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Electron spin-lattice relaxation rate in $Y(Gd)Ba_2Cu_4O_8$: Evidence for *d*-wave pairing in high-T_c materials

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Using an original modulation technique, the longitudinal (spin-lattice) relaxation of the impurity Gd^{3+} ions has been investigated in the superconducting state of $Y_{0.99}Gd_{0.01}Ba_2Cu_4O_8$ magnetically aligned powders. The results agree well with the linewidth analysis performed on a single crystal. At low temperatures ($T<60$ K) the relaxation rate T_1^{-1} is found to be proportional to T^3, suggesting *d*-wave superconducting pairing. The data are consistent with previous Knight shift (^{Gd}K) measurements that revealed a linear temperature dependence of the uniform spin susceptibility. The Korringa relation between T_1 and ^{Gd}K is confirmed indicating the validity of the Fermi-liquid model.

The orbital state of the superconducting Cooper pairs remains one of the most important problems concerning high-T_c superconductors (HTSC's). Despite growing evidence supporting *d*-wave symmetry (see, for example, Refs. 1–4), there are still some open questions concerning the origin of gaps in the energy and spin spectrum. The comparison of the ''true'' superconducting gap which opens at T_c with the so-called spin gap (or pseudogap) arising in the underdoped HTSC's at higher temperatures such as $T^* \sim 180-200$ K has attracted much attention. If both gaps have the same *d* symmetry then there should be nodes along definite wave-vector directions, leading to a linear energy dependence of the density of states down to the Fermi energy. As a result, activated (exponential) freezing of normal excitations which is typical of conventional ''low-T_c'' *s*-wave superconductors should not occur in HTSC's, even at $T \ll T_c$. Instead, a moderate decrease of the normal carrier concentration is expected. This should be reflected in a corresponding behavior of the uniform spin susceptibility, χ^0, and spin-lattice relaxation rate, $(T_1)^{-1}$. In particular, theory[3–5] predicts a linear temperature dependence of χ^0 and a power law $T_1^{-1} \propto T^n$ with $n \approx 3$ for the relaxation rate at $T \ll T_c$.

The NMR relaxation measurements performed on $^{63,65}Cu$ and ^{17}O nuclei in both slightly overdoped $YBa_2Cu_3O_7$ and underdoped $YBa_2Cu_4O_8$ gave some evidence for *d*-wave pairing.[3,6] However, the nuclear spin-lattice relaxation rate at low temperatures may be influenced by localized paramagnetic centers that are frequently found in HTSC's.[7] So it would be of interest to repeat such experiments with electron paramagnetic resonance (EPR) and electron spin-lattice relaxation on electron-spin probes introduced in a HTSC material.

As a convenient electron-spin probe, a small concentration of isovalent Gd^{3+} ions (electron spin $S=7/2$) was used. The impurity ions substitute for Y^{3+} between two adjacent CuO_2 planes in YBaCuO compounds. The corresponding EPR spectra were reported in many papers starting in 1987 (see, for example, Refs. 8–12); among them, investigation of the EPR fine structure on a single crystal[10] and the analysis of the relaxation broadening in the normal state[11,12] are noteworthy. The temperature dependence of the Gd^{3+} EPR Knight shift, ^{Gd}K (proportional to χ^0), was measured recently[13,4] both on $Y_{0.99}Gd_{0.01}Ba_2Cu_3O_7$ and $Y_{0.99}Gd_{0.01}Ba_2Cu_4O_8$. The most accurate data were obtained in the latter case:[4] using EPR measurements at various frequencies (75–225 GHz), the diamagnetic contributions in the superconducting state were successfully subtracted. As a result, a linear temperature dependence of χ^0 was found between $10\text{ K} < T < 40\text{ K}$.

Attempts were also made to measure the Gd^{3+} spin-lattice relaxation time in the superconducting phase of YBaCuO type materials. The extremely short T_1 values present the main obstacle for such experiments and made it impossible to measure T_1 directly by standard pulse or cw methods. This difficulty has been overcome by using an original modulation technique with radio-frequency detection of the longitudinal component $M_z(t)$ of the spin magnetization.[14,15] This method [which is a version of the idea suggested by Hérve and Pescia as early as 1960 (Ref. 16)] enables one to measure directly electron T_1 values as short as $10^{-7}-10^{-10}$ sec. Experiments[17] performed on the underdoped $Y_{0.99}Gd_{0.01}Ba_2Cu_3O_{6+x}$ samples (at $x=0.59$ and 0.95) revealed the spin gap opening at 180–200 K; however, at $T \ll T_c$, the temperature dependence of T_1 was affected by some nonsuperconducting phase.

Unlike $YBa_2Cu_3O_{6+x}$, the underdoped $YBa_2Cu_4O_8$ (Y124) system is known as a stoichiometric and stable compound; it often serves as a reference high-T_c material for the most precise and fundamental experiments. In this paper, this material was chosen to obtain information on the electron

spin-lattice relaxation of the Gd^{3+} impurity ions at $T<T_c$. This information is then related to the published data on the EPR Knight shift in the same material,[4] and a conclusion is made concerning the symmetry of superconduction pairing.

Three Y124 samples doped with 1% Gd were used in our experiments. Two of them (hereafter referred as 01 and 02; $T_c=82$ K) were powders magnetically aligned along the crystallographic c axis and embedded in epoxy resin. The sample 01 was prepared by G. Böttger and M. Guttmann (ETH Zurich, Switzerland); the preparation technology together with some T_1 data are described in Ref. 17. The sample 02 was fabricated by G. V. M. Williams (New Zealand Institute for Industrial Research and Development, Lower Hutt, New Zealand); this was exactly the same sample as used previously for precise $^{Gd}K(T)$ measurements.[4] The third sample (03) was an untwinned single crystal with a surface of about 1 mm^2; it was prepared by the flux flow method under 600 bar oxygen pressure at 1100 °C at Northern Illinois University. $T_c=80$ K and a 10–90 % transition width of 1.5 K was measured by ac susceptibility. All the samples were tested by x rays and showed good single-phase characteristics.

The T_1 experiments were carried out on the 01 and 02 samples with the external magnetic field $\mathbf{B}_0$ directed along the c axis. The homemade X-band apparatus (microwave frequency $\omega/2\pi=9.4$ GHz) employs a microwave power modulation technique[14,15] with longitudinal detection of $M_z(t)$ at modulation frequency $\Omega\sim10^7$ rad/sec. The ''phase'' operation mode was used: the T_1 value of interest was found from the phase lag of the longitudinal magnetization response relative to the modulation voltage. T_1 is obtained from the following relation:[14,15]

$$\frac{V}{U}=\Omega T_1, \tag{1}$$

where U and V are, respectively, the in-phase and out-of-phase components of the longitudinal magnetization response relative to the modulation wave form. An appropriate data averaging and computer processing were used to record the rather weak longitudinal signals. To check the reliability of the obtained data, some measurements were repeated at two different modulation frequencies, $\Omega/2\pi=1.65$ MHz and 370 kHz; in both cases, the same T_1 values were found within the experimental error (~20%).

The 03 sample was used to perform accurate measurements of the Gd^{3+} EPR linewidth, thus providing independent information on the electron-spin relaxation. These measurements were carried out at $\omega/2\pi=225.0$ GHz using standard audio modulation detection. Since penetration depth is small, signals were averaged for a few hours at each temperature.

The three central fine-structure lines of the crystal-field split Gd^{+3} EPR spectrum of sample 03 at $\omega/2\pi=225.0$ GHz, $\mathbf{B}_0\|c$, and $T=50$ K are shown in Fig. 1. In the following we will focus only on two central lines (the $-\frac{1}{2}\rightarrow+\frac{1}{2}$ and $\frac{1}{2}\rightarrow\frac{3}{2}$ transitions) which were measured between 40 and 65 K. (At higher temperatures, the fine structure begins to collapse due to exchange interaction with delocalized charge carriers, in agreement with the Barnes-Plefka mechanism[18]). A more detailed account of the single-crystal work will be published elsewhere.[19]

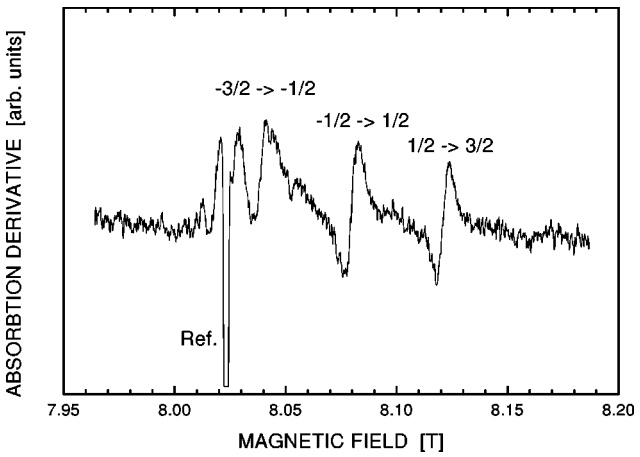

FIG. 1. Three central EPR transitions of the Gd^{3+} fine structure of an $Y(Gd)Ba_2Cu_4O_8$ single crystal at 225.0 GHz and 50 K. The absorption derivative of the Gd^{3+} EPR lines is shown. Ref. denotes a field reference free radical.

At $\omega/2\pi=9.4$ GHz, however, some EPR lines belonging to a nonsuperconducting phase[17] with relatively slow spin-lattice relaxation overlap the central EPR transition of the Gd^{3+} spectrum. This makes it impossible to perform appropriate T_1 measurements on the $\frac{1}{2}\rightarrow-\frac{1}{2}$ transition below T_c. Instead, we carried out the modulation experiments on two fine-structure satellites corresponding to the $\pm\frac{3}{2}\rightarrow\pm\frac{5}{2}$ transitions observed (at X band) at $B_0=0.18$ and 0.4 T, respectively. Below T_c, these satellites were resolved well enough to allow accurate measurements of the in-phase and out-of-phase components of the longitudinal magnetization response at the modulation frequency.

It should be emphasized that the technique employed[14,15] measures the relaxation of the total longitudinal spin magnetization $M_z(t)$, regardless of what particular EPR transition is excited by the modulated microwave power. In the case of a fine structure ($S>\frac{1}{2}$) and under the condition that the partial relaxation probabilities W_{ij} are governed by the magnetic selection rules

$$W_{ij}\propto S(S+1)-m(m+1), \tag{2}$$

(where i, j are energy levels with magnetic quantum numbers m, $m+1$), it can be shown that the evolution of $M_z(t)$ is determined by a single characteristic time T_1 which is just the same as for the case $S=\frac{1}{2}$. This conclusion can be proved by analysis of the corresponding rate equations (for instance, the coupled local-moment-conduction-electron Bloch equations, as shown in Ref. 20).

For comparison of the T_1 data obtained by the longitudinal detection with those determined from the EPR linewidth, it is significant that the partial relaxation probabilities W_{ij} in the multilevel Gd^{3+} energy spectrum obey the magnetic dipolar selection rules, Eq. (2). In such a case, as shown in Refs. 18 and 20, the relaxational broadening of the EPR fine-structure lines from $m=-\frac{7}{2}$ to $+\frac{5}{2}$ are consecutively (for $S=\frac{7}{2}$):

$$7:12:15:16:15:12:7, \tag{3}$$

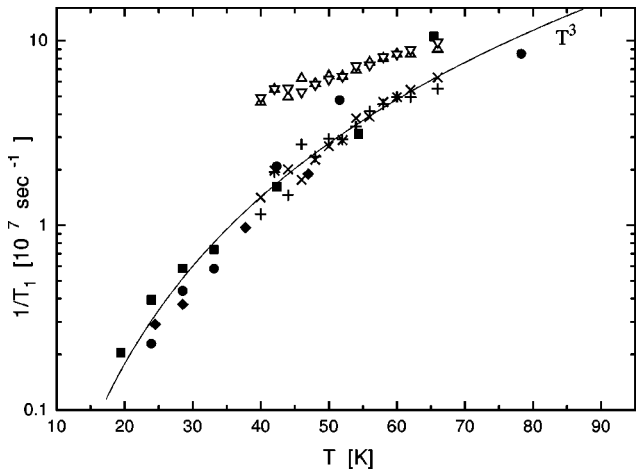

FIG. 2. Temperature dependence of the Gd^{3+} spin-lattice relaxation rate in $Y_{0.99}Gd_{0.01}Ba_2Cu_4O_8$. Data obtained by the modulation technique, Eq. (1) (filled symbols): sample 01, $B_0=0.18$ T (squares); sample 02, $B_0=0.18$ T (circles), $B_0=0.4$ T (diamonds). Data obtained from the EPR line width, Eq. (5) (sample 03): assuming $\Delta B^0=0$: $\pm\frac{1}{2}$ transition (up triangles), $\frac{1}{2}\rightarrow\frac{3}{2}$ transition (down triangles); assuming $\Delta B^0=3.2$ mT: $\pm\frac{1}{2}$ transition (+), $\frac{1}{2}\rightarrow\frac{3}{2}$ transition ($\times$). The solid curve represents Eq. (4) with the best fit parameters reported in the text.

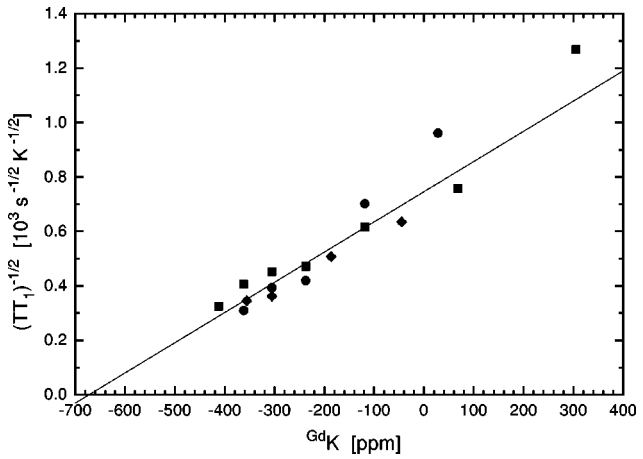

FIG. 3. Square root of the normalized Gd^{3+} spin-lattice relaxation rate as a function of the EPR Knight shift in $Y_{0.99}Gd_{0.01}Ba_2Cu_4O_8$. The symbols are the same as in Fig. 2. The Knight shifts are measured (Ref. 4) on sample 02. The straight line represents the best-fit linear approximation (see the text).

where T_1^{-1}, the relaxation rate of the total longitudinal spin magnetization, is taken as unity.[20]

The temperature dependence of T_1^{-1} in the 01 and 02 samples is shown in Fig. 2. It is seen that the data obtained on both samples and both fine-structure satellites fall on the same curve which can be well fitted by the power law

$$T_1^{-1}=AT^n \tag{4}$$

with $n=3.0\pm0.3$ and $A=(220\pm20)$ $s^{-1}K^{-3}$. As mentioned above, this is consistent with the predictions based on the *d*-wave pairing.

These T_1 data can be compared with those extracted from the temperature dependence of the EPR linewidth. Taking into account Eq. (3) and assuming a Lorentzian line shape, one has

$$RT_1^{-1}=\gamma(\Delta B-\Delta B^0), \tag{5}$$

where $R=16$ and 15 for the $-\frac{1}{2}\rightarrow+\frac{1}{2}$ and $\frac{1}{2}\rightarrow\frac{3}{2}$ EPR transitions, respectively; γ is the magnetogyric ratio; ΔB is the measured half-width at half-amplitude; and ΔB^0 is a temperature-independent contribution to the linewidth due to dipole-dipole interactions and inhomogeneous broadening.

For a most accurate comparison, the temperature dependence of ΔB was measured on the single crystal (03) sample, at 225 GHz, on both $\pm\frac{1}{2}$ and $\frac{1}{2}\rightarrow\frac{3}{2}$ EPR lines. A limited temperature range could only be used (40–65 K); at higher temperatures, the relaxation collapse begins to distort the EPR line, whereas at $T<40$ K irreversible diamagnetic effects cannot be ignored. The results are plotted in the same Fig. 2, both with and without the correction, ΔB^0, for an inhomogeneous contribution in Eq. (5). As seen, without the subtraction of ΔB^0, the relaxation data obtained from the linewidths are found to be of the same order of magnitude as the directly determined T_1^{-1} values, but lie a bit higher and demonstrate weaker temperature dependence. Assuming $\Delta B^0=3.2$ mT and using Eq. (5), the relaxation rates obtained from the linewidths are in excellent agreement with the T_1^{-1} data obtained directly with the modulation technique. Note that the Gd-Gd dipolar broadening in our samples is[21] about 1.5 mT, and the remainder can be readily attributed to inhomogeneous sources such as magnetic vortices, etc. Also, the suppression of T_c by a few K in the 8 T field of the 225 GHz EPR results in a small difference between the two measurements of T_1.

A much-debated question[3,22,23] in magnetic resonance studies of HTSC's is whether the spin-lattice relaxation time and the Knight shift satisfy the Korringa relation

$$T_1TK_{\rm spin}^2=\kappa\frac{\hbar}{4\pi k_B}\left(\frac{\gamma_e}{\gamma_s}\right)^2, \tag{6}$$

where $K_{\rm spin}$ is the spin part of the Knight shift; k_B is the Boltzman constant; γ_e and γ_s are, respectively, the gyromagnetic factors of the delocalized spins of charge carriers and of the localized spin species under investigation; and κ is a factor close to unity ($\kappa=1$ within the free-electron model). In our case, both γ_e and γ_s are related to electron spins, so one can suppose $\gamma_e/\gamma_s=1$. Equation (6) can be rewritten as

$$\sqrt{(TT_1)^{-1}}=\left(\frac{C}{\sqrt{\kappa}}\right)(^{\rm Gd}K-^{\rm Gd}K_0), \tag{7}$$

where $^{\rm Gd}K$ is the measured Gd^{3+} EPR Knight shift; $^{\rm Gd}K_0$ is its orbital part determined as the $^{\rm Gd}K$ value extrapolated to zero temperature; and C is the appropriate combination of the fundamental constants.

The plot of $(TT_1)^{-1/2}$ against $^{\rm Gd}K$ is shown in Fig. 3 (the $^{\rm Gd}K$ values were measured[4] on the 02 sample). The linear relation predicted by Eq. (7) is clearly satisfied. The best fit to the Korringa relation is achieved for $^{\rm Gd}K_0=-672$ ppm (this value is close to that estimated in Ref. 4) and $\kappa=1.34$. Thus, the electronic system behaves like a Fermi liquid, at least far away from the antiferromagnetic wave

vector (note that antiferromagnetic fluctuations of planar copper are cancelled at the Y^{3+} position occupied by the Gd^{3+} ions). Bankay *et al.*[3] concluded that planar ^{17}O and ^{63}Cu in $YBa_2Cu_4O_8$ obey a Korringa law with $\kappa = 1.34$ although, as they remark, the result is sensitive to the choice of K_0. On the other hand, Alloul *et al.*[23] and Takigawa *et al.*[22] argued that at the ^{89}Y site (at least above T_c in the $YBa_2Cu_3O_{6+x}$ materials) the Korringa law is not obeyed but rather the product T_1TK_{spin} is constant.

In conclusion, the Gd^{3+} spin-lattice relaxation has been investigated in the superconducting state of $Y_{0.99}Gd_{0.01}Ba_2Cu_4O_8$. The directly measured relaxation time of the total longitudinal magnetization is shown to be in accord with the theoretically predicted[18] relaxational broadening of the fine-structure transitions. A nearly cubic power temperature dependence of the relaxation rate is found at $T < 60$ K; this is consistent with the previous Knight-shift data[4] and supports the idea of *d*-wave pairing. Proportionality between $(TT_1)^{-1/2}$ and $^{Gd}K_{spin}$ is very well satisfied suggesting the validity of the Korringa relation and Fermi liquid model, at least at low temperatures for the Y sites that are not sensitive to the antiferromagnetic correlations.

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