

## LONG-RANGE POLARIZATION EFFECTS IN RARE-EARTH-DOPED PALLADIUM

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We have found that the magnetic polarization around paramagnetic impurities has a much greater effective range in palladium than in ordinary metals. In our experiments we find that this polarization is essentially uniform over several hundred lattice sites, which is a far larger range than the Ruderman-Kittel-Yosida (RKY) theory predicts. These findings are based on the electron paramagnetic resonance (EPR) spectrum of Gd in rare earth (R.E.) doped palladium, and corroborated by susceptibility measurements. The shift of the resonance lines measures the strength of the polarization, and the broadening contains information about its range. A simple molecular field description of dilute paramagnetism in Pd becomes possible because of the long interaction range. Within this description we explain the observed susceptibility behavior of some mixed R.E. impurities in Pd as well as the observation that the Gd resonance is shifted by the magnetic ions due to other R.E. but not by the one due to Gd itself.

The  $g$  factor  $g_{\text{Gd}}$  of Gd in solution in Pd is shifted by  $\Delta g_0 = -0.10$ . This shift is caused by a negative scalar interaction  $J(\mathbf{r})\vec{S} \cdot \vec{s}$  between the spin of the itinerant electrons  $\vec{s}$  and the gadolinium ion spin  $\vec{S}$ .<sup>1</sup>

Introducing the Fourier transform  $\bar{J}(q)$  of  $J(r)$ , and setting  $\bar{J}(0) = \bar{J}$ , we can write

$$\Delta g_0 = \bar{J} \chi_{\text{Pd}} / 2\beta^2 n_0 = \lambda_{\text{Gd}} \chi_{\text{Pd}} g_{\text{Gd}},$$

where  $\lambda_{\text{Gd}}$  is a molecular field constant,  $\chi_{\text{Pd}}$  is the susceptibility of undoped Pd, and  $n_0 = 6.8 \times 10^{22}$  is the number of atoms per cc. If Pd is now doped with other R.E. besides Gd, we can extend our description by introducing the rare-earth susceptibilities  $\chi_{\text{R.E.}}$  and the additional molecular field constants  $\lambda_{\text{R.E.}}$  and write

$$\Delta g = \Delta g_0 + \sum \Delta g_{\text{R.E.}} = \Delta g_0 (1 + \sum \lambda_{\text{R.E.}} \chi_{\text{R.E.}}).$$

The sum goes over the additional R.E. and does not include the term  $\lambda_{\text{Gd}} \chi_{\text{Gd}}$ . This can be deduced from a two-sublattice calculation and the fact that the rapid itinerant-electron relaxation must take place toward the instantaneous value of the rare-earth magnetization.<sup>1</sup>

Figure 1 shows the resonance shift plotted against the positions of the R.E. in the periodic

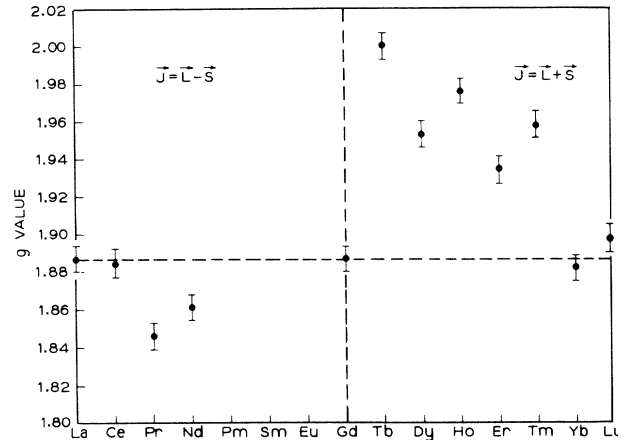


FIG. 1.  $g$  value of Gd in the alloys 96% Pd, 2% Gd, 2% R.E. at 20° K.

system. Figure 2 shows, for the cases of Tb and Pr, that the shifts are indeed proportional to  $\chi_{\text{R.E.}}$ . The constants  $\lambda_{\text{R.E.}}$  are seen to change signs as we progress from the left to the right side of Gd. This shows that  $\bar{J}_{\text{R.E.}}$  acts on  $\vec{S}_{\text{R.E.}} = \vec{J}_{\text{R.E.}} - \vec{L}_{\text{R.E.}}$  in the rare-earth ions, and not on the total spin  $\vec{J}_{\text{R.E.}}$ . Hence we write

$$\lambda_{\text{R.E.}} = \bar{J}_{\text{R.E.}} (g_{\text{R.E.}} - 1) / 2n_0 \beta^2 g_{\text{Gd}}.$$

A similar situation exists in the case of the rare earth induced Knight shifts of the nuclear magnet resonance (NMR) in R.E. Al<sub>2</sub>.<sup>2</sup> Some values of  $\bar{J}_{\text{R.E.}}$  are shown in Table I. From  $\Delta g_0 = -0.10$  and the present measurements, it follows that  $\bar{J}_{\text{R.E.}}$  is negative for all the observed R.E. As a consequence, the magnitude of the total shift,  $|\Delta g|$ , increases if those R.E. are added whose  $\vec{S}$  is antiparallel to the external field, and decreases for the R.E. with parallel spins. Since  $\bar{J}_{\text{R.E.}}$  is negative, it is not due to the simple atomic exchange mechanism. Instead, its origin may lie in the configuration mixing effects suggested by Anderson and Clogston and briefly discussed in reference 1.

A new feature in our experiments is that we observe our shifts in alloys with the R.E. in as much as two-hundred-fold dilution. In GdAl<sub>2</sub>, a dilute substitution of other R.E. for Gd produces broadenings of the ionic Gd resonance that are

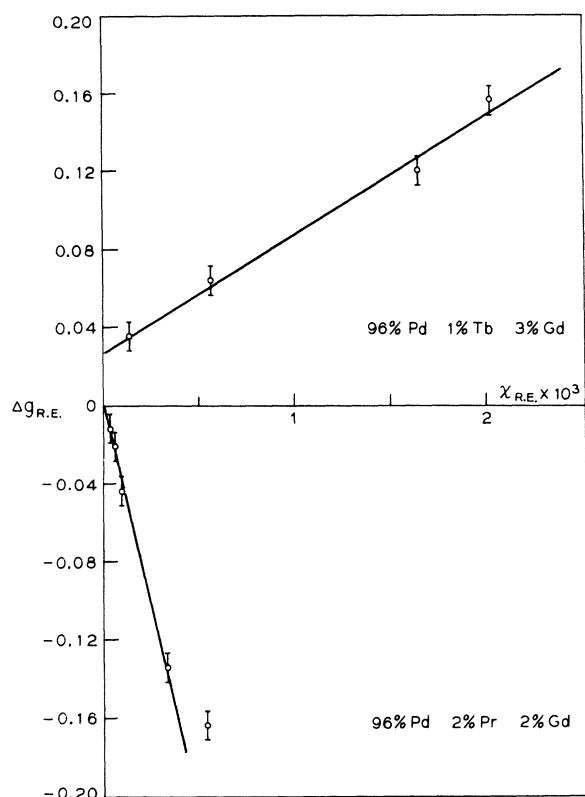


FIG. 2. The change of the  $g$  value,  $\Delta g_{R.E.}$ , in the alloys 96% Pd, 1% Tb, 3% Gd and 96% Pd, 2% Pr, 2% Gd as function of the volume susceptibilities  $\chi_{Tb}$  and  $\chi_{Pr}$ , respectively.  $\Delta g_{R.E.}$  and  $\chi$  are parametric functions of the temperature. The susceptibilities were measured in 1% Tb, 99% Pd and 2% Pr, 98% Pd and the Pd susceptibility subtracted. The  $g$  value of the undoped samples of Gd in Pd was used as reference; it is essentially constant over the shown range.

larger than any shift.<sup>3</sup> The EPR line shape of Gd in Pd,  $\rho(t)$ , gets transformed by the addition of other R.E. into  $h(s) = \int \rho(t) y(s-t) dt$ . The function  $y(s-t)$  represents the probability that  $\rho(t)$  is shifted by  $(s-t)$  by the joint action of all R.E. impurity atoms. The first moment is the shift and the variance is the square of the width of  $y(s)$ . These two quantities, being semi-invariants, are simply the sum<sup>4</sup> of the corresponding quantities contributed by each R.E. atom.

If we adopt a simplified model by setting  $J(r)$  constant for  $r < r_0$ ,  $J(r) = 0$  for  $r > r_0$ , we find that  $y(s)$  is given by an equidistant set of  $\delta$  functions whose strengths follow a Poisson distribution and that the ratio of shift to width,  $z$ , for  $y(s)$  is given by  $z = (4\pi c r_0^3 / 3)^{1/2} = n^{1/2}$ . Here,  $c$  is the number of R.E. per cc and  $n$  is the number of R.E. within the "sphere of interaction" around each Gd ion. ( $c/n_0 \ll 1$  is here assumed.) For

Table I. The interaction parameter  $\bar{J}_{R.E.}$  deduced from  $\Delta g_{R.E.}$ . There is satisfactory agreement between the measurements reported here and the values obtained for  $\bar{J}_{R.E.}$  in R.E.  $Al_2$  by NMR<sup>a</sup> and EPR<sup>b</sup> techniques.

Element	$\bar{J}_{R.E.}$ (eV)
Pr	$-0.22 \pm 0.03$
Nd	$-0.13 \pm 0.03$
Gd <sup>c</sup>	$-0.03 \pm 0.005$
Tb	$-0.025 \pm 0.005$
Ho	$-0.102 \pm 0.01$

<sup>a</sup> See reference 2.

<sup>b</sup> See reference 3.

<sup>c</sup> The value for  $\bar{J}_{Gd}$  is discussed in reference 1. It is derived using the specific heat density of states rather than  $\chi_f$ .

large  $n$ ,  $y(t)$  can be smoothed out and the central limit theorem predicts that it approaches a Gaussian function. This made it possible to extract by graphical methods from our EPR lines the values:  $z \approx 3$ ,  $n \approx 9$ , and  $r_0 \approx 15 \text{ \AA}$ .

The more realistic range function,  $[\sin(2k_f r) - (2k_f r) \cos(2k_f r)] / (2k_f r)^3$ , proposed by Yosida,<sup>5</sup> leads to  $z = (\pi/2)(3c/k_f^3)^{1/2}$ , where  $k_f$  is the Fermi momentum of the itinerant electrons. In order to get the same  $z$  as in the previous model, we have to set  $k_f = 1.21/r_0$ . This leads to  $k_f = 8.1 \times 10^6 \text{ cm}^{-1}$  from our experiments, a value that is much too small, particularly in view of the high susceptibility and specific heat of Pd, since it would allow for only 0.01  $d$  holes per Pd ion. We therefore conclude that the independent electron theory by Ruderman-Kittel-Yosida cannot be applied to the long-range polarization effects in Pd. This is in contrast to our measurements in other metallic systems, such as  $GdAl_2$ ,<sup>3</sup> Gd in Ag and Cd,<sup>1</sup> Gd in  $LaAl_2$  where we found that doping by the R.E. produces broadening only, in accord with the prediction of the RKY theory.<sup>3</sup>

The main errors of our measurements come from the approximate nature of the model, the limited signal to noise ratio and the possibility of exchange narrowing. The latter effect is of the same origin and order of magnitude as the observed effect and could falsify the results by a factor of two. Further study of the concentration dependence of the effect will reduce this margin of error.

Our calculation implies that in the case of more than one kind of R.E. impurity the  $g$  shift will be the sum of the contributions of each im-

purity. This effect has been observed and it has been possible to produce a cancellation between the Tb- and the Pr-induced shifts. This experiment further demonstrates the long range of the magnetic interaction involved.

Such an interaction should produce magnetic ordering even in the most dilute R.E. - Pd samples. Susceptibility measurements on 3% Gd in Pd indicate indeed  $\theta = +12^\circ\text{K}$  in  $\chi = C/(T - \theta)$ . For a given temperature (70°K), the susceptibility of Pd<sub>98</sub>Gd<sub>2</sub> is increased by the admixture of 2% Tb and decreased by the admixture of 2% Nd; this is another consequence of the change of sign in  $\vec{L} \cdot \vec{S}$  which results here in a change of sign of the indirect coupling between Gd and the different R.E. The long-range effects have so far only been observed in the host metal Pd and some of its alloys, where  $\chi_p$  is about 100 times higher than in ordinary metals. The effect appears approximately in the range of alloys where the dilute transition elements produce anomalous magnetic moments, Curie temperatures, and  $\theta$  values.<sup>6</sup> The fact that the R.E. show paramagnetic moments consistent with the ionic Landé  $g$  factors suggests, however, that the transition element-Pd interaction is considerably larger than the R.E. - Pd interaction re-

ported here.

A simple extension of the RKY independent-particle calculation to include anomalous density-of-state functions does not appear capable of accounting for the range observed in Pd. It was, however, shown by Wolff<sup>7</sup> that these effects could considerably modify the range function if the electron-electron interaction is taken into account.

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## ELECTRIC DIPOLE SPIN TRANSITIONS IN InSb

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The conduction band magnetic moment in InSb has been predicted to be very large, isotropic, and negative.<sup>1</sup> This has led to proposals<sup>2</sup> for its application to tunable infrared lasers. This material is one of a large class of (in general, anisotropic) solids with highly anomalous paramagnetic properties, which might be of interest in this area.

The theoretical predictions have received several indirect experimental confirmations<sup>3-5</sup>; however, the sign of the magnetic moment for the important intraband transitions has not received direct confirmation.

The writer attempted this measurement using circularly polarized radiation at 72 kMc/sec, the lowest frequency for which plasma effects<sup>6</sup> can be avoided in the purest materials available. These attempts were for some time unsuccessful,

the spin resonance absorption being not significantly affected by a change from left to right circular polarization. The right-left symmetry, taken together with the fact that the strength of the spin transition unexpectedly increased on moving the sample away from the microwave magnetic field maximum (node of electric field) led to the conclusion that the transition being observed was of an electric dipole character. It now appears that these results can be explained on the basis of the band structure calculations for InSb of Kane.<sup>7</sup> Experimental confirmation of the negative magnetic moment was finally obtained by confining the sample to a cut-off region carrying only microwave magnetic field (Fig. 2).

Figure 1 shows the broad cyclotron resonance obtained at 1.3°K with a disk-shaped sample of