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Crystalline-Field Effects in the EPR of Er in Various Cubic Metals[*]

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Electron-spin-resonance measurements on the dilute alloys Ag:Er, Au:Er, Rh:Er, and Ir:Er exhibit a change in slope of the Er-resonance thermal broadening above $\sim$ 7 K. This behavior is interpreted in terms of off-diagonal matrix elements of the exchange coupling between the Γ_7 ground state and the $\Gamma_8^{(1)}$ first-excited state.

In a previous paper[1] (referred to as I), the effect of a low-lying excited crystalline-field-split level on the thermal broadening of the ground-state EPR spectrum was discussed. The exchange interaction [of the form $J(\vec{S}\cdot\vec{s})$] between the spin of the localized moment and the conduction electrons can induce transitions between the ground and the excited levels. This results in a larger thermal broadening than would be the case for an isolated ground state even at temperatures smaller than the energy separation Δ between the ground and the excited state. Thus, the temperature dependence of the EPR linewidth can provide a method to determine the crystalline-field splitting in a dilute magnetic alloy.

In I Au : Er was chosen for the following reasons: (i) the separation Δ is relatively small (only 16 K according to susceptibility measurements[2]) so an appreciable effect was expected even at low temperatures; and (ii) the small thermal broadening and residual width, as well as the excellent signal-to-noise ratio, enabled detection of the resonance at high temperature (25 K).

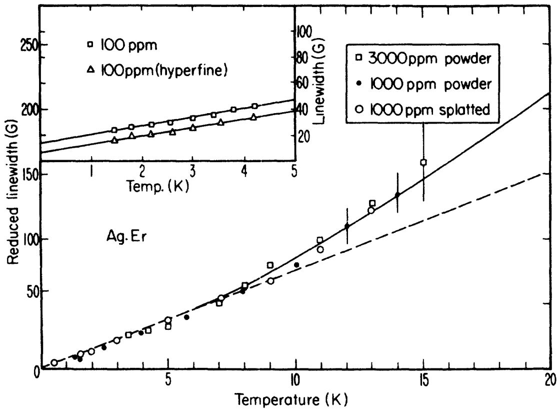

FIG. 1. Effect of low-lying crystalline-field excited level on the thermal broadening of Ag : Er dilute alloys. The residual widths for the various alloys (80 G for the 3000-ppm powder, 40 G for the 1000-ppm powder, and 28 G for the 1000-ppm splatted sample) were subtracted from the total linewidth and shown in the figure. The solid line is the theoretical fit [Eq. (3) in I] to the experimental data with a value $\Delta = 35$ K and over-all splitting of 207 K. The dashed line is the Korringa rate for an isolated doublet verified by measurements at low temperatures and small Er concentrations (see inset). The triangle in the inset represents the linewidth extracted from one of the hyperfine lines of Ag : Er^{167} sample.

In the present addenda, we present our measurements on other Er dilute alloys: Ag : Er, Rh : Er, and Ir : Er, all exhibiting a Γ_7 ground state. We found that the signal-to-noise ratio in the present cases was not as good as for Au : Er. Nevertheless, the linewidth clearly deviates from a linear temperature dependence which we attribute to transitions to excited crystalline-field levels. The departure from linearity, however, was much smaller than observed for Au : Er. Correlations with previous EPR measurements on Dy in the same hosts enable us to estimate the crystalline-field parameters. For comparison, our previous data on Au : Er, as well as new measurements on

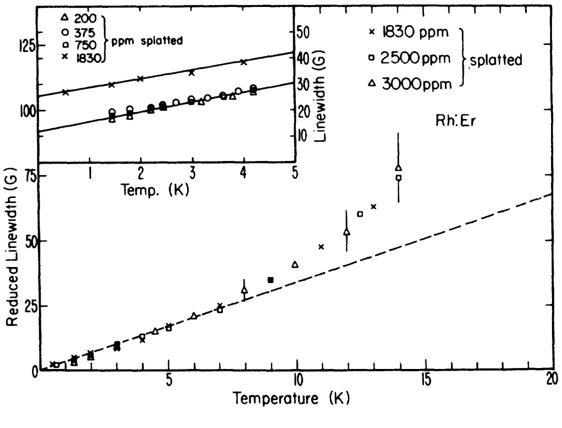

FIG. 2. Reduced linewidth (obtained by subtracting the residual width) for Rh : Er as a function of temperature. The residual widths are 25, 41, and 42 G for the 1830-, 2500-, and 3000-ppm sample, respectively. All the samples were splatted. The dashed lines are the Korringa rate expected for isolated Γ_7 doublet. This Korringa rate was obtained from measurement at low temperature and concentrations (see the inset).

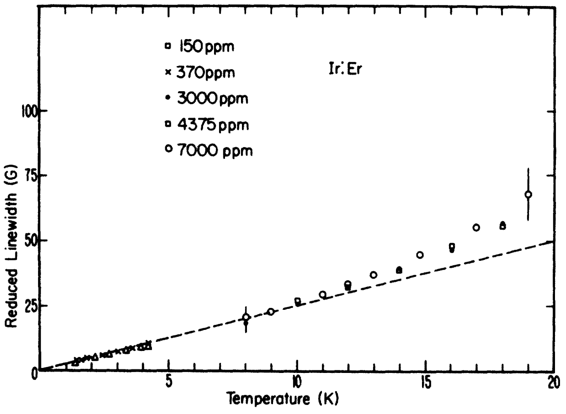

FIG. 3. Reduced linewidth (obtained by subtracting the residual width) for Ir : Er as a function of temperature. The residual widths are 31, 37, and 40 G for the 3000-, 4375-, and 7000-ppm samples, respectively. The dashed line is the thermal broadening expected for an isolated Γ_7 doublet, extrapolated from low temperatures and low concentrations (150 and 370 ppm) measurements.

Au : Gd, are also presented.

Ag : Er. At low temperatures ($1.4 \leq T \leq 4.2$ K) and small Er concentrations (to reduce the possibility of ordering), the linewidth was fitted to the formula $a + bT$. To obtain the thermal broadening, we subtracted the quantity a (residual width) from the total linewidth. The results for Ag : Er are exhibited in Fig. 1. The thermal-broadening slope expected for an isolated Γ_7 doublet (verified at low temperatures and concentrations) is equal to b. We find $b = 7$ G/K for Ag : Er, which is slightly smaller than that obtained previously by Chui *et al.*[3] At higher temperatures an increase in the thermal-broadening slope was observed which can be explained quantitatively by Eq. (3) in I. Using the value of 207 K for the over-all crystal-field splitting, given by Williams and Hirst,[2] we find a value $\Delta \simeq 35 \pm 7$ K. This is to be compared to the susceptibility analysis of Williams and Hirst[2] who found $\Delta = 35$ for Ag : Er. Our value for Δ corresponds to the parameter $x = -0.35$, where x is proportional to the ratio of the fourth- and the sixth-order crystalline-field coefficient and is defined by Lea, Leask, and Wolf.[4] The solid line in Fig. 1 is the fit using our values for the relevant parameters in Eq. (3) of I.

Rh : Er and Ir : Er. EPR measurements on Rh : Er and Ir : Er dilute alloys have been reported previously[5,6] in the temperature range ($1.4 \leq T \leq 4.2$ K). In the present work we extend these measurements to higher temperatures (limited by the signal-to-noise ratio). Figures 2 and 3 exhibit our data for Rh : Er and Ir : Er, respectively. The samples were measured in splatted form. The thermal broadening for very low temperature and very low concentrations, yield the values $b_{\mathrm{Rh:Er}} = 3.5 \pm 1$ G/K and $b_{\mathrm{Ir:Er}} = 2.5 \pm 0.5$ G/K, respectively. The value of b for Ir : Er is slightly smaller (but still within the error bar) than reported previously by us[6] (3 ± 1 G/K). Assuming that these values correspond to an isolated Γ_7 doublet (dashed lines in Figs. 2 and 3), the crystalline-field effect

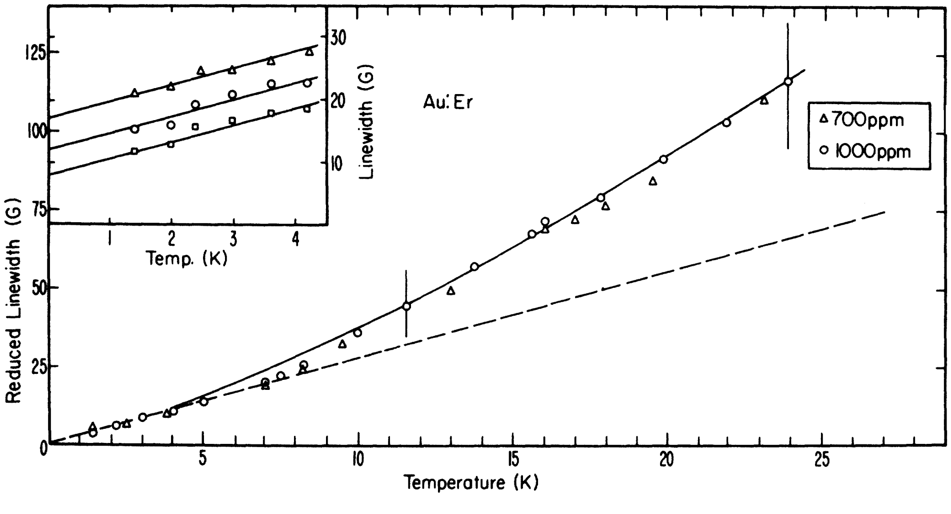

FIG. 4. Reduced linewidth (obtained by subtracting the residual width) for Au : Er as a function of temperature. The residual widths are 21 and 27 G for the 700- and 1000-ppm samples, respectively. The solid line is the theoretical fit with $\Delta = 16$ K (assuming an over-all splitting of 105 K). The dashed line is the Korringa rate expected for an isolated Γ_7 doublet, extrapolated from measurements at low temperatures ($1.4 \leq T \leq 4.2$ K) and small Er concentrations as shown by the inset.

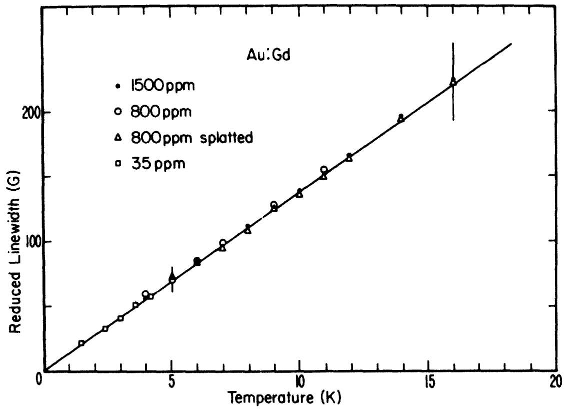

FIG. 5. Reduced linewidth (obtained by subtracting the residual width) for Au : Gd as a function of temperature. The residual widths are 28, 32, 58, and 80 G for the 35-ppm powdered, 800-ppm splatted, 800-ppm powdered, and 1500-ppm powdered samples, respectively. The data for high Gd concentrations and low temperatures were omitted because of interaction effects.

is clearly seen by virtue of the slightly higher slope at high temperatures (Figs. 2 and 3).

The analysis of the data is complicated because of the absence of susceptibility or other information on these systems (in particular, absence of knowledge of the over-all crystalline-field splitting W). However, a very rough estimation can be obtained as follows: The EPR of Rh : Dy and Ir : Dy indicate a Γ_7 ground state for Dy^{+3} in these hosts.[5,6] Following Williams and Hirst[2] we assume that the crystalline-field parameters do not vary much for the same host matrix, and for different rare-earth impurities. From the curves of Lea, Leask, and Wolf,[4] observation of a Γ_7 for both Er and Dy in Rh and Ir results only if the cubic crystal-field coefficients C_4 and C_6 are negative and positive, respectively (similar to that for rare earths in noble metals, but different from rare earths in Pd[7]). Further, for these values of C_4 and C_6 the first excited state is $\Gamma_8^{(1)}$ or Γ_6. However, the latter does not affect the thermal broadening because the exchange coupling has no matrix element between Γ_7 and Γ_6. As a result of this hierarchy of levels, the analysis used earlier in this paper for Ag : Er applied to Rh : Er and Ir : Er.

It is clearly seen from Figs. 1–3 that the relative increase in the thermal broadening at high temperatures for Ir : Er is roughly the same as Ag : Er; for Rh : Er, however, the relative increase in the thermal broadening is slightly larger. In the absence of information about the over-all splitting, we shall adopt a "reasonable" value for the over-all splitting $W \simeq 200$ K (as for Ag : Er). We obtain from our data (Figs. 2 and 3) $\Delta \simeq 35 \pm 10$ K and $\Delta \simeq 25 \pm 10$ K for Ir : Er and Rh : Er, respectively. It is clear that one further piece of information (e.g., W as determined by susceptibility measurements) is sufficient to determine Δ. In the absence of such data the above prediction is the most that magnetic resonance can yield.

Au : Er and Au : Gd. Finally, we shall compare our previous published data on Au : Er with new measurements of Au : Gd dilute alloys. The appreciable increase in the thermal broadening observed for Au : Er (Fig. 4) was interpreted in I by crystalline-field effect with a separation $\Delta = 16 \pm 5$ K (using the over-all splitting of 105 K).

For Au : Gd, however, a linear thermal broadening is expected because of the very small crystalline-field splitting of S-state ions.[8] This is in agreement with our observations for Au : Gd shown in Fig. 5. We find that the thermal broadening at low temperatures and low Gd concentrations (to eliminate possibility of ordering effects) coincide with that observed at higher temperatures at, however, larger Gd concentrations. The observed thermal broadening of 14 ± 4 G/K does not agree with a previous report[8] based on measurements over a much smaller temperature range. The discrepancy is probably due to the existence of interaction effects in the previous work. The linear thermal broadening observed for Au : Gd gives us complete confidence that the deviation observed for Er dilute alloys are associated with crystalline-field effects.

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