins under study is due to the so-called "transferred hyperfine interaction." To extend this approach to the electron-spin-lattice relaxation of Gd^{3+} ions, it is sufficient to replace the hyperfine interaction by the exchange one. This does not change the form of the Mila-Rice Hamiltonian and hence the relaxation model, though all characteristic energies and rates become several orders of magnitude greater.

Following Millis, Monien, and Pines (MMP) (Ref. 18) (see also Refs. 2, 19–21) we write for the relaxation rate of the paramagnetic centers

$$W\equiv(T_1T)^{-1}=W_0+W_{AF}+W'\ . \tag{9}$$

Here the term W_0 is due to the quasiparticle contribution from the entire Brillouin zone except the vicinity of $\mathbf{k}_{AF}\equiv(\pi/a,\pi/b)$, and the W_{AF} term represents the contribution of the antiferromagnetic fluctuations with $\mathbf{k}\approx\mathbf{k}_{AF}$, where $\mathbf{k}$ is the wave vector and a and b are lattice constants in the CuO_2 plane (note that the interplane AF correlations are also possible).

The Gd^{3+} ions are located between two adjacent CuO_2 planes in $GdBa_2Cu_3O_{6+x}$, similarly to Y sites in $YBa_2Cu_3O_{6+x}$. These sites are symmetric relative to eight nearest Cu(2) atoms, so their AF correlations do not create any fluctuating field seen by ^{89}Y nuclei. Thus one supposes $W_{AF}=0$ for ^{89}Y nuclear relaxation.[2] However, as seen from Fig. 2, the $W(T)$ curves at $x<0.84$ resemble rather the data for ^{63}Cu(2) relaxation[16,22,23] which are governed just by the AF contribution. So to fit our experimental data both W_0 and W_{AF} terms in Eq. (9) should be retained. Finally, the W' term is added to be "on the safe side" in the case of any foreign relaxation mechanisms.

In the subsequent discussion, one needs to assume an explicit form for the temperature variations of W_0 and W_{AF}. Within the MMP model[18,19] modified by taking into account the opening of a "gap" in magnetic excitation spectrum[20,21] we write

$$W_{AF}=W^0\phi_{AF}(T)f_g(T)\ , \tag{10a}$$

$$W_0=rW^0f_g(T)\ , \tag{10b}$$

where the function

$$f_g(T)=1-\tanh^2\left[\frac{\Delta}{2k_BT}\right] \tag{11}$$

describes the "freezing" of the magnetic excitations because of the gap opening (Δ is the gap energy),[21] and

$$\phi_{\mathrm{AF}}(T)=\frac{300+\theta}{T+\theta} \tag{12}$$

reflects the temperature dependence of the AF correlation length and characteristic energy.[21] The function $\phi_{\mathrm{AF}}(T)$ has a Curie-Weiss-like form (θ is the Curie-Weiss temperature); the numerator in Eq. (12) is chosen for convenience sake, in order to normalize $\phi_{\mathrm{AF}}(T)$ to unity at 300 K. The common factor W^0 in Eqs. (10a) and (10b) gives the scale of the relaxation rates whereas the factor r determines the ratio W_0/W_{AF} at $T=300$ K.

So the procedure of fitting Eqs. (9)–(12) to the experimental data (Fig. 2) includes five parameters (Δ, θ, r, W^0, and W') and at first glance seems rather ambiguous. In fact, however, the situation is not so bad. First, the Curie-Weiss-like function $\phi_{\mathrm{AF}}(T)$ is known from comparison between ^{63}Cu and ^{17}O relaxation rates in $\mathrm{YBa_2Cu_3O_{6+x}}$;[16,22] this gives $\theta \approx 20-30$ K. Such low θ values hardly affect the fitting at rather high temperatures (77–300 K) where Eq. (12) is close to Curie law. Hereafter we shall use $\theta=20$ K for all samples.

Second, the common factor W^0 has no influence on temperature variation of relaxation rate. And, finally, the W' term will not be used except for the sample $x=0.40$. So we have to fit the experimental curves with only two real parameters, Δ and r.

The best fit obtained is shown in Fig. 2 by solid curves; the corresponding parameters are given in Table I. One can see that a good agreement is achieved with the same value $\Delta/k=200$ K for all samples. Note that the Δ/k_B values reported for the YBaCuO system fall between 150 and 280 K.[2,21]

Unlike Δ, the r value depends strongly on the oxygen content. As seen from Table I, the relative contribution of the AF fluctuations (r^{-1}) increases from 0.4 at $x=0.84$ to 2.0 at $x=0.78$ and becomes much more than unity for the less oxygenated samples, where the term W_0 is negligible. Finally at $x=0.40$ (near the boundary between superconducting and AF phases in the "123" system[24]) the temperature variation $W(T)$ becomes so gentle that it cannot be described without the "foreign" term W' in Eq. (9). To fit the data, we added a constant value $W'=1.9\times10^{6}\ \mathrm{s^{-1}\,K^{-1}}$. The nature of such a Korringa term is not clear; note that similar flattening of the temperature dependencies at low x was also reported by Alloul, Ohno, and Mendels[7] for ^{89}Y NMR.

The rise of the nonzero term W_{AF} can be explained by an incomplete filtering of the AF fluctuations sampled by the $\mathrm{Gd^{3+}}$ spins. This may be related to the finite size of $\mathrm{Gd^{3+}}$ $4f$ electron orbitals as opposed to a ^{89}Y nucleus. An increase of the AF contribution at lower x values (see Fig. 2 and Table I) could be due to symmetry breaking caused by random distribution of oxygen vacancies in the Cu-O chains. Although these perturbations occur only in the next nearest environment of the $\mathrm{Gd^{3+}}$ ions, their effect can be essential, as seen from the observed influence of oxygen vacancies on the EPR spectrum in $\mathrm{Gd_{0.01}Y_{0.09}Ba_2Cu_3O_{6+x}}$.[25]

Now we shall estimate the extent to which the AF fluctuations are not cancelled at $\mathrm{Gd^{3+}}$ site. Following Refs. 17–21, the ratio W_{AF}/W_0 reads

$$\frac{W_{\mathrm{AF}}}{W_0}=\frac{F_{\mathrm{AF}}\langle I(\mathbf{k},\omega)\rangle_{\mathrm{AF}}}{F_0\langle I(\mathbf{k},\omega)\rangle_0}\ . \tag{13}$$

Here $F_{\mathrm{AF},0}$ are the form factors representing the efficiency of $\mathrm{Gd^{3+}}$-Cu(2) exchange coupling in a given part of the $\mathbf{k}$ space; $I(\mathbf{k},\omega)$ is the spectral density of spin fluctuations, and $\langle\ \rangle$ means the $\mathbf{k}$ average. The subscripts AF and 0 indicate, as previously, the areas of summation (for the form factors) and averaging (for the spectral densities): near and away from $\mathbf{k}_{\mathrm{AF}}$, respectively. The expression used in Eq. (13) implies that the $\mathbf{k}$ dependence of $I(\mathbf{k},\omega)$ is weak enough within the two separate areas.

Suppose that $I(\mathbf{k},\omega)$ is nearly the same in both Y- and Gd-123 systems and, besides, it is not changed significantly as ω increases from NMR to EPR. Under these assumptions we can estimate the ratio $\langle I(\mathbf{k},\omega)\rangle_{\mathrm{AF}}/\langle I(\mathbf{k},\omega)\rangle_0$ using the data on nuclear-spin-lattice relaxation of ^{63}Cu(2), ^{17}O, and ^{89}Y in $\mathrm{YBa_2Cu_3O_{6+x}}$. In particular at $T=300$ K one has $^{63}W/^{17}W \simeq 20$ (Refs. 16 and 22) and $^{63}W/^{89}W \simeq 5\times10^{4}$.[26] With the known values of F factors and hyperfine constants for these nuclei[2] we get $\langle I(\mathbf{k},\omega)\rangle_{\mathrm{AF}}/\langle I(\mathbf{k},\omega)\rangle_0 \approx 12$. Comparing this quantity with our experimental values of $r=W_0/W_{\mathrm{AF}}$ at 300 K (see Table I), we can estimate, using Eq. (13), the ratio F_{AF}/F_0 for $\mathrm{Gd^{3+}}$ ions: this is of the order of 0.04 for $x=0.84$ and 0.2 for $x=0.78$. These quantities give an idea about the penetration of the AF fluctuations within the volume occupied by the $\mathrm{Gd^{3+}}$ $4f$ orbitals.

To provide an additional test of the model employed it would be worthwhile to compare the relaxation rates with a static part of the spin susceptibility $\chi_s(\mathbf{k}=0)$ which can be determined by measuring the Knight shift K. Unfortunately, it is impossible to measure K for Gd EPR in our samples because of the huge broadening of the EPR line. So we made use of the results obtained on ^{89}Y NMR in $\mathrm{YBa_2Cu_3O_{6+x}}$ by Alloul, Ohno, and Mendels.[7]

In Fig. 3, our W values for $\mathrm{GdBa_2CuO_{6+x}}$ are plotted against the ^{89}Y NMR Knight shifts, ^{89}K, taken from Ref. 7. The points in Fig. 3 refer to pairs of the samples: ($\mathrm{GdBa_2Cu_3O_{6+x}}$, this work), [$\mathrm{YBa_2Cu_3O_{6+x}}$ (Ref. 7)] with closely related oxygen contents. The ^{89}K values are obtained by interpolating the experimental points of Ref. 7. One can see that at low temperatures (to the left in Fig. 3) and high x values the dependence of W(Gd) on ^{89}K is nearly linear. As T increases, the linearity fails, especially for low x. This behavior can be readily explained by the W_{AF} contribution because the Knight shifts, as opposed to the relaxation rates, cannot be affected by the AF fluctuations.

To verify this suggestion, the "quasiparticle" part of the Gd relaxation rate (W_0) is shown in the same figure. The W_0 values are calculated according to Eqs. (10b) and (11) and using the parameters listed in Table I for $x=0.84$ and 0.78; the Knight shifts at corresponding temperatures and x values are taken from Ref. 7. As seen, the dependence of W_0 (Gd) on ^{89}K is linear for both x values and within the entire temperature range. Extrapolation to $W_0=0$ (that is, to $T=0$) gives ^{89}K(0)

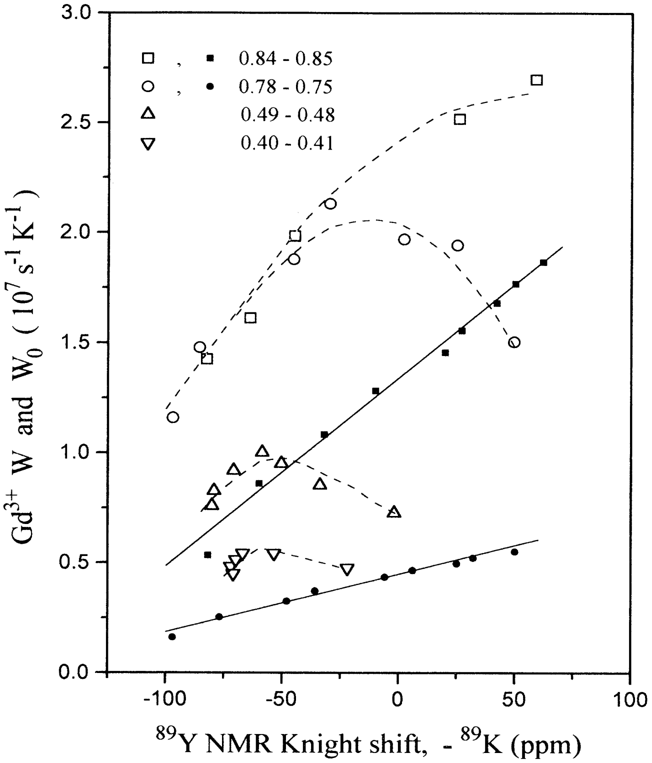

FIG. 3. Gd^{3+} spin-lattice relaxation rate per degree Kelvin $W=(T_1T)^{-1}$ (open symbols) and its "quasiparticle" component W_0 (filled symbols) in $GdBa_2Cu_3O_{6+x}$ versus ^{89}Y NMR Knight shift in $YBa_2Cu_3O_{6+x}$ (Ref. 7). The corresponding x values are indicated in the figure (two columns at the top). The dashed curves are guides to the eyes.

$=(165\pm5)$ ppm for both lines; this value determines the chemical shift which seems quite reasonable. Note that the proportionality between W(Gd) and $^{89}K_s = {}^{89}K - {}^{89}K(0)$ in the temperature range (80–160 K) was reported by Jánossy, Brunel, and Cooper for 1% Gd-doped YBaCuO.[6]

Finally, we shall discuss one of the most striking results of this work, the insensitivity of spin-lattice relaxation rate to dipolar and exchange interactions between Gd^{3+} ions in the GdBaCuO system. It is commonly supposed (see, for example, Ref. 27) that at $J/\hbar \gg \omega$, ω_d an EPR line experiences the exchange narrowing which leads to $T_1^{-1} \sim T_2^{-1} \sim \omega_d^2/J$ (here ω_d is a root-mean-square value of dipole-dipole interactions). The estimates for $GdBa_2Cu_3O_{6+x}$ seem to be in reasonable agreement with the observed linewidth (see above, Sec. III A). So one would expect $T_1 \approx T_2 \approx 3\times10^{-11}$ s, in contradiction with the reported T_1 values.

A possible explanation may be as follows. In fact, the exchange Hamiltonian commutes with the Zeeman one and so cannot affect T_1 directly. An accurate calculation should take into account both secular and nonsecular dipole-dipole interactions which serve as intermediates between the exchange and Zeeman operators. The efficiency of such a complicated process is not clear *a priori,* but in any case the equality $T_1 = T_2$ cannot be fulfilled automatically.

On the other hand, the characteristic time of the coupling between Zeeman (Z) and exchange (J) subsystems may be very short indeed (of the order of 10^{-10} s), but the relaxation process may have its bottleneck between the unified ($Z+J$) system and the "lattice" (spin fluid). In such a case, if the coupling between the J subsystem and the "lattice" is weak enough, the exchange interactions cannot affect T_1 values as measured by saturation technique. Obviously, this problem is not yet clear at present.

V. CONCLUSION

The main results of this work may be summarized from three different points of view.

(i) As far as methodical aspects are concerned, an effective technique has been developed for measuring extremely short electron spin-lattice relaxation times (up to the rates of the order of 10^{10} s^{-1}). This enables one to investigate longitudinal spin relaxation both in normal metals and superconductors.

(ii) In terms of high-T_c superconductivity, information is obtained about the relative contributions of quasiparticles and AF fluctuations to the Gd^{3+} spin-lattice relaxation rate in $GdBa_2Cu_3O_{6+x}$. We succeeded in separating both these contributions for the same site in the crystalline lattice and following the increase of the ratio W_{AF}/W_0 with a decrease in the oxygen content. The temperature variation of this ratio was found to obey the Curie-Weiss law, in accordance with MMP model.[18–21]

The experimental data provide an additional support to the concept of a gap opening in the magnetic excitation spectrum. The magnitude of the gap was found to be about 200 K for both AF and quasiparticle contributions; this implies that the gap does not depend strongly on the wave vector within the range $0 \le \mathbf{k} \le \mathbf{k}_{AF}$. It is also found that there exists a very good linear relationship between the quasiparticle part W_0 of the Gd^{3+} relaxation rate and the Knight shifts ^{89}K measured for ^{89}Y NMR in the YBaCuO system.[7]

(ii) Finally, from the standpoint of radiospectroscopy and magnetic resonance, the most interesting observation is the lack of any influence of rather strong spin-spin interactions between Gd^{3+} ions on their longitudinal spin relaxation time T_1 in $GdBa_2Cu_3O_{6+x}$. Apart from other aspects, this makes it possible to employ paramagnetic ions as effective spin probes even at 100% concentration when their EPR and u signals are sufficiently large and convenient for measuring. At the same time, the dipolar and exchange interactions in the GdBaCuO system are to be studied in more detail elsewhere.

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