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Paramagnetic resonance of Gd in Lu single crystals*

K. Baberschke and J. Nagel
Fachbereich Physik, Freie Universität Berlin-West Berlin, West Germany

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The spin resonance of dilute Gd in Lu single crystals has been measured. It shows a single-line spectrum. The field for resonance, as well as the linewidth, change as a function of crystal orientation. The experimental results are concentration independent (unbottlenecked) and can be described by $g = 2.10(1)$, a thermal broadening of the linewidth $b = 80$ (8) G/K and an axial crystal field parameter $D = -63(6)$ G. The results are compared with those in Y and Sc.

I. INTRODUCTION

Electron-spin resonance of localized moments (Gd) in metals enables us to determine the static and dynamic transverse susceptibility on a microscopic scale. The magnetization of the conduction electrons at the Gd site acts as an additional field and is measured as a shift of the field for resonance. The relaxation of the localized moment to the lattice via the conduction electrons is determined by the thermal broadening of the linewidth. If the experiment is performed on single crystals instead of in powder, the interaction of the paramagnetic ion with the crystalline electric field can be determined in addition. In contrast to the classical methods (specific heat, magnetization, etc.) which measure macroscopic averages and require relatively concentrated samples, the ESR method permits a microscopic determination of the properties of impurities in very dilute magnetic alloys.

The paramagnetic resonance of[1] Gd and other rare-earth ions (i.e., Er and[2] Dy) has been observed in single crystals of pure metals (i.e., Y,[3] Sc,[4] and[5] Mg). The theory of ESR spectra in dilute magnetic alloys including the crystalline-field structure has been developed by Plefka[6] and Barnes.[7] There are two limits: a completely resolved spectrum (Gd^{3+} with $S=J=\frac{7}{2}$ produces 7 lines) and a completely collapsed single-line spectrum caused by exchange narrowing. The condition for an exchange-narrowed spectrum is given by[6]

$$|\omega_M - \omega_{M'}| \ll \delta_{ie},$$

where $\omega_M, \omega_{M'}$ are the resonance frequencies for the different fine-structure transitions and δ_{ie} the relaxation rate from the impurity ion (here Gd) to the conduction electrons:

$$\hbar\delta_{ie} = \pi N^2(E_F)\langle J^2_{\mathrm{eff}}(q)\rangle kT .$$

That means the fine-structure splitting, caused by the crystalline electric field, has to be small compared to the thermal broadening of the linewidth δ_{ie}.

We report electron-spin-resonance measurements on Gd^{3+} in single crystals of hexagonal Lu and polycrystalline samples in the temperature range between 1.8 and 14 K. The resonance is a single line; the resonance field H_0, the linewidth ΔH, and the line-shape change as a function of the crystal orientation with respect to the applied field. In a Gd concentration range of 600–7800 ppm no change for the thermal broadening of the linewidth and for the g factor was observed.[1] Y, Sc, and Lu are isostructural (hcp), and the free atoms have a similar electronic structure: core, nd^1, $(n+1)s^2$. This is a rare-earth-like configuration, which makes these three metals favorable as diamagnetic diluents for rare-earth ions. Recent magnetization measurements[8] of dilute Tb, Dy, and Er in Y, Sc, and Lu studied the systematic of crystal-field parameters. Furthermore, ESR measurements have been performed on Sc: Er,[9] and Lu: Er.[10] In Sec. II we describe the single-crystal growing and susceptibility measurements on the undoped host. As will be shown in Sec. III, our ESR results of Lu: Gd show no bottleneck behavior in the relaxation mechanism in contrast to the Y: Gd and Sc: Gd resonance. Therefore in Lu: Gd the unbottlenecked g shift and thermal broadening can be detected easily. Both quantities were not determined in Sc: Gd,[4] and only extrapolated for the Y: Gd system.[3] In Sec. IV we compare the results with other host metals which are summarized in the table.

II. SAMPLE PREPARATION AND PROPERTIES OF HOST

The starting materials were lutetium, produced by the Ames Laboratory, and gadolinium with 99.9% purity. The impurity concentration for the lutetium was ~10 ppm for rare-earth metals and 15 ppm for other impurities.

The single crystals were prepared by melting the appropriate amounts of Gd and Lu in an arc furnace. A sample of ~4 g of the alloy was then remelted in a water-cooled copper crucible in a rf furnace. The single crystals were grown by slowly cooling to a temperature just below the melting point and keeping the sample at this temperature for some hours (similar to Ref. 8). By this method we got ingots of ~4 cm length and 5 mm diam which consisted of crystal grains several mm in diameter. For our purpose, the single-crystalline ends of the ingots were cut off with a crystal saw. Only the section plane was etched in concentrated H_3PO_4, and the sample was annealed again. The advantage of this method is that only ~10% of the surface of the crystal suffered etching or mechanical working. Using this technique we got better ESR results (larger signal intensity and smaller background signals) than by etching the total surface. The stated Gd concentrations are the nominal ones, which agree within 5% with the concentrations determined by saturation magnetization measurements.

The single crystals were oriented by Laue diagrams and measured in a conventional Varian *X*-Band ESR spectrometer. The orientation was changed by rotating the crystal in the Dewar. For the coefficient of the Lu electronic specific heat we used[11] $\gamma = 10.2$ mJ/mol K^2. Neglecting electron-phonon enhancement we get from the specific-heat data the conduction-electron density of states $N(E_F) = 2.3$ states/(eV atom spin). Our susceptibility measurements on undoped polycrystalline Lu yield $\chi_{\mathrm{exp}} = 20.5 \times 10^{-5}$ emu/mol ± 5% which was temperature independent in the range 2 K to room temperature. From this we get for the susceptibility of the conduction electrons $\chi_{\mathrm{ce}} = 22.2 \times 10^{-5}$ emu/mol, using[12] $\chi_{\mathrm{dia}} = -1.7 \times 10^{-5}$ emu/mol:

$$\chi_{\mathrm{exp}} - \chi_{\mathrm{dia}} = \tfrac{2}{3}\chi_s^{\mathrm{spin}} + \chi_d^{\mathrm{spin}} + \chi_{\mathrm{orb}} ,$$

where χ_s^{spin}, the Pauli spin susceptibility of the conduction-band *s* electrons, is enhanced by $1/(1-\alpha)$.

In the presence of a narrow *d* band at the Fermi energy the spin of this band contributes to the susceptibility $\chi_d^{\mathrm{spin}}(T)$. This contribution is temperature dependent. Our experiments show no temperature dependence, therefore we assume $\chi_d^{\mathrm{spin}}(T)$ to be negligible. Depending on the band structure of the conduction electrons, the orbital part of the conduction electrons can also contribute to the susceptibility χ_{orb}. In the absence of further information we have no possibility to determine the orbital contribution χ_{orb} and the enhancement factor $\alpha = U\chi(0)$. (U: Coulomb interaction, $\chi(q)$: dynamic susceptibility.) If we calculate χ_s^{spin} from the free-electron gas using $N(E_F) = 2.3$ states/(eV atom spin) and assume alternatively that α and χ_{orb} are small we get $\chi_{\mathrm{orb}} = 12.3 \times 10^{-5}$ emu/mol or $\alpha \approx 0.5$.

III. EXPERIMENTAL RESULTS AND ANALYSIS

The ESR spectrum of the S state ion Gd^{3+} (ground state $^8S_{7/2}$) in a hexagonal host can be described by the spin Hamiltonian

$$\mathcal{H} = g\mu_B H_0 S_z + D[S_z^2 - \tfrac{1}{3}S(S+1)] . \qquad (1)$$

The contributions of the fourth- and sixth-order crystalline field are neglected. Assuming $D \ll H_0$ (which will be justified by the analysis of the experimental results, see also Ref. 3), first-order perturbation theory can be used to obtain the eigenvalues. Off-diagonal contributions are smaller than the experimental error. Neglecting these, one gets

$$\mathcal{H} = g\mu_B H_0 S_z + \tfrac{1}{2}D[S_z^2 - \tfrac{1}{3}S(S+1)](3\cos^2\theta - 1) , \qquad (2)$$

where θ is the angle between H_0 and the c axis.

In the case of a completely collapsed spectrum we get a single resonance line at the center of gravity of all the fine-structure lines. The first moment $\langle\!\langle \omega \rangle\!\rangle$ describes the temperature and frequency dependence of the resonance:

$$\hbar\langle\!\langle \omega \rangle\!\rangle = \sum_n C_n(E_n - E_{n-1}) \Big/ \sum_n C_n ,$$
$$C_n = (e^{-E_{n-1}/kT} - e^{-E_n/kT}) \, |\langle n | S_x | n-1 \rangle|^2 . \qquad (3)$$

The angular variation of the field for resonance is obtained from $\langle\!\langle \omega \rangle\!\rangle - \omega_0$, which is proportional to $(3\cos^2\theta - 1)$, using (2) and (3).

The linewidth ΔH shows three contributions in the absence of a bottleneck:

$$\Delta H = a + \Delta H_k + \Delta H(\theta) , \qquad (4)$$

with the residual width a, the thermal broadening $\Delta H_k = bT$, and an additional width depending on the second moment $\langle\!\langle \Delta\omega^2 \rangle\!\rangle$ of the collapsed line. Using the moment method, the angular-dependent part of the linewidth equals[13]

$$\Delta H(\theta) \propto \langle\!\langle \Delta\omega^2 \rangle\!\rangle^{1/2} \propto |3\cos^2\theta - 1| . \qquad (5)$$

In the case of extreme exchange narrowing $\Delta H(\theta)$ is given by the theory of Plefka[6]:

$$\Delta H(\theta) = \langle\!\langle \Delta\omega^2 \rangle\!\rangle / 3\Delta H_k \propto (3\cos^2\theta - 1)^2 . \qquad (6)$$

For an angle $\theta = 54.5°$ all angular-dependent contibutions to the linewidth and the field for resonance vanish. We first analyzed spectra at this angle to determine the g shift and the thermal broadening b.

A. Determination of *g* factor and thermal broadening

Figure 1 shows the spectra for different angles: A computer analysis proves that the line shape for

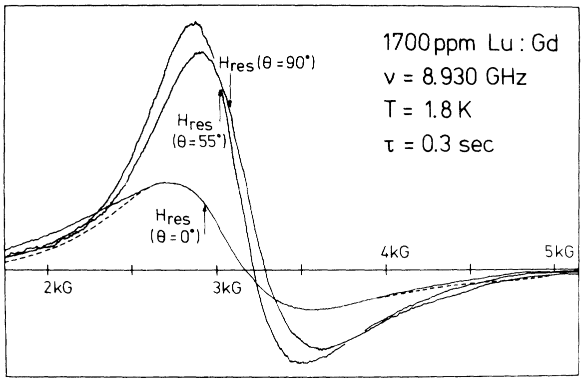

FIG. 1. Resonance spectrum at three different angles θ, where θ is the angle between the magnetic field direction and the c axis. The dashed line is the Lorentz fit for the $\theta = 0°$ line. The recorder traces for $\theta = 55°$ and 90° coincide with the Lorentz fit.

the $\theta \approx 55°$ spectra is perfectly (error <1%) Lorentzian. The g value is determined as $g = 2.10(1)$. No concentration or temperature dependence of the g value was detected. Figure 2 shows the linewidth as a function of temperature. The single-crystal data (Δ, O) show a slope of $b = 80$ G/K and no concentration dependence. To confirm that there was no concentration dependence of the thermal broadening and the g shift we measured several polycrystalline samples in a range of Gd concentraton between 600 and 7800 ppm. Figure 2 shows constant slope for all samples independent of c (besides "ordering" effect for high concentrations). This leads to the conclusion that the ESR of Lu: Gd (in the range of concentration we measured) does not show a bottleneck effect in the relaxation mechanism. The thermal broadening for the polycrystalline samples does not show a Lorentzian line shape. Therefore a determination of the linewidth is not so reliable.

The best fit for the resonance of the single-crystal sample (Figs. 1 and 2) yields the parameters

$$\Delta g = N(E_F)J(0) = +0.108(10) ,$$

$$b = (\pi k / g\mu_B)\langle J^2(q)\rangle N^2(E_F)$$

$$= 80(8) \text{ G/K} ,$$

where $N(E_F)$ is the conduction-electron density of states for one spin direction at the Fermi level. $J(q)$ is the wave-vector-dependent exchange parameter. The average $\langle\ \rangle$ is taken over the Fermi surface $0 < q < 2k_F$.

Furthermore, because of the discrepancy between the specific heat and susceptibility of the Lu host (Sec. II), the presence of an exchange enhancement has to be assumed:

$$J_{\text{eff}}(0) = J(0)/1 - U\chi(0) = 0.047 \text{ eV} ,$$

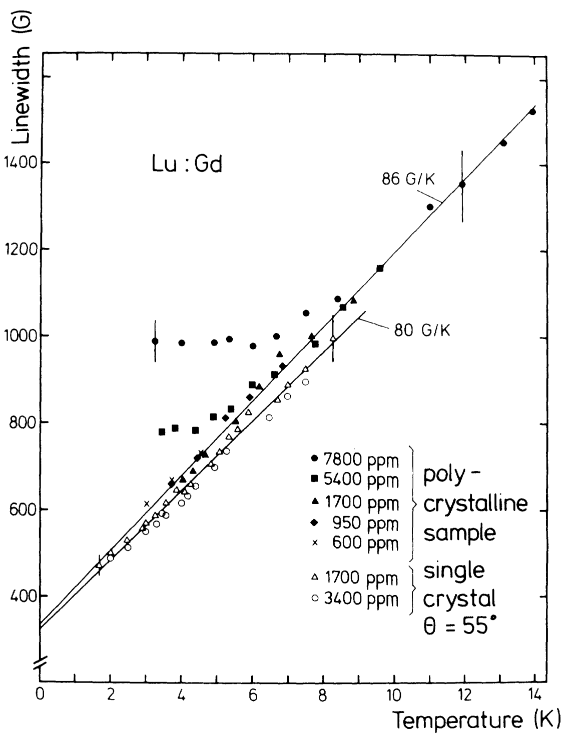

FIG. 2. Linewidth as a function of temperature for polycrystalline samples and single crystals. The high-concentration samples show at low temperatures "ordering" effects. This is consistent with our susceptibility measurement. For the 7800-ppm sample we measured a paramagnetic Curie temperature of $T_c = +3$ °K.

$$\langle J^2_{\text{eff}}(q)\rangle = \langle (J(q)/ - U\chi(q)])^2\rangle$$

$$= 6.8 \times 10^{-4} \text{ eV}^2 .$$

Here[11] $N(E_F) = 2.3$ states/(eV atom spin) was assumed.

B. Determination of crystalline-field parameter

Using formulas (2) and (3) the field for resonance yields

$$H_{\text{res}}(\theta) = g\mu_B H_0 + \langle\!\langle \Delta\omega \rangle\!\rangle ,$$

$$\langle\!\langle \Delta\omega \rangle\!\rangle = (\langle\!\langle \omega \rangle\!\rangle - \omega_0)\,\alpha(3\cos^2\theta - 1) . \tag{7}$$

For the temperature and frequency given in Fig. 3 and $\theta = 0°$, $\langle\!\langle \Delta\omega \rangle\!\rangle = 1.4D$, $\langle\!\langle \omega^2 \rangle\!\rangle = 12.8D^2$ and $\langle\!\langle \Delta\omega^2 \rangle\!\rangle = 10.85D^2$. This angular dependence of the resonance field $H_{\text{res}}(\theta)$ is shown in Fig. 3(a). The experimental results are in good agreement with the expected angular dependence. The best fit yields $D = -63$ G. Figure 3(b) shows the linewidth $\Delta H(\theta)$ as a function of orientation. The experimental linewidth as well as the field for resonance were determined by fitting a Lorentzian line shape to the recorder trace. As shown in Fig. 1 the spectrum for $\theta = 0$ deviates from a Lorentzian line

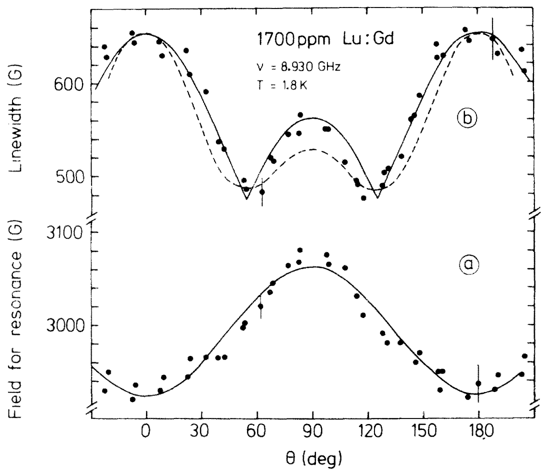

FIG. 3. (a) Field for resonance as a function of the angle θ. The curve is calculated using formula (7) and $D=-63$ G. (b) Linewidth as a function of angle θ for the same sample. The full line is the square root of the second moment [Eq. (5)] for $|D|=55$ G. The dashed line shows the Plefka theory in the limit of extreme exchange narrowing [Eq. (6)] for $|D|=82$ G.

shape.

The variation of linewidth as a function of θ is shown in Fig. 3(b). Because the crystal-field splitting is of the same order of magnitude as the thermal broadening [$\Delta H_k(1.8\text{ K})=144$ G], the extreme exchange narrowing [Eq. (6)] will not describe the angular dependence of the linewidth very well. For the dashed line we used Eq. (6) and $|D|=82$ G; the full line shows Eq. (5) and $|D|=55$ G. As can be seen from Fig. 3(b), none of these equations describes the angular dependence of the linewidth very well. The most reliable determination of the crystalline-field parameter is given therefore by the variation of the field for resonance using the first moment method, which gave $D=-63(6)$ G.

IV. DISCUSSION

In the Table I we summarize the experimental results and compare them with those of Y, Sc, and La (the resonance of Gd in the polycrystalline fcc phase of La has been reported recently by this group[14]). In this table we show furthermore the electronic specific-heat γ and susceptibility χ data. Our own susceptibility measurements are in agreement with the literature. All four metals show a positive g shift. We believe that negative contributions to the exchange integral ($J_{\text{cov.mix.}}$) are negligible.[15] Therefore these numbers give a good possibility to determine J_{atm}, the positive Heisenberg exchange interaction. The specific-heat data show that the conduction-electron density of states at the Fermi surface is roughly the same for all metals $N(E_F)\approx 2.2$ states/(eV atom spin). Consequently the amount of g shift should be the same assuming that there is no big change in $J_{\text{atm}}(0)\approx 55$ meV. The susceptibility measurements show slightly different results and may be explained by the electron-electron enhancement (Sec. II). Using this number the thermal broadening b can be calculated $b=(\Delta g)^2\pi k/g\mu_B\approx 260$ G/K. The experimental results (also for Y, see Table I and Sec. III) are smaller by a factor 2–4. This is a general experimental fact and may be explained by the wave-vector dependence of $J(k,k')$. But a quantitative analysis for these metals seems not to be meaningful because of the complicated Fermi surface.

In the last row we show the crystalline-field pa-

TABLE I. Specific-heat, susceptibility, and ESR parameters of Gd in Y, La, Sc, and La. The crystalline-field parameter is given in units of field (for $g=2.10$, 100 G correspond to 98×10^{-4} cm^{-1}).

	Y	Lu	Sc	La hcp	La fcc
c/a	1.571	1.585	1.594	1.616	⋯
γ (Ref. 11) (mJ/mol K^2)	10.1	10.2	10.8	9.4	11.5
χ [a] (10^{-5}emu/mol)	21 [b]	20.5 [b]	40 [c]	13 [c]	15 [c]
$\Delta g_{\max}$	(+0.15) [d]	+0.108(10)	>0 [e]	⋯	+0.117(10) [f]
b (G/K)	250(75) [d]	80(8)	⋯	⋯	75(8) [f]
D (G)	−150(20) [d]	−63(6)	≈(−120) [e]	⋯	⋯

[a] At 30 K, uncorrected.

[b] No temperature dependence up to 300 K.

[c] χ decreases with increasing temperature the corresponding values for 300 K are: 32(Sc), 7.3(La hcp), and 9.6 (La fcc).

[d] Reference 3, the g shift is extrapolated.

[e] Reference 4, D was extracted from the data given in the reference.

[f] Reference 14, and private communication.

rameter D. The fact that Eq. (5) fits better the experimental results seems to indicate that the line broadening is rather caused by superposition, and exchange narrowing is less important. This is in accordance with the results of Barnes[7] who predicts for the bottlenecked case a larger narrowing than for the nonbottlenecked case. This is also confirmed by the fact that the values of D determined from the field for resonance and the line broadening agree better than in the Mg: Gd and Y: Gd experiments. The negative sign is in agreement with the point-charge model. If there exists a valence difference between the paramagnetic ion and the host a change in the sign of the crystal-field parameter can be observed (i.e., for Mg^{2+}: Gd^{3+}, $D = +140$ G). This may be explained by a screening of the conduction electrons. A quantitative comparison with other rare-earth ions in the same host material seems to be difficult because the origin of the crystal-field splitting for the "S-state" ions is quite different. A comparison with insulators shows that the crystal-field splitting in these metals is smaller (in La ethylsulfate $D \approx +240$ G).

In summary we have detected the spin resonance of dilute Gd in single crystals of Lu. In the range of concentration we used the system is unbottlenecked. Therefore the full g shift and thermal broadening were easily detected. If we assume that the spin-flip scattering of the conduction electrons at the Gd ion δ_{ei} is of the same order of magnitude for all four metals[16] (Y, Sc, La, Lu), the reason for the nonbottlenecked behavior has to be due to a larger electron-lattice relaxation δ_{eL} in Lu compared to the other ones. This can be caused by imperfections in the samples (strain). The large residual linewidth $a = 320$ G supports this idea.

Note added in proof. Recent ESR measurements of Sc: Gd at two microwave frequencies and different Gd concentrations yield an axial crystalline field parameter of $D \approx -330$ G. Detailed results will be published.

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