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ESR and spin-lattice relaxation of Nd³⁺ in a metallic host: LaRh₂

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We report the first ESR observation of Nd³⁺ in a metal: cubic LaRh₂. The resonance arises from a Γ_6 ground state and exhibits hyperfine splitting at low temperature, allowing for positive identification. Above about 12 K, the ESR linewidth increases exponentially with temperature. We attribute this increase to the resonance phonon relaxation process involving the first excited state at 125 ± 10 K.

I. INTRODUCTION

We have observed for the first time the magnetic resonance of Nd in a metal and obtained evidence of phonon-driven spin relaxation in this metallic host. The observed resonance arises from the Γ_6 ground state of Nd³⁺ in the cubic metal LaRh₂. Below 4.2 K, the linewidth is a linear function of temperature, typical for metals in which the spin relaxation is dominated by exchange with the conduction electrons. Above about 12 K, the linewidth exhibits a nonlinear rise with increasing temperature. The rise is too rapid to be accounted for by conduction-electron exchange scattering involving higher crystal-field levels.[1,2] We attribute the observed effect to a resonance relaxation phonon process. We are also able to observe the hyperfine structure of both ¹⁴³Nd and ¹⁴⁵Nd. This confirms our identification of the ESR signal and allows us to deduce values for the hyperfine coupling constants. For purposes of comparison, we have also measured the resonance of Gd in the same host.

II. SAMPLE PREPARATION AND ESR RESULTS

Samples were prepared by arc-melting the weighed constituents on a copper hearth in an argon atmosphere. Except as noted in Table I, all concentrations reported are nominal, based on the starting weights. The purity of the rhodium used is 99.99%, but the lanthanum is only 99% pure. The bulk of the impurity in the lanthanum is expected to be calcium, but the ESR of nominally pure LaRh₂ shows about 30 at.ppm of Nd and about 50 at.ppm of Gd. The samples were crushed in an agate mortar, placed in quartz sample tubes, and dispersed in paraffin immediately before measurement.

ESR measurements were made with a conventional reflection spectrometer at a frequency of 9.2 GHz. Fields were determined by a Hall probe, calibrated against proton NMR. Temperatures from 1.5 to 4.2 K were obtained by pumping on the liquid helium in which the samples were immersed. The temperature was determined by measuring the vapor pressure. Temperatures above 5 K were achieved with a commercial gas flow cryostat.[3] A Au-0.07-at.%-Fe vs Cu thermocouple, embedded in the paraffin used to disperse the sample, was used to measure temperatures in this range. The thermocouple was calibrated against a germanium resistance thermometer in a separate Dewar system. Measured spectra were analyzed by the method of Peter et al.[4] to obtain the the true linewidth, $\Delta H = 1/\gamma T_2$, and g value.

Below 4.2 K, the Nd linewidth can be described by a function of the form $a + bT$. The values of a, b, and the observed g value are tabulated for several samples in Table I. The value of a depends strongly on Nd concentration. The value of b is essentially independent of Nd concentration, but is increased somewhat by addition of Th impurities. The g value is independent of both Nd and Th concentration over the range examined. The significance of these observations will be discussed below.

At 1.5 K and low concentration, the line is sufficiently narrow to allow observation of the hyperfine structure due to the two $I = \frac{7}{2}$ isotopes: ¹⁴³Nd (12.2% abundant) and ¹⁴⁵Nd (8.3% abundant). There is considerable overlap between the two sets of hyperfine lines and some interference from the $I = 0$ line, but it is possible to measure the positions of several hyperfine lines accurately. The resulting spectrum fits the Breit-Rabi formula well, giving the hyperfine constants $A(^{143}\text{Nd}) = 212 \pm 1$ G and $A(^{145}\text{Nd}) = 131 \pm 1$ G. These A values are somewhat larger than observed in insulating CeO₂,[5] a trend observed in other metallic systems as well.[6]

Figure 1 shows the linewidth data over the full temperature range of our observations, after subtracting the residual width a appropriate to each concentration. The data can conveniently be described by the function

$$\Delta H = bT + c\Delta/(e^{\Delta/T} - 1), \tag{1}$$

TABLE I. Summary of ESR data for the various LaRh$_2$ alloys studied. Concentrations are specified as La$_{1-x-y}$R$_x$Th$_y$Rh$_2$, where R is Gd or Nd. The error bars are $\pm 2\sigma$ limits from a least-squares fit. Values for Nd are derived from data in the range 1.5–4.2 K; for Gd, data in the range 6–50 K were used to avoid interaction effects.

R	$10^{-2}x$	$10^{-2}y$	g	a(G)	b(G/K)
Nd	0.003[a]	0	2.63 ± 0.01	14 ± 1	5.5 ± 0.6
Nd	0.003[a]	0	2.63	15 ± 1	4.0 ± 0.8
Nd	0.013	0	2.63	13 ± 1	4.8 ± 0.3
Nd	0.025	0	2.63	13 ± 1	5.0 ± 0.3
Nd	0.05	0	2.63	14 ± 1	4.5 ± 0.2
Nd	0.10	0	2.63	15 ± 1	4.4 ± 0.4
Nd	0.20	0	2.63	21 ± 2	4.4 ± 0.2
Nd	0.50	0	2.63	34 ± 3	4.1 ± 0.6
Nd	1.0	0	2.63	36 ± 3	4.3 ± 0.2
Nd	0.025	1.5	2.63	27 ± 2	5.8 ± 0.5
Nd	0.025	5.0	2.64	84 ± 8	6.5 ± 1.0
Nd	0.05	1.0	2.63	25 ± 2	5.6 ± 0.4
Gd	0.05	0	1.99 ± 0.01	6 ± 0.5	1.7 ± 0.1
Gd	0.50	0	1.99	19 ± 2	1.6 ± 0.05
Gd	1.0	0	1.99	36 ± 3	1.6 ± 0.05
Gd	0.05	1.0	1.99	13 ± 1	1.7 ± 0.1

[a]Residual impurity concentration, estimated from ESR intensity.

where Δ is the energy of the excited state relative to the ground state. The solid line in Fig. 1 is a plot of Eq. (1) for a particular choice of b, c, and Δ. The data shown are accurately described by (1) using $b = 4.5 \pm 0.2$ G/K, $c = 120 \pm 40$ G/K, and $\Delta = 125 \pm 10$ K. As discussed below, c will contain a factor of Δ^2 if the phonons produce the relaxation,
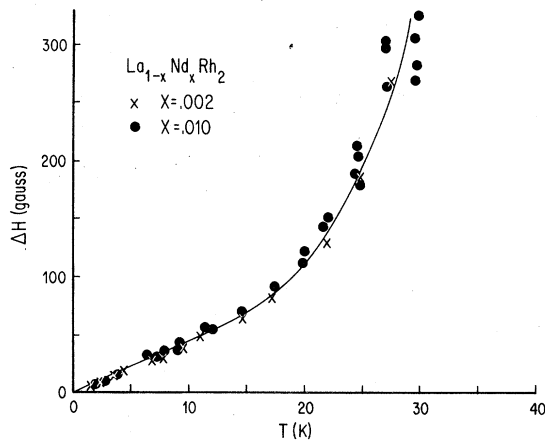

FIG. 1. Temperature-dependent part of the measured ESR linewidth for two concentrations of Nd in LaRh$_2$. The values plotted have been corrected by subtracting the residual widths a given in Table I. The solid line is a typical fit of Eq. (1) to the data, using $b = 4.5$ G/K, $c = 140$ G/K, and $\Delta = 135$ K.

but will be independent of Δ if only the conduction electrons contribute.

The resonance data for Gd are also contained in Table I. The linewidth is again of the form $a + bT$, but now over the entire temperature range from 6 to 50 K. The linewidth for the lowest concentration samples remains linear at lower temperatures, but the higher concentration samples show decreasing slope at low temperature, and even minima in linewidth versus temperature, indicative of magnetic ordering. Note that both the g value and high-temperature linewidth slope are independent of Gd and Th concentration for the samples examined.

III. DISCUSSION

In a metallic host, it is usually assumed that the local moment is coupled to the host conduction electrons by an exchange interaction, expressed here in the form $-(g_J - 1)J_{fs}\vec{J} \cdot \vec{s}$. In the absence of a magnetic resonance bottleneck, this interaction leads to a linear dependence of the resonance linewidth on temperature given by[7]

$$b = (\pi g k_B / \mu_B)[(g_J - 1)/g_J]^2 (J_{fs}\eta)^2 \qquad (2)$$

for an isolated doublet ground state. Here, g is the effective resonance g value, η is the density of states per spin, and b is the coefficient in $a + bT$. There will also be a temperature independent g shift, given by[7]

$$\Delta g = g[(g_J - 1)/g_J]J_{fs}\eta . \qquad (3)$$

The electronic density of states, which appears in both (2) and (3), can be estimated from the measured electronic susceptibility of LaRh$_2$, $\chi_e = 7.3 \times 10^{-5}$ cgs/mole.[8] This yields $\eta = 1.1$ state/(eV spin molecule). There are also effects arising from the exchange enhancement of the conduction electron susceptibility[9] which should appear in (2) and (3). Lack of data for this host forces us to ignore these effects, except as they may be present in the experimental χ_e. We have also neglected any dependence of J_{fs} on the conduction electron scattering wave vector.[10]

This simple model seems to account for the behavior of the Gd resonance reasonably well. Taking the average value of $b = 1.6$ G/K and the value of η deduced above, we find $J_{fs} = 0.008 \pm 0.001$ eV/molecule by using Eq. (2). This value is small, but not unreasonable in comparison with other results.[11] Using this value for J_{fs}, (3) would predict $\Delta g < 0.01$. Indeed, no shift relative to the usual $g = 1.99$ is seen. The insensitivity of the observed resonance to Gd and Th concentration indicates that a bottleneck is not present for this system. The linear temperature dependence of the line-

width over the entire temperature range indicates that the host is will behaved, and the observed non-linear behavior of the Nd linewidth must be a property of that ion.

Proceeding in the same way for Nd, Eq. (2) yields $J_{fs} = 0.015 \pm 0.002$ eV/molecule, using the average value of $b = 4.6$ G/K. This value of J_{fs} implies a g shift of -0.016 ± 0.002 due to the conduction electrons, assuming that J_{fs} is positive. (The Landé factor g_J is less than unity for Nd^{3+}.) The observed shift relative to the Γ_6 g value of[12] 2.667 is considerably larger, $g = -0.037 \pm 0.01$. The theoretical value does not take into account changes in the ionic g value due to the breakdown of Russell-Saunders coupling and due to host-dependent bonding effects.[13,14] The effect of intermediate coupling can be calculated from the wave functions for the free Nd^{3+} ion.[15] One finds an increase in g of 0.8%. Bonding effects can be estimated from measurements in other hosts, but there is little data for Nd. Measurements of Er in MgO imply a reduction of 1.4%.[14] Another method, applied to Er in Al,[16] leads to a reduction of 0.6%. Assuming that the bonding effects are the same for Nd as for Er, we arrive at a total change in the Γ_6 g value between $+0.2\%$ and -0.6%, referred to $g = 2.667$. By comparison the measured g shift is -1.4%. We conclude that the conduction electron contribution to the g shift is negative, and therefore J_{fs} is positive (ferromagnetic). Further analysis, and in particular any estimate of the wave-vector dependence of the exchange,[10] is clearly not warranted in view of the large uncertainties in the g shift.

The concentration dependence of b shown in Table I is near the limits of our measurement error, but we believe that it is real. Concentration dependence could be caused by several factors: changes in host η due to doping; interaction effects as observed for Gd; or dynamic coupling to the conduction electrons. The first possibility is unlikely, since it is expected to arise only in materials with a large d-like density of states. Small changes in the Fermi energy caused by doping can then produce large changes in the density of states. This effect is not expected to be large for LaRh$_2$ because η is too small to indicate a large d contribution, unlike LaRu$_2$,[8] where the change in η on doping has been observed.[17] Changes in η would also be expected to affect the Nd g shift and Gd linewidth slope. Neither effect is seen. We conclude, therefore, that η is effectively constant. Interaction effects are somewhat more likely. In the presence of noise, a small amount of curvature in the low-temperature linewidth vs temperature plots could be mistaken for decreasing slope. The addition of Th would tend to break

up the RKKY coupling between Nd spins, thus restoring the full linewidth slope. It does not appear possible to rigorously exclude this explanation. Finally, the exchange coupling to the conduction electrons can give rise to dynamic effects which are not included in (2) and (3). When the impurity and conduction electron resonance g values are equal, or nearly so, the dynamic effects produce the well-known resonance "bottleneck."[18] If the g values are different, as is the case here, it is still possible to estimate the effects of this coupling on the impurity resonance by using the more general methods of Ref. 19. Unfortunately, it is necessary to know the conduction electron resonance g value and several relaxation times to perform these calculations. Plausible assumptions for the necessary quantities reproduce the observed dependence of linewidth on concentration, and the observed constant Nd g value, but there are too many free parameters for this treatment to be taken seriously. In the absence of more direct measurements of the conduction electron g value and the pertinent relaxation times, this possibility must remain speculative. We can only conclude that the small concentration dependence observed may be due either to interactions or to dynamic coupling to the conduction electrons.

The sharp rise in the linewidth vs temperature plot shown in Fig. 1 is presumably connected with the existence of the Γ_8 excited crystal-field level in Nd^{3+}. Two mechanisms could produce such a rise: transitions to the excited level driven by the conduction electrons[1,2] or by the host phonons, the well-known resonance relaxation process. The first mechanism has been observed in several metallic systems[2] and the second is common in insulators.[20] Although the crystal-field parameters for Nd in LaRh$_2$ are not known, we can infer a certain amount from the ESR results. Over the range of interest, the temperature is large compared to the Zeeman splittings. We can therefore ignore the Zeeman splittings and write the linewidth due to conduction electron exchange coupling in a cubic system as[2]

$$\Delta H = \left(\frac{\pi k_B}{2 g \mu_B} (g_J - 1)^2 (J_{fs}\eta)^2 \right) \left(b'T + c' \frac{\Delta}{e^{\Delta/T} - 1} \right), \quad (4)$$

where g is the effective g value of the ground-state doublet, Δ is the energy of the first excited state, and

$$b' = 2 |\langle + | J_+ | - \rangle|^2,$$

$$c' = \tfrac{1}{2} \sum_i |\langle i | J_- | + \rangle|^2 + |\langle i | J_+ | + \rangle|^2$$

$$+ |\langle i | J_- | - \rangle|^2 + |\langle i | J_+ | - \rangle|^2$$

$$+ 2 |\langle i | J_z | + \rangle|^2 + 2 |\langle i | J_z | - \rangle|^2. \quad (6)$$

The ground doublet wave functions have been labeled by $|\pm\rangle$ and the excited-state wave functions by $|i\rangle$. The b' term, together with the prefactor, is equivalent to Eq. (2). As noted above, the experimental linewidth has a temperature dependence of the same form as Eq. (4), if we take $\Delta = 125$ K. Knowing Δ, we can characterize the shape of the temperature dependence by the ratio c'/b', which is determined in the theory only by matrix elements. Using the tabulated[12] wave functions, one finds that the ratio $c'/b' < 1.1$, the precise ratio depending on the (unknown) crystal-field parameters. This is much less than the observed value of $c'/b' = 27 \pm 9$, from which we conclude that there must be additional contributions to the relaxation.

The resonant phonon relaxation process is approximately described by[20]

$$1/T_1 = (3k_B^3 |M|^2/2\pi\hbar^4\rho v^5)\Delta^3/(e^{\Delta/T} - 1), \qquad (7)$$

where ρ is the host density and v is the speed of sound in the host. M is a sum of matrix elements which characterizes the strength of the orbit-lattice coupling between the ground and first excited states. The prefactor in (7) is difficult to calculate, but the order of magnitude can be estimated from experiments on Nd^{3+} in insulators. For values of Δ from 90–160 K, the prefactor is found to be in the range 3.5×10^4–3.6×10^5 s^{-1}/K^3.[21] Our experimental values, $c = 120$ G/K and $\Delta = 125$ K, correspond to a prefactor of 1.8×10^5 s^{-1}/K^3. Recent measurements[22] indicate that the strength of

the orbit-lattice coupling in metals, and hence the quantity M, can be comparable to that in insulators. Consequently, a substantial part of our experimental value of $c = 120$ G/K can reasonably be attributed to the resonant phonon relaxation process. Sugawara and Huang[23] have recently reached a similar conclusion for Ce in LaAs.

In conclusion, the resonance of Nd in a metallic host, LaRh$_2$, has been seen for the first time. At low temperatures, the Γ_6 ground-state spectrum exhibits a clear hyperfine structure, characterized by the hyperfine coupling constants $A_{143} = 212 \pm 1$ G and $A_{145} = 131 \pm 1$ G. At higher temperatures, resonant phonon relaxation occurs, leading to a very rapid broadening of the resonance.

Note added in proof. S. Stalinski and H. Drulis [Bull. Pol. Acad. Sci., 19, 729 (1971)] have observed a resonance in metallic LaH$_x$ which they attribute to the Γ_8 state of Nd^{3+}. The line is sensitive to hydrogen concentration, but no temperature dependence is reported.

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