# Effect of superconductivity on spin dynamics in $(Y_{1-x}R_x)Rh_4B_4$

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(Received 12 October 1982)

An adiabatic—field-cycle method for $^{11}B$ nuclear magnetic relaxation has been used to study the spin dynamics of rare-earth ions in dilute $(Y_{1-x}R_x)Rh_4B_4$. Longitudinal dipolar fluctuations of rare-earth moments are found to be the main source for the spin-lattice relaxation time of $^{11}B$. The variation of $T_1$ in the superconducting state is attributed to the reduction of the electronic spin-relaxation time $\tau_m$, which is mainly determined by the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction mediated by the conduction electrons. The remarkable reduction of the RKKY coupling below $T_c$ is discussed in connection with the reduction of the conduction-electron spin susceptibility $X(q)$.

## I. INTRODUCTION

Since the discovery of reentrant superconductivity in $ErRh_4B_4$ (Ref. 1) and $HoMo_6S_8$ (Ref. 2) there have been numerous experimental and theoretical investigations on the interaction of superconductivity and magnetism in ternary compounds.[3] The origin of magnetism in these compounds is associated with the unfilled $4f$ electron shell of the rare-earth ions, and the interaction between localized moments is thought to be due to the indirect Ruderman-Kittel-Kasuya-Yosida (RKKY)[4] interaction mediated by the conduction electrons. Since one expects a reduction of the electron spin susceptibility $X(q)$ in the superconducting state, the indirect RKKY interaction will be modified by superconductivity. Such an effect may be responsible for the depression of $T_M$ in the reentrant regions of $ErRh_4B_4$ and in $(Lu_{1-x}R_x)Rh_4B_4$ ($R$ represents Ho and Er).[5]

In this paper we report on the spin dynamics of rare-earth ions measured with the $^{11}B$ nuclear magnetic relaxation in dilute $(Y_{1-x}R_x)Rh_4B_4$ ($R$ represents Gd and Er). Because of the relatively small $s$-$f$ exchange coupling and the small hyperfine coupling of $^{11}B$ in those compounds, the relaxation time for small $x$ is long enough to study the relaxation behavior in low applied fields with an adiabatic demagnetization-remagnetization field-cycle method.[6] Since the nuclear relaxation is found to be dominated by the fluctuations of the local dipole fields due to the localized rare-earth moments, we are able to follow the detailed magnetic field and temperature dependence of the local-moment spin-correlation times in the normal and superconducting states. Thus detailed information is obtained about the indirect coupling of the local moments, i.e., the

nonlocal susceptibility, in the superconducting state. Such information is critically important for a complete understanding of magnetic superconductors.

## II. EXPERIMENTAL PROCEDURE

### A. Sample preparation

The $Y_{1-x}R_xRh_4B_4$ samples were prepared by arc-melting stoichiometric quantities of the constituent elements. The starting materials had the following purities: Rh, 99.95 at. %; B, 99.0 at. %; Y, 99.98 at. %; Gd, 99.9 at. %; Er, 99.9 at. %. The concentration of the rare-earth atoms was between $x = 0.0002$ and $0.005$. The arc-melted buttons were wrapped in Ta foil and homogenized at 1100 °C under an argon atmosphere for five days. Samples for both x-ray analysis and NMR measurement were crushed and passed through a 325-mesh sieve. The x-ray diffraction investigation indicated that the samples contained the primitive tetragonal structure[7] and were close to single phase.

Superconducting transition temperatures $T_c$ have been measured on the samples used for NMR studies. These measurements were made using a low-frequency mutual inductance bridge. Upper critical fields $H_{c2}$ were also measured in a superconducting magnet. The results of these measurements are summarized in Table I. Dilute concentrations of the magnetic rare-earth atoms have very little effect on $T_c$ and $H_{c2}$.

### B. NMR measurements

NMR measurements were made with a pulsed phase-coherent spectrometer at a frequency of 12 MHz. Because $^{11}B$ has large NMR signals and long

TABLE I. Superconducting transition temperatures.

| $T_c$ $(H)$ | $LuRh_4B_4$ | $YRh_4B_4$ | $(Y_{1-x}Gd_x)Rh_4B_4$ | | | $(Y_{1-x}Er_x)Rh_4B_4$ | |
|---|---|---|---|---|---|---|---|
| | | | 0.0002 | 0.002 | 0.005 | 0.0002 | 0.002 |
| $T_c$ (0) | 10.85 | 10.45 | 10.38 | 10.36 | 10.34 | 10.42 | 10.40 |
| $T_c$ (8.8 kOe) | | | | | 7.27 | 7.44 | 7.51 |

($\sim$sec) spin-lattice relaxation times $T_1$, we have used an adiabatic demagnetization and remagnetization cycle to study the relaxation behavior in various external fields. For a $T_1$ measurement in low field, the procedure allows the nuclear-spin system to come to thermal equilibrium at high field $\sim 8.8$ kOe in a superconducting solenoid. The field is then cycled to a low field in a few msec. The time at low field is the independent parameter to be varied. The field is then cycled back to the original high field in about 110 msec and the nuclear magnetization decay is measured with the spin-echo signal of $^{11}B$ using a $\frac{1}{2}\pi$-$\pi$ pulse sequence. We have also measured $T_1$ in high field with the field-cycle method. In this case, the field is kept at zero field for a long time compared to $T_1$ and then cycled quickly to high field. The nuclear magnetization recovery is measured with a $\frac{1}{2}\pi$-$\pi$ pulse sequence as a function of time at high field.

The field-cycle method has several advantages for the measurement of $T_1$. First, $T_1$ can be measured in various magnetic fields which include the mixed and normal state, and enable us to sample different parts of the spectral density of the local-moment fluctuations. Second, we do not suffer from the difficult analyses required in determining $T_1$ under an incomplete saturation condition that occurs in the presence of a strong quadrupolar coupling. In strongly quadrupolar-broadened NMR spectra the saturation of the entire powder-pattern line profile is difficult with the pulse-train method. The recovery curve of the nuclear magnetization does not show single exponential behavior for the $^{11}B$ $(I = \frac{3}{2})$ under an incomplete saturation condition. With the field-cycle method, a unique initial spin temperature is established at high and low fields. Therefore, we can obtain accurate values of $T_1$ even in the compounds doped with magnetic ions.

## III. RESULTS AND ANALYSES

### A. Nuclear relaxation in undoped compounds

In the undoped $YRh_4B_4$ and $LuRh_4B_4$ the magnetization recovery curves show the existence of a fast component of the relaxation. As it will be ex-

plained later, this component has an $\exp[-(t/\tau_1)^{1/2}]$ dependence and is indicative of the presence of the equivalent of about 25 ppm of Gd paramagnetic impurities. The intrinsic behavior was analyzed using the long-time part of the recovery curve, which is well described with an $\exp(-t/T_1)$ relation.

Figure 1 shows the temperature dependence of $T_1$ of $^{11}B$ at 8.8 kOe and 300 Oe in $YRh_4B_4$ and $LuRh_4B_4$. In the normal state (above 10 K), $T_1^{-1}$ is proportional to temperature as expected for the Korringa relaxation in metals and alloys. The Korringa constant is found to be $T_1 T = 46$ sec K at 8.8 kOe for both $YRh_4B_4$ and $LuRh_4B_4$. The Korringa relaxation rate is given by
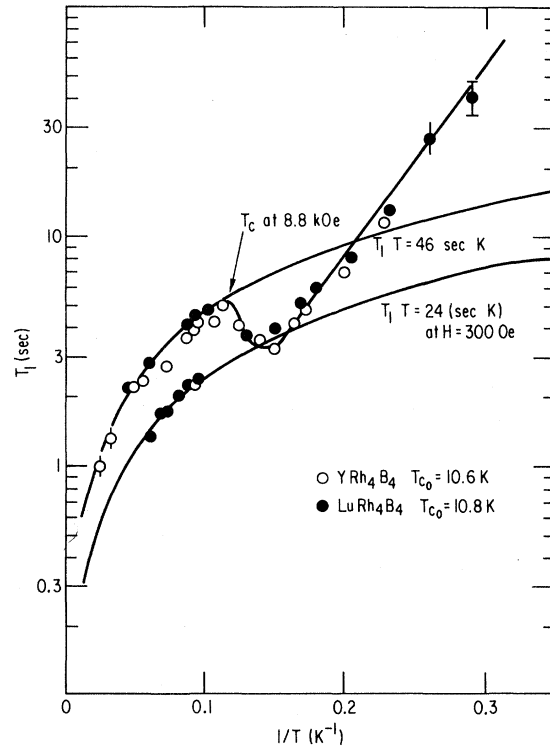


FIG. 1. Temperature dependence of nuclear relaxation time $T_1$ of $^{11}B$ in undoped samples. The arrow indicates the $T_c(H)$ at 8.8 kOe. The upper and lower data are obtained at 8.8 kOe and 300 Oe, respectively.

$$\frac{1}{(T_1)_K}=4\pi h\gamma_n^2 H_{hf}^2 N_s(0)^2 k_B T \ ,$$

where $\gamma_n$ is the nuclear gyromagnetic ratio, $H_{hf}$ is the hyperfine constant, and $N_s(0)$ is the density of states at the Fermi surface. Using the free-atom value of $H_{hf}=1.0\times10^6$ atom Oe/$\mu_B$,[8] we obtain $N_s(0)=0.02$ states/eV atom. The band-structure calculation[9] gives the density of states $N_b(0)\sim0.35$ state/eV atom. Therefore, the contribution of the 2s electrons to $N_b(0)$ at the B site is about 6% of the total density of states at the Fermi level.

$T_1$ obtained at high field (8.8 kOe) decreases just below the superconducting transition and then increases exponentially with decreasing temperature. This behavior of $T_1$ is in accordance with BCS theory. The superconducting energy gap is obtained for both compounds from $T_1^{-1}\propto\exp(-\Delta/k_B T)$ and found to be $2\Delta/k_B T_c=3.5\pm0.3$. This can be compared to the BCS value of $2\Delta(0)/k_B T_c=3.52$.

The [11]B nuclear-spin–lattice relaxation time was measured also at a field of 300 Oe. Because of the large nuclear electric quadrupolar interaction, a unique spin temperature and the adiabatic conditions could not be maintained for field cycles down to zero field. That is, as the Zeeman splitting of the $I=\frac{3}{2}$ manifold becomes small compared to the quadrupole splitting, the energy levels become unevenly split and the $\Delta m=\pm1$ spin flips become difficult. Thus the time to establish a common spin temperature becomes long at fields below 300 Oe. For this reason, we measured $T_1$ at external fields of 300 Oe or greater, i.e., $\gtrsim Hc_1$.

In the normal state the Korringa relaxation time for both YRh$_4$B$_4$ and LuRh$_4$B$_4$ at a field of 300 Oe is given by $T_1 T=24$ sec K, which is 52% of the high-field value. The low-field relaxation is given by the expression[10]

$$T_1(H)=\frac{H^2+H_D^2+H_Q^2}{H^2+2H_D^2+3H_Q^2}T_1(\infty) \ .$$

The dipolar field $H_D$ can be ignored compared to the quadrupolar field $H_Q$ in the compounds. Thus we obtain $H_Q=280$ Oe from the above relation, which is in good agreement with the results obtained from the NMR spectrum at high temperature.[11]

At low fields the Korringa relaxation time in the superconducting state becomes difficult to determine from the long-time part of the recovery curve because the magnetic contribution from a trace amount of impurities dominates the nuclear magnetic recovery in the superconducting state, as will be described later.
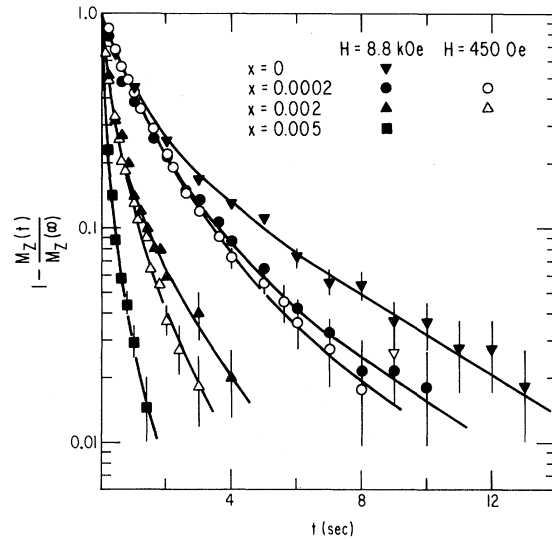


FIG. 2. Magnetization recovery curves as a function of time $t$ in the normal state ($T=11$ K) for various concentrations of $(Y_{1-x}Gd_x)Rh_4B_4$ at 8.8 kOe (closed symbols) and 450 Oe (open symbols).

## B. Nuclear relaxation due to the paramagnetic moments

The presence of paramagnetic rare-earth ions affects the resonance properties of [11]B in several ways. First, the time dependence of the magnetization recovery changes. Second, the relaxation due to the magnetic moments is characterized by a well-defined dependence on the impurity concentration $x$, magnetic field $H$, and temperature $T$. Third, the resonance line is observed to broaden and the signal intensity decreases at low temperature.

Figure 2 shows the magnetization recovery curves for various concentrations of $(Y_{1-x}Gd_x)Rh_4B_4$ at 11 K. The time dependence of the recovery curve is not described by single exponential relaxation. Similar results at various fields and temperatures have been obtained for doping with other rare-earth atoms.

The observed behavior of $M_z(t)$ results from the combination of host and impurity relaxation effects. The contribution from the magnetic moments can be separated from the host relaxation by assuming that the Korringa and impurity relaxation process are independent.[12] The paramagnetic ion-induced component of the [11]B recovery $P(t)$ is obtained as follows:

$$P(t)=\left[\frac{M_z(\infty)-M_z(t)}{M_z(\infty)-M_z(0)}\right]\exp\left[\frac{t}{(T_1)_K}\right] \ .$$

$P(t)$ of $(Y_{0.9998}Gd_{0.0002})Rh_4B_4$ is plotted semilogarithmically as a function of $\sqrt{t}$ in Fig. 3. $P(t)$ does
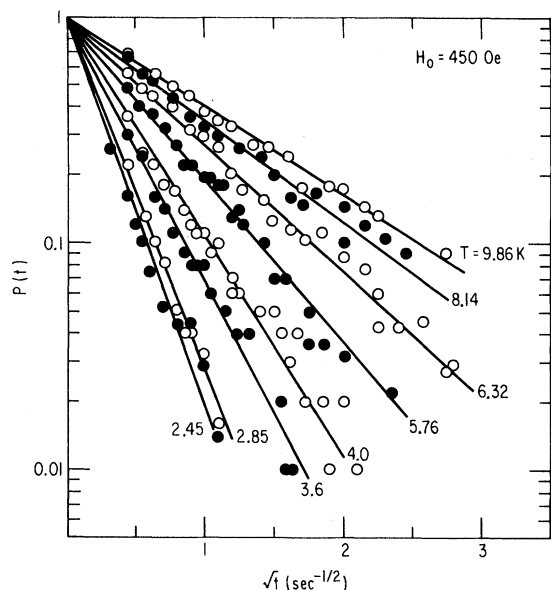
FIG. 3. Impurity component of the magnetization recovery $P(t)$ as a function of $\sqrt{t}$ in $(Y_{0.9998}Gd_{0.0002})Rh_4B_4$ at various temperatures.



FIG. 4. Temperature dependence of nuclear relaxation time due to the localized magnetic moments as a function of temperature in $(Y_{1-x}Gd_x)Rh_4B_4$.

not change exponentially against $t$, but has the form $\exp[-(t/\tau_1)^{1/2}]$. All the data obtained in various fields, temperatures, and concentrations have the same time dependence. We obtain the parameters $\tau_1$ from the slope of $t^{1/2}$ decay curves.

In many solids the nuclear-spin—nuclear-spin interaction is strong and energy in the nuclear-spin system can diffuse from one position to another by mutual nuclear-spin flips. However, in the case of $Y_{1-x}R_xRh_4B_4$-type compounds, the quadrupolar and the inhomogeneous magnetic-hyperfine interactions unequally split the energy levels of neighboring $^{11}B$ and thus tend to suppress mutual nuclear-spin flips and reduce spin diffusion. According to the analysis based on the diffusionless case,[12,13] $P(t)$ has the time dependence of the form

$$P(t) \propto \exp\left[ -\frac{t}{\tau_1} \right]^{1/2} ,$$

where $\tau_1^{-1}$ is given by $(\frac{4}{3}\pi^{3/2}N_0 x)^2 C$, $N_0$ is the density of rare-earth sites, $x$ is the concentration of the paramagnetic rare-earth atoms, and $C$ is the interaction strength which will be described later. The $\exp[-(t/\tau_1)^{1/2}]$ dependence of the magnetization recovery demonstrates the lack of spin diffusion between nuclear spins in the dilute $(Y_{1-x}R_x)Rh_4B_4$ compounds. This enables us to unambiguously separate the relaxation due to the paramagnetic moment from the Korringa relaxation process which has an $\exp[-(t/T_1)]$ dependence. Furthermore,
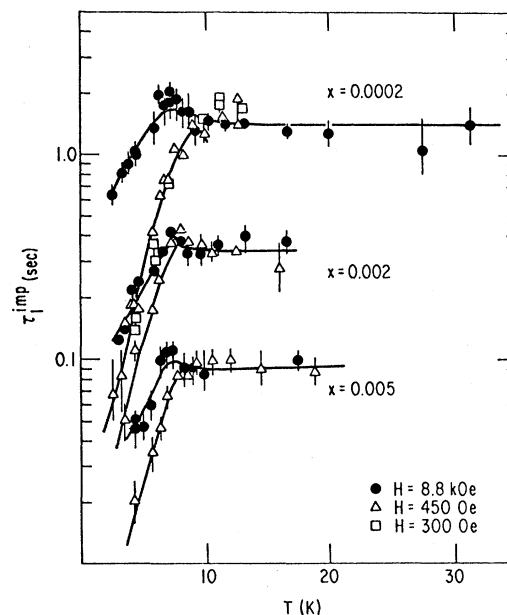
since $\tau_1$ is independent of the details of the spin-diffusion process the analysis of the data is simple.

We have measured the $^{11}B$ relaxation time $\tau_1$ as a function of $x$, $T$, and $H$. Figures 4 and 5 show the temperature dependence of $\tau_1$ for $(Y_{1-x}Gd_x)Rh_4B_4$ and $(Y_{1-x}Er_x)Rh_4B_4$, respectively. $\tau_1$ is indepen-
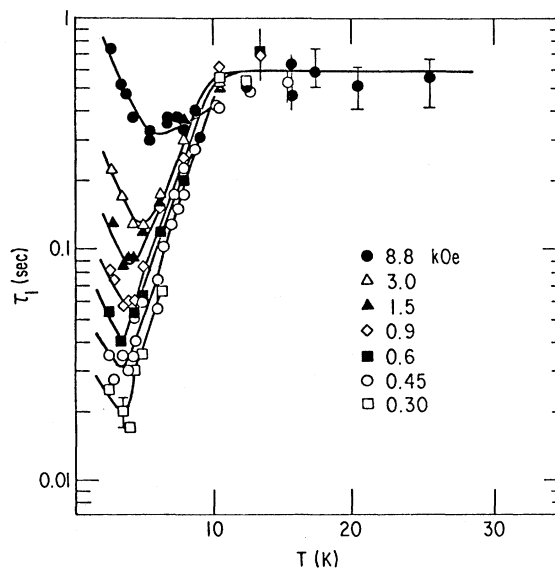


FIG. 5. Temperature dependence of nuclear relaxation time due to the localized magnetic moments as a function of temperature in $(Y_{1-x}Er_x)Rh_4B_4$.

dent of external field and temperature in the normal state and decreases with increasing concentration of the magnetic moments. In the superconducting state, $\tau_1$ of $(Y_{1-x}Gd_x)Rh_4B_4$ is strongly reduced with decreasing temperature and external field. In the case of $(Y_{1-x}Er_x)Rh_4B_4$, $\tau_1$ decreases at first and then increases with decreasing temperature in the superconducting state and is dependent on the external field. We would like to point out that $\tau_1$ is shorter for Er than for Gd for the same concentration. This indicates that the magnitude of $^{11}B$ nuclear relaxation rate is related to the value of the magnetic moment $(g_J J)$, not to the spin projection $(g_J - 1)J = S$, which implies that the local-moment—nuclear-moment interaction is dominated

by the dipolar interaction instead of the RKKY interaction.

There are various paramagnetic-induced relaxation mechanisms that contribute to nuclear relaxation. Paramagnetic impurity-induced relaxation mechanisms in metals have been reviewed by Giovannini et al.[14] Relaxation of the host nuclei can occur via any of the following processes: the longitudinal (LD) or the transverse (TD) fluctuations of the impurity dipole moment, the RKKY polarization of the conduction electrons discussed by Benoit et al. (BGS),[15] or the virtual scattering process discussed by Giovannini and Heeger (GH).[16] Expressions for the relaxation rates accompanying these processes are

$$\left[\frac{1}{T_1(r,\theta)}\right]_{LD} = \frac{1}{r^6}\left[9(\gamma_e\gamma_n h)^2 S^2 \frac{\partial B_s(X)}{\partial X}\frac{\tau_{m1}}{1+(\omega_n\tau_{m1})^2}\right]\sin^2\theta\cos^2\theta \ ,$$

$$\left[\frac{1}{T_1(r,\theta)}\right]_{TD} = \frac{1}{r^6}\left[\tfrac{1}{2}(\gamma_e\gamma_n h)^2 S^2 \frac{B_s(X)}{X}\frac{\tau_{m2}}{1+(\omega_e\tau_{m2})^2}\right][(1-3\cos^2\theta)^2+9\sin^4\theta] \ ,$$

$$\left[\frac{1}{T_1(r)}\right]_{BGS} = \frac{1}{r^6}\left[\left[\frac{2\pi A \mathscr{J} N^2(E_F)}{hk_F^3}E_F\right]^2 S^2\frac{B_s(X)}{X}\frac{\tau_{m2}}{1+(\omega_e\tau_{m2})^2}\right] \ ,$$

$$\left[\frac{1}{T_1(r)}\right]_{GH} = \frac{1}{r^5}\left[\left[\frac{2\pi A \mathscr{J} N^2(E_F)}{hk_F^3}E_F\right]^2 S^2\frac{B_s(X)}{X}\frac{hk_F}{E_F}\right] \ .$$

Here $\tau_{m1}$ and $\tau_{m2}$ are the longitudinal and transverse paramagnetic impurity relaxation times, respectively, $\omega_n$ and $\omega_e$ are the host nuclear and rare-earth electronic resonance frequencies, respectively, $\gamma_n$ and $\gamma_e$ are the corresponding gyromagnetic ratios, $A$ is the host hyperfine-coupling constant, $\mathscr{J}$ is the conduction-electron—$4f$-electron exchange, $B$ is the Brillouin function $X \sim H/T$, and $r$ and $\theta$ are defined by the paramagnetic moment to the nuclear-moment vector relative to the magnetic field direction.

The order of magnitude of the relaxation rate from the various processes can be estimated using the parameters given in Table II. From the inspection of the relaxation rate it is obvious that the LD and TD mechanism will be stronger than the BGS and GH mechanism because of the small $s$-$f$ exchange interaction $N(E_F)\mathscr{J}$ found in the rhodium borides and small hyperfine constant of $^{11}B$.

For the TD mechanism, $(\omega_e\tau_{m2})^{-2}$ factor is dominant in the case of $\omega_e \gg \tau_{m2}^{-1}$. ($\omega_e$ is larger than $\omega_n$ by $\sim 10^3$.) In this case, the relaxation rate should have an $H^{-2}$ field dependence ($\omega_e \propto H$) and greatly reduced relaxation rate in a large magnetic field. The absence of field dependence of the relaxation

rate in the normal state is inconsistent with the TD mechanism. Therefore, we can conclude that the LD mechanism is the dominant relaxation process in the rare-earth-doped $YRh_4B_4$ compounds. The same mechanism has been found to be important in host nuclear relaxation in $La(Gd)Al_2$ (Ref. 12), $La_3(Gd)Al$ (Ref. 17), and $La(Gd)X_3$ ($X=$ In, Sn, and Pb).[18]

In order to take into account the temperature and field dependence of the derivative of the Brillouin function in the LD equation, we define $\tau_0$ by

$$\frac{1}{\tau_1} = \frac{1}{\tau_0}\frac{\partial B(X)}{\partial X}$$

and obtain $\tau_0$ for the LD mechanism,[12]

$$\left[\frac{1}{\tau_0}\right]_{LD} = \frac{16}{9}\pi^3(\gamma_n g_J \mu_B J N_0 x)^2\frac{\tau_m}{1+(\omega_n\tau_m)^2}$$

$$\equiv Cx^2\frac{\tau_m}{1+(\omega_n\tau_m)^2} \ .$$

A powder average was taken and $g_J$ and $J$ are the Landé $g$ factor and total angular momentum of the paramagnetic ion, respectively. (Note we have dropped the subscript 1 on the longitudinal relaxa-

TABLE II. Characteristic parameters for $(Y_{1-x}R_x)Rh_4B_4$.

| Rare-earth atom density[a] | $N_0 = 9.47 \times 10^{21}$ | $cm^{-3}$ |
|---|---|---|
| Fermi momentum[b] | $k_F = 1.61 \times 10^8$ | $(cm)^{-1}$ |
| Fermi energy[b] | $\epsilon_F = 9.9$ | (eV) |
| Density of states at the Fermi level[c] | $N(0) = 0.35$ | (states/eV atom) |
| [11]B nuclear gyromagnetic ratio | $\gamma_n = 8.59 \times 10^3$ | $(sec\ Oe)^{-1}$ |
| Gd electric gyromagnetic ratio | $\gamma^{Gd} = 1.76 \times 10^7$ | $(sec\ Oe)^{-1}$ |
| Hyperfine constant[d] | $A = 1.0 \times 10^6$ | $(Oe/\mu_B)$ |

[a]Reference 7.
[b]From the free-electron model assuming $z$ equals three electrons.
[c]Reference 9.
[d]Reference 8.

tion time $\tau_m$ of the local moment.) Throughout the remainder of this paper it is to be understood that $\tau_m \equiv \tau_{m1}$.

With the parameters in Table II, the constant $C$ is determined to be $1.52 \times 10^{15}$ and $2.54 \times 10^{15}$ for $(Y_{1-x}Gd_x)Rh_4B_4$ and $(Y_{1-x}Er_x)Rh_4B_4$, respectively. $C$ will also be checked experimentally in the analysis of the field and temperature dependence of $\tau_0$ in the superconducting state, which will be described in the next section.

By assuming the values of $\partial B(X)/\partial X$ given by the free-ion model, the experimental values of $\tau_0$ are calculated from the data of $\tau_1$ for each compound. For the case of the Er as well as the other $L \neq 0$ rare

earths, a full crystal-field treatment will be given in a planned forthcoming paper. The temperature dependence of $\tau_0$ with various fields in $(Y_{1-x}Gd_x)Rh_4B_4$ and $(Y_{1-x}Er_x)Rh_4B_4$ are shown in Figs. 6 and 7, respectively. Because of the small variation of $\partial B(X)/\partial X$ for the temperatures and fields measured, the essential features of the temperature and field dependence of $\tau_0$ are similar to the behavior of $\tau_1$. The concentration dependence of $\tau_0$ in the normal state is shown in Fig. 8. $\tau_0^{-1}$ is proportional to the concentration of the rare-earth moments and is equal to. $4.4 \times 10^3 x$ and $2.5 \times 10^4 x$ for $(Y_{1-x}Gd_x)Rh_4B_4$ and $(Y_{1-x}Er_x)Rh_4B_4$, respectively.
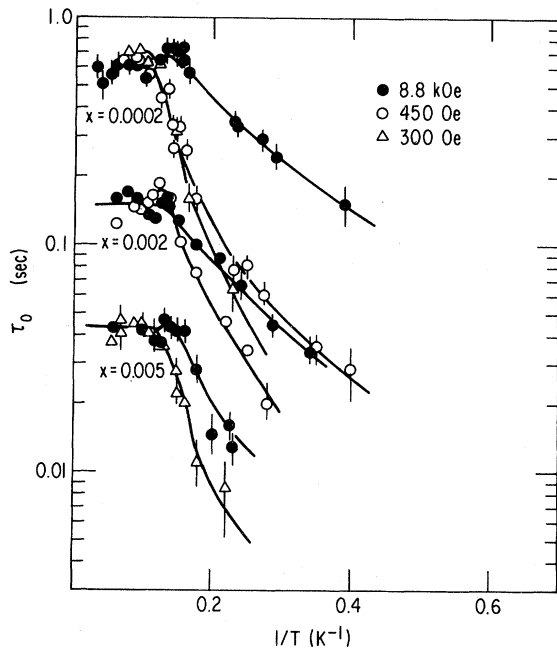


FIG. 6. Nuclear relaxation time due to the longitudinal dipolar fluctuations $\tau_0$ as a function of reciprocal temperature in $(Y_{1-x}Gd_x)Rh_4B_4$.
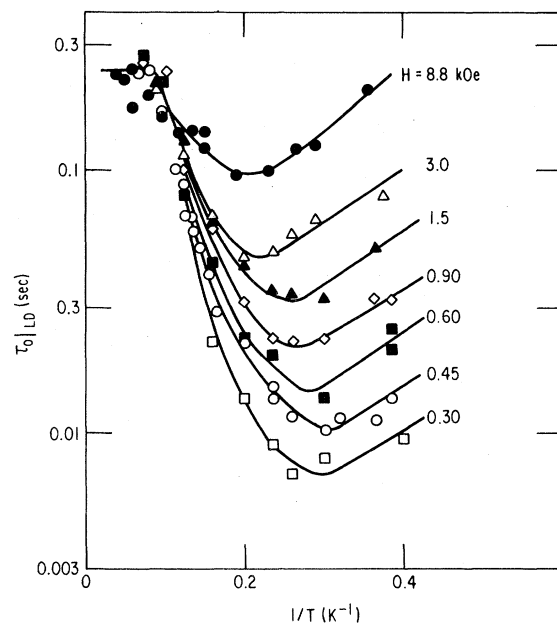


FIG. 7. Nuclear relaxation time due to the longitudinal dipolar fluctuations $\tau_0|_{LD}$ as a function of reciprocal temperature in $(Y_{1-x}Er_x)Rh_4B_4$.
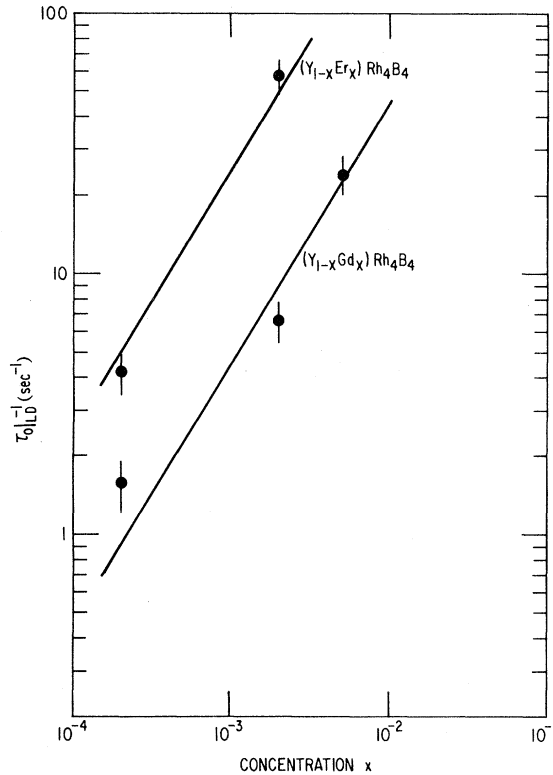
FIG. 8. Concentration dependence of $\tau_0 |_{\rm LD}^{-1}$ in the normal state.

## C. Spin dynamics

We obtain the field and temperature dependence of $\tau_m^{-1}$ from the experimental results by inverting the equation for $\tau_0^{-1}$. As can be seen in Figs. 6 and 7, $\tau_0$ is independent of temperature and field in the normal state. In the superconducting state, $\tau_0$ decreases monotonically with decreasing temperature in $(Y_{1-x}Gd_x)RhA_4B_4$, while $\tau_0$ of $(Y_{1-x}Er_x)Rh_4B_4$ decreases and then increases with decreasing temperature. The different behavior of $\tau_0$ with temperature between the two systems can be understood if $\tau_m^{-1}$ decreases drastically in the superconducting state. In the normal state of $(Y_{0.9998}Er_{0.0002})Rh_4B_4$ the electronic relaxation rate $\tau_m^{-1}$ is larger than the magnitude of the nuclear Larmor frequency $\omega_n$. $\tau_m^{-1}$ decreases below $T_c$ such that $\tau_m^{-1}$ becomes equal to $\omega_n$ at the temperature of the minimum of $\tau_0$. Further decreases of temperature yield $\omega_n\tau_m \gg 1$, and $\tau_0$ increases as $\tau_0 \propto \omega_n^2\tau_m$. The field dependence of $\tau_0$ in the superconducting state comes primarily from the $\omega_n^2$ $(\propto H^2)$ factor.

On the contrary, $\tau_m^{-1}$ of $(Y_{1-x}Gd_x)Rh_4B_4$ is rather large compared to that in the Er-doped com-

pound. $\tau_m^{-1} \gg \omega_n$ is satisfied even at the highest field (8.8 kOe) in the entire temperature range measured. Since $\tau_0^{-1}$ is proportional to $\tau_m$ in the case of $\omega_n\tau_n \ll 1$, $\tau_0$ decreases monotonically with decreasing $\tau_m^{-1}$ in the superconducting state.

As the minimum position of $\tau_0$ corresponds to the condition $\tau_m^{-1} = \omega_n$, we can determine experimentally the constant of $C$ to be $1/x^2(2\omega_n/\tau_0)$. The values of $C$ are calculated to be $3.0\times10^{15}$, $4.3\times10^{15}$, and $6.6\times10^{15}$ in units of $\sec^{-2}$ at $H_0=300$ Oe to 1.5, 3, and 8.8 kOe, respectively, for $x_{\rm Er}=0.0002$. The value of $3.0\times10^{15}$ at low field is in good agreement with the calculated value obtained using the parameters in Table II. We would like to emphasize again that the LD mechanism is found to be dominant in $(Y_{1-x}Er_x)Rh_4B_4$ from the analysis of the field and temperature dependence of $\tau_0$.

The change of $C$ with field in $(Y_{1-x}Er_x)Rh_4B_4$ may be attributed to the anisotropic nature of Er atoms. We have calculated $\tau_0$ with $\partial B(X)/\partial X$ for the isotropic free-ion model. However, this is only a valid approximation for the case of an $S$-state ion such as Gd. Er has an orbital angular momentum which can couple to the crystalline electric field (CEF) to produce anisotropy in the magnetization for these tetragonal compounds. Highly anisotropic magnetization has been found in $ErRh_4B_4$. The effect of the crystalline field should be taken into account in calculating $\partial B(X)/\partial X$ and in averaging the angular functions in the LD equation. The details of the effects of CEF will be discussed in a planned second paper dealing with the spin dynamics of Pr-, Nd-, Sm-, Tb-, Dy-, Ho-, Er-, and Tm-doped $YRh_4B_4$.

The coupling constant $C$ for the LD mechanism is proportional to $(g_JJ)^2$. The constant $C$ for $(Y_{1-x}Gd_x)Rh_4B_4$ is obtained from the ratio of $[(g_JJ)^{\rm Gd}/(g_JJ)^{\rm Er}]^2C^{\rm Er}$ and is found to be $1.8\times10^{15}$ $\sec^{-2}$ where we have used $C^{\rm Er}=3.0\times10^{15}$ $\sec^{-2}$.

We have calculated the electronic relaxation times $\tau_m$ for both the Er-doped and Gd-doped compounds. Figure 9 shows the temperature dependence of $\tau_m$ for various fields in $(Y_{1-x}Gd_x)Rh_4B_4$ and $(Y_{1-x}Er_x)Rh_4B_4$ $(X=0.0002)$. In the normal state, $\tau_m^{-1}$ is independent of temperature and field and is proportional to the concentration of the magnetic ions. $\tau_m^{-1}$ decreases remarkably with decreasing temperature in the superconducting state. A field dependence of $\tau_m$ is also found in both systems. The strong suppression of $\tau_m$ in the superconducting state is the most striking result in the present investigation.

For dilute paramagnetic moments in the normal metallic state two electronic spin-relaxation mechanisms are usually operative. One is the relaxation mechanism arising from the $s$-$f$ exchange interac-
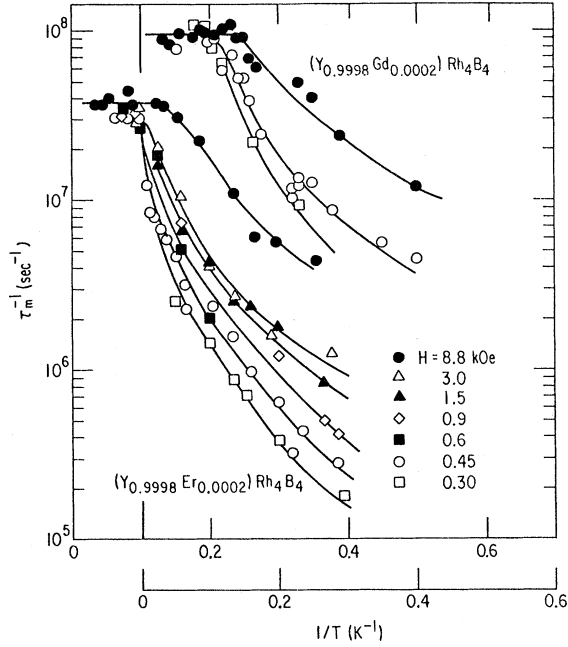
FIG. 9. Longitudinal relaxation rate $\tau_m^{-1}$ of the local moment as a function of reciprocal temperature for $(Y_{0.9998}Gd_{0.0002})Rh_4B_4$ and $(Y_{0.9998}Er_{0.0002})Rh_4B_4$ at various external fields. Note shifted reciprocal temperature axis for the Gd-doped compounds.

tion $\mathscr{J}$ between the localized moment and the conduction electrons.[19] This Korringa relaxation rate is given by

$$\left[\frac{1}{\tau_m}\right]_K = \frac{\pi}{h}[\mathscr{J}N(0)]^2 k_B T \ ,$$

which is linear in temperature and independent of concentration of the localized moment. The other mechanism is due to the spin-spin interaction, which is usually dominated by the RKKY interaction between spins,[12]

$$\left[\frac{1}{\tau_m}\right]_{RKKY} = \frac{8h^2}{3}\left[\frac{\pi(g_J-1)^2 J(J+1)}{6}\right]^{1/2}$$

$$\times \frac{E_F N_0 [\mathscr{J}N(0)]^2}{hk_F^3} x \ .$$

The RKKY rate is independent of temperature but linear in concentration in the normal state.

The linear concentration dependence of $\tau_m^{-1}$ suggests that the spin-spin relaxation time arising from the RKKY interaction is dominant in $Y_{1-x}R_x Rh_4B_4$ above $T_c$. (Estimates of direct dipole-dipole coupling between impurity moments are an order of magnitude smaller.) The Korringa

relaxation of the local moment has, however, been reported in $SmRh_4B_4$ at high temperatures.[20] The ratio of $\tau_m^{Er}/\tau_m^{Gd}$ gives directly the ratio of the strength of the $s$-$f$ exchange interaction $N(0)\mathscr{J}$ after we correct for the magnitude of the spin projection $[(g_J-1)^2 J(J+1)]^{1/2}$ with the use of the ratio of $\tau_m^{Er}/\tau_m^{Gd}=0.39$ obtained in the normal state, $[N(0)\mathscr{J}]^{Er}/[N(0)\mathscr{J}]^{Gd}$ is found to be equal to 1. This means that the $s$-$f$ exchange interaction is nearly the same and independent of the rare-earth atom for Gd and Er. The magnitude of $N(0)\mathscr{J}$ using the parameters in Table II is $8\times10^{-2}$.

## IV. DISCUSSION

The nuclear-spin—lattice relaxation time in a BCS superconductor has been described in a general form,

$$\frac{T_1^N}{T_1^S} = \frac{2}{k_B T}\int \frac{(EE'+\Delta^2)f(E)[1-f(E)]}{[(E^2-\Delta^2)(E'^2-\Delta^2)]^{1/2}}dE \ ,$$

$$E'=E\pm\hbar\omega_n$$

where $\Delta$ is the superconducting energy gap and $f(E)$ is the Fermi-Dirac distribution function of the quasiparticle excitation energy $E$. This relaxation, due to the nuclear hyperfine interaction with the conduction electrons (Korringa relaxation), shows an enhancement just below $T_c$ due to the sharp peak in the density of states at the gap edge, and an exponential behavior on temperature at low temperature. Such a behavior in the undoped compounds is shown in Fig. 1. In the superconducting state we would expect the very dilute concentration of paramagnetic impurity to have little effect on the Korringa-type relaxation well below $T_c$. Therefore, we have analyzed the relaxation behavior using the same value of $(T_1)_K$ as in the undoped compounds.

The effect of pair breaking on the density of states and hence on the spin-lattice relaxation was calculated by Griffin and Ambegaokar[21] based on the Abrikosov-Gor'kov theory. Machida[22] also investigated the Korringa relaxation rate within the depairing theory. Their results bear out the qualitative expectation that the enhancement of the relaxation rate just below $T_c$ should be depressed by magnetic impurities. When the superconducting transition temperature is suppressed below $0.6T_c^0$ ($T_c^0$ is the transition temperature in the pure sample), the relaxation rate decreases monotonically as temperature is lowered. The results of $^{139}La$ relaxation in the superconducting $La(Gd)Al_2$ (Ref. 23) are consistent with the theoretical results. However, the change of the Korringa relaxation rate due to the pair-breaking effect by impurities is smooth at $T_c$ and is small in magnitude. In addition, because of

the small hyperfine coupling constant of $^{11}B$, the Korringa relaxation rate is much smaller than the additional mechanism that comes from the dipolar interaction with the paramagnetic ions described in the preceding section. Therefore, in spite of the lack of information about the change of the Korringa relaxation in the paramagnetic doped compounds, we can conclude that the error in determining $P(t)$ due to the change of $T_{1K}$ by impurities is negligible.

According to the theory by Matsui and Masuda,[24] the nuclear relaxation time due to the indirect coupling between nuclei and impurities (i.e., the BGS and GH mechanism) is modified by superconductivity, because the indirect coupling is related to the conduction-electron spin susceptibility which is expected to change in the superconducting state. However, the expressions for the LD and TD mechanism in the superconducting state are the same as those in the normal state. The reason for this comes from the fact that the LD and TD coupling arise from the classical electromagnetic dipolar interaction between nuclei and impurities, which is affected little by superconductivity.

The most important experimental observation is found to be the dramatic reduction of the electronic spin-relaxation time $\tau_m$ in the superconducting state. The interesting question is how superconductivity affects the spin dynamics of the localized moment, and, therefore, how the expression of $(\tau_m)_{RKKY}$ changes as a function of temperature and external field in the superconducting state. Although no theoretical study is presently available with which to compare present results, we would expect that the reduction of $\tau_m^{-1}$ due to the RKKY interaction in the superconducting state can be attributed to the reduction of the conduction-electron spin susceptibility $X(q)$.

The indirect exchange interaction of the localized moments is expressed in terms of the nonlocal spin susceptibility

$$H_{ex} = -\frac{\mathscr{J}^2}{g_J^2\mu_B^2}(\vec{S}_1 \cdot \vec{S}_2)$$

$$\times \int \frac{d^Bq}{(2\pi)^3} X(q)\exp-[iq\cdot(\vec{r}_1-\vec{r}_2)] ,$$

where $\mathscr{J}$ is the exchange integral and $X(q)$ is the Fourier transform of the conduction-electron susceptibility investigated by Anderson and Suhl[25] in a pure superconductor. $X(q)$ at $q=0$ should vanish because of the singlet ground state of the superconducting Cooper pairs, which modifies $X(q)$ over the range of $q < \xi_0^{-1}$ ($\xi_0$ is the coherence length). Qualitatively, one would expect a reduction in $H_{ex}$ as $X(q)$ is reduced. The temperature dependence is discussed by Matsui and Masuda.[24] In the pure limit

the reduction is proportional to $\tanh[\Delta(T)/2T]$. We would expect in the mixed state that $\Delta$ would be reduced as $H$ increases, i.e., $\Delta$ is spatially averaged over the vortices. Such a dependence on $H$ and $T$ qualitatively fits our data for $\tau_m^{-1}$ below $T_c$.

For large $q$, $X(q)$ approaches that of the normal state. In the strong spin-orbit coupling limit, Machida and Matsubara[26] calculated $X(q)$ in a dirty superconductor and showed that the overall features of $X(q)$ look like that in the normal state, because the strong spin-orbit scattering mixes the spin-up and -down states of the superconducting ground state. As the spin-orbit coupling is considered to be large in the ternary superconductors, one can expect that the exchange-type interaction may not be changed by the onset of superconductivity.

However, the considerations of $X(q)$ described above are made at small values of $q$. The main contribution to $H_{ex}$ comes from large $q \sim 2k_F$, where $k_F$ is the Fermi momentum. The expression for $X(q)$ for an arbitrary wave vector is required for the derivation of the exchange interaction $H_{ex}(r_1-r_2)$ in the superconducting state.

Recently, Kochelaev et al.[27] investigated the spatial dispersion of the spin susceptibility of the conduction electrons in a pure and dirty superconductor, and obtained the expression for the nonlocal susceptibility and for the RKKY interaction. The expression for the RKKY interaction in pure superconductors is given for $k_Fr \gg 1$,

$$H_{ex} = \frac{\mathscr{J}^2}{2}\left[\frac{N(E_F)\pi}{k_Fr}\right]^2 T$$

$$\times \sum_{\omega}\left[\frac{\omega^2\cos(2k_Fr)}{\omega^2+\Delta^2} + \frac{\Delta^2}{\omega^2+\Delta^2}\right]$$

$$\times \exp\left[-\frac{\omega^2+\Delta^2}{\epsilon_F}k_Fr\right](\vec{S}_1\cdot\vec{S}_2) ,$$

where $r$ is the distance between the interacting moments, $k_F$ and $\epsilon_F$ are the Fermi momentum and energy, respectively, and $2\Delta$ is the energy gap. The first oscillatory term is the expression for the RKKY interaction in the normal state, when $\Delta$ goes to zero. The second term, which vanishes at $\Delta=0$, is due to the superconducting correlations of the conduction electrons; this term is nonoscillatory and decreases at $r^{-2}$; in a Fourier transform for $q \rightarrow 0$, it tends to cancel the first term. The cutoff factor is of the order of $\exp(-r/\xi_0)$, where $\xi_0$ is the coherence length in the pure superconductor.

In the case of dirty superconductors, an additional term appears. This term, which is nonoscillating, decreases with distance as $r^{-1}$, and is exponentially

cutoff at distances on the order of the modified coherence length $\xi \sim (\xi_0 l)^{1/2}$, where $l$ is the mean free path. The nonoscillating behavior of this term is due to the joint action of the superconducting correlation and of the scattering by the magnetic impurities on the phase shifts of the electron wave functions. Thus the effective radius of the indirect exchange interaction, which is equal to mean free path in the normal state, increases sharply to the new length $\xi$ on going into the superconducting state. The results obtained by Kochelaev *et al.* show the importance of the nonlocal spin correlation in the superconducting state.

Finally, we would like to point out that the electromagnetic interaction has been proposed to explain the anomalous nature of magnetic superconductors.[28] According to the theory by Tachiki *et al.*, the spin-spin interactions acting between the rare-earth ions are strongly screened by the superconducting persistent currents through the electromagnetic interaction. The effect of such interactions on the spin dynamics should be included in theoretical studies.

*Note added in proof.* For the concentrations of Gd or Er of interest in this investigation, the important regime for $T < T_c$ is that of $r \approx \xi$. A. J. Fedro (private communication) has recently calculated $H_{ex}(r, \xi)$ and demonstrated the large reduction of the interaction between rare-earth moments from an oscillatory $r^{-3}$ dependence for very large $\xi$ to a damped $\exp(-r/\xi)$ asymmetric oscillatory dependence for $\xi \leq r$. We are presently calculating the full temperature and field dependence of the rare-earth spin correlation function based on $H_{ex}[r, \xi(T)]$ in order to quantitatively explain our results for $\tau_m$ in the superconducting state.

## ACKNOWLEDGMENTS

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