Electron-spin resonance of a localized moment in the superconducting state: $B\,Ru_2$: Gd (B = La, Ce, Th)†

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The electron-spin-resonance spectrum of Gd in the type-II cubic superconductors $LaRu_2$, $CeRu_2$, and $ThRu_2$ has been observed in both the normal and superconducting regimes. Upon transition from the normal to the superconducting state, the spectra exhibit (a) a change in line shape (A/B ratio), (b) an increase in thermal broadening immediately below $T_c(H)$, and (c) a change in g value. Comparison with experiments performed by others, as well as a preliminary interpretation of the data, is presented.

I. INTRODUCTION

In a previous letter[1] (referred to as I), observation of the magnetic resonance of a localized moment (Gd) in the type-II superconductor $LaRu_2$ (intermetallic compound) was reported. It was shown that, upon transition from the normal to the superconducting state (a) the g shift decreased from -0.17 to -0.155; (b) the thermal broadening increased from 23 to 40 G/K, and (c) the line shape (A/B ratio, in the notation of Feher and Kip[2]) changed from $(A/B)_{\text{normal}} \simeq 2.5$ to $(A/B)_{\text{super}} \simeq 1.2$ at $T = 1.4$ K. The experiments were performed in the temperature range $1.4 \leq T \leq 20$ K. The superconducting transition temperature in the presence of the resonance magnetic field ($H_0 \simeq 3000$ G) was $T_c(H) = 3.5$ K. Thus, the over-all range of temperature available for measurement in the superconducting state was less than 2 K (see below). It was of extreme importance, therefore, to extend the measurements to lower temperatures.

In this paper we report further EPR measurements, not only on $LaRu_2$: Gd, but also on $CeRu_2$: Gd and $ThRu_2$: Gd in the He^3 range, i.e., to 0.52 K. To our knowledge, this is the first report of EPR of localized moments in metals at such temperatures. Our results for $LaRu_2$ indicate that the thermal broadening increases as T is lowered only in the immediate vicinity of $T_c(H)$. At significantly lower temperatures the temperature dependence of the thermal broadening is roughly the same as that observed in the normal state. The appreciable change in the A/B ratio, and the changes in the g shift, noted previously in the He^4 regime in I, were also observed in the He^3 temperature range.

Our results for $CeRu_2$: Gd and $ThRu_2$: Gd indicate that the line shape and linewidth behave in a manner similar to that of $LaRu_2$: Gd, while the change in the g shift upon transition to the superconducting state appears to be different for the three alloys. The different direction of the shifts can be understood, however, by assuming a two-band model. Thus, the EPR properties in the superconducting state as exhibited in I appear to be typical of a localized moment in a superconductor. Finally, a comparison with previous experiments performed by others[3] on $CeRu_2$: Gd will be presented, as well as a preliminary interpretation of the data.

II. COMPARISON OF EXPERIMENTAL RESULTS

All of the measurements were performed at X-band frequency. The temperature was changed continuously from 0.5 to approximately 25 K (limited by the intensity of the EPR signal). The samples were prepared by arc melting, followed by annealing at a temperature of $T = 1100$ K for 24 h. X-ray examination indicated a single phase.

The transition from the normal to the superconducting state appears in our EPR spectra as a strong field-dependent signal, providing a measure of the upper critical field. Around $T_c(H_0)$ (H_0 is the field for resonance), this signal overlaps with the Gd EPR signal and makes the extraction of a meaningful measurement almost impossible. More explicitly, the EPR g shift and linewidth are strongly dependent on the resonance line shape (i.e., the A/B ratio), as shown by Peter *et al.*[4] Our results display appreciable A/B ratio changes upon transition from the normal to the superconducting state. In order to find the A/B ratio, the "baseline" should be "almost" horizontal.[4] The baseline is obtained by sweeping the magnetic field over a range much larger than the linewidth. (The width of the EPR resonance itself is determined from a sweep over a much smaller range, once the A/B ratio is known.) An accurate measurement of the g shift and linewidth is therefore impossible in the temperature range where the baseline sweep range (2500 G) overlaps the (broad) upper critical field transition. In Fig. 1 we plot the upper critical field as determined from our microwave measurements, together with the width of the transition. The temperature ranges over which EPR signals are impossible to measure are also displayed. It is clearly seen from Fig. 1, that, for $ThRu_2$, measurements were impossible for a 1-K variation of temperature immediately below

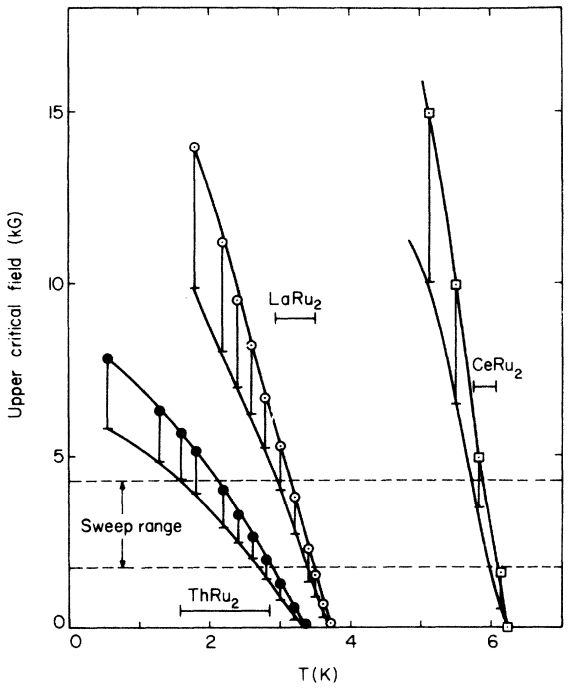

FIG. 1. Upper critical field as measured at microwave frequency. The closed circles represent measurements on $ThRu_2$: Gd; the open circles represent measurements on $LaRu_2$: Gd; the rectangles represent $CeRu_2$: Gd. (The Gd concentration is 200 ppm.) The vertical solid lines represent the width of the transition. The dashed lines are the EPR magnetic field sweep range limits. It is clearly seen that for $ThRu_2$ the sweep range overlaps with the critical field transition over wider range of temperature than for $LaRu_2$ or $CeRu_2$. The temperature ranges over which the upper critical field overlaps with the sweep range are shown by horizontal solid lines for the three compounds.

$T_c(H)$. For $LaRu_2$ and $CeRu_2$, however, the range is much smaller.

In the following paragraph we shall describe in detail the experimental results for $CeRu_2$, partly because of the relatively large T_c which enables us to measure over a wide temperature range in the superconducting state, and also because of the small range of temperature over which the critical field and the EPR signal overlap (Fig. 1). For $CeRu_2$ this range is roughly equal to the accuracy in the measurement of temperature so that no overlap is effectively present. We shall compare these results with measurements on $LaRu_2$ (extended to lower temperatures than in I) as well as $ThRu_2$.

A. Linewidth

1. $CeRu_2$:Gd

The EPR linewidth of Gd in $CeRu_2$ is plotted against temperature in Fig. 2. An increase in the thermal broadening was observed immediately below $T_c(H)$. This effect is clearly seen by plotting the linewidth over an enlarged scale of temperature (Fig. 3).

At still lower temperatures $[T < T_c(H)]$ the rate of thermal broadening observed for samples with very low Gd concentration (less than 200 ppm) is roughly the same as in the normal state. For higher Gd concentrations, a decrease in the thermal broadening rate, or even an increase in the linewidth, has been observed at low temperatures. These effects are probably due to ordering. Figures 4 and 5 (exhibiting the same low-temperature data as Fig. 4 but over a larger temperature scale) demonstrate these effects by comparing the linewidth versus temperature for samples with 150 and 800-ppm-Gd concentration. The experimental points for high concentration samples at low temperatures are therefore omitted in Figs. 2 and 3.

The EPR of $CeRu_2$: Gd has been observed recently by Engel *et al.*[3] Their results indicate a leveling off of the linewidth at low temperatures even at very low Gd concentrations in disagreement with our results. In addition, they found the thermal broadening in the normal state to be $(\Delta H/\Delta T)_n$

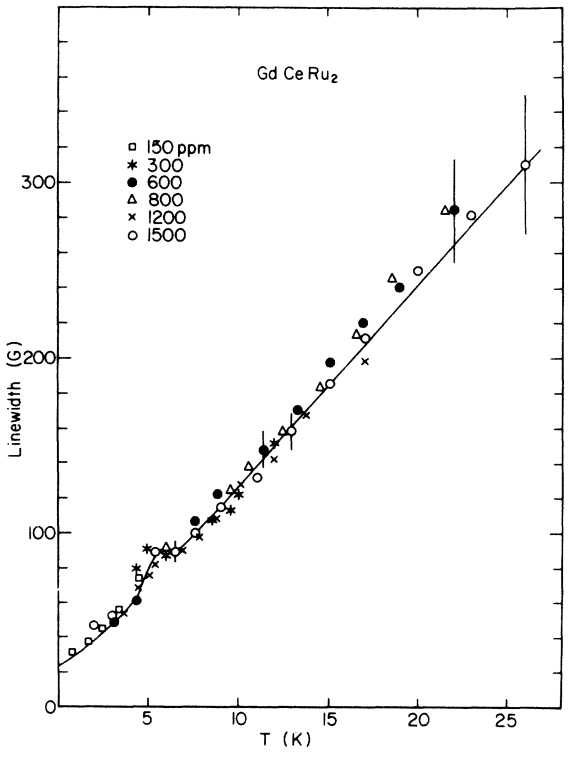

FIG. 2. EPR linewidth of Gd in $CeRu_2$ as a function of temperature for various Gd concentrations. Our data for high Gd concentration at low temperatures are omitted as explained in the text.

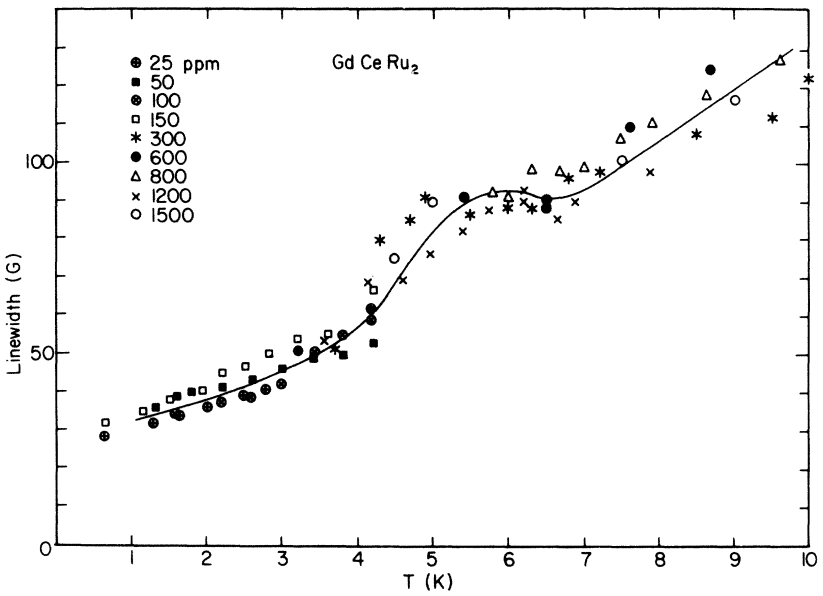

FIG. 3. EPR linewidth of Gd in $CeRu_2$ as a function of temperature using expanded ordinate. Our data for high Gd conconcentrations at low temperatures are omitted (see text).

= 4 G/K. We find a value $(\Delta H/\Delta T)_n = 12 \pm 3$ G/K. We have performed experiments on one of their samples (80-ppm $CeRu_2$: Gd kindly provided to us by Baberschke). Although it was difficult to determine the thermal broadening in the normal state because of small signal-to-noise ratio, the general behavior of the data agreed with our observations on our own samples.

2. *$LaRu_2$:Gd and $ThRu_2$:Gd*

The linewidth of $LaRu_2$: Gd exhibits the same behavior with temperature as $CeRu_2$ and it is shown in Fig. 6. In $ThRu_2$, however, we were not able to measure immediately below $T_c(H)$ (see above), but the thermal broadening rate in the superconducting state ($T < T_c(H)$) is the same as in the normal state, consistent with the other two hosts. It should be mentioned that for all three systems we found the thermal broadening to be independent of concentration in the normal state, indicating that BRu_2: Gd (B = Ce, La, Th) are unbottlenecked in the normal state.

B. Line shape, A/B ratio

The A/B ratio for various $Gd_xCe_{1-x}Ru_2$ samples are exhibited in Fig. 6(a). It is clearly seen that upon transition from the normal to the superconducting state the A/B ratio changes from approximately 2 (a value of 2.55 is expected for a localized moment in a metal according to Dyson theory[2,5]) to $\simeq 1$. Similar behavior has been observed for $LaRu_2$: Gd and $ThRu_2$: Gd (see Table I).

C. g value

Though the linewidth and the line shape (A/B ratio) behave in roughly the same way for all the three systems, the g shift is quite different. For $LaRu_2$, we observed a decrease in the g shift upon the transition from normal to the superconducting ($\Delta g_n = -0.17$, $\Delta g_s = -0.155$). The subscripts n and s label normal and superconducting, respectively. For $CeRu_2$, the opposite effect occurs, the g shift increasing from $\Delta g_n = -0.05$ to $\Delta g_s = -0.065$ [see also Fig. 7(b)] in agreement with the observation of Engel *et al.*[3] The change in the g value for $ThRu_2$: Gd is much smaller than the error limits, but it appears to be in the same direction as in $CeRu_2$ (Table I). The increase in Δg for $CeRu_2$: Gd and the decrease for $LaRu_2$: Gd were observed for temperatures much smaller than $T_c(H)$ (Fig. 7). For $ThRu_2$: Gd, however, $T_c(H) \approx (2 \pm 0.2)$ K (Fig. 1), so that at the lowest temperature measured (0.6 K) one may not be sufficiently below the transition region. This could explain the small shift observed for $ThRu_2$: Gd. It should be mentioned that our experimental data were analyzed using the method suggested by Peter *et al.*[4] According to this method, the field for resonance is appreciably dependent on the A/B ratio. Because of the change in the A/B ratio in our experiment, there is a possible danger of induced shift (by virtue of the A/B change) that has nothing to do with the exchange induced shift if the line is not Lorentzian or systematic baseline errors are present. This difficulty, however, is certainly not present in our experiments on $ThRu_2$ — a decrease in the A/B ratio was observed with almost no change in the g value.

III. DISCUSSION

Unfortunately, a complete theory for the EPR of localized moment in the superconducting states is not yet available though significant progress has

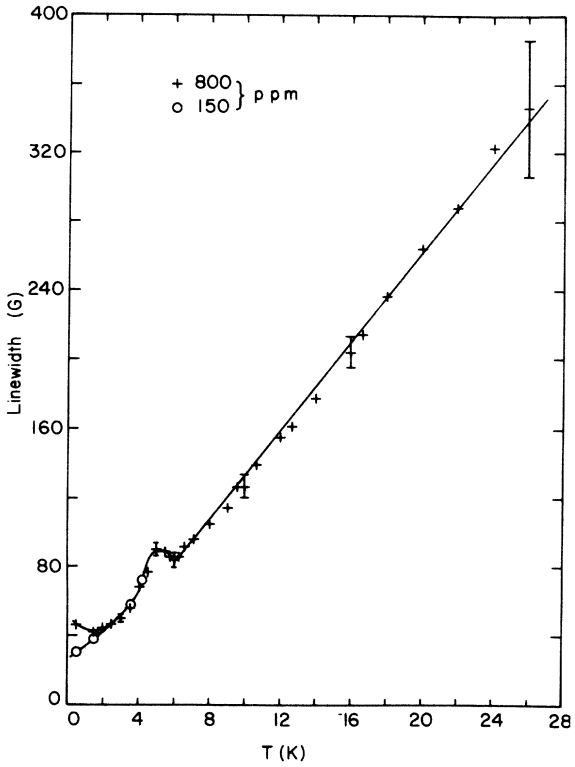

FIG. 4. Comparison of the linewidth as a function of temperature for 800 and 150 ppm Gd concentration in $CeRu_2$. The comparison suggests that the leveling off of the linewidth observed by Engel *et al.* (Ref. 3) at low temperature is probably associated with ordering effects (see text).

recently been made by Maki[6] on the conduction-electron relaxation rate as well as the EPR line shape.

In the absence of complete theory (which explicitly includes the spatial dependence of the order parameter in the vicinity of the magnetic impurity) we use the calculations of Maki as well as these appropriate to NMR (T_2) to interpret our results.

An attempt to understand the A/B ratio has been presented by Maki.[7] He generalized the Dyson calculation to a type II superconductor in the vortex state and was able to show (for the case of thick slab) that if the oscillating electric field associated with the microwave field, E_ω, is parallel to the external magnetic field, the London-Pippard equation would yield an A/B ratio equal to 1. This does not occur if E_ω is perpendicular to H_0; in such an orientation $A/B \approx 2.5$, the normal state result. In our experiments (cylindrical cavity with the sample roughly along the cylindrical axis) both geometries are simultaneously present. We are trying at present to verify Maki's predictions by performing experiments with geometries appropriate separately to the limiting cases considered by him.

The observed increases in the thermal broadening immediately below $T_c(H)$ are in agreement with T_2 calculations by Cyrot[8] and Maki[6] in the gapless regime. No calculation is available yet for the EPR linewidths further below $T_c(H)$.

The most interesting result is the behavior of the g shift. As pointed out above, the g value shifts in different directions for $CeRu_2$ and perhaps $ThRu_2$ than for $LaRu_2$, upon transition from the normal state to the superconducting state. This behavior can be explained by a two-band model (s and d electrons) as follows.

Specific-heat measurements[9] in $LaRu_2$ and $CeRu_2$ indicate that the total density of states η (corrected for phonon enhancement using MacMillan theory[10]) is roughly the same for $CeRu_2$ ($\eta_{CeRu_2} \simeq 2.5$ states/atom eV spin and $LaRu_2 \simeq 2$ states/atom spin eV). Unfortunately, the specific heat of $ThRu_2$ has not been measured yet. However, it can be estimated from the formula[10]

$$T_c = \Theta_D e^{-1/\eta V} , \tag{1}$$

where Θ_D is the Debye temperature and V is the attractive Coulomb interaction. As demonstrated by Joseph *et al.*,[9] V does not vary much across the BRu_2 (B = La, Ce, Th) series. As for Θ_D, it can be estimated from the isotope effect. Thus, using (1) we can deduce a value for η for $ThRu_2$ of $\simeq 2.2$ states/eV atom spin. These densities of states are much larger than those expected on the basis of free-electron models, and are probably due to large state densities of d electrons (associated with the Ru ions) at the Fermi level for all the three hosts.

Further evidence for this picture is provided by the normal state g shift in BRu_2 (B = La, Ce, Th). The g shift is usually written (in the absence of bottleneck effects) as the sum of the negative d contribution and the positive s contribution,

$$\Delta g = J_{f\text{-}s}(0)\eta_s + J_{f\text{-}d}(0)\eta_d = \Delta g_s + \Delta g_d , \tag{2}$$

where $J_{f\text{-}s}(0)$ and $J_{f\text{-}d}(0)$ are the f-s and f-d exchange interaction and η_s and η_d are the densities of states of the s and d electrons, respectively. It is believed that the magnitude of $J_{f\text{-}s}(0)$ (positive) is much larger than that of $J_{f\text{-}d}(0)$ (negative). The negative g shift observed in all the three intermetallic compounds is therefore most probably associated with the dominance of η_d over η_s, in agreement with the arguments above.

Shaltiel *et al.*[11] have measured the NMR Knight shift of La and the EPR g shift of Gd in the system $La_xTh_{1-x}Ru_2$. They found an appreciable decrease in the negative Knight shift and Gd g shift as x was decreased from $x = 1$. Their experiment can be interpreted by an increase in the s-electron density with little change in the d-electron density at

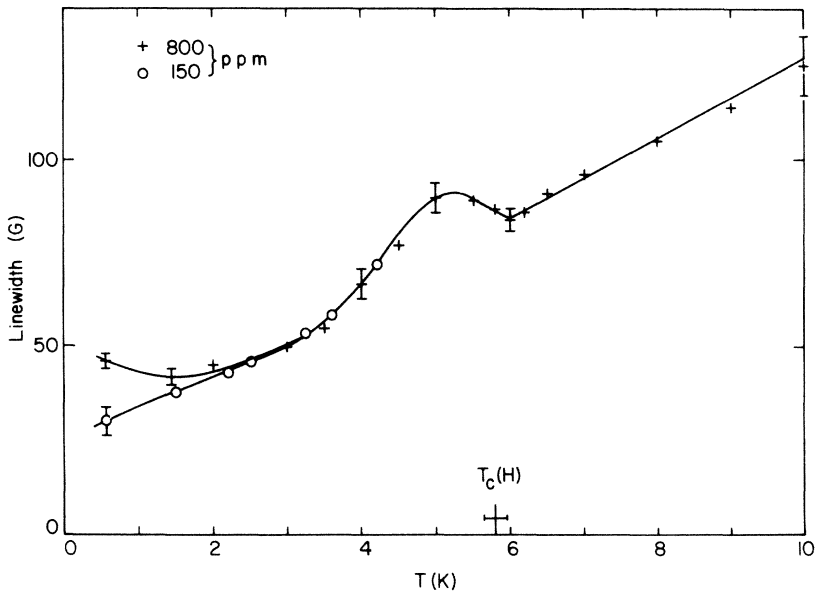

FIG. 5. Same as in Fig. 4 but with an expanded ordinate.

the La (or Gd) site. The increase of the s-electrons density of states at the La or Gd site can be understood on the basis that Th is a tetravalent ion and therefore contributes one extra electron (relative to the La) to $La_xTh_{1-x}Ru_2$. Equation (2) indicates that any small change in η_s can change Δg appreciably because of the dominance of J_{f-s} over J_{f-d}. This interpretation of Shaltiel's experiment, however, appears to be inconsistent with the thermal broadenings (Table I), if one assumes that in cubic metals the s and d contributions to the linewidth do not interfere. The total thermal broadening is then the sum of their separate contributions.[12] If this is the case, we would expect a larger thermal broadening for $ThRu_2$: Gd over that of $LaRu_2$: Gd because the s-electron density is larger on the Gd site in the former as compared to the latter. This is in disagreement with the experimental results (Table I). Although no complete calculation is available yet, in the presence of a wave-vector-dependent exchange interaction the separation into separate s and d wave contributions to the linewidth is no longer possible, and the discrepancy may not exist.[13] The expression for the g shift [Eq. (2)], however, still holds, at least formally.

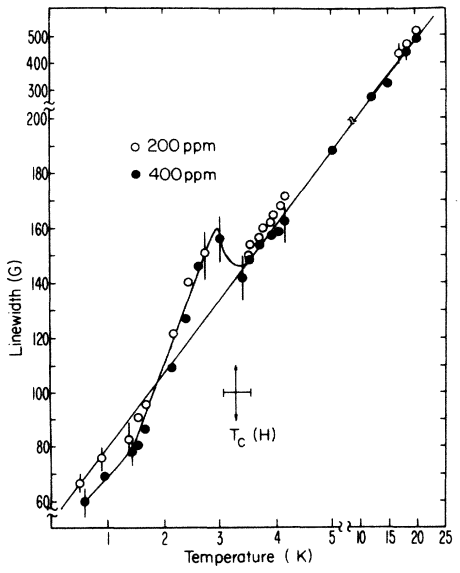

FIG. 6. EPR linewidth of Gd in $LaRu_2$ as a function of temperature.

With the assumption that the s-electrons density of states at the Gd site is larger in $ThRu_2$: Gd (or $CeRu_2$: Gd, Ce is also tetravalent) than in $LaRu_2$: Gd, we are in position to analyze the different behaviors of the g values in the three compounds.

Upon transition from the normal to the superconducting state a reduction in the spin susceptibility of the superconducting electrons is expected. The spin susceptibility at the superconducting state, however, does not vanish at $T = 0$ because of the spin-orbit scattering. This scattering rate depends on, in addition to the spin-orbit coupling itself, the amount of admixture of the conduction electrons with the core states responsible for the scattering. We expect, therefore, a larger reduction of the g shift associated with the s electrons than that associated with the d electron upon transition from the normal to the superconducting state This is because of the smaller admixture of the former, as compared to the latter, with the core

TABLE I. The EPR g shift, A/B ratio, and thermal broadening of Gd in $B\mathrm{Ru}_2$ (B = Ce, Th, La)—a comparison between the normal state and superconducting state.

	Normal state			Superconducting state	
	Δg	A/B	$\frac{\Delta H}{\Delta T}$(G/K)	Δg (0.6 K)	A/B (0.6 K)
CeRu_2	-0.050 ± 0.005	2.0 ± 0.2	12 ± 3	-0.065 ± 0.003	1.1 ± 0.2
ThRu_2	-0.035 ± 0.004	2.6 ± 0.3	8 ± 2	-0.038 ± 0.003	1.7 ± 0.2
LaRu_2	-0.172 ± 0.005	2.5 ± 0.3	23 ± 4	-0.155 ± 0.004	1.2 ± 0.2

states. This can explain the increase in the negative shift observed in CeRu_2. The decrease in the negative shift observed in LaRu_2 is understood by the very small s-electrons density of states at the Gd sites such that, upon transition to the superconducting state, the decrease in the density of states is mainly associated with the d electrons. Following the above discussion, one also expects an increase in the negative shift for ThRu_2, and indeed a small effect in the right direction has been observed (Table I). The smallness of the effect may be due to the fact that the temperature at which this shift was observed is *not* much smaller than $T_c(H)$, as was the case in CeRu_2 and LaRu_2.

Another possible explanation for the different behaviors of the g shift upon transition from the normal to the superconducting state is that s electrons are responsible for the superconductivity in CeRu_2, while in LaRu_2, superconductivity is due to d electrons. This interpretation, however, disagrees with the picture of Benneman and Garland for CeRu_2.[14] Maki[6] has demonstrated recently that, upon transition from the normal to the superconducting state, the exchange scattering rate increases and the spin-orbit scattering rate decreases. Thus, a system which is unbottlenecked in the normal state might be bottlenecked in the superconducting state. This effect might explain our experimental results if the f-s exchange interaction is bottlenecked (in the superconducting state) in the system CeRu_2: Gd but unbottlenecked in LaRu_2: Gd. At present, no further support is available for this interpretation.

Finally, Engel *et al.*[3] attributed the increase in the magnitude of the g shift in CeRu_2 to "the pairing of the s electrons in the vicinity of the rare-earth sites is larger than that of the d electrons." The above discussion indicates, however, much larger *depairing* of the s electrons because of the large $J_{f\text{-}s}$ exchange as compared to $J_{f\text{-}d}$.

In summary, although the EPR of localized moment in the superconducting state is not yet completely understood, the systematics achieved by measurements on three different systems indicate that the results in I are not accidental but characterize the general behavior of a localized moment in the superconducting state. A full interpretation must await band calculations for the three host compounds, similar to that performed by Switendick[15] for the cases of $B\mathrm{Al}_2$ (B = La, Y, La).

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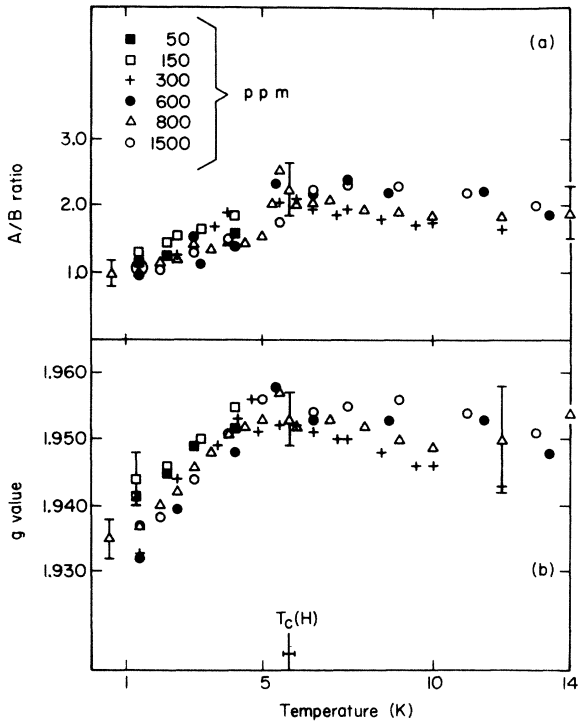

FIG. 7. (a) A/B ratio; (b) g value for CeRu_2: Gd samples as a function of temperature.

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