Electron spin–lattice relaxation in high-T_c superconductors: Cu^{2+} in Y–Ba–Cu–O

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A new method for measuring very short electron spin–lattice relaxation times in the range $T_1 \sim 10^{-6}$–10^{-10} s is described. The method is based on recording the oscillating longitudinal magnetization of the sample under conditions of weak ESR saturation by an amplitude-modulated microwave field. This technique is used to determine the value of T_1 for Cu^{2+} ions in the nonconducting compound Y$_2$BaCuO$_5$ (the "green phase") and in a series of samples of high-T_c superconductors having the formula YBa$_2$Cu$_3$O$_{6+x}$ with various oxygen contents. In the former case the relaxation time equals 9×10^{-10} s and does not depend on the temperature in the 77–300 K range, as is characteristic of ESR spectra with strong exchange narrowing. In the latter case three types of Cu^{2+} centers (I, II, and III) having similar ESR spectra, but different spin–lattice relaxation rates, are found. The centers of type I ($T_1 \sim 10^{-6}$ s) are nonconducting impurities. The value of T_1 for the centers of type II nearly coincides with the results for the green phase. Acceleration of the relaxation to $\sim 5 \times 10^{-10}$ s is discovered for the centers of type III in the 120–160 K temperature range. An interpretation, which takes into account structural defects and clusters in the Y–Ba–Cu–O system, including the local replacement of Ba^{2+} by Y^{3+} (centers of type II) and fragments of Cu–O chains (centers of type III), is proposed. © *1995 American Institute of Physics.*

1. INTRODUCTION

The investigation of the spin–lattice relaxation of nuclei and paramagnetic centers in solids is known to yield unique information on internal fields, atom–molecule dynamics, electronic states, etc. One example is provided by the numerous studies on nuclear spin–lattice relaxation in high-T_c superconductors, which have made possible considerable progress in understanding the physics of these materials (see, for example, Ref. 1 and the literature cited therein). On the other hand, few data have hitherto been obtained on electron spin–lattice relaxation in high-T_c superconductors. This is clearly due to the fact that the standard methods of continuous or pulsed saturation are practically inapplicable in this case. In fact, for an ESR linewidth $\Delta B \simeq 10$–100 mT, which is typical of high-T_c superconductors, and the expected spin–lattice relaxation times $T_1 \sim 10^{-9}$ s, totally unrealistic levels of microwave pumping equal to more than 1 kW would be needed to achieve a value of the saturation factor $s \equiv (\gamma B_1)^2 g(\omega) T_1$ of order unity [here γ is the gyromagnetic ratio, B_1 is the half-amplitude of the microwave magnetic field, and $g(\omega)$ is the shape factor of the ESR line]. For just this reason, the only method for evaluating T_1 in high-T_c superconducting materials has hitherto been measurement of the temperature-induced broadening of ESR spectra.[2–4] It is clear, however, that determination of the relaxational linewidth superposed on other sources of broadening (primarily, inhomogeneous broadening) is far from always possible and that, in addition, it allows determination only of the transverse relaxation time T_2, which does not necessarily coincide with T_1.

In the present work, developing a very old, but almost never applied idea of Herve and Pescia[5] (see also Ref. 6), we created an alternative method for measuring T_1, which

makes it possible to work at extremely low saturation levels ($s \sim 10^{-3}$–10^{-4}) and to directly measure extremely short times in the range $T_1 \sim 10^{-9}$-10^{-10} s. The essence of this technique is described in Sec. 2, and in the ensuing sections we describe the results of its application to the investigation of the spin–lattice relaxation of Cu^{2+} paramagnetic centers, first in the nonconducting green phase of Y$_2$BaCuO$_5$ and then in the well known high-T_c semiconducting material YBa$_2$Cu$_3$O$_{6+x}$, at 77–300 K.

The purpose of this investigation is to elucidate the nature of the paramagnetic centers just mentioned in YBa$_2$Cu$_3$O$_{6+x}$. This question is still controversial: some investigators presume[3,7–9] that the observed ESR spectrum, which is typical of Cu^{2+} ions, is caused by certain defects or clusters, which are incorporated into the main lattice of the 1–2–3 system. Others conjecture[10–13] that the only source of this spectrum is parasitic contamination by the so-called green phase of Y$_2$BaCuO$_5$, which forms in an uncontrolled manner during the synthesis of samples of the high-T_c superconductors. We recall that x-ray methods do not allow such small amounts of an impurity phase to be detected (on the order of 0.1%). Clearly, a comparison of the spin–lattice relaxation rates in Y$_2$BaCuO$_5$ and YBa$_2$Cu$_3$O$_{6+x}$ should provide new information and help to resolve this problem.

2. METHOD FOR MEASURING T_1

The procedure which we employed to measure very short spin–lattice relaxation times is as follows. The sample under investigation is placed in a microwave cavity of special design, which is located in an external magnetic field B_0. Before entering the cavity with the sample, the microwave power at the ESR frequency is subjected to deep amplitude modulation with a frequency $\Omega/2\pi \sim 10^6$ Hz. This

results in corresponding modulation of the saturation factor s, and, consequently, in the appearance in the sample of an oscillating longitudinal magnetization

$$M_z(t) = u \cos \Omega t + v \sin \Omega t, \qquad (1)$$

where u and v are the amplitudes of the components of the magnetization which oscillate in phase and with a $\pi/2$ shift relative to the modulation, respectively. The signals u and v are clearly proportional to the real and imaginary parts of the spin susceptibility at the frequency Ω. The essence of the method is the measurement of these components using a pickup coil oriented along the field $\mathbf{B}_0$ and tuned to the frequency Ω.

By solving the elementary rate equations for the populations of the magnetic sublevels or the Bloch equations, one can easily show[5] that when the conditions

$$s \ll 1, \qquad (2a)$$

$$T_1^{-1} \ll \gamma \Delta B \qquad (2b)$$

are satisfied, the signals induced in the pickup coil have the form

$$U = A M_0 (\gamma B_1)^2 g(\omega) \Omega T_1 \frac{1}{1 + (\Omega T_1)^2}; \qquad (3a)$$

$$V = A M_0 (\gamma B_1)^2 g(\omega) \Omega T_1 \frac{\Omega T_1}{1 + (\Omega T_1)^2}. \qquad (3b)$$

Here A is an instrumental factor, and M_0 is the equilibrium spin magnetization of the paramagnetic centers which contribute to the ESR spectrum under investigation. From (3a) and (3b) it follows directly that

$$\frac{V}{U} = \Omega T_1, \qquad (4)$$

which makes it possible to determine T_1 at once, if the values of U and V are measured with sufficient accuracy. Of course, this requires appropriate amplification and subsequent synchronous detection of the signals induced in the pickup coil.

The method under discussion was first proposed in the "phase" version described above back in 1960 (Ref. 5) and was subsequently employed on rare occasions in a few laboratories.[6] We do not know of its use to measure T_1 in metals, and certainly not in superconductors. Such application of this method is, in fact, associated with definite difficulties.

First, when metals are investigated, the radio-frequency field produced by the variable magnetization $M_z(t)$ passes through the conducting medium, creating an additional phase shift, which distorts the results. A careful analysis, however, reveals that this difficulty is surmountable. In fact, the oscillating magnetization $M_z(t)$ appears only in the part of the volume of the sample into which the saturating microwave field penetrates, i.e., in a skin layer of thickness $\delta(\omega)$ in the case of a normal metal. Since the thickness $\delta(\Omega)$ of the skin layer at radio frequencies is far greater than $\delta(\omega)$, the phase shift at the modulation frequency will be negligibly small. In the case of a superconductor, the question becomes more complicated. However, the calculations which we performed show that the impedance of samples of typical high-T_c superconductors is determined mainly by dissipation in viscous motions of the magnetic vortices for $B_0 \cong 0.3$ T (the ESR range) and when the temperature is, at least, not far from the superconducting transition temperature T_c.[14] As a result, the situation is similar to a normal metal $[\delta(\omega) \ll \delta(\Omega)]$ and there are no significant phase distortions in the reception of U and V. As will be seen below, this conclusion is confirmed experimentally.

Second, a more fundamental problem arises in measurements of very short relaxation times. The fact is that due to the finite transmission band of a microwave cavity (in practice its quality factor cannot be less than 10^2), the modulation frequency has an upper bound: $\Omega \leqslant 10^7$ s^{-1}. Therefore, for $T_1 < 10^{-8}$ s the inequality

$$\Omega T_1 \ll 1 \qquad (5)$$

is satisfied. In this case, as is seen from (3) and (4), virtually only the synphase component U remains in the longitudinal magnetization signal, so that the ratio V/U turns out to be nearly zero and cannot be measured on a background of the unavoidable parasitic phase shifts in the instrumentation. The method ceases to work.

We were able to overcome this difficulty using an "amplitude" version of the modulation method, which combines measurement of the oscillating longitudinal magnetization $M_z(t)$ with recording of the ordinary ESR absorption signal P. As we know, in the weak saturation limit the latter quantity can be written in the form

$$P = C M_0 (\gamma B_1)^2 g(\omega), \qquad (6)$$

where C is another (different from A) instrumental factor and the remaining notation is the same as in (3). We stress that we are dealing with the absorption signal, rather than its derivative dP/dB_0, which is usually recorded in standard ESR spectrometers.

Taking into account the condition (5), from (3) and (6) we can easily obtain

$$\frac{U}{P} = \frac{A}{C} \Omega T_1. \qquad (7)$$

The latter relation makes it possible to determine T_1, only if the ratio of the instrumental factors A/C is known. It, in turn, can be found by measuring the signals U and P from a special reference sample having a clearly isolated ESR line and a known spin–lattice relaxation time. In particular, a widely used ESR reference, such as the free radical DPPH, for which the value of T_1 is independent of the temperature over a broad range and can easily be measured using the first (phase) version of the modulation method, can be employed.

We note, however, that the values of T_1 and T_2 for DPPH and substances like it are often of the same order of magnitude, so that the second of the conditions (2) is violated and the relations (3) and (4) must be corrected. For this reason, we present here more exact expressions, which follow from the Bloch equations under the conditions of amplitude modulation of the microwave field for $s \ll 1$:

$$\frac{V}{U} = \frac{\Omega[T_1 + \frac{1}{2}T_2(1 + \Omega^2 T_1 T_2)]}{1 - \frac{1}{2}\Omega^2 T_2(T_1 - T_2)} ,$$ (8a)

$$Z \equiv (V^2 + U^2)^{1/2}$$

$$= AM_0(\gamma B_1)^2 g(\omega)\Omega T_1 \left[\frac{1 + \frac{1}{4}(\Omega T_2)^2}{(1 + \Omega^2 T_1^2)(1 + \Omega^2 T_2^2)} \right]^{1/2} .$$ (8b)

The transverse relaxation time T_2 is determined in this case from the width of the ESR line of the reference. The corresponding corrections to Eq. (7) are obvious.

A necessary condition for applicability of the second (amplitude) version of the modulation method is the performance of both measurements (of U and P) under strictly identical conditions, i.e., with the same positioning of the main and reference samples in the microwave cavity, at the same temperature, etc. We note that the spatial nonuniformity of the microwave field is then of no significance: as is seen from a comparison of (3) and (6), the multiplier $(\gamma B_1)^2$ cancels out in Eq. (7).

One great advantage of the amplitude version is its insensitivity to the parasitic phase shifts in the modulator and detector circuits. When such shifts can significantly alter the value of U, it is helpful to measure the absolute value of the longitudinal magnetization Z [see (8b)], whose value does not depend on the phase shifts.

It is interesting to compare the versions of the modulation technique described here with the classical procedures for measuring T_1, viz., the pulsed- and continuous-saturation methods.[15] It is not difficult to see that the first (phase) version, especially if it is supplemented by measurements at different values of Ω, is basically a Fourier analog of the pulsed-saturation method: the relaxation response of the spin system is simply transformed from the time scale to the frequency scale. At the same time, the amplitude version can be regarded as a further development of the continuous-saturation method, since in both cases the saturation factor s is actually measured, and the ESR absorption line is essentially used to extract the value of T_1.

Application of the amplitude version makes it possible, at least in principle, to measure longitudinal relaxation rates up to 10^{10} s^{-1}: the restriction appears only due to the ESR frequency. Of course, as is seen from (3), the sensitivity drops as T_1 shortens. However, as will be shown below, this problem can be solved for the samples actually used.

3. EXPERIMENT

3.1. Samples and experimental technique

The samples for the investigations ($YBa_2Cu_3O_{6+x}$ and Y_2BaCuO_5) were obtained from two sources: the Moscow Institute of Radio Engineering, Electronics, and Automation (they are denoted in the following by the letter M) and the Institute of Single Crystals of the Ukrainian Academy of Sciences, Khar'kov (they are denoted by the letter K). They were prepared by standard solid-phase synthesis methods. The single-phase state of the samples was monitored by x-ray diffraction with an accuracy of about 1%. The oxygen

TABLE I. Parameters of the samples investigated and the spin-lattice relaxation times.

No.	Formula	T_c, K	c, %	T_1, 10^{-9} s	
				$T = 295$ K	$T = 77$ K
6.90K	$YBa_2Cu_3O_{6.90}$	90	0.27	0.9±0.2	1.1±0.2
6.85K	$YBa_2Cu_3O_{6.85}$	88	0.50	1.2±0.2	···
6.85M	$YBa_2Cu_3O_{6.85}$	91	0.75	1.0±0.2	0.95±0.2
6.69K	$YBa_2Cu_3O_{6.69}$	75	0.75	1.0±0.2	···
6.55K	$YBa_2Cu_3O_{6.55}$	60	0.18	1.3±0.2	1.1±0.2
6.30K	$YBa_2Cu_3O_{6.30}$	···	0.80	1.3±0.2	1.3±0.2
GPM	Y_2BaCuO_5	···	100	0.90±0.06	0.95±0.06

content in the samples of the $YBa_2Cu_3O_{6+x}$ system (which will be called the 1–2–3 system below) was determined by x-ray spectroscopy from the lattice constant and chemically by an iodine titration. The temperature of the superconducting transition (if it occurred) was determined from the appearance of low-field microwave absorption, which is characteristic of high-T_c superconductors. The parameters of the samples investigated are presented in Table I.

The measurements of the ESR spectra and the spin-lattice relaxation were performed in the $\lambda = 3.2$ cm wavelength range ($\omega/2\pi = 9.4$ GHz) at 77–300K. The samples were prepared in the form of powders with a particle size less than 10 μm. The powder was fixed in paraffin (the ratio was 1:2) and enclosed in a toroidal container with a working volume of about 100 mm^3, which was placed at the antinode of the microwave magnetic field of a coaxial cavity resonator with a length of $3\lambda/4$. The axis of the cavity was aligned in the direction of the field B_0, so that the circular force lines of the microwave magnetic field would be perpendicular to B_0, as required for the observation and saturation of ESR. The outer cylindrical surface of the cavity was cut by longitudinal slits, which have almost no influence on the Q factor of such a microwave cavity ($Q \approx 150$), but render its walls permeable to the high-frequency magnetic field induced by the longitudinal spin magnetization $M_z(t)$. The pickup coil, which was tuned to the frequency Ω, was wound directly on the cavity, so that its axis would be parallel to B_0.

The spin–lattice relaxation time T_1 was measured by both versions of the modulation technique described above, viz., the phase and amplitude versions. In the latter case the measurements of the ESR absorption were performed with the same cavity and under the same conditions as the recording of the relaxation signals U and V. A standard Bruker ER-200 ESR spectrometer was used to obtain the more precise spectra needed for a detailed analysis of the line shape.

The free radical DPPH, as well as the quasi-one-dimensional conductor orthorhombic Rb_1C_{60} (o-Rb_1C_{60}), which was kindly supplied by Dr. L. Forro (Laboratoire de Physique des Solides Semicristallins, Lausanne, Switzerland), were employed as reference samples in the measurements of T_1 by the "amplitude" method. In the latter case an ESR line with a width of 0.3–0.6 mT, which belongs to the conduction electrons,[16] was used; detailed data on this substance will be published separately. To avoid the systematic error associated with different spatial locations of the main
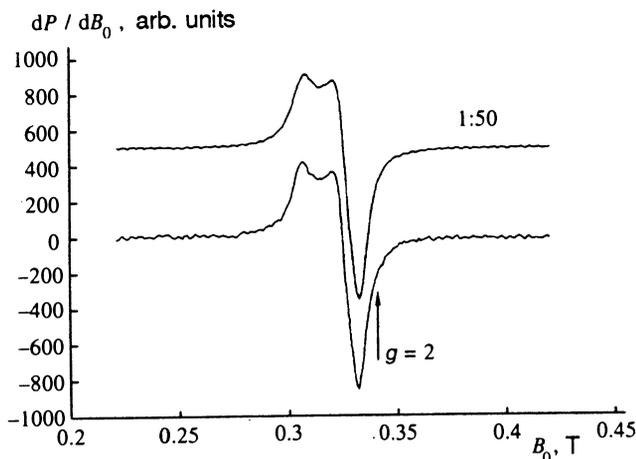
FIG. 1. ESR spectra of samples of Y_2BaCuO_5 (upper spectrum) and $YBa_2Cu_3O_{6.69}$ (lower spectrum) at room temperature.

FIG. 2. ESR spectrum of a sample of $YBa_2Cu_3O_{6.85}$ (No. 6.85M) at $T = 100$ K (upper spectrum) and result of the subtraction of the ESR line shown in Fig. 1 from it (lower spectrum). The dashed line on the lower spectrum is the result of a calculation with the parameters indicated in the text.

and reference samples in the high-frequency pickup coil, the two samples were mixed in a single container.

3.2. ESR spectra

All the samples investigated produced ESR spectra at 77–300K which are characteristic of Cu^{2+} ions and have been described repeatedly in the literature.[2,7–10,12] Typical results are shown in Fig. 1, which presents the ESR spectra of Y_2BaCuO_5 and $YBa_2Cu_3O_{6.69}$ powders at room temperature. Practically the same spectra (differing only in intensity) were observed in the range $77 \leqslant T \leqslant 300$ K for the other samples listed in Table I, with the exception of sample 6.85M, which will be discussed separately. As is seen from Fig. 1, the ESR line shapes for the 1–2–3 system and the green phase practically coincide. They correspond completely to the calculated spectrum of a powder with the g tensor components $g_z = 2.222$, $g_x = 2.050$, and $g_y = 2.094$ and with the individual width $\Delta B_{pp}^0 = 7.0$ mT for the Lorentzian line from individual crystallites, in agreement with the ESR data for Y_2BaCuO_5 single crystals.[17] At the same time, both spectra in Fig. 1 are described satisfactorily by an axial g tensor with the components $g_\parallel = 2.20$ and $g_\perp = 2.06$ (Refs. 2,7,12). The concentration (c) of paramagnetic centers relative to the total number of copper atoms was determined from the ESR intensity and is indicated in Table I.

The ESR line shape of one of the samples (6.85M, see Table I) differed somewhat from that shown in Fig. 1. This difference reached a maximum at $T \approx 100$ K. At that temperature it is possible to separate the ESR spectrum into two lines, one of which coincides in shape with the line shown in Fig. 1, while the other, which corresponds to approximately 40% of all the Cu^{2+} paramagnetic centers in the sample, is similar to the spectrum of the powder with the parameters $g_\parallel = 2.27$, $g_\perp = 2.03$, and $\Delta B_{pp}^0 = 7.0$ mT (see Fig. 2). When the temperature is raised to 300 K, the distinct structure of the additional line seen in Fig. 2 is smeared, attesting to a significant increase in its width ΔB_{pp}^0.
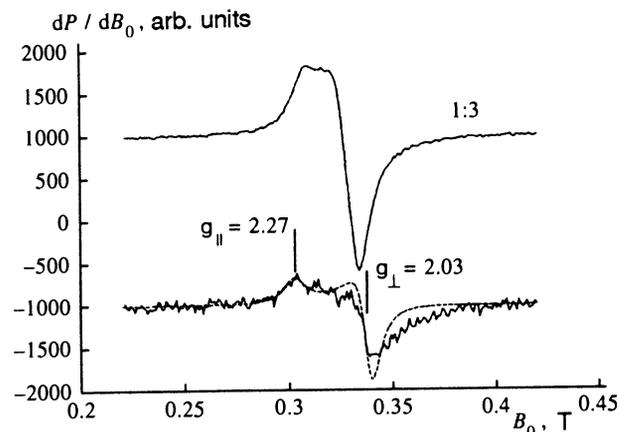
The parameters presented for the additional ESR line, as well as the increase in ΔB_{pp}^0 with increasing temperature, are very reminiscent of the recently published data on the ESR spectrum of $YBa_2Cu_3O_{6+x}$ single crystals.[18,19] They indicate that this line most probably belongs to Cu^{2+} ions in so-called $Cu(1)$ sites, which appear within fragments of Cu–O chains. It was shown in Ref. 19 that such paramagnetic centers are characteristic of only a narrow range of oxygen concentrations, $x \approx 0.75$–0.85, which appears to account for the absence of the additional line in most of our samples.

3.3. Spin–lattice relaxation in Y_2BaCuO_5

A typical experimental trace, which was used to determine the value of T_1 for the Cu^{2+} ions in the green phase, is shown in Fig. 3, which presents the results of the measurements of U and V, as well as the ESR absorption spectra at $T = 300$ K, as a function of the external magnetic field B_0 as it passes through the resonance region. The modulation frequency was equal to 1.6 MHz ($\Omega = 10^7$ s^{-1}), and the time constant of the detector (with consideration of signal accumulation) was about 5 s. As is seen from the figure, the relaxation response of Y_2BaCuO_5 contains practically only the synphase signal U, whose shape, as predicated by Eqs. (3), coincides with the shape of the ESR absorption line. This means that the condition (5) is satisfied in the present case, i.e., $T_1 \ll 10^{-7}$, and the amplitude version of the method should be used to measure it [see (7)]. The multiplier A/C in this formula was determined from a comparison of the relaxation signals U and V (Fig. 3b) with the amplitude of the ESR absorption (Fig. 3a) for the reference sample of DPPH; the value $T_1(DPPH) = 6.3 \times 10^{-8}$ s was obtained from Fig. 3b using (8). We finally get

$$T_1(Y_2BaCuO_5) = (9.0 \pm 0.5) \cdot 10^{-10} \text{ s}.$$

The results of similar measurements in the temperature range $77 \leqslant T \leqslant 300$ K are shown in Fig. 4. It is seen that the
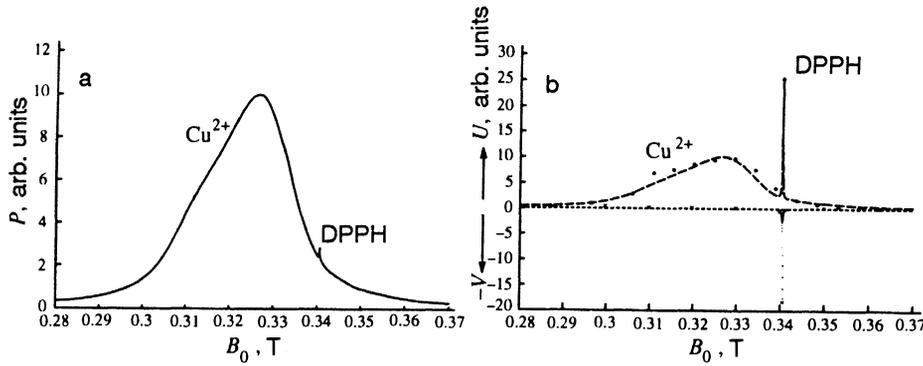
FIG. 3. a—ESR absorption signals from a mixture of Y_2BaCuO_5 (broad line) and DPPH (narrow line); b—relaxation signals U (circles, dashed line) and V (crosses, dotted line) from the same substances under identical conditions. $T=300$ K; $\Omega=10^7$ s^{-1}. For convenience, U and V are plotted on different sides of the horizontal axis.

value of T_1 for the Cu^{2+} ions in the green phase does not depend on the temperature to within the accuracy of the measurement.

We note that the value of T_1 obtained leads to relaxational broadening of the ESR line in accordance with the relation

$$\Delta B_{pp} = \frac{2}{\sqrt{3}} (\gamma T_1)^{-1}, \qquad (9)$$

which gives $\Delta B_{pp} = 6.8 \pm 0.4$ mT, a value practically coinciding with the experimentally measured ESR linewidth for Y_2BaCuO_5 single crystals.[17] We put off a more detailed discussion until Sec. 4.

3.4. Spin–Lattice relaxation in $YBa_2Cu_3O_{6+x}$

The procedure used to measure T_1 in 1–2–3 samples with different oxygen contents (see Table I) scarcely differs from that described in the preceding section. The only additional difficulty was the decrease in the amplitude of the signals by approximately two orders of magnitude, which required a corresponding increase in the number of acquisitions and, of course, caused an increase in the error.

The investigations showed that the $YBa_2Cu_3O_{6+x}$ samples which we used contain at least three types of Cu^{2+} paramagnetic centers having similar ESR spectra, but significantly different spin–lattice relaxation rates.

The centers of the first type (the "slowly relaxing" centers, which will be referred to as type I below) are character-

ized by values of T_1 on the order of $10^{-6}-10^{-7}$ s, which are highly temperature-dependent. These data were presented in our first paper.[20] A further investigation showed that the centers of type I make only a small (about 1%) contribution to the observed ESR line, and their predominance in the relaxation signals U and V observed in Ref. 20 is attributed to the use of the relatively low modulation frequency $\Omega/2\pi = 0.3$ MHz [see Eq. (3)]. It was found that the concentration of the centers of type I increases as the samples are dehydrated. They are apparently nonconducting decomposition products of the 1–2–3 system, and we shall not discuss them further.

An increase in the modulation frequency to 1.5–2 MHz, the use of samples of better quality, and the transition to the amplitude version of the measurement method made it possible to discover and investigate two more types of centers, which are designated as centers of types II and III below.

Centers of type II were discovered in all the samples studied, and they make the largest (and often the only) contribution to the intensity of the ESR line. Our measured values of T_1 for these centers are presented in Table I for two temperatures: 77 and 300 K. At intermediate temperatures the data are similar. We stress that no special features were observed in T_1 upon passage through the superconducting transition temperature. It is seen that the values presented in the table agree to within the error both with one another and with the results for the green phase. (We note that in our preliminary data[21] all these values of T_1 were overestimated by approximately 20% due to the spatial separation of the main and reference samples, but this has practically no influence on the interpretation of the results).

At the same time, sample 6.85M, which has anomalies in the ESR spectrum (see Fig. 2), also exhibited features in its spin–lattice relaxation, which allowed us to postulate the presence of one more type of paramagnetic center (III). The temperature dependence of T_1 for this sample is shown in Fig. 5. It is seen that acceleration of the relaxation exceeding the instrumental error is observed in the 120–160 K range. At the same time, the results at both edges of the 77–300 K range studied coincide with one another and scarcely differ from those presented in Table I.
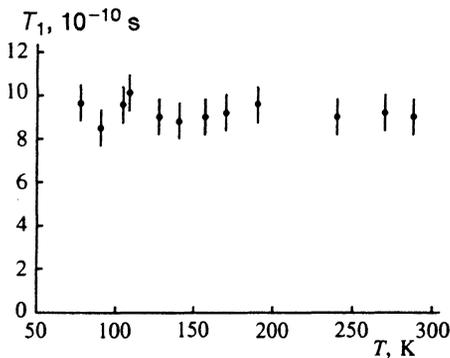

FIG. 4. Results of the measurements of the spin–lattice relaxation time of the Cu^{2+} ions in Y_2BaCuO_5 in the 77–300 K temperature range.

4. DISCUSSION OF RESULTS

We begin the discussion from the spin–lattice relaxation data for the green phase, Y_2BaCuO_5. The unit cell of this compound is known[22] to contain two Cu^{2+} ions occupying
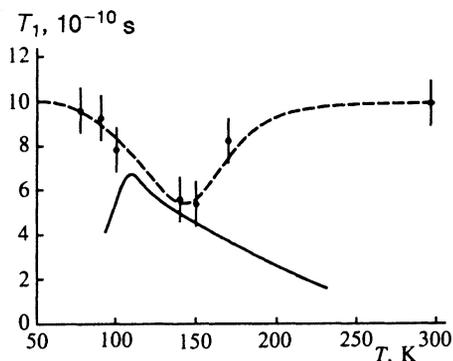
T_1, 10^{-10} s

FIG. 5. Temperature dependence of the spin–lattice relaxation time of Cu^{2+} ions in sample 6.85M. The dashed curve was drawn through experimental points. The solid curve depicts the transverse relaxation time for the ESR line assigned to fragments of Cu–O chains (according to the data in Ref. 18).

magnetically inequivalent positions. In both positions the local environment of the paramagnetic ion has the form of a pyramid of five oxygen atoms with an almost square base; however, the axes of these pyramids are at a 58° angle relative to one another. Reinen and Wegwerth[23] reported a transformation of the ESR spectrum of Cu^{2+} ions in the isomorphic compound $Y_2BaZn_{1-y}Cu_yO_5$: when the copper concentration (y) increases, the exchange interaction between the Cu^{2+} ions causes the spectra from the two inequivalent positions to gradually merge into a single line, for which the magnetic z axis is aligned along the bisector between the axes of the coordination pyramids.

Thus, the ESR spectrum of Y_2BaCuO_5 is characterized by strong exchange narrowing. This is consistent with the fairly high Weiss constant ($\theta \simeq -50$ K) and Néel temperature ($T_N \simeq 14$ K) for this compound.[17,24] In such a case it is perfectly natural that the ESR line for the single crystals would have a nearly Lorentzian shape,[17] for which T_1 and T_2 are equal to one another and are specified by Eqs. (9) and (10). It is also well known that in systems with strong exchange narrowing the relaxation times frequently do not depend on the temperature, since they are determined by the thermal contact between the Zeeman and exchange subsystems (a typical example is DPPH). Thus, both the absolute value and the temperature-dependent behavior of T_1 in the green phase are completely consistent with our expectations.

Let us now turn to the $YBa_2Cu_3O_{6+x}$ system. Since the centers of type I clearly do not belong to the principal lattice of this substance, we shall concentrate on a discussion of the centers of type II, especially since they make the main contribution to the observed ESR spectrum.

As is seen from Table I, T_1 for these centers scarcely differs from that for the green phase, either in its value or in the absence of a temperature dependence. This is certainly very strong evidence in support of the hypothesis in Refs. 10 and 12 that the source of paramagnetic centers of type II is a trivial impurity of macroscopic inclusions of the green phase, which forms during the synthesis of the 1–2–3 system.

Without ruling out such a possibility, we note, however, that some investigators[2,8] emphasize the differences between the ESR spectra of Y_2BaCuO_5 and $YBa_2Cu_3O_{6+x}$, which may attest to a relationship between the latter and microscopic internal defects or clusters incorporated in the 1–2–3 lattice. There have also been reports of magnetic orientation of the ESR spectrum of a $YBa_2Cu_3O_{6+x}$ powder, the z axis of the g tensor being aligned along the crystallographic c axis.[2] There is also convincing evidence of the existence of paramagnetic centers which accelerate nuclear spin relaxation in an oxygen-deficient 1–2–3 lattice.[25]

Speaking of the structural defects which might be responsible for the appearance of the paramagnetic centers of type II in $YBa_2Cu_3O_{6+x}$, we should bear in mind that our spin–lattice relaxation data greatly restrict the list of permissible models. Explanations are needed not only for the form of the ESR spectrum, but also for the observation that T_1 depends on the temperature, which is clearly attributable to strong exchange narrowing similar to the exchange narrowing in the green phase. In other words, only the Cu^{2+} clusters in the 1–2–3 structure which are most similar to the Y_2BaCuO_5 lattice are suitable candidates.

One such possibility is illustrated in Fig. 6. A fragment of an ordinary 1–2–3 lattice, which includes portions of CuO_2 planes [Cu(2) copper sites] and a CuO chain [a Cu(1) site], is depicted on the left. As we know, in a defect-free lattice none of these sites produces an ESR spectrum due to antiferromagnetic exchange with their neighbors.

Now we assume that a Ba^{2+} ion occupying a site between a CuO_2 plane and the CuO chain is replaced by a Y^{3+} ion (it should normally be located between two adjacent CuO_2 planes). In order to provide for the ordinary eightfold coordination of the Y^{3+} ion in the new site, O(4) oxygen sites must become vacant, and empty O(5) sites must become occupied (see Fig. 6b). Thus, a fragment of a CuO_2 plane appears instead of the portion of the CuO chain. The Cu^{2+} ion involved is found at the center of a square of four oxygen atoms. Addition of the O(4) atom belonging to the next layer gives a coordination pyramid, which is very similar in shape and even with respect to the lengths of its interatomic distances to the environment of the Cu^{2+} ions in the green phase (compare with Ref. 17).

The replacement of several neighboring Ba^{2+} ions by Y^{3+} ions would signify growth of the CuO_2 fragment. The exchange interaction in such a cluster can have a corresponding influence on the ESR line shape and lead to temperature-independent spin–lattice relaxation. We note that the axes of the coordination pyramids in Fig. 6b are aligned along the c axis, in agreement with the observed symmetry of the g tensor in $YBa_2Cu_3O_{6+x}$ (Ref. 2).

As we know, the mutual replacement of cations in complicated oxides is fairly common, so that the existence of such defects in the 1–2–3 system is not only possible, but inevitable. This model is also supported by the fact that the synthesis of a 1–2–3 system with a Ba deficiency, as well as the replacement of a small portion of the Ba ions by La, produce an ESR spectrum of the type under discussion.[9] The proposed model can also account for the increase in the intensity of similar spectra following prolonged storage of the
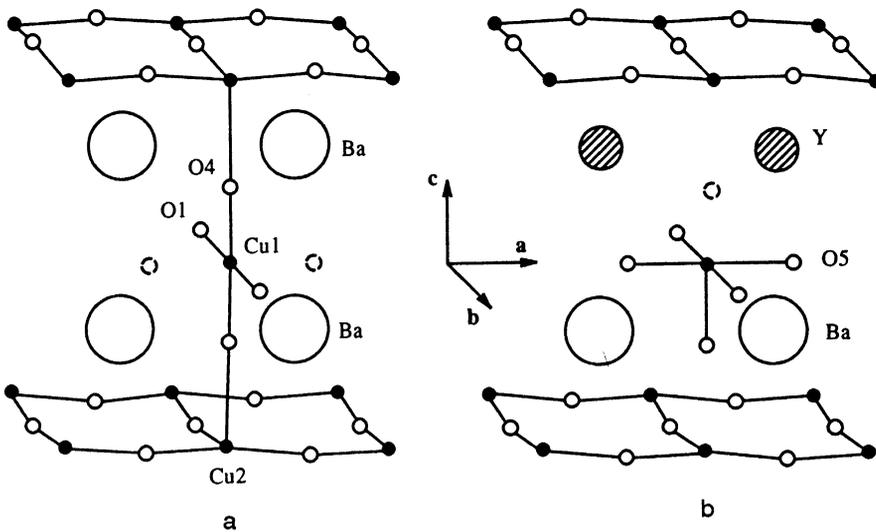
FIG. 6. a—Fragment of the crystal structure of $YBa_2Cu_3O_{6+x}$ illustrating the local environment of a copper atom in a Cu(1) site. b—Proposed restructuring of the environment when two Ba^{2+} ions are replaced by Y^{3+}. Dashed circles—oxygen vacancies.

samples at room temperature:[26] it is clearly due to redistribution of the oxygen atoms, which gradually occupy the vacant O(1) and O(5) sites in Fig. 6b.

Let us move on the centers of type III, whose contribution was manifested in the features of the spin–lattice relaxation in sample 6.85M (see Fig. 5). It is natural to associate these features with the additional ESR line identified in Fig. 2, which is assigned to Cu^{2+} ions in Cu(1) sites (fragments of Cu–O chains).[18,19] To test this hypothesis, we compare our results with the temperature dependence of

$$T_2 = \left(\frac{\sqrt{3}}{2} \gamma \Delta B_{pp} \right)^{-1}, \tag{10}$$

where ΔB_{pp} is the width of the ESR line measured in the spectra of $YBa_2Cu_3O_{6+x}$ single crystals in Ref. 18. The results of calculations based on Eq. (10) are illustrated in Fig. 5 by the solid line. It is seen that for $100\ K < T\ 150$ K the temperature dependence of T_1 correlates with the variation of the ESR linewidth. Moreover, the absolute values of T_1 exhibit close agreement with (10), which can be interpreted as a result of the relaxational broadening of the ESR line from the "chain" Cu^{2+} ions. This is consistent with the relaxation model proposed for these centers in Ref. 27.

The broadening of the "additional" ESR line on both sides of the 100–150 K temperature range is so strong that the amplitude of this line drops sharply, and the centers of type III can no longer have a significant influence on the results of the measurements of T_1 performed by the method used here. This accounts for the observable "restoration" of the relaxation time to the 9×10^{-10} s level at both nitrogen and room temperatures.

5. CONCLUSIONS

The results of the present work can be considered from two standpoints. First, an effective method for measuring very short electron spin–lattice relaxation times has been devised and successfully tested. In our opinion, it can significantly expand the range of applications of ESR spectroscopy, especially in case of metals and high-T_c superconductors. A

real possibility for supplementing pure spectral information, which pertains only to static or averaged characteristics, with relaxation data, which depend on the dynamics of the internal fields in the materials investigated, has become apparent. We believe that practically all ESR-spectroscopic investigations of high-T_c superconductors can now be supplemented by measurements of T_1.

Second, new information on the ESR spectra of Cu^{2+} ions in layered cuprates has been obtained. Here the main result is the agreement of absolute values and temperature-dependent behavior of T_1 for the most prevalent centers (type II) in $YBa_2Cu_3O_{6+x}$ with the analogous data for the green phase. Convincing support has been obtained for the simplest explanation for this finding, viz., macroscopic contamination; however, it cannot yet be considered conclusively proved. Further investigations are needed here, and experiments on oriented samples might be especially informative.

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