Magnetic Resonance of a Localized Magnetic Moment in the Superconducting State: $LaRu_2$:Gd†*

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The magnetic resonance of dilute $LaRu_2$:Gd has been observed in both the superconducting and normal states. A reduction in the g shift and an increase in the thermal broadening were observed, upon going from the normal to the superconducting regime. The spin-orbit scattering rate, $1/\tau_{s.o.}$, is estimated from both EPR and the re-entrant behavior of the upper critical field in $LaRu_2$:Gd.

We wish to report the first unequivocal observation of ESR of a localized moment in the superconducting state. Our results immediately below T_c are in agreement with theoretical predictions valid in that region, but originally developed for NMR in dirty superconductors. We discuss the implications of these measurements, and propose future work which could shed considerable light on the dynamics of conduction electrons in the superconducting state.

We have observed the magnetic resonance of dilute amounts (200–40 000 ppm) of Gd in $LaRu_2$ (superconducting below 3.9°K) from 1.4 to 20 K. The measurements were performed at X-band frequency. The $LaRu_2$ intermetallic compounds were prepared by arc melting in an argon atmosphere, and then annealed for 2 days at a temperature of 1200°C. X-ray examination indicated the existence of only a single phase. The samples were measured in the form of balls or powder. In addition, superconductivity measurements performed on our samples indicated that the reduction in T_c upon alloying with Gd was $\frac{1}{7}$ as much as occurred in $LaAl_2$, in agreement with previous measurements.[1] This relatively weak coupling allows the observation of magnetic resonance with a T_c in the middle of the He regime. This also enables us to work at relatively high Gd concentrations where appreciable conduction-electron polarization can be expected. This polarization is responsible for the re-entrant critical-field behavior.

Our EPR results exhibit the following features:

(1) A large negative g shift was observed in the normal state (we find $g_{\mathrm{normal}} = 1.82 \pm 0.005$). The linewidth was approximated by the formula $\Delta H = a + bT$ where both a and b are temperature independent. We found the thermal broadening $b = b_n = 23 \pm 4$ G/deg (the subscript n denoting normal values). Both the g value and b_n are concentration independent for low Gd concentration (less than 2000 ppm). This indicates the absence of a bottleneck in the normal state.

(2) Upon transition to the superconducting state our measurements at low Gd concentrations exhibit an 11% reduction in the g shift, $g_s = 1.84 \pm 0.005$ (the subscript s denoting superconducting values) and an initial increase in the slope of the linewidth by a factor of 2 to $b_s = 50 \pm 10$ G/deg.[2] The change in the g shift decreases with increasing Gd concentration. The line shape (A/B ratio) of the EPR signal was found to change appreciably upon transition from the normal ($A/B = 2$) to the superconducting state ($A/B \simeq 1.2$).

The experimental linewidths for two samples (200 and 400 ppm are summarized in Fig. 1. Similar results have been obtained for at least three other $LaRu_2$:Gd samples for Gd concentrations less than 2000 ppm. For higher Gd concentrations, however, a broadening was observed with decreasing temperature. This broadening at low temperatures is probably associated with ordering effects, in agreement with high-field measurements.[3] The lack of data between about 3.2 and 2.8°K (see Fig. 1) is caused by overlap of the transition to the superconducting state with the magnetic resonance line. This former appears in our EPR spectra as a strong field-dependent signal which provides us with a measure of the upper critical field. As the temperature is further reduced, the upper critical field increases and the field for resonance lies entirely within the superconducting state.

Low-frequency upper-critical-field measurements were made in the temperature range 0.5°K $\leqslant T \leqslant$ 4.2°K on the same samples and show some deviation from those at microwave frequency. For relatively high Gd concentration ($c \geqslant 2\%$) these measurements indicate re-entrant critical-field behavior. The decrease in the critical field

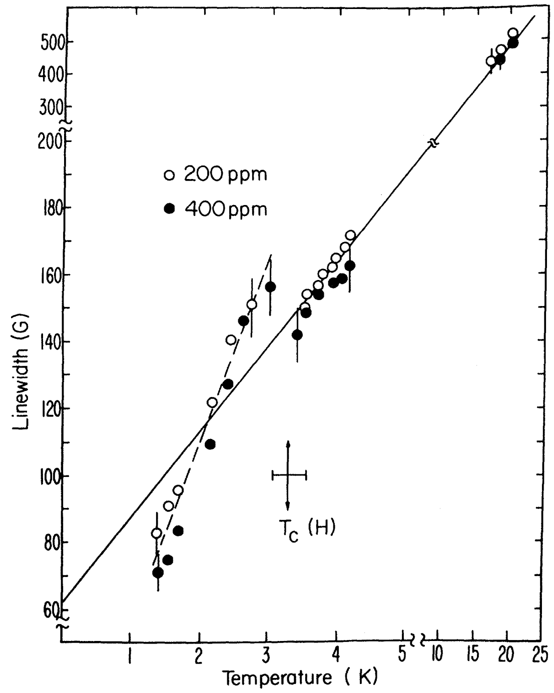

FIG. 1. Linewidth as a function of temperature for two $LaRu_2$:Gd samples. The 200-ppm sample was measured in the form of a powder; 400-ppm, in the form of a ball. The value of $T_c(H)$ is shown. Solid line, fit to our data in the normal state; dashed line, in the superconducting state.

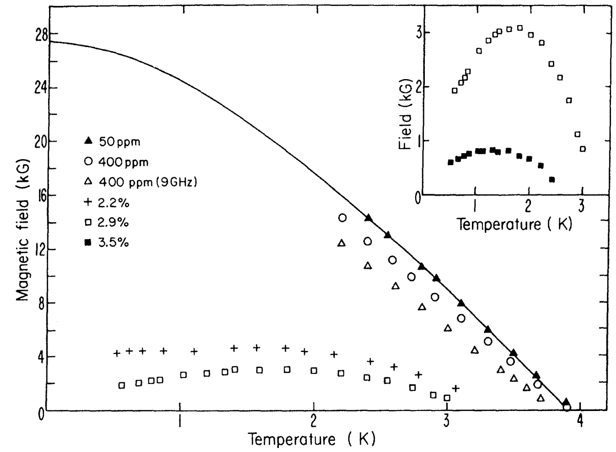

FIG. 2. Upper critical field as a function of temperature. All the measurements represented here (except those denoted by open triangles) were performed at low frequency (80 Hz). Open triangles, measurements on the 400-ppm sample at microwave frequencies. Solid line, Abrikosov-Gor'kov fit to H_{c2} measurements on $LaRu_2$:Gd for a 50-ppm Gd concentration. Inset, high-concentration results with expanded ordinate.

with decreasing temperature (Fig. 2) is probably due to Pauli pair breaking from the internal field of the polarized Gd impurities.[4]

Specific-heat measurement of $LaRu_2$ yield $\gamma = 13.85$ mJ/g atom $°K^2$.[5] The density of states (corrected for the electron-phonon mass enhancement using the McMillan formula) is $\eta = 2$ states/eV atom spin. This value is larger by a factor of 2 relative to the free electron value, assuming 6.33 electrons per atom,[5] and is indicative of a complicated band structure. The value of $J(0)$ (the $\vec{q} = 0$ component of the exchange interaction, including enhancement) was estimated from the expression for the g shift.[6] We find $J(0) = -0.087$ eV. The thermal broadening of the EPR linewidth in the normal state enables us to extract the conduction-electron exchange scattering, $1/\tau_{ex}$, using the detailed-balance relation.[6] We find $1/\tau_{ex} = 2.5 \times 10^7$/sec ppm. The value extracted from the depression of T_c by alloying with Gd is $1/\tau_{ex} = (1.7 \pm 0.5) \times 10^7$/sec ppm. The absence of a bottleneck[6] in the normal state (even for 1% Gd in $LaRu_2$) yields, therefore, a lower limit on $1/\tau_{s.o.}$: $1/\tau_{s.o.} \gg 1/\tau_{ex} = 2.5 \times 10^7$/sec ppm.

We believe that the large negative g shift observed in the normal state $\Delta g_n = -0.17$ (measured relative to $g = 1.993$) is associated with a narrow d band. This conclusion is based on systematics found in many transition-metal alloys.[7,8] In the superconducting state a reduction of the spin susceptibility is expected.[9] This reduction was calculated by Anderson[9] and Abrikosov and Gor'kov.[10] Anderson demonstrated that, in the presence of spin-orbit coupling, the spin susceptibility in the superconducting state, $\chi^{(s)}$, does not vanish at $T = 0$ but satisfies (in the dirty limit $\xi_0 > v_F \tau_{s.o.}$) the relation[9]

$$[\chi^{(n)} - \chi^{(s)}(0)]/\chi^{(n)} = 2v_F\tau_{s.o.}/\pi\xi_0, \tag{1}$$

where ξ_0 is the coherence length and v_F is the Fermi velocity.[11] The reduction in the g shift upon going from normal to superconducting state is, therefore, consistent with the reduction in the spin susceptibility of the superconducting electrons, provided that d electrons are responsible for superconductivity in $LaRu_2$. The small magnitude of change of the g shift (11%) at low concentrations of Gd (200 ppm) is an evidence for strong spin-orbit scattering, as evinced already by the absence of bottleneck effects in the normal state. The reduction in the jump of the g shift with increasing Gd concentration in the superconducting state is consistent with (1), as $1/\tau_{s.o.}$ increases with increasing Gd concentration.

Using the relation $H_{c2}(0) = \varphi_0/2\pi\xi_0^2$,[12] where φ_0 is the fluxoid quantum ($\varphi_0 = 2.07 \times 10^{-7}$ G cm^2), we estimate $\xi_0 \simeq 100$ Å. Then (1) yields $1/\tau_{\rm s.o.} \approx 4 \times 10^{14}$/sec. Use of the BCS theory ($\xi_0 \approx 1000$ Å) would predict $1/\tau_{\rm s.o.} \approx 4 \times 10^{13}$/sec. All these estimates are based on a free-electron model. As shown above, this may not be a very good approximation for $LaRu_2$, and may be responsible for the order of magnitude range for $1/\tau_{\rm s.o.}$ at low (200–400 ppm) concentrations. The values for $1/\tau_{\rm s.o.}$ are consistent with the lower limit estimated in the normal state from the absence of the the bottleneck ($\gg 1/\tau_{\rm ex} = 2.5 \times 10^7$/sec ppm) for these concentrations. Recently, Maki[13] has derived expressions for the spin-orbit rate $1/\tau_{\rm s.o.}$ and exchange spin-flip rate $1/\tau_{\rm ex}$ for conduction electrons in dirty gapless superconductors. These rates control the conditions which determine the presence or absence of the magnetic resonance bottleneck. His results show that $1/\tau_{\rm s.o.}$ is reduced, while $1/\tau_{\rm ex}$ is increased, upon passing from the normal to the superconducting state. A system in the superconducting state could in principle be bottlenecked (i.e., $1/\tau_{\rm ex} > 1/\tau_{\rm s.o.}$), and in the normal state not, the condition $1/\tau_{\rm s.o.} > 1/\tau_{\rm ex}$ then being satisfied. Because of the experimentally observed large difference between $1/\tau_{\rm s.o.}$ and $1/\tau_{\rm ex}$ in $LaRu_2$:Gd, however, this is not the situation in our case.

The change in the thermal broadening upon transition from the normal to the superconducting state (Figs. 1 and 2) can be interpreted using the theories of Griffin and Ambegaokar,[14] Cyrot,[15] and Maki[16] for NMR relaxation in gapless type-II superconductors. Unfortunately, these theories were developed for fields immediately below H_{c2} and at temperatures immediately below $T_c(H)$. Our data extend to greater field deviations and lower temperatures, and the theory for this region has not yet been put in tractable form. What theory has been worked out does predict an increase in the thermal broadening ($1/T_2$) in the superconducting state immediately below T_c, in agreement with our experiment. Previous NMR measurements in type-II superconductors indicate broadening of the line below the upper critical field due to magnetic-field distributions in the mixed state. This effect was not observed in our experiment.

The upper-critical-field measurements[17] enable us to extract the value of $1/\tau_{\rm s.o.}$ as follows: The value of H_{c2} as a function of temperature in the presence of three depairing mechanisms, (a) external magnetic field, (b) magnetic impurities, and (c) Pauli susceptibility polarization, is given by the Abrikosov-Gor'kov (AG)[4,17] formula as

$$\ln(T_c/T_{c0}) + \psi(\tfrac{1}{2}+\rho) - \psi(\tfrac{1}{2}) = 0, \tag{2}$$

where

$$\rho = 0.140\,\frac{T_{c0}}{T_c}\left[\frac{\tau_{\rm tr} H_{c2}(T)}{\tau_{\rm tr0} H_{c20}(0)} + \frac{n}{n_{\rm cr}} + \frac{P}{P_{\rm cr}}\right], \tag{3}$$

and $\tau_{\rm tr}$ is the transport collision time. $P/P_{\rm cr}$ is the polarization term, given by

$$\frac{P}{P_{\rm cr}} = \frac{\tau_{\rm s.o.} n^2 J^2(0) S^2}{\pi T_{c0}/3\gamma} B_S{}^2\left(\frac{\mu H_{c2}}{k_B T}\right). \tag{4}$$

Here, B_S is the Brillouin function, and H_{c20} and T_{c0} are the upper critical field and transition temperature in "pure" $LaRu_2$, respectively. At low Gd concentrations and relatively high temperatures, $P/P_{\rm cr}$ can be neglected. This enables us to estimate the value of $|\tau_{\rm tr} H_{c2}(T)/\tau_{\rm tr0} H_{c20}(0)|$ as a function of temperature, and also to estimate its magnitude for high Gd concentration and very low temperatures (the value of $n/n_{\rm cr}$ is already known from T_c measurements). Thus, by comparing the theoretical prediction of the AG formula in the absence of polarization with the actual experimentally observed H_{c2}, we are able to extract $P/P_{\rm cr}$ (see Fig. 2). Using the EPR value $|J(0)| = 0.087$,[18] (4) yields $1/\tau_{\rm s.o.} = (2 \pm 1) \times 10^{14}$ sec for the 2.9% sample. This high concentration value should be much larger than that extracted from EPR measurements on the more dilute alloys if the Gd impurity is responsible for $1/\tau_{\rm s.o.}$. A spread of values for $1/\tau_{\rm s.o.}$ is obtained from the g-shift measurements (4×10^{13}–4×10^{14}/sec at low concentrations). Along with other possible sources for $1/\tau_{\rm s.o.}$, this is sufficient to account for the relative values of $1/\tau_{\rm s.o.}$ as obtained from the two methods. The high concentration value is still large enough to avoid a bottleneck in the normal state ($1/\tau_{\rm ex} = 10^{12}$/sec at this concentration).

In conclusion, (a) we have observed the magnetic resonance in the superconducting state. These measurements, as well as EPR measurements in the normal state, provide information about $1/\tau_{\rm s.o.}$ and $1/\tau_{\rm ex}$. Both these parameters were also extracted from superconductivity measurements (the re-entrant critical field gives us information about $1/\tau_{\rm s.o.}$ while the reduction of T_c by alloying with Gd ions enables us to estimate $1/\tau_{\rm ex}$). Order of magnitude agreement for $1/\tau_{\rm s.o.}$ between the methods was achieved (the best that could have been expected using free-electron parameters).

(b) The theory of Maki predicts increasing $1/\tau_{\rm ex}$

and decreasing $1/\tau_{s.o.}$ upon going from the normal to the superconducting state. Therefore, the existence of a bottleneck in the superconducting state can be determined from the thermal broadening of the linewidth in this state. Now that magnetic resonance has been observed in the superconducting state, it should be possible to make measurements on bottlenecked systems (e.g., $LaAl_2$:Gd at He^3 temperatures) or on nonbottlenecked systems in the normal state, but which become bottlenecked in the superconducting state when the spin-orbit cross section reduces (or the reverse if the primary spin-flip scattering mechanism is exchange). One has the exciting prospect of direct determination of the (temperature dependent) dynamics of the conduction-electron spins in the superconducting state by making use of the changing magnetic-resonance bottleneck conditions.

(c) The reduction of the negative g shift in the superconducting state, as well as the correlation between EPR and superconductivity, gives some evidence that $LaRu_2$ is a "d-band" superconductor. Previous arguments were based on the relatively small reduction of T_c upon substitution of Gd for La, as well as by analogy with the equistructural superconductor $CeRu_2$.[19]

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