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ESR Observation of the Γ_6 Excited State of Er^{3+} in the Dilute Alloy PdEr

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We report the first ESR signal of an excited crystalline state (Γ_6) in a metal (PdEr). The intensity of the Γ_6 isotropic resonance compared to the $\Gamma_8^{(3)}$ resonances of the ground-state quartet allows the determination of the energy scaling parameter W of the crystalline field. A more precise value is deduced from the splitting of the transitions $1 \to 2$ and $3 \to 4$ of the $\Gamma_8^{(3)}$ ground state: $W = -0.163 \pm 0.015$ °K, in accordance with the work of Praddaude.

The effect of excited crystalline-field states on the relaxation rate of the ground-state multiplet has recently been observed in dilute alloys. Davidov et al.[1] measured the temperature dependence of the Er^{3+} ESR linewidth in AuEr and from this deduced a value of the energy separation Δ between the Γ_7 ground-state doublet and the first-excited $\Gamma_8^{(1)}$ quartet. In a previous paper Devine, Zingg, and Moret[2] measured the ESR in PdEr single crystals. The ground state of Er^{3+} was found to be a $\Gamma_8^{(3)}$ quartet. We have since observed a new resonance signal in PdEr, whose g value and temperature behavior indicate that it is due to the first-excited Γ_6 doublet. The amplitude of the signal is related to the energy separation between the $\Gamma_8^{(3)}$ and Γ_6 levels, and allows a direct determination of the crystalline-field energy scaling parameter W.

The Er^{3+} free ion has a $J = \frac{15}{2}$ multiplet ground state which reduces in a cubic crystalline field to three Γ_8 quartets, one Γ_7 doublet, and one Γ_6 doublet. Devine, Zingg, and Moret[2] observed all possible transitions in the $\Gamma_8^{(3)}$ ground-state quartet and interpreted them with the effective-spin-Hamiltonian formalism[3] ($\tilde{S} = \frac{3}{2}$). They found an x value as defined by Lea, Leask, and Wolf[4]
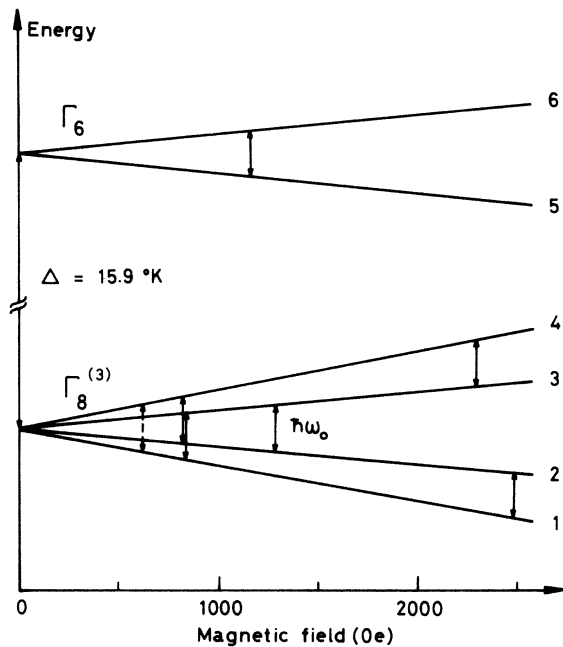
FIG. 1. Zeeman energy levels of the ground and first excited states of Er^{3+} in a cubic crystal field. The magnetic field is applied along [111] and the crystal field parameters are $x = +0.47$, $W = -0.16°K$. The possible transitions at a microwave frequency $\omega_0/2\pi = 9500$ MHz are indicated. The transition $1 \to 4$ is forbidden when $\tilde{H} \parallel [111]$.

FIG. 2. ESR spectra of Er^{3+} in Pd. Spectra a to d, obtained with sample A (1500 ppm) and $\tilde{H}$ along [111]. The low-field line corresponds to the excited doublet (transition $5 \to 6$) and the high-field one to transition $2 \to 3$ of the $\Gamma_8^{(3)}$ ground quartet. The increase of the relative intensity of the excited state with temperature is readily seen. Spectra e to g, obtained with sample B (1000 ppm) at constant temperature $T = 9.3°K$. The high-field line (transition $2 \to 3$) changes position according to the orientation of H whereas the low-field line (transition $5 \to 6$) has an isotropic g value.

equal to 0.47. However, this formalism does not explain the observed splitting between the transition $1 \to 2$ and $3 \to 4$ (see Fig. 1), nor does it give any information on the energy scaling parameter W. Instead, the spin Hamiltonian for the full ground-state J multiplet is to be used, as Praddaude demonstrated first for PdDy and also for PdEr (see Praddaude and co-workers[5-7]).

New ESR measurements were made on PdEr single crystals with nominal concentrations 1500 ppm (sample A), 1000 ppm (sample B), and 800 ppm (sample C). The dilute alloys were prepared in an arc furnace under an argon atmosphere. Sample A was grown by the floating-zone technique; samples B and C were prepared by recrystallization. Previous results on sample C were reported in Ref. 2. The sample was glued onto the vertical wall of a rectangular cavity (TE_{102} mode), the microwave magnetic field $\tilde{H}_1(t)$ being vertical and parallel to the crystal axis $[1\bar{1}0]$. The static magnetic field $\tilde{H}$ rotated in the horizontal plane.

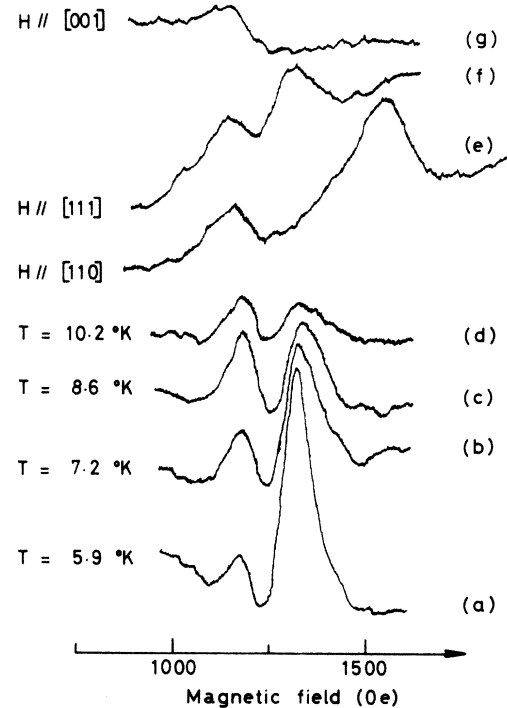In addition to the $\Gamma_8^{(3)}$ resonance lines we observed an isotropic resonance signal at $g = 5.8$

± 0.1, which appears at approximately $5.5°K$ and broadens beyond detection at about $12°K$. Figure 2 (spectra $a-d$) shows the evolution of the signal as a function of temperature with $\tilde{H}$ parallel to the [111] axis. We also give the observed spectra ($e-g$) for different orientations of the magnetic field at constant temperature. The striking feature of the signal is the increase of its amplitude relative to that of the strong $2 \to 3$ transition of the ground-state quartet when increasing the temperature (see Fig. 3). This strongly suggests that the isotropic signal is due to an excited state.

A well-defined splitting of $1 \to 2$ and $3 \to 4$ transitions has already been observed for sample C (see Fig. 3 in Ref. 2). From the dependence of their intensities as a function of temperature we can conclude that the high-field line corresponds to the transition $1 \to 2$. It has been sug-
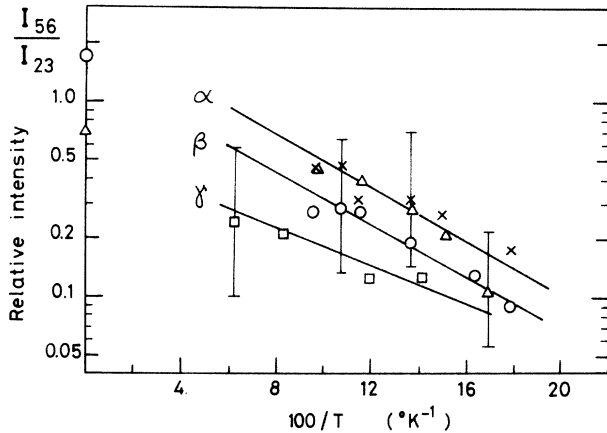
FIG. 3. Ratio of intensities of Γ_6 excited state (transition $5 \to 6$) and transition $2 \to 3$ of ground-state quartet as a function of inverse temperature. The values should be on a straight line whose slope gives the energy separation Δ between the ground and first excited states. The straight line α corresponds to 1500 ppm (crosses) and 1000 ppm (triangles) with $\vec{H}$ along [111], β to 1000 ppm (circles) with $\vec{H}$ along [110], and γ to 800 ppm (squares) with $\vec{H}$ along [110]. The points on the vertical axis ($T = \infty$) correspond to the theoretical transition-probability ratios W_{56}/W_{23} in the [110] (circles) and [111] (triangles) directions.

FIG. 4. Resonance fields of the transitions $1 \to 2$ and $3 \to 4$ as a function of angle for 800-ppm PdEr. The magnetic field rotates in the plane $(1\bar{1}0)$ and forms an angle θ with [001]. The theoretical curves were calculated with the parameters $x = 0.47$, $W = -0.16°$K, and $g_J' = 1.135$ for a microwave frequency $\omega_0/2\pi = 9500$ MHz.

gested[8] that the recrystallization technique could leave a uniaxial distortion in the crystal which was laminated before recrystallization. In sample C the splitting along the two equivalent directions [111] and [11$\bar{1}$] is the same; this seems to exclude any distortion effect. We will show that the observed splitting can be explained by the proximity of the excited state. We give in Fig. 4 the resonance fields of the transitions $1 \to 2$ and $3 \to 4$ as a function of the magnetic-field orientation for sample C. Even at the lowest temperature the transitions $1 \to 2$ and $3 \to 4$ were not split in samples A and B where only one broad line was observed ($\Delta H \simeq 420 \pm 100$ Oe).

The Hamiltonian of the Er^{3+} ion in a cubic crystal field and in the presence of a magnetic field $\vec{H}$ is

$$\mathcal{H} = \mathcal{H}_{free} + W\left[xO_4/F_4 + (1 - |x|)O_6/F_6\right]$$
$$+ g_J'\mu_B\vec{H}\cdot\vec{J}, \qquad (1)$$

where $\vec{J}$ is the total angular momentum of the ion, g_J' is an "isotropic" effective Landé factor which takes into account the exchange interaction with the conduction electrons, O_4 and O_6 are the fourth- and sixth-degree cubic operators, and F_4 and F_6 are multiplying factors, respec-
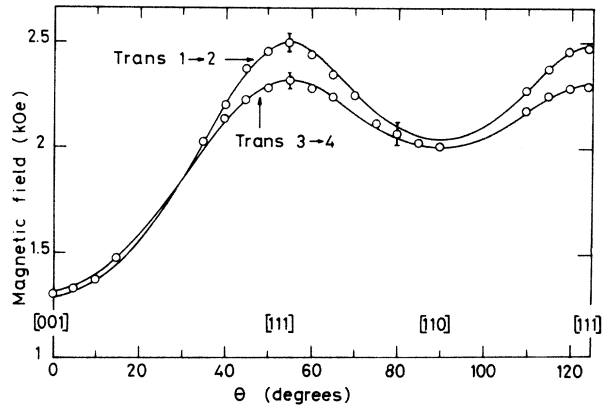
tively 60 and 13 860 for Er^{3+}. In the case of PdDy, Praddaude and co-workers[5,6] suggested that the energy levels of the ground-state multiplet are significantly modified by the proximity of the excited crystalline levels. We diagonalized the full Hamiltonian (1) within the subspace formed by the sixteen $(2J + 1)$ eigenvectors $|J, M_i\rangle$ of the operator J_z. The energy levels and wave functions depend on x, on W, and on the magnitude and orientation of the static field $\vec{H}$ with respect to the axis of quantization (z direction), chosen as the crystallographic [001] axis. The calculation shows that the g value of the $2 - 3$ transition is virtually W independent; using the experimental resonance fields for this transition we find the parameter $x = + 0.47 \pm 0.005$ and $g_J' = 1.135 \pm 0.01$. For $x = + 0.47$ the first excited state is a Γ_6 doublet. The calculated energy separation of the transition $5 \to 6$ does not depend much on W and yields an isotropic g value equal to $g_{theor} = 5.67$ (with $g_J' = 1.135$). Given the error on g_J', this value is in good agreement with the measured g value for the new line: $g_{exp} = 5.8 \pm 0.1$.

The intensity of a magnetic dipole transition between two states $|k\rangle$ and $|l\rangle$ is given by

$$I_{kl} = W_{kl} \frac{\exp(-E_k/kT)}{\sum_i \exp(-E_i/kT)}$$
$$\times [1 - \exp(-\hbar\omega_{kl}/kT)], \qquad (2)$$

where the transition probability per unit time W_{kl} (multiplied by a Boltzmann factor) is pro-

portional to $|\langle l|\vec{H}_1\cdot\vec{J}|k\rangle|^2$, with $|k\rangle$ and $|l\rangle$ eigenvectors of the full Hamiltonian (1) and H_1 the magnitude of the rf field. The intensity ratio between transitions $5 \to 6$ and $2 \to 3$ is then given to a very good approximation by $(W_{56}/W_{23})\exp(-\Delta/kT)$. As a function of $1/T$ it is a straight line with a slope $-\Delta/k$ in a semilogarithmic plot. In Fig. 3 we give the best straight-line fits for three cases; from their slopes we find $\Delta = (14 \pm 4)°K$ corresponding to $W = (-0.143 \pm 0.04)°K$. Large errors in the determination of the intensities do not allow us to assign a more accurate value to Δ. The intensity ratio at high temperatures can be calculated with the known W_{kl} values. The agreement is not good for the straight lines α and γ (see Fig. 3); also, we do not understand exactly why the relative intensities for sample C are smaller (see discussion below).

A better determination of W is possible by utilizing the splitting of the resonance lines of transitions $1 \to 2$ and $3 \to 4$ in sample C. This has a maximum value of 185 ± 20 Oe when $\vec{H}$ is parallel to $[111]$. We calculated the splitting as a function of W by diagonalizing (1) with $\vec{H}$ along $[111]$. On fitting with the measured splitting we obtain $W = (-0.163 \pm 0.015)°K$, which is in good agreement with that obtained from the intensity behavior. For this value of W we have drawn on Fig. 4 the theoretical resonance fields for the transitions $1 \to 2$ and $3 \to 4$. The agreement with the measured angular dependence is excellent and shows that the observed splitting in sample C is indeed due to the proximity of the excited doublet.

As mentioned in the experimental part no splitting was observed in samples A and B. It is possible that local distortions in these crystals lead to a spread in the energy separation Δ. The resonance fields for transitions $2 \to 3$, $1 \to 3$, $2 \to 4$, $1 \to 4$, and $5 \to 6$ do not depend appreciably on W; we thus expect narrow lines even in the presence of a distribution of W values. However, transitions $1 \to 2$ and $3 \to 4$ depend considerably on W, and a distribution of W could explain the observed broad lines in samples A and B. Such local distortion could also partially explain the difference in the intensities of the excited-state resonance line between samples A or B and C.

We also looked for possible deviations of the linear relation between temperature and linewidth; there is no such observable deviation in PdEr. This is in good agreement with a calculation, generalizing Hirst's formula,[9] of the effect of excited crystalline states on the linewidth of the ground-state multiplet. More details will be reported later.

Knowing W one can calculate the fourth- and sixth-order crystal field parameters C_4 and C_6. We find $C_4 = Wx/F_4\beta = (-26.4 \pm 3)°K$ and $C_6 = W(1 - |x|)/F_6\gamma = (-2.73 \pm 0.3)°K$, where for Er^{3+} the values β and γ, respectively, are 4.44×10^{-5} and 2.07×10^{-6}. C_4 and C_6 have a sign opposite to the prediction of a naive point-charge model. This points to the strong contribution of the conduction and $5d$ electrons.[10]

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