Paramagnetic resonance of Gd^{3+} as a probe of exchange and crystal-field effects in singlet-ground-state systems*

K. Sugawara and C. Y. Huang
Department of Physics, Case Western Reserve University,† Cleveland, Ohio 44106

Bernard R. Cooper
Department of Physics, West Virginia University, Morgantown, West Virginia 26506

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We have studied the use of paramagnetic resonance of dilute Gd impurities as a probe of exchange and crystal-field effects in the singlet-ground-state systems Tm*X* and Pr*X* (where *X* is one of the group-V*A* elements, P, As, Sb, Bi), i.e., the thulium and praseodymium monopnictides of NaCl structure. Analysis of the temperature-dependent resonance *g*-value behavior yields values for the Gd-Tm and Gd-Pr exchange interactions. The Gd-Tm exchange changes sign with increasing lattice parameter (on going from the phosphide and arsenide to the antimonide and bismuthide); while the Gd-Pr exchange becomes increasingly negative with increasing lattice parameter. Analysis of the temperature dependence of the linewidth yields values for the crystal-field splitting of Tm^{3+} and Pr^{3+} in agreement with those from neutron scattering. We briefly mention recent experiments using EPR of Gd in TbP to probe the behavior of the staggered susceptibility in the critical region.

I. INTRODUCTION

There has been much interest in recent years in the magnetic properties of rare-earth systems where the rare earth has a crystal-field-only singlet ground state.[1,2] The occurrence of magnetic ordering in such systems depends on a competition between exchange and crystal-field effects.[1] While the dominance of crystal-field effects explains the lack of magnetic ordering in compounds such as the thulium and praseodymium monopnictides and this dominance also explains the basic features of susceptibility and high-field magnetization measurements, understanding of the magnetic behavior is not complete, particularly with regard to the role played by exchange in dynamic effects. We have used two types of paramagnetic resonance experiments to study paramagnetic singlet-ground-state systems. In one type of experiment, as recently reported,[3(a)] we study the paramagnetic resonance in one of the crystal-field excited states of the rare earth in a pure concentrated paramagnetic singlet-ground-state system. In the second type of experiment, as reported here, we study the paramagnetic resonance of dilute Gd impurities used as a probe of the magnetic behavior of such a system.[3(b)] These studies provide information on the exchange and crystal-field effects in the singlet-ground-state systems of interest. Obtaining this information depends on the fact that the resonance *g* values and line widths of the Gd impurities serve to probe the behavior of the isothermal and isolated susceptibilities of the host materials. (The isothermal susceptibility is the susceptibility measured under circumstances where the spin system remains in thermal equilibrium with the lattice during the measurement period. This means that the thermal populations of the various crystal-field levels adjust themselves in a way corresponding to the change in Boltzmann factors as the energies of the levels change with magnetic field. The isolated susceptibility is that measured when the thermal populations of the levels do not change. The effect measured is due to the change in wave functions, and hence moments, with field, i.e., the polarization effect.)

As shown in Fig. 1, the ground state of both Tm^{3+} and Pr^{3+} with fourth-order crystal-field anisotropy

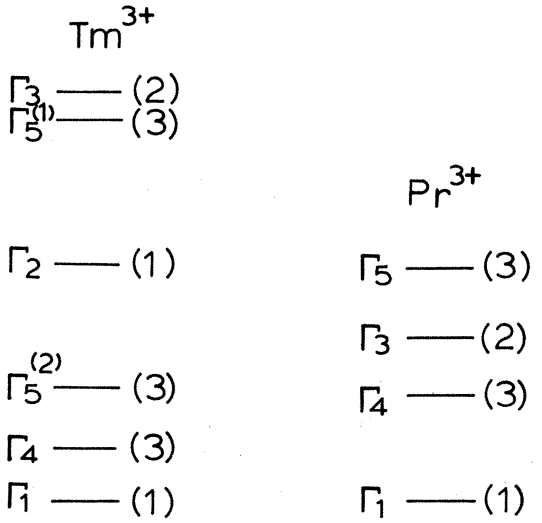

FIG. 1. Crystal-field energy levels for Tm^{3+} and Pr^{3+} in octahedral environment when fourth-order crystal-field anisotropy is dominant.

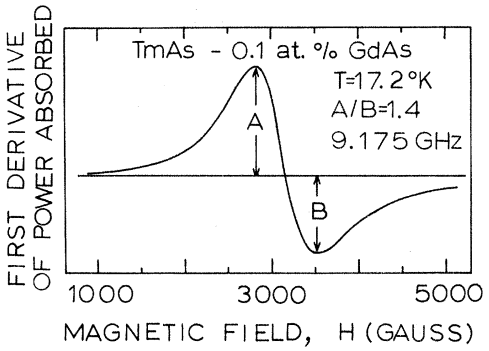

FIG. 2. Shape of the EPR absorption of Gd^{3+} for TmAs–0.1-at.% GdAs at 9.1 GHz.

dominant in the NaCl-structure monopnictides is a singlet Γ_1 state; and the order of magnitude of the energy separation between the ground state and the first excited state is between 10 and 100 °K. Therefore one expects that the most interesting behavior of the EPR of the Gd impurities would occur in the temperature range between 4.2 and 300 °K. We have studied the EPR of Gd^{3+} with nominal concentration between 0.05 and 10 at.% in PrP, PrAs, PrSb, and PrBi and with nominal concentration between 0.1 and 10 at.% in TmP, TmAs, TmSb, and TmBi. We have used our results for temperature dependence of the Gd^{3+} EPR g shift and linewidth to obtain values for the Gd–Pr and Gd–Tm exchange interaction and for the crystal-field splitting in the host monopnictide.

II. SAMPLE PREPARATION AND EPR SPECTROMETER

A number of samples of n-at.% GdX in TmX and n-at.% GdX in PrX (n is less than 10, X = P, As, Sb, Bi) were prepared in powdered form. The alloys $Gd_\xi R_{1-\xi}$, where R is Pr or Tm, were first made by using an electric induction heater. The two constituents, Gd and R, were heated in a tantalum crucible under argon atmosphere for about

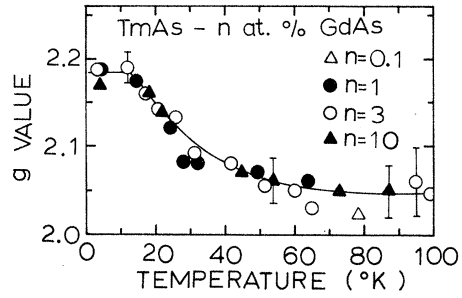

FIG. 4. Temperature dependence of EPR g value of Gd^{3+} in TmAs–n-at.% GdAs (n = 0.1, 1, 3, 10).

1 h for $Gd_\xi Pr_{1-\xi}$ and for about 20 or 30 min for $Gd_\xi Tm_{1-\xi}$. For $Gd_\xi Tm_{1-\xi}$, because of the high vapor pressure of Tm metal, it was necessary to use an argon pressure of 2 or 3 atm. After making the alloys in this manner, turnings of the alloys were prepared. Thereafter the process for making the intermetallic compounds with the group-VA elements is as given by Jones.[4] The purities of the rare-earth metals and group-VA elements used were higher than 99.9% and 99.999%, respectively. Standard x-ray powder diffraction techniques were used to confirm that the samples had the correct rock-salt structure and lattice constants.

Our EPR spectrometer is a conventional one operating at 9.1 GHz.

III. REVIEW OF THE THEORY g SHIFT DUE TO Gd-HOST EXCHANGE AND OF THEORY OF THE RESONANCE LINE WIDTH

Our major interest is to study the exchange interaction between Gd^{3+} ion and the surrounding host rare-earth ions and to study the crystal-field splitting of the host rare-earth ions. The isothermal susceptibility of the host rare-earth ion affects the g value of Gd^{3+} via the exchange interaction between them; and the spin fluctuations of the host ion determine the linewidth of Gd^{3+}. In

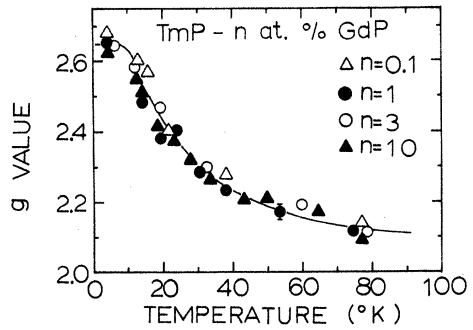

FIG. 3. Temperature dependence of EPR g value of Gd^{3+} in TmP–n-at.% GdP (n = 0.1, 1, 3, 10).

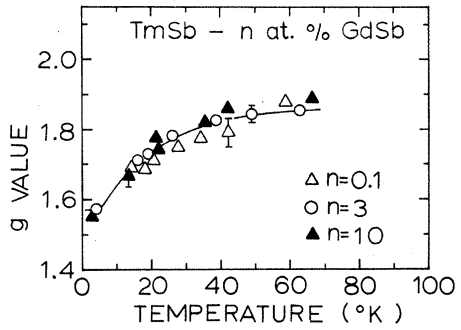

FIG. 5. Temperature dependence of EPR g value of Gd^{3+} in TmSb–n-at.% GdSb (n = 0.1, 3, 10).

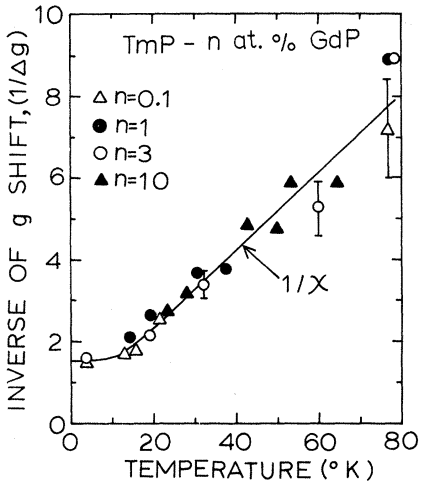

FIG. 6. Comparison between the g shifts of Gd^{3+} ions in TmP and the magnetic susceptibility of TmP. $1/\chi$ is in arbitrary units.

this section we would like to review some existing theories on the g value and the linewidth.

A. g-shift due to Gd-host exchange

We consider the situation in which the exchange interaction between a Gd^{3+} ion and the surrounding rare-earth ions is isotropic. The Hamiltonian of Gd^{3+} is written

$$\mathcal{H} = g_{Gd}\mu_B \vec{S}_{Gd}\cdot\vec{H} + \sum_j J_j \vec{S}_{Gd}\cdot\vec{S}^j_{RE}\ , \tag{1}$$

where the first and second terms represent the Zeeman and exchange energies, respectively. g_{Gd} is the g value of the isolated Gd^{3+} ion; μ_B is the Bohr magneton; S_{Gd} and S^j_{RE} represent the spin of Gd^{3+} and the host rare-earth ion, respectively; and J_j is the exchange interaction coefficient of Gd^{3+} and its jth host rare-earth neighbor.

Following the theory of Hutchings *et al.*,[5] the g shift of Gd^{3+} at zero temperature can be given as

$$\Delta g = \frac{J(0)}{\mu_B H}\langle 0'|S^z_{RE}|0'\rangle\ , \tag{2}$$

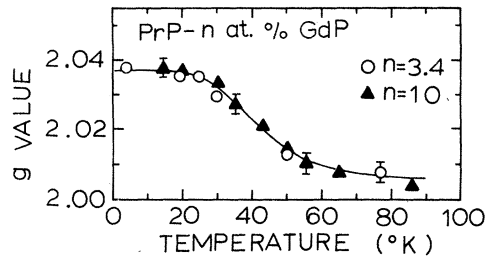

FIG. 7. Temperature dependence of the g value of Gd^{3+} in PrP–n–at.% GdP (n=3, 4, 10).

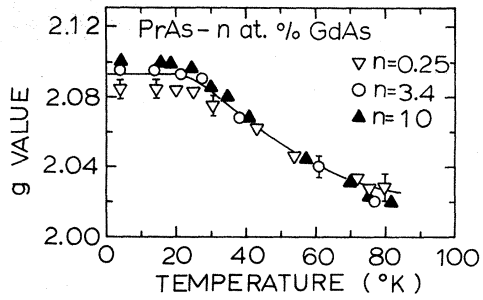

FIG. 8. Temperature dependence of the g value of Gd^{3+} in PrAs–n–at.% GdAs (n=0.25, 3, 4, 10).

with

$$J(0) \equiv \sum_j J_j\ , \tag{3}$$

where we have considered that the applied magnetic field is along the z-axis, and $|0'\rangle$ represents the perturbed wave function of the ground state of a host rare-earth ion in the magnetic field.

$$|0'\rangle = |0\rangle + \sum_m \frac{\langle m|\mathcal{H}_z|0\rangle}{E_0 - E_m}|m\rangle\ , \tag{4}$$

with

$$\mathcal{H}_z = \mu_B \vec{H}\cdot(\vec{L}_{RE} + 2\vec{S}_{RE}), \tag{5}$$

where $|0\rangle$ and $|m\rangle$ represent the crystal-field-only wave functions[6] of the host ground state and the host excited state, respectively. Equation (2) can be interpreted as meaning that the g shift of Gd^{3+} is proportional to the isothermal susceptibility of the host rare-earth ion; and the exchange interaction coefficient $J(0)$ can be obtained if we measure the g shift of Gd^{3+} at zero temperature and if the wave functions and the crystal-field splittings of the host rare-earth ions are known. As long as the exchange energy $J(0)\,S_{Gd}S_{RE}$ ($S_{Gd} = \frac{7}{2}$; for Pr^{3+} and Tm^{3+}, $S_{RE}=1$) is small compared to the crystal-field splittings, where in practice the only important comparison is to the crystal-field splitting from the ground to the first excited

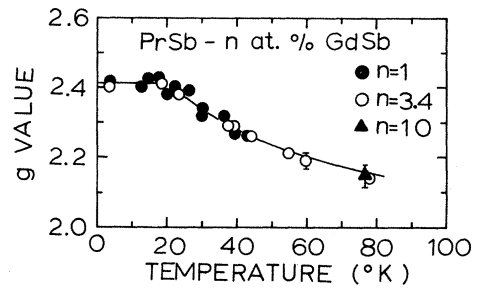

FIG. 9. Temperature dependence of the g value of Gd^{3+} in PrSb–n–at.% GdSb (n=1, 3.4, 10).

state, this theoretical prediction, that the g shift of Gd^{3+} is proportional to the isothermal susceptibility of the host-rare-earth ion, holds at any temperature. The generalization of Eq. (2) to all temperatures is

$$\Delta g = \frac{\lambda - 1}{\lambda} \frac{J(0)}{\mu_B^2} \chi_{CF} , \tag{6}$$

where λ and χ_{CF} are the Landé factor of the host and the crystal-field-only susceptibility of the host, respectively.

The isothermal crystal-field-only susceptibility has been calculated[7] for Tm^{3+} and Pr^{3+} in the NaCl structure, and there are a number of measurements[8,9] of the isothermal susceptibility of the thulium and praseodymium monopnictides. Both the theoretical and experimental isothermal susceptibilities are of the Van Vleck type and are almost temperature independent below liquid-He temperature. This indicates that one may obtain $J(0)$ by measuring the g shift of Gd^{3+} at liquid-He temperature. (In fact, as discussed below, we have measured the g shift over a substantial range of temperature, and the value of $J(0)$ giving the scaling between Δg and χ at the lowest temperatures also gives excellent agreement for increasing temperature.)

When there are exchange interactions between the host rare-earth ions, Eq. (6) becomes

$$\Delta g = \frac{\lambda - 1}{\lambda} \frac{J(0)}{\mu_B^2} \chi_{CF} \Big/ \left[1 - 2J'(0) \left(\frac{\lambda - 1}{\lambda} \right)^2 \frac{\chi_{CF}}{\mu_B^2} \right] , \tag{7}$$

where $J'(0)$ is the total exchange interaction coefficient between the host rare-earth ions.

B. Theory of the linewidth

The theory of the temperature dependence of the linewidth for a magnetic impurity in a magnetic host has been investigated by Moriya and Obata.[10] Their theory predicts that the EPR linewidth of the magnetic impurity is proportional to the autocorrelation function of the spin fluctuations of the host magnetic ion. They concluded that the autocorrelation function is approximately given by kT times the difference between the isothermal and isolated susceptibilities of the host material,

$$\Delta H = AkT(\chi_T - \chi_{iso}) . \tag{8}$$

Here A is a constant, and χ_T and χ_{iso} are the isothermal and isolated susceptibilities of the host magnetic ion, respectively. The physical significance of Eq. (8) is that the population fluctuation in the excited states of the Pr^{3+} and Tm^{3+} ions contributes to the line broadening of the Gd^{3+} impurity. This means that we expect the linewidth of Gd^{3+} to increase sharply as the temperature is raised to the order of the crystal-field splitting to the first excited state of the host rare-earth ions; and if the temperature is high compared to the

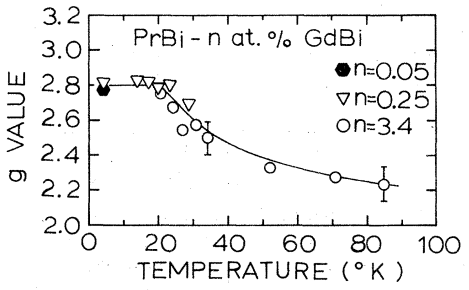

FIG. 10. Temperature dependence of the g value of Gd^{3+} in PrBi—n-at.% GdBi ($n = 0.05, 0.25, 3.4$).

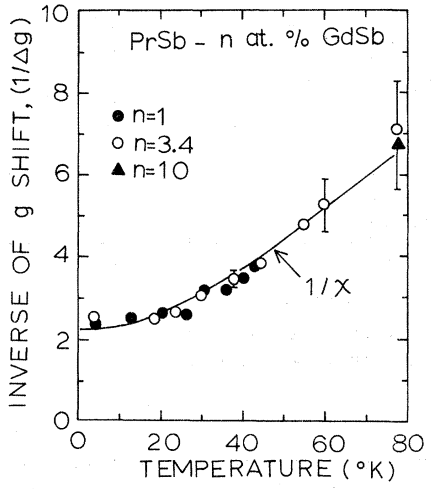

FIG. 11. Comparison between the g shifts of Gd^{3+} ions in PrSb and the magnetic susceptibility of PrSb. $1/\chi$ is in arbitrary units.

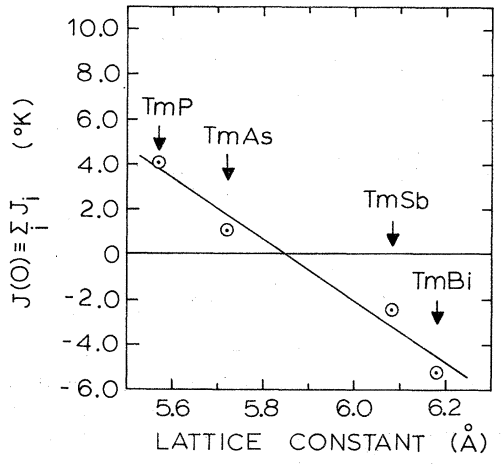

FIG. 12. Exchange interaction between Gd^{3+} and Tm^{3+} in TmX. The horizontal axis is lattice constant.

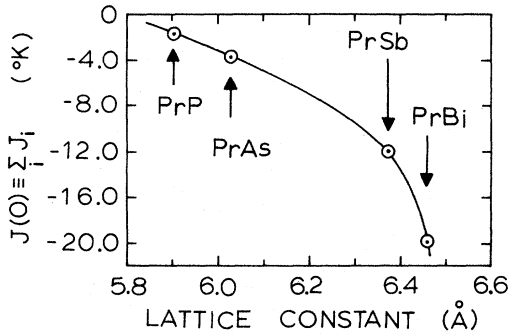

FIG. 13. Exchange interaction between Gd^{3+} and Pr^{3+} in PrX. The horizontal axis is lattice constant.

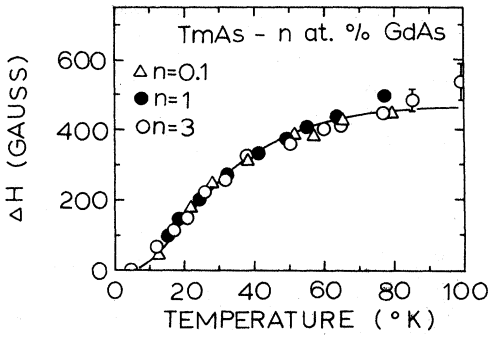

FIG. 15. Temperature dependence of the EPR linewidths of Gd^{3+} in TmAs–n-at.% ($n = 0.1, 1, 3$). The solid curve represents a fit of the data to the equation $\Delta H = 1178\ (0.25\, e^{-28/T} + 3.6\, e^{-61.6/T} + 0.36\, e^{-218/T})/Z$ G, where $Z = 1 + 3\, e^{-28/T} + 3\, e^{-61.6/T} + e^{-180/T} + 3\, e^{-218/T} + 2\, e^{-225/T}$.

overall crystal-field splitting, we expect the linewidth to be temperature independent. As discussed in the next section, the isothermal and isolated susceptibilities are directly related to the crystal-field splittings. This means that the measurements of the EPR linewidth of Gd^{3+} can give very useful information about the crystal-field splittings of the host rare-earth ion.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

The observed EPR line shapes are Dysonian. However, as can be seen from Fig. 2, the shapes are not markedly different from true Lorentzian. In this case, the resonant field can be found using the analysis method of Peter *et al.*[11] Occasionally, when the linewidths are relatively wide, we have used a modification[12] of the technique of Peter *et al.* to obtain the resonant fields.

The temperature dependence of the experimentally observed g values for Gd diluted in TmX (X = P, As, Sb) are shown in Figs. 3–5. The g shifts with respect to the high temperature behavior are positive for TmP and TmAs hosts, and are negative for TmSb as host, As discussed below, this indicates a change in sign of the Gd^{3+}–Tm^{3+} exchange interaction on going from phosphide and arsenide to the antimonide and bismuthide.

At low temperatures the variation of the g values with temperature flattens out as expected for the Van Vleck type host susceptibility. The g shifts Δg are found by subtracting the value for the isolated Gd^{3+} ion, 1.991, from the experimentally observed g values. As shown in Fig. 6, as predicted by the theory given in Sec. III A, for Gd^{3+} in TmP the temperature dependence of $1/\Delta g$ is in close agreement with that of[8] $1/\chi$, the inverse of the isothermal susceptibility. Similar behavior is found[12] for Gd^{3+} in TmAs and TmSb. In addition, we have also observed the Gd^{3+} resonance in TmBi at 4.2 °K with the g value equal to 1.04 ± 0.02.

The g-value variation with temperature in the PrX compounds is shown in Figs. 7–10. The g shifts are large for PrSb and PrBi, while they are

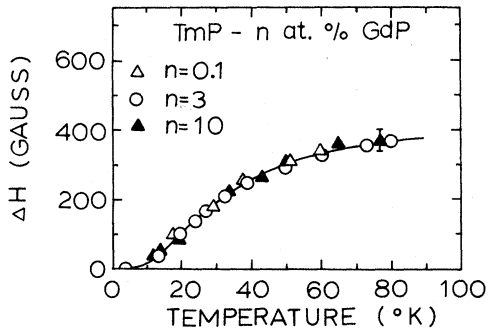

FIG. 14. Temperature dependence of the EPR linewidths of Gd^{3+} in TmP–n-at.% GdP ($n = 0.1, 3, 10$). The solid curve represents a fit of the data to the equation $\Delta H = 970\ (0.25\, e^{-30/T} + 3.6\, e^{-66/T} + 0.36\, e^{-240/T})/Z$ G, where $Z = 1 + 3\, e^{-30/T} + 3\, e^{-66/T} + e^{-193/T} + 3\, e^{-234/T} + 2\, e^{-240/T}$.

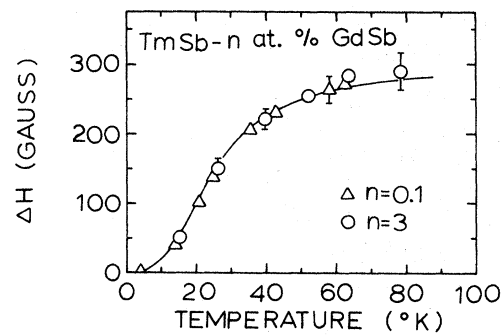

FIG. 16. Temperature dependence of the EPR linewidths of Gd^{3+} in TmSb–n-at.% GdSb ($n = 0.1, 3$). The solid curve represents a fit of the data to the equation $\Delta H = 743\ (0.25\, e^{-25/T} + 3.6\, e^{-55/T} + 0.36\, e^{-195/T})/Z$ G, where $Z = 1 + 3\, e^{-25/T} + 3\, e^{-55/T} + e^{-160/T} + 3\, e^{-195/T} + 2\, e^{-201/T}$.

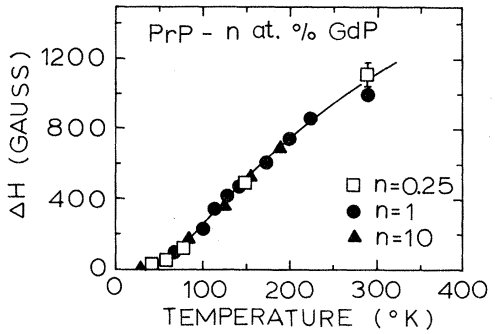

FIG. 17. Temperature dependence of the EPR linewidths of Gd^{3+} in PrP–n-at.% GdP ($n=0.25,1,10$). The solid curve represents a fit of the data to the equation $\Delta H=2797\ (0.25\,e^{-128/T}+6.25\,e^{-400/T})/Z$ G, where $Z=1+3\,e^{-128/T}+2\,e^{-224/T}+3\,e^{-400/T}$.

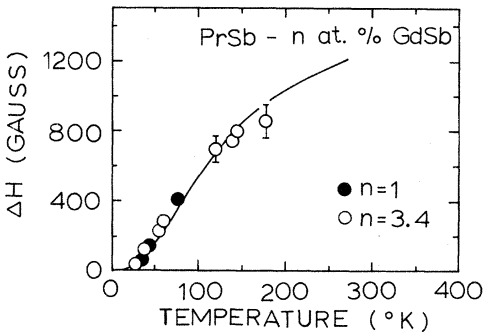

FIG. 19. Temperature dependence of the EPR linewidths of Gd^{3+} in PrSb–n-at.% GdSb ($n=1,3.4$). The solid curve represents a fit of the data to the equation $\Delta H=2520\ (0.25\,e^{-73/T}+6.25\,e^{-239/T})/Z$ G, where $Z=1+3\,e^{-73/T}+2\,e^{-127/T}+3\,e^{-239/T}$.

small for PrP. As shown in Fig. 11, just as for the TmX hosts, the temperature dependence of $1/\Delta g$ is in good agreement with that of[13] $1/\chi$ for PrSb as host. Just as for the TmX-host results, Δg here is the difference between the experimental g value and 1.991. Similar behavior[12] is found for PrP, PrAs, and PrBi as hosts.

The total exchange interaction $J(0)$ between a Gd^{3+} ion and the surrounding host rare-earth ions can be obtained from the value of the g shift at liquid-He temperature. This information is obtained from Eq. (7) by using the measured g shifts and susceptibilities.[8,9,13(a)] Figures 12 and 13 show the relationship between $J(0)$ and the host lattice constant. For PrX, $J(0)$ increases in magnitude (becomes more negative) with increasing lattice parameter, while for TmX, $J(0)$ changes sign from positive to negative with increasing lattice parameter.

The exchange-induced g shifts are quite large and recall those observed[13(b),13(c)] for Eu^{2+}, Gd^{3+}, and Mn^{2+} in the singlet-ground-state semiconductors SmS, SmSe, and SmTe. The functional dependence of the observed exchange on lattice parameter is quite different from the semiconductor case,[13(c)] however. This difference could be related to the metallic nature of the monopnictides studied in the present work.

The temperature dependence of the experimentally observed EPR linewidths of Gd^{3+} in TmP, TmAs, TmSb, PrP, PrAs, PrSb, and PrBi are shown in Figs. 14–20, respectively. (The linewidths are plotted after subtracting the residual linewidth, ΔH at $T=0$ °K, from the observed linewidths.) Qualitatively, the most striking feature of these results is the sharply increasing linewidth with increasing temperature (exponentially increasing at temperatures lower than the energy splitting to the first crystal-field excited state of the host rare-earth ion).

The theoretical linewidth is given by Eq. (8). Using the nomenclature of Ref. 7 (see Eqs. 39–41

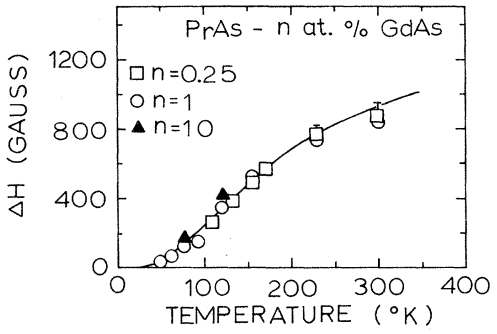

FIG. 18. Temperature dependence of the EPR linewidths of Gd^{3+} in PrAs–n-at.% GdAs ($n=0.25,1,10$). The solid curve represents a fit of the data to the equation $\Delta H=2250\ (0.25\,e^{-115/T}+6.25\,e^{-360/T})/Z$ G, where $Z=1+3\,e^{-115/T}+2\,e^{-203/T}+3\,e^{-360/T}$.

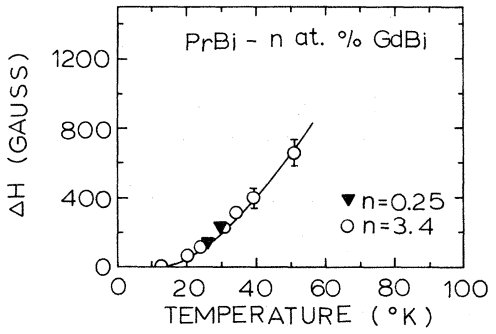

FIG. 20. Temperature dependence of the EPR linewidths of Gd^{3+} in PrBi–n-at.% GdBi ($n=0.25,3.4$). The solid curve represents of the data to the equation $\Delta H=7600\ (0.25\,e^{-67/T}+6.25\,e^{-203/T})/Z$ G, where $Z=1+3\,e^{-67/T}+2\,e^{-116/T}+3\,e^{-203/T}$.

TABLE I. Experimentally observed $E(\Gamma_4)-E(\Gamma_1)$ crystal-field splitting of Tm^{3+} in TmX and Pr^{3+} in PrX (X=P, As, Sb, Bi) intermetallic compounds.

	Tm^{3+} $E(\Gamma_4)-E(\Gamma_1)$ (°K)			Pr^{3+} $E(\Gamma_4)-E(\Gamma_1)$ (°K)	
	Present experiment (linewidth analysis	Neutron scattering[a]		Present experiment (linewidth analysis)	Neutron scattering[b]
TmP	30±3	≃32	PrP	128±15	127±12
TmAs	28±3	≃31	PrAs	115±15	117±8
TmSb	25±3	≃25	PrSb	73±10	73±4
			PrBi	67±10	67±4

[a]Reference 14.

[b]Reference 15.

of Ref. 7), the difference $\chi_T-\chi_{iso}$ is equal to χ_R, the repopulation contribution[7] to the susceptibility. Therefore we take the linewidth as being proportional to χ_R. For the crystal-field parameter[6] x, giving the ratio of fourth to sixth-order anisotropy close to -1, as is indicated experimentally for the rare-earth monopnictides, this gives

$$\Delta H = a(0.25e^{-E(\Gamma_4)/kT}+3.6e^{-E(\Gamma_5^{(2)})/kT} + 0.36e^{-E(\Gamma_5^{(1)})/kT})/Z \text{ (for } Tm^{3+}) \quad (9)$$

$$\Delta H = b(0.25e^{-E(\Gamma_4)/kT}+6.25e^{-E(\Gamma_5)/kT})/Z \text{(for } Pr^{3+}), \quad (10)$$

where a and b are some numerical coefficients, and Z is the single-ion partition function.

Generally, accurate calculations of a and b are very complicated. However, we are interested in the determination of $E(\Gamma_4)$ [since determining $E(\Gamma_4)$ fixes all the crystal-field splittings for specified x] and not in the scaling factors a and b. Let us consider Fig. 14 [TmP–n-at. % GdP] as an example. The experimental data fit, for TmP–n-at. % GdP,

$$\Delta H = 970(0.25e^{-30/T}+3.6e^{-66/T}+0.36e^{-240/T})/Z \text{ G}. \quad (11)$$

Here the value of the scaling factor, 970, was chosen by adjusting the scaling factor a in Eq. (9) until the theoretical curve fits the experimental data at all temperatures. This result indicates that the Γ_4 and $\Gamma_5^{(2)}$ states are at 30 and 66 °K above the Γ_1 ground state, respectively. These values are consistent with our values[3(a)] obtained by performing the EPR in the excited $\Gamma_5^{(2)}$ state of Tm^{3+} in TmP.

Similar analyses of the linewidth behavior have been performed for all samples, and the results for the crystal-field splittings of Tm^{3+} are tabulated in Table I. The present results agree quite well with those obtained from neutron scattering.[14,15]

In all the experiments described above, Gd was used as the probe impurity. We also considered the possibility of using Dy or Er as the probe impurity, but for reasons we will briefly describe, rejected this. To investigate that possibility, we prepared several samples of the type n at.% DyX in YX, n at. % DyX in LaX, and n at.% GdX in YX, where the host is nonmagnetic and n is less than 10. EPR experiments were done in the temperature range between 4.2 and 150 °K for Dy, and between 4.2 and 300 °K for Gd. (Our experimental results show that the ground state of Dy^{3+} in LaX and YX is Γ_6, consistent with the experimental results of Davidov *et al.*[16]) We found that the experimentally observed peak-to-peak linewidth of Dy^{3+} increases sharply ($\partial\Delta H_{pp}/\partial T \simeq 5$ G/°K, and 8 G/°K for Dy^{3+}: YX, and Dy^{3+}: LaX, respectively) above 20 °K, and the increase is almost linear in T. Because of this line broadening, Dy^{3+} is not suitable as a probe. On the other hand, the linewidth for the EPR of Gd^{3+} diluted in YX shows little variation with temperature.[12] The temperature-dependent contribution to the linewidth, presumably due to Korringa-type relaxation via the conduction electrons, is 10% or less of that for Dy^{3+}. This small Korringa-type linewidth for the EPR of Gd^{3+} in the YX compounds shows that Gd^{3+} is an appropriate choice of magnetic impurity probe for the EPR experiments of interest in the paramagnetic hosts. In fact, the lack of Gd^{3+} concentration dependence of the linewidths shown in Figs. 14–20 indicates that the Korringa-type contribution to the temperature-dependent line width is even smaller for Gd^{3+} in TmX and PrX.

Our discussion in this paper has been confined to the case where the host material is paramagnetic. However, our experimental method can be applied to antiferromagnetic host materials such as

$Tb_\xi Y_{1-\xi} X(\xi \geq 0.4)$ and CeX. Our preliminary results[17] for TbP–5-at. % GdP indicate that the Gd^{3+} g shifts are strongly affected by the staggered susceptibility. We did not see any line broadening of Gd^{3+} near the Néel temperature.

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