Electron spin resonance of $Gd_xLa_{1-x}Pd_3$ intermetallic compounds

Jang W. Kim and James S. Karra
Department of Physics, Temple University, Philadelphia, Pennsylvania 19122
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We have extended our ESR study of Gd in the intermetallic compound $Gd_xLa_{1-x}Pd_3$ to samples annealed at 940 °C and cooled rapidly to room temperature. We have measured the ESR linewidths and g shifts as a function of temperature and concentration of Gd. They were found to exhibit Korringa-like thermal broadening between 6 and 40 °K. We have deduced the average value of J_{eff} for the effective-exchange integral to be 0.24 ± 0.03 eV. We have calculated also the magnitudes of the conduction-electron relaxation rates to the lattice, (i) due to the undisturbed host lattice, (ii) by spin-flip scattering due to the magnetic impurity Gd, and (iii) by spin-flip scattering due to the nonmagnetic impurity Th.

I. INTRODUCTION

The exchange interaction between the spins of the conduction electrons and those of the paramagnetic impurities in the intermetallic systems is given by the following Hamiltonian[1–5]:

$$H = J\vec{S}_i \cdot \vec{S}_c \ , \tag{1}$$

where S_i and S_c are the spins of the paramagnetic ions and the conduction electrons, respectively, and J is the exchange-interaction integral between the two spin systems. As explained in a previous paper,[6] the exchange interaction gives rise to the Korringa-like thermal broadening ΔH of the ESR line of the Gd ion and the resonance frequency shift (g shift) Δg.

Our present work is an extension of the ESR study of Gd^{3+} in the host lattice of $LaPd_3$.[6] This intermetallic compound $Gd_xLa_{1-x}Pd_3$ annealed at 940 °C and cooled rapidly to room temperature contrasted with our previous study[6] of the two sets of samples annealed at 740 and 840 °C and cooled rather slowly to room temperature. The spin-lattice relaxation rates and g shifts were studied as a function of temperature and concentration of Gd. The concentration of Gd was varied from 0.27 to 2.0 at.%. The effective average value J_{eff} (0.24 ± 0.03 eV for the present samples) was deduced and found to be larger than the J_{eff}values (0.16 ± 0.03 eV) reported for the samples annealed at 740 and 840 °C.[6]

We have added thorium metal (nonmagnetic) to the intermetallic compound to form $Gd_xTh_yLa_{1-x-y}Pd_3$ system. The concentration (y) of Th was varied from 1 to 16 at.% to introduce additional spin-flip scattering due to the nonmagnetic impurity Th^{4+} and to open up the bottleneck in the relaxation process of the conduction electrons.

II. THEORIES

We quote below only the final expressions[7–15] for the linewidth ΔH and g shift Δg as functions of temperature and concentrations of Gd and Th impurities.

$$\Delta g_{\max} = J_{\text{eff}}(0)\eta \ , \tag{2}$$

$$\gamma \Delta H_{\max} = (\pi/\hbar)\eta^2 J_{\text{eff}}^2 kT = \delta_{ic} \ , \tag{3}$$

$$\Delta g = [x^2/(1+x)^2 + y^2]\Delta g_{\max} \ , \tag{4}$$

$$\Delta H = \tfrac{3}{2}[\eta \delta_{cl} kT/\gamma S(S+1)C_{\text{Gd}}] \ , \tag{5}$$

$$\left[\frac{d(\Delta H)}{dT}\right]_{\text{exp}} = \frac{d(\Delta H_{\max})/dT}{6.014 \times 10^{15} J_{\text{eff}}^2} \times \left[\frac{\delta_{cl}^0}{C_{\text{Gd}}} + \frac{\partial \delta_{cl}}{\partial C_{\text{Gd}}} + \left[\frac{\partial \delta_{cl}}{\partial C_{\text{Th}}}\right]\frac{C_{\text{Th}}}{C_{\text{Gd}}}\right] . \tag{6}$$

All the notations here are the same as those of the Ref. 6. From the above expressions, we have deduced the effective-exchange integral J_{eff} and the conduction-electron relaxation rates to the lattice.

III. EXPERIMENT

Our samples were prepared in an argon arc furnace in the same manner as we prepared the two previous sets of samples.[6] The procedure in annealing the previous two sets of samples was to heat them for about 100 h at 740 and 840 °C and then gradually lower the furnace temperature over a period of 6 to 7 h. However, the present samples have been cooled at a faster rate (about 1 h) after they were annealed at 940 °C.

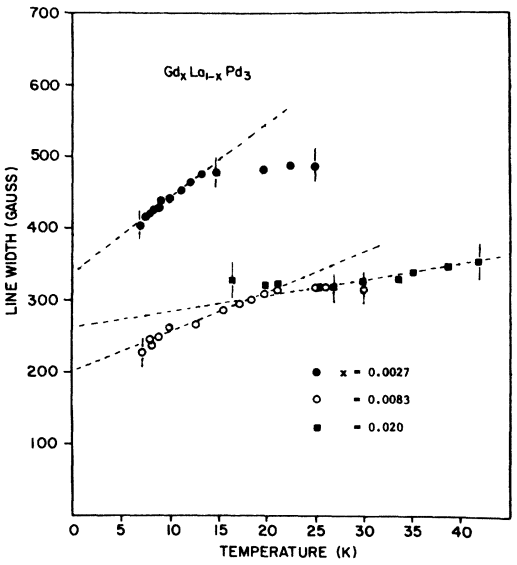

FIG. 1. ESR linewidth ΔH of Gd^{3+} in $Gd_xLa_{1-x}Pd_3$ annealed at 940 °C as a function of temperature for various Gd concentrations.

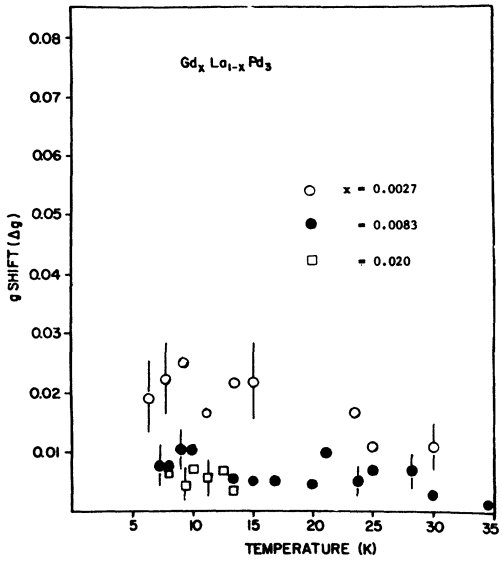

FIG. 2. ESR g shifts Δg of Gd^{3+} in $Gd_xLa_{1-x}Pd_3$ annealed at 940 °C as a function of temperature for three Gd concentrations.

The crystal structure of the samples was investigated by the x-ray diffraction technique.

IV. RESULTS

Thermal broadening of the linewidths of the samples annealed at 940 °C increases linearly with the temperature and reaches a plateau finally at some higher temperatures. Samples with different concentration of Gd reach a plateau in ΔH at different temperatures ranging from 15 to 50 °K. In our calculation we have taken into account only the linear portions of the linewidth versus temperature plots in Fig. 1. The parameters, $x, d(\Delta H_{max})/dT$, and Δg_{max} were deduced from the data of ΔH and Δg in Figs. 1 and 2 as described elsewhere[4,6,16]

$$x = 2.88; \quad \frac{d(\Delta H_{max})}{dT} = \frac{18.6\ \text{G}}{^\circ\text{K}}; \quad \Delta g_{max} = 0.035 \ .$$

Substituting the above values into the Korringa relation and the Eq. (3), we find

$$J_{eff} = 0.24 \pm 0.03 \text{ eV}$$

from ΔH measurement ,

$$J_{eff}(0) = 0.29 \pm 0.1 \text{ eV}$$

from Δg measurement .

The conduction-electron relaxation rates to the lattice due to the pure host lattice (δ_{el}^0) and by spin-flip scattering due to magnetic impurity Gd $[\partial(\delta_{el})/\partial(C_{Gd})]$ are deduced from the thermal broadening $d(\Delta H)/dT$ vs $1/C_{Gd}$ plot in Fig. 3 and found to be

$$\delta_{el}^0 = (8.8 \pm 2.0) \times 10^{11} \text{ sec}^{-1} \ ,$$

$$\frac{\partial(\delta_{el})}{\partial(C_{Gd})} = \frac{(1.4 \pm 0.5) \times 10^{11} \text{ sec}^{-1}}{(\text{at.\% Gd})} \ .$$

A similar plot (Fig. 4) with thorium as an additional nonmagnetic impurity gives the spin-lattice relaxation rate to the lattice by spin-flip scattering due to Th:

$$\frac{\partial(\delta_{el})}{\partial(C_{Th})} = \frac{(2.2 \pm 1.0) \times 10^{11} \text{ sec}^{-1}}{(\text{at.\% Th})} \ .$$

V. DISCUSSION

From the previous and present data on the three sets of samples prepared and annealed at three different temperatures, we find the host lattice to be strongly dependent on the annealing and cooling process. The linewidth of the samples annealed at 740 °C decreases linearly with temperature from around 50 down to 20 °K and then begins to increase with further decreases in temperature, whereas the samples annealed at 840 and 940 °C do not show such minima in their variation of the linewidth down to 6 °K. We attribute the increase in ΔH of the samples annealed at 740 °C at lower temperature to the ordering effects due to the presence of impurity ions existing in clusters rather than dispersed homogeneously in the entire lattice. The annealing at lower temperature could be the cause of the inhomogeneous dispersion of impurity ions.

Although the experimental parameters such as ΔH and Δg were found to be sensitive to the annealing temperature of the sample, the average value J_{eff} is al-

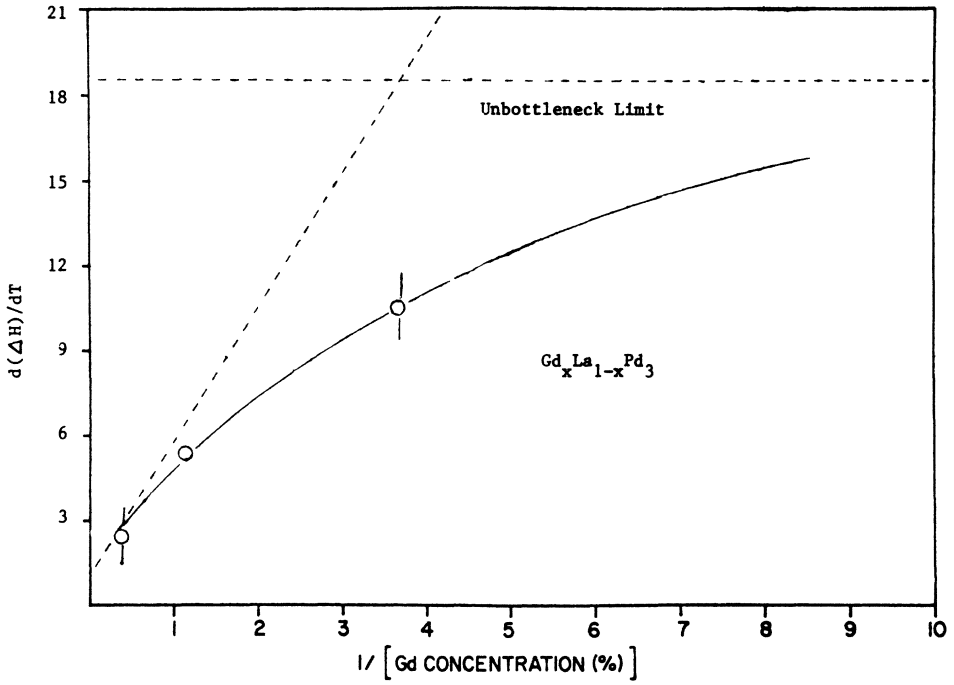

FIG. 3. Thermal broadening $d(\Delta H)/dT$ of the ESR linewidth of Gd^{3+} in $Gd_xLa_{1-x}Pd_3$ annealed at 940° as a function of $1/C_{Gd}$(C_{Gd}:Gd concentration).

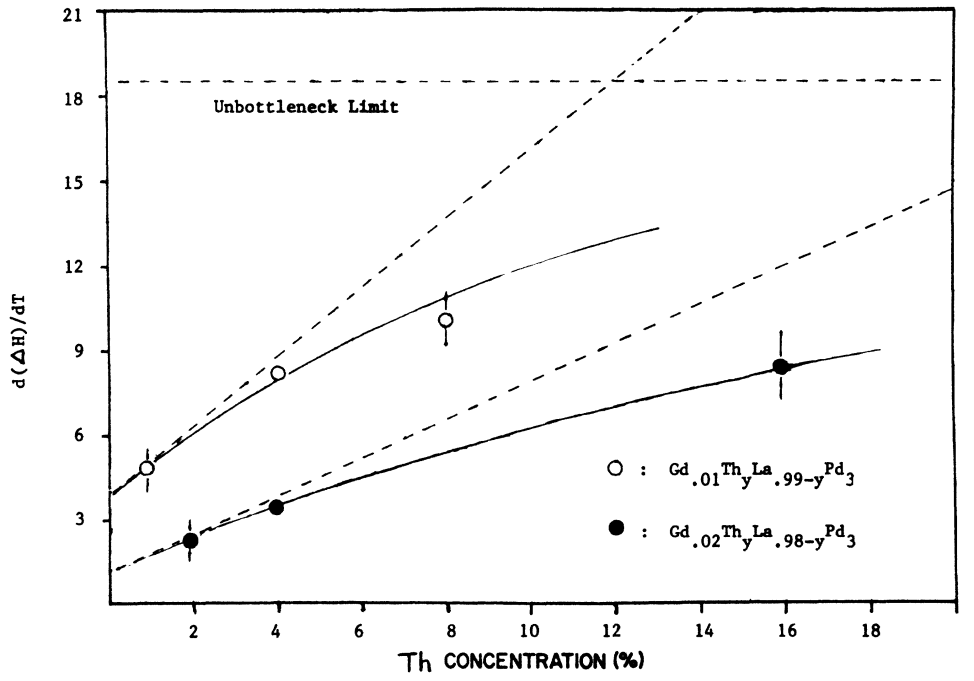

FIG. 4. Thermal broadening $d(\Delta H)/dT$ of the ESR linewidth of Gd^{3+} in $Gd_xTh_yLa_{1-x-y}Pd_3$ annealed at 940°C as a function of Th concentration.

most the same for the sets of samples annealed at 740 and 840 °C ($J_{eff}=0.16$ eV)[6], and is slightly larger in the present set of samples ($J_{eff}=0.24$ eV). However, the conduction-electron relaxation rate δ_{cl}^0 of the pure host lattice varies considerably depending on the annealing temperature: $(2.9\pm0.7)\times10^{11}\text{sec}^{-1}$ for the first set, $(3.7\pm0.9)\times10^{11}$ sec^{-1} for the second set, and $(8.8\pm2.0)\times10^{11}$ sec^{-1} for the present set. For the $LaPd_3$ system the fcc crystal structure (disordered state) may be transformed into the ordered cubic structure ($AuCu_3$type)[6] under the proper annealing process. This indicates that the samples of our previous work (annealed at 740 and 840 °C) may be structurally ordered to a lesser extent than the one annealed at 940 °C.

However, the faster cooling process may result in more lattice defects in some cases. Our result of a higher value for the δ_{cl}^0 in the sample annealed at 940 °C indicates that there are more scattering centers for the conduction-electron relaxation in the pure host lattice. The spin-flip scattering rate varies directly with the number of scattering centers.[17] Therefore we may have introduced more defects due to faster cooling. We assume that the residual linewidth ΔH_r is present when extrpolated to 0 °K in Fig. 1 and is due to the lattice stresses, the dipolar broadening and the unresolved hyperfine structure.

VI. CONCLUSION

The thermal broadening of the linewidth ΔH and the g shift due to the concentration of Gd show that samples with high Gd concentration (0.83 at.% or more) do suffer from the bottleneck effect. No temperature dependence of Δg (dynamic effect) was observed in all the samples in the temperature range of 6 °K and above. Since all the g shifts observed are positive, we conclude that the main contribution to the g shift is from the s-band[3] conduction electrons and that the exchange integral J_{eff} is positive.

The J_{eff} values calculated from the thermal broadening of the line-width ΔH are quite different from the ones calculated from the g-shift data for the previous two sets of samples. By contrast, we get almost the same value for J_{eff} when we use either g-shift data or ΔH data for the present set of samples.

ACKNOWLEDGMENT

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[1] M. Peter, J. Dupraz, and H. Cottet, Helv. Phys. Acta. 40, 301 (1967).
[2] H. K. Schmidt, Z. Naturforsch. A 27, 191 (1972).
[3] D. Davidov, A. Chelkowski, C. Rettori, R. Orbach, and M. B. Maple, Phys. Rev. B 7, 1029 (1973).
[4] C. Rettori, H. M. Kim, E. P. Chock, and D. Davidov, Phys. Rev. B 10, 1826 (1974).
[5] H. Cottet, P. Donze, J. Dupraz, B. Giovannini, and M. Peter, Z. Angew. Phys. 24, 249 (1968).
[6] J. W. Kim and J. S. Karra, Phys. Rev. B 15, 2538 (1977), B 16, 1293 (1977).
[7] J. Korringa, Physica 16, 601 (1950).
[8] H. Hasegawa, Prog. Theor. Phys. 21, 483 (1959).
[9] A. C. Gossard, A. J. Heeger, and J. H. Wernick, J. Appl. Phys. 38, 1251 (1967).
[10] B. Giovannini, Phys. Lett. A 26, 80 (1967).
[11] A. Overhauser, Phys. Rev. 89, 689 (1953).
[12] T. Moriya, J. Phys. Soc. Jpn. 18, 516 (1963).
[13] A. Narath and H. T. Weaver, Phys. Rev. 175, 373 (1968).
[14] R. W. Shaw, Jr. and W. W. Warren, Jr., Phys. Rev. B 3, 1562 (1971).
[15] J. Zitkova-Wilcox, Phys. Rev. B 7, 3203 (1973).
[16] M. Peter, D. Shalteil, J. H. Wernick, H. J. Williams, J. B. Mock, and R. C. Sherwood, Phys. Rev. 126, 1395 (1962).
[17] J. Winter in *Magnetic Resonance in Metals* (Clarendon, Oxford 1971), p. 168.