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THE CRYSTAL FIELD SPLITTING BETWEEN THE Γ_8–Γ_7 LEVELS OF Dy^{3+} IN CaF_2: AN INDIRECT EPR MEASUREMENT

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The angular variation of the gyromagnetic factor of the Γ_7 level of Dy^{3+} in CaF_2 has been measured at 35 GHz. The data have been fitted with a spin Hamiltonian which includes linear and cubic terms in the magnetic field. This gives an estimated value of $\Delta = 9.5 \pm 0.4$ cm^{-1} for the energy splitting between the ground Γ_8 quartet and the next Γ_7 excited doublet.

1. INTRODUCTION

WHEN ions of Dy^{3+} are diluted in a crystalline environment of cubic symmetry, the ground $^6H_{15/2}$ state of the free ion is split in to three Γ_8 quartets and two doublets of Γ_7 and Γ_6 symmetry. Bierig and Weber found the ground state to be a Γ_8 quartet for Dy^{3+} in CaF_2.[1] Using the g-values of the resonance lines within the Γ_8 levels they have estimated $x = 0.6$ (x being the ratio between the fourth and sixth order terms of the crystal field Hamiltonian). According to Lea, Leask and Wolf[2] (LLW), a quartet Γ_8 and the doublet Γ_7 are the ground and first excited states respectively.

Several papers (see Table 2 for references) indicate that for this system, the energy gap between these two levels is of only a few cm^{-1} and they are both split in the presence of a magnetic field. At the same time, some mixing between them is also induced by the Zeeman interaction, the largest effects being obtained for large magnetic field. Due to the anisotropic nature of the Zeeman splitting of the Γ_8 level, its admixing with the doublet Γ_7 will produce a small angular variation in the position of the EPR line for this state.[3]

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The angular dependence of the EPR field can be expressed in terms of linear combinations of spherical harmonics transforming like the Γ_1 irreducible representation of the O_h symmetry group. Retaining terms up to 4th order we get:

$$H_{res} = A^{(0)}Y_0^0(\theta,\phi) + A^{(4)}\left(\frac{1}{2}\sqrt{\frac{7}{3}}\right)\left[Y_4^0(\theta,\phi) + \sqrt{\frac{15}{4}}\left(Y_4^4(\theta,\phi) + Y_4^{-4}(\theta,\phi)\right)\right] \quad [1(a)]$$

$$\equiv \frac{A^{(0)}}{\sqrt{4\pi}} + A^{(4)}\left(\frac{1}{16}\sqrt{\frac{21}{4\pi}}\right)(35\cos^4\theta - 30\cos^2\theta + 3 + 5\,\mathrm{sen}^4\theta\cos 4\phi).$$

In the (001) plane this expression reduces to:

$$H_{res} = A^{(0)}\left(\frac{1}{\sqrt{4\pi}}\right) + A^{(4)}\left(\frac{1}{2}\sqrt{\frac{21}{4\pi}}\right) \times [1 - 5\,\mathrm{sen}^2\theta + \tfrac{15}{4}\,\mathrm{sen}^4\theta] \quad [1(b)]$$

where θ is the angle between the direction of the magnetic field and the |001| crystal axis.

The spin Hamiltonian for a Γ_7 doublet ($S = 1/2$) in cubic symmetry, can be written as:[4]

$$\mathcal{H} = g\beta\bar{S}\cdot\bar{H} + A\beta^3[S_xH_x^3 + S_yH_y^3 + S_zH_z^3 - \tfrac{3}{5}|H|^2\bar{S}\cdot\bar{H}] + B\beta^3|H|^2\bar{S}\cdot\bar{H} \quad (2)$$

where we have retained up to cubic terms in the magnetic fields.

Transforming this Hamiltonian to a system where the z axis is parallel to the magnetic field and taking its diagonal part we can evaluate the constants of equation (1) in terms of the spin Hamiltonian parameters:

$$K = A^{(4)}\left(\frac{1}{2}\sqrt{\frac{21}{4\pi}}\right) = -\left(\frac{2}{5}\right)\beta^3\frac{H_0}{h\nu}\cdot A$$

and

$$g\beta H_0 + \beta^3 H_0^3 B = h\nu$$

with

$$H_0 = \frac{A^{(0)}}{\sqrt{4\pi}}$$

2. EXPERIMENTAL RESULTS

Measurements of the angular variation of the resonance field for the Γ_7 doublet were performed at 4.2 K using a conventional EPR spectrometer operating at Q-Band[5] ($\nu = 35.181$ GHz).

The experimental results are plotted in Fig. 1 and from a minimum square fitting procedure of the data with equation [1(b)] we obtain:

$$H_0 = (3372 \pm 2)\,\text{G}$$

$$K = 9.8 \pm 0.4\,\text{G}$$

or equivalently

$$g + B\beta^2 H_0^2 = 7.45 \pm 0.01$$

$$A = -2.18 \pm 0.08\ \text{cm}^2.$$

3. THE Γ_8–Γ_7 ENERGY GAP

From the energy shift of the Γ_7 due to the mixing with the ground Γ_8, as obtained by third order perturbation theory in the Zeeman interaction, we get:

$$A = +(9/2)g_J^3(M_{12}/\Delta)^2(M_{22} - (1/3)M_{33})$$

$$B = -\tfrac{1}{5}g_J^3(M_{12}/\Delta)^2(M_{22} + 3M_{33} + 10M_{11})$$

$$g = 2g_J M_{11}$$

where $g_J = 4/3$ is the Landé factor for the $^6H_{15/2}$ state and M_{11}, M_{22}, and M_{33} are given by

$$M_{11} = \langle\Gamma_7\alpha''|J_z|\Gamma_7\alpha''\rangle \quad M_{33} = \langle\Gamma_8\lambda|J_z|\Gamma_8\lambda\rangle$$

$$M_{22} = \langle\Gamma_8\kappa|J_z|\Gamma_8\kappa\rangle \quad M_{12} = \langle\Gamma_7\alpha''|J_z|\Gamma_8\nu\rangle.$$

From the wave functions of LLW for $x = 0.6$ the values of M_{11}, M_{22} and M_{33} can be calculated. These quantities can also be identified (provided they have been obtained from low field experiments) with the experimental parameters: g_{Γ_7}, P and Q defined by Ayant *et al.*,[6] the relation being

$$M_{11} = g_{\Gamma_7}/2g_J \quad M_{22} = P \quad M_{33} = Q.$$

Both calculated and experimental values for these quantities are tabulated for comparison in Table 1. From these relations and the experimental g, P, and Q, we get:

$$A = (-51.3 \pm 1.0)(M_{12}/\Delta)^2\ \text{cm}^2 \qquad (3)$$

and

$$B = (-17.1 \pm 0.1)(M_{12}/\Delta)^2\ \text{cm}^2. \qquad (4)$$

M_{12} was then calculated exactly from LLW's wave functions. To this value we assigned an arbitrary dispersion margin of 2 per cent, similar to that found for M_{11}, M_{22} and M_{33}, as shown in Table 1. From equation (3) and the value of A obtained in our experiment we get:

$$\Delta = E(\Gamma_7) - E(\Gamma_8) = (9.5 \pm 0.4)\ \text{cm}^{-1}$$

for the energy splitting Δ.

Using this value of Δ we estimate the field dependent isotropic contributions to the g factor as:

$$B\beta^2H^2|_{Q\text{-band}} = -0.018 \pm 0.002$$

and

$$B\beta^2H^2|_{X\text{-band}} \cong -0.001$$

for 35 and 9 GHz, respectively.

The difference between our value $g = (7.45 \pm 0.01)$ for Q-band, and that of 7.47 ± 0.03 given by Low[7] for X-band, is consistent with these estimations.

4. CONCLUDING REMARKS

The $E(\Gamma_7) - E(\Gamma_8)$ splitting has also been determined from other experiments and the values provided by these methods are given in Table 2. A large discrepancy between our result and that of Low can be observed. In order to examine this discrepancy we have recalculated this splitting by direct diagonalization of the Γ_7–Γ_8 Zeeman matrix using the experimental data of Low,[8] obtaining $\Delta = 9.2\ \text{cm}^{-1}$ instead of the $7.3\ \text{cm}^{-1}$ value quoted in that paper. Presumably this difference is due to the neglect of

Table 1. Energy splitting $\Delta = E(\Gamma_7) - E(\Gamma_8)$

Method	Experimental value (cm^{-1})	Reference
Intensity of EPR line	8.5 ± 1.0	1
High field EPR	7.3 ± 0.2	8
Fluorescence	8	9
g-factor anisotropy	9.5 ± 0.4	This paper
Thermoluminescence	8.3 ± 1.0	10

Table 2. Results for the matrix elements as used in this paper

Matrix element	Theor. value $x = +0.600$	Exp. value	Ref.
M_{11}	2.833	2.80 ± 0.01	7
		2.82 ± 0.02	1
M_{22}	5.029	5.14 ± 0.10	8
		5.25 ± 0.30	1
M_{33}	0.960	0.986 ± 0.02	1
M_{12}	1.965	–	–

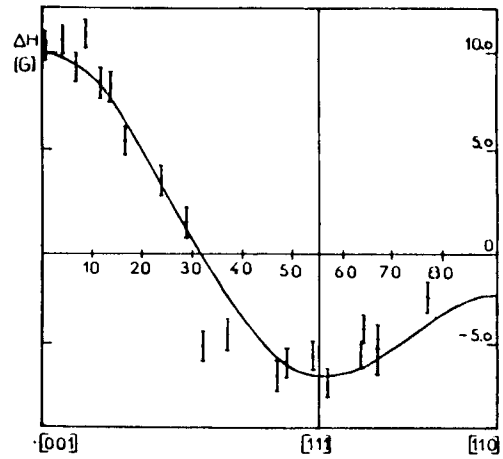

FIG. 1. Angular variation of the *Q*-band EPR line of the Γ_7 level for Dy^{3+} in CaF_2. Units in Gauss.

the Zeeman mixing of the Γ_7–Γ_8 levels in their calculations since the value $\Delta = 7.3\ cm^{-1}$ is consistent with this assumption. As a final remark we should mention that by complete diagonalization of the crystal field and Zeeman interaction within $J = 15/2$ for $H = 3400$ G, we were able to observe that the presence of the remaining Γ_8 and Γ_6 states affect our results in only 1–2 per cent which justifies the neglect of those levels in our third order perturbations calculations.

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