Paramagnetic resonance of Gd in single crystals of Pd in the very dilute limit and at high microwave frequency*

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The ESR of 300- and 25-ppm Gd in single crystals of Pd at 35 and 9 GHz below 4.1 °K is reported. It is shown that at 1.35 °K and at 35 GHz a simple single-ion spectrum was obtained that is straightforward to analyze. The Gd collective resonance line (cluster line) at 35 GHz and 1.35 °K shows a different behavior than at 9 GHz.

INTRODUCTION

Recently, Devine *et al.*[1] and Moret *et al.*[2] have investigated the EPR spectrum of Gd in single crystals of Pd at concentrations of 1500–300 ppm and at *X* band. A resolved spectrum was reported below 4 °K. The spectrum was explained[2] as the superposition of two spectra: (a) the resolved EPR spectra of individual Gd ions in Pd and (b) a collective resonance line of interacting Gd atoms due to the Gd-Gd spin-spin interaction. The intensity of the collective resonance line (called cluster line) decreases by lowering the Gd concentration and its g value is very close to the g value ($g = 1.795$) of the single Gd ion. The spectrum of the Gd single ion was calculated by Moret *et al.*[2] using the Barnes theory[3] which shows that at pumped-helium temperatures and around the [100] and [111] directions, the $-\frac{1}{2} \rightarrow \frac{1}{2}$ line does not appear due to the large $\Delta M_S = \pm 1$ spin-flip matrix elements for small M_S levels of the Gd ions. Hence, the resolved resonance line observed close to $g = 1.795$ is due to the cluster line only.[2]

The existence of the collective resonance line even for low concentrations could be anticipated, since it is known[4] that the spin-spin interaction via the indirect exchange coupling of Gd in Pd is long range. Using a model of spherical range of interaction, Moret *et al.*[2] have estimated that the sphere of interaction is enclosed in a volume of 200 lattice sites. For the Gd concentration of 1500 and 300 ppm, 16% and 6% of the ions correspondingly should belong to the cluster line.[2]

In this work we report the investigations of the EPR Gd in Pd single crystals in extremely dilute alloys down to 25 ppm at 9 and 35 GHz. This is an extension of the experimental work reported earlier.[2] By reducing the concentration to 25 ppm the interaction between the Gd ions is reduced and therefore the intensity of the cluster line should be very small (less than 0.5% in a sphere of interaction of 200 lattice sites). The use of the 35 GHz simplifies the spectrum of the Gd single-ion spectra: At 1.35 °K only the three lowest Gd $S_{7/2}$ levels are significantly populated, therefore, the single-ion spectrum should contain fewer lines and should be easier to analyze. We, therefore, expect to study the behavior of the cluster line without it being superimposed on the spectrum of the individual ion.

EXPERIMENTAL RESULTS

Single crystals of Pd with a nominal concentration of 300- and 25-ppm Gd that were grown by the recrystallization method[2] were measured at *X*-band and *Q*-band frequencies and at liquid-helium temperatures. One of the 25-ppm samples was small enough ($1.5 \times 5 \times 0.3$ mm) to be measured both at *X*-band and *Q*-band frequencies.

Figure 1 shows the experimental results for the 25-ppm sample at *Q*-band and 1.35 °K frequency, for the magnetic field in the [100] direction and for the collapsed angle direction. (H is 30° from the [100] direction and perpendicular to the $[0\bar{1}1]$ direction.) The high-field line in the [100] direction corresponds to the $-\frac{7}{2} \rightarrow -\frac{5}{2}$ transition. The low-field line corresponds to the exchange narrowed $-\frac{5}{2} \rightarrow -\frac{3}{2}$ and $-\frac{3}{2} \rightarrow -\frac{1}{2}$ transitions. The other transitions were not observed because of depopulation of higher levels. At *X* band and 1.7 K the intensity of the resonance line at the collapsed angle was large. However, the signals at the [100] and [111] directions were weak. At these two directions we could identify a line at a position where the $-\frac{1}{2} \rightarrow \frac{1}{2}$ transition should occur. Other transitions were also identified, but due to their weak intensities they will not be discussed further.

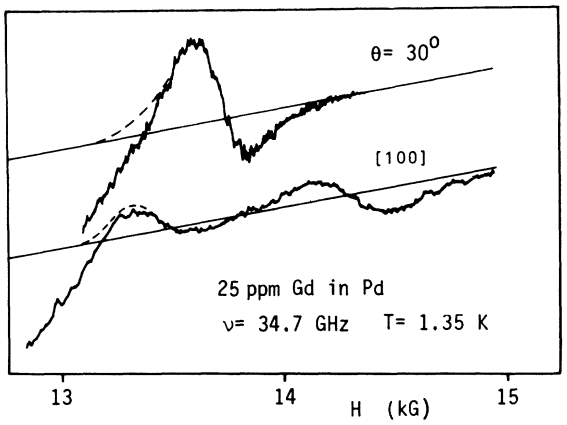

FIG. 1. ESR spectrum of 25-ppm Gd in a Pd single crystal at Q band and 1.35 °K in the [100] and the collapsed-angle direction. The solid straight line indicates the baseline. At the low-field part of the signal a background signal starts. The dashed line shows the corrected resonance line.

Figure 2 shows the EPR spectrum of the 300-ppm sample at 35 GHz and 1.35 °K in the [111], collapsed angle, and the [100] directions. The results are similar to those of the 25-ppm sample. From these results we calculate $b_4 = 29 \pm 1$ G and $g = 1.795 \pm 5$, assuming that the position of the exchange narrowed line, $-\frac{5}{2} \rightarrow -\frac{3}{2}$ and $-\frac{3}{2} \rightarrow -\frac{1}{2}$, is in the center of gravity of these two transitions. These results are in good agreement with previous ones.[1,2] The spectrum in the [100] and [111] directions were simulated using the calculated b_4 and g value, predetermined linewidth and Boltzmann factors, and neglecting exchange. Figure 2(b) shows the spectrum in the [100] direction at a slightly higher temperature $T = 2.13$ °K: an additional small line is observed. This spectrum was also simulated under the same assumptions as at 1.35 °K. The small additional line corresponds to the $-\frac{1}{2} \rightarrow \frac{1}{2}$ transition. At X band and 1.7 °K the spectrum of the 300-ppm sample in the [100] direction was similar to the spectrum shown in Fig. 1 in the Moret *et al.* paper[2] and it includes the line in the $-\frac{1}{2} \rightarrow \frac{1}{2}$ position.

The linewidth (Fig. 3) of the 25-ppm samples at the collapsed angle had a Korringa broadening of 8 ± 1 G/°K. The residual linewidth for the sample was affected by the preparation. First the big sample was measured at X-band frequency. Afterwards it was cut into two pieces (a and b) and annealed. Sample a was measured at Q band, also. All results showed the same thermal broadening but different residual linewidth: 58 G for sample a or b at X band (38 G before cutting), 158 G for sample a at Q band. The linewidth of the 300-ppm sample at the collapsed angle had a minimum at about 2.5 °K and therefore did not show a Korringa behavior.

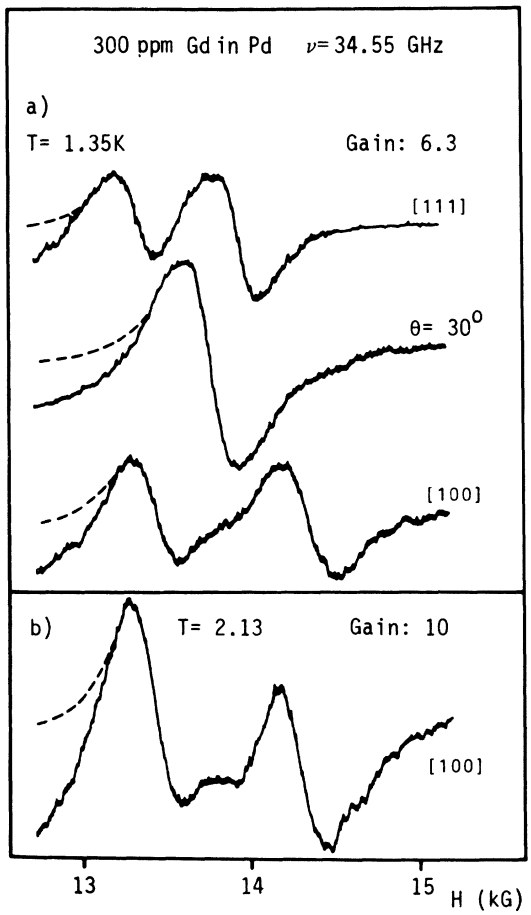

FIG. 2. ESR spectrum of 300-ppm Gd in a Pd single crystal at Q band and 1.35 °K in the [100], [111], and collapsed-angle directions, see (a). The dashed line shows the resonance line corrected for the background.

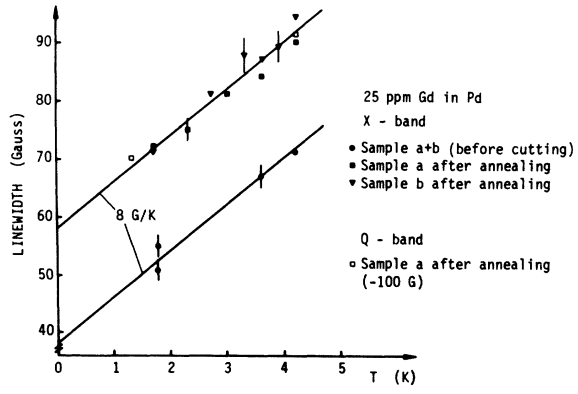

FIG. 3. Thermal broadening of the linewidth for the 25-ppm samples at the collapsed-angle direction at 9 and 35 GHz. A width of 100 G was subtracted from the results at 35 GHz.

DISCUSSIONS

At 35 GHz and 1.35 °K only the lowest Gd $S_{7/2}$ levels: $-\frac{7}{2}$, $-\frac{5}{2}$, and $-\frac{3}{2}$ are significantly populated. This has an advantage for the study of the Gd spectra, particularly in cubic-field symmetry. For Gd in cubic environment in the [100] direction two lines $-\frac{5}{2} \rightarrow -\frac{3}{2}$ and $-\frac{3}{2} \rightarrow -\frac{1}{2}$ are very close and on one side of the center of the spectrum the other line $-\frac{7}{2} \rightarrow -\frac{5}{2}$ is on the other side. For Gd in Pd at Q band we have obtained a very simple spectrum consisting of two lines: the $-\frac{7}{2} \rightarrow -\frac{5}{2}$ and the exchange narrowed line $-\frac{5}{2} \rightarrow -\frac{3}{2}$ and $-\frac{3}{2} \rightarrow -\frac{1}{2}$. From these spectra were obtained the crystal-field parameters with 3% accuracy in a straightforward calculation (without the need for the quite complicated calculation of Barnes,[4] used by Moret *et al.*). Measuring at Q-band, therefore, has an advantage in obtaining a better resolved Gd spectra in cubic symmetry that is simple to analyze. Chock *et al.*[5] have reported a partly resolved spectra for Gd in Au at X band. Measuring at Q band should produce a better resolved spectra and may clarify some controversy about the signs of b_4 for Gd in Au.[6]

The linewidth observed at the $-\frac{1}{2} \rightarrow \frac{1}{2}$ position for the 25-ppm Gd in Pd sample, at X band and in the [100] direction, was too narrow to be attributed to a real $-\frac{1}{2} \rightarrow \frac{1}{2}$ transition and we therefore attribute it to a cluster line. Using the criteria of a Gd-Gd sphere of interaction of 200 unit cells we obtain a stronger intensity for this line than expected from a random distribution of the Gd atoms. This might indicate a metallurgical clustering even at such low Gd concentrations.

The most interesting result is the disappearance of the cluster line for the 25- and 300-ppm sample at 35 GHz and 1.35 °K in the [100] direction [Figs. 1 and 2(a)]. The relative intensity of the cluster line for the 300-ppm sample at 1.35 °K at X band is about 8%. The cluster line is clearly observed for the 300-ppm sample at Q band and 2.13 °K [Fig. 2(b)]. A possible explanation for the decrease in intensity of the cluster line with decreasing temperature at 35 GHz is the depopulation of the higher levels of the $S_{7/2}$ state. The depopulation in the case of cubic field symmetry, produces an effective increase of the distance between adjacent lines of the Gd spectra. Thus the exchange narrowing between these lines is decreased and the intensity is distributed between the $-\frac{7}{2} \rightarrow -\frac{5}{2}$ and the exchanged narrowed $-\frac{5}{2} \rightarrow -\frac{3}{2}$ and $-\frac{3}{2} \rightarrow -\frac{1}{2}$ transition. More experiments at Q band at higher Gd concentrations are needed in order to verify these assumptions.

A Korringa broadening of 8 ± 1 G/ °K obtained for the 25-ppm sample between 1.4 °K (at X band and Q band) is slightly smaller than the value of 9.3 ± 0.4 G/°K obtained at above helium temperatures as reported by Moret *et al.*[1] The smaller value reported here may result from some magnetic ordering at helium temperatures even for samples with such a low concentration. The approach to ordering in the 300-ppm sample at helium temperature is expressed by the minimum in the linewidth at 2.5 °K.

The residual linewidth of 38 G observed at X band in one of the 25-ppm samples is remarkably small; for lower concentration in carefully grown crystals smaller residual linewidths should be obtained. Recently, Dahlberg[7] has analyzed the residual linewidth of Er in Ag as a function of concentration and frequency assuming dipole-dipole interaction and oscillations of the charge density. A similar study is intended in order to understand the origin of the residual linewidth in Pd whose range of interaction is long.

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