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THE EPR OF EUROPIUM METAL

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ABSTRACT

The signs of the g-shifts of Gd and Eu (negative for Gd and positive for Eu) are discussed in terms of a simple model with s and d bands . The g-shift of metallic Eu determined by extrapolation to $T \rightarrow \infty$ is 0.038 ± 0.004 ; $DH/T = 1.9 \pm 0.3 \text{ G K}^{-1}$. The experimental difficulties involved in EPR measurements in concentrated spin systems are also considered.

The purpose of this note is to suggest an interpretation for the sign of the g-shift in metallic europium and to compare the contributions to Δg in Eu and Gd. We have re-measured the EPR spectrum of europium to resolve a discrepancy in the sign of Δg reported by other workers (1,2). The experimental aspects of the work with concentrated spin systems like pure Gd and Eu are also discussed.

The present measurements give a positive g-shift for europium of 0.038 ± 0.004 using a value of 1.992 for the g in insulating crystals (3,4). The sign of Δg is negative for Gd, in agreement with other measurements in the literature (5,6,7). Both metals have seven 4f electrons, and therefore the ground state is an S state.

The g-shifts are given (8) within a model electronic structure with s and d electrons by

$$\Delta g = (J_s \chi_s + J_d \chi_d) / g_e \mu_B^2 \quad |1|$$

with effective parameters $J_s > 0$ and $J_d < 0$.

In concentrated gadolinium metallic systems, like GdAg and GdCu, the negative g-shifts are explained by assuming that the s-electron contribution is almost completely bottlenecked and Δg_d is the only term observed (9,10).

The calculated electronic densities of state for metallic Gd and Eu (11,12) show that at the Fermi level there is a peak in the case of gadolinium and a minimum in the case of europium. We therefore attribute the posi-

tive g-shift in Eu to the fact that χ_d is much reduced in this case. The s contribution (which is positive) even though largely bottlenecked, may then dominate the d contribution to Δg .

The origin of negative parameters J in these systems has been discussed elsewhere (13).

EXPERIMENTAL DETAILS

The measurements were performed on disk-shaped samples of Eu and Gd cut under an argon atmosphere from 99.5% purity ingots (supplied by Rare Earth Products Ltd.). The X-band EPR spectrometer (a Varian E9) was calibrated using an NMR gaussmeter. The spectra were computer fitted to a sum of absorption and dispersion lorentzian lines of variable proportion; the fits gave the position and width of the lines, as well as the ratio of dispersion to absorption. The measured g-factors are displayed in Fig. 1 and the dependence of linewidth on temperature in Fig. 2. The apparent g values (Fig. 1) vary with temperature as expected from the variation in magnetization. The linewidth at high temperatures shows a linear dependence with T typical of metallic systems, showing that the Korringa mechanism dominates at these temperatures.

MEASUREMENTS IN CONCENTRATED SPIN SYSTEMS

The analysis of EPR measurements in metallic Gd and Eu presents certain difficulties which arise from the fact that in the pure metals the 4f moments are concentrated. Consequently, the susceptibility due to the localized moments is large; a substantial magnetization results under the applied

magnetic field, of the order of 3500 G at resonance. This non-negligible magnetization in the paramagnetic phase is responsible for two instrumental effects: 1) the apparent g values are displaced by the local fields, and 2) the spread in the local fields from grain to grain (in powdered samples) gives an extra contribution to the linewidth.

The total magnetic field acting on the rare-earth ion is a sum of the applied field H_0 and a local field H_{loc} . H_{loc} consists of H_{dm} , the demagnetizing field, $H_{Lorentz}$, the field due to dipoles on the Lorentz cavity, and H_{dip} , the field due to the dipoles inside this cavity. These terms are proportional to the magnetization, and should therefore vary as $(T - T_p)^{-1}$, if we take into account only the f magnetization (T_p is the paramagnetic Curie temperature). The temperature dependence of the apparent g is therefore of the form

$$g_{app} = g (1 + A(T - T_p)^{-1}) \quad |2|$$

Consequently the real g value (g) can be obtained by extrapolating the experimental points to $T \rightarrow \infty$; this procedure was used by Davidov and Shaltiel (14) in the study of some gadolinium intermetallic compounds. The agreement between Eq. |2| and our experimental data is fairly good, suggesting that local order effects and the variation of the electronic susceptibility with T are not important in the range of temperatures displayed (Fig. 1).

In a dispersed powdered sample the only contribution to the local field that varies from grain to grain is $H_{dm} = D_i M$, since for each shape there corresponds a demagnetizing factor D_i . Although H_{dm} will vary from

point to point within a grain if its shape is not ellipsoidal, we can assume that the resulting distribution of fields arises from an equivalent ensemble of ellipsoids. The resulting broadening of the EPR lines is then related to the width of the distribution of the D_i . The absorption lines corresponding to each grain are expected to have lorentzian shapes; the broadened line is obtained through the convolution of this shape and the distribution of the values of $D_i M$. For small broadenings one can assume that the width of the broadened line is a sum of the original width plus the width of the distribution of $D_i M$ (this would be a good approximation if the $D_i M$ had a lorentzian distribution). This approximation appears to be valid since spectra obtained with powdered samples give good fits with lorentzian lines. The values of D vary between 0 and 4π , these extremes corresponding to flat grains with magnetic field parallel and perpendicular to their planes, respectively. The maximum possible width of the distribution of D_i is then 4π ; this means, for example, that the contribution to DH in Gd at 400°K is less than 30 G, and at 500°K , less 10 G. These contributions would modify the experimental value of DH/T by approximately $0.2 \text{ G } ^\circ\text{K}^{-1}$. Samples with different forms may therefore give rise to different values of the slope. We have observed in our powdered Gd samples a slightly smaller value of DH/T than that obtained with a disk (4.3 G K^{-1}) but the difference may not be significant. By extrapolation we obtained $g = 1.972 \pm 0.004$ with powdered Gd, and $g = 1.987 \pm 0.004$ with a disk, starting in either case from the same ingot annealed in vacuo for 10 hours at 1000°C ; the value for the powder agrees very well with that derived by correcting for the demagnetization field (7). In the case of the disk the extrapolated value is significantly larger, however.

The experimental slope observed with Eu metal was of $1.9 \pm 0.3 \text{ G K}^{-1}$

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FIGURE CAPTIONS

Fig. 1 Variation of the apparent g factor with temperature. The straight lines are computer fits to Eq. |2| , with T_p fixed ($T_p = 108^\circ\text{K}$) in the case of europium, and adjustable in the gadolinium samples: $T_p = 309 \pm 3^\circ\text{K}$ for the powder and $T_p = 318 \pm 4^\circ\text{K}$ for the disk.

Fig. 2 Variation of the linewidth with temperature for Eu disk and Gd powder; the Gd disk showed a similar behaviour (DH is the half width at half maximum of the lorentzian absorption curve).

