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Paramagnetic Resonance of Dysprosium in Cubic and Axial Fields in CaF_2

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The paramagnetic resonance spectrum of dysprosium in CaF_2 has been investigated at 9.6 kMc/sec at liquid-helium temperatures. In a site of cubic crystal field symmetry, the Dy^{3+} ground state is a Γ_8 quartet. The observed g values and their angular dependences are in general agreement with predicted values derived from Bleaney's Γ_8 spin Hamiltonian. The first excited state is a Γ_7 doublet 8.5 ± 1 cm^{-1} above the ground state with an isotropic $g=7.52\pm0.05$. The fourth and sixth degree parameters describing the cubic crystal field are $A_4\langle r^4\rangle\sim-200$ cm^{-1} and $A_6\langle r^6\rangle\sim30$ cm^{-1}, respectively. The Dy^{163} hyperfine structure constant determined from the Γ_7 resonance is $(280\pm10)\times10^{-4}$ cm^{-1}. Two groups of lines exhibiting trigonal symmetry about the [111] crystallographic axes are observed with (I) $g_{\parallel}=16\pm1$, $g_{\perp}<1$, and (II) $g_{\parallel}=4.93\pm0.05$, $g_{\perp}=1.50\pm0.05$. A site with tetragonal symmetry about [100] axes is also observed with $g_{\parallel}=1.78\pm0.05$, $g_{\perp}=2.84\pm0.05$. Attempts to measure the spin-lattice relaxation time T_1 indicate $T_1<3$ μsec at 2°K. Possible relaxation mechanisms and estimates of their magnitude and temperature dependence are discussed.

INTRODUCTION

Electron paramagnetic resonance and optical studies[1] of various rare-earth impurities in CaF_2 have shown that trivalent rare-earth ions, which enter the lattice substitutionally for divalent calcium, may occupy sites having cubic, tetragonal, or trigonal local crystal field symmetry depending upon the nature of the charge compensation. From an investigation of the electron paramagnetic resonance (EPR) spectrum of Dy^{3+} in CaF_2, resonances arising from ions in sites having these three different symmetries have been identified.[2] The cubic field spectrum has been examined in greatest detail. It is of particular interest since the ground state is a Γ_8 quartet and, as Bleaney[3] has pointed out, the Zeeman splitting of such a quartet may be useful for maser applications.

Measurements were made at 9.6 kMc/sec and at liquid-helium temperatures. Four different dysprosium-doped CaF_2 single crystals, two grown by Optovac, Inc., and two in this laboratory by the Bridgeman-Stockbarger technique, were examined. The resonance spectra of these samples were in general similar and, as shown in Fig. 1, quite complex. The dysprosium content of the samples which were studied in detail was 0.17% and any other iron or rare-earth transition group elements, if present, were in fractional concentrations $\lesssim10^{-5}$ as determined from spectrochemical analysis.

In addition to the resonances reported below, which exhibit cubic, trigonal, and tetragonal symmetry and derive from trivalent dysprosium, several other lines and broad resonances were observed. Due to the difficulty in investigating many of these lines, either because of their low relative intensities or because of overlapping resonances, their origin and nature is not understood at present. Dysprosium is known to enter the CaF_2 lattice in a divalent state. In the cubic field of the CaF_2 lattice, the lowest Stark level of the $^5I_8$ ground multiplet of Dy^{2+} may be either a nonmagnetic Γ_3 doublet or a Γ_5 triplet state; hence, paramagnetic resonance from Dy^{2+} may be observable if the magnetic Γ_5 triplet is populated. No correlation between the additional lines in the spectrum and the possible presence of divalent dysprosium has been made.

CUBIC FIELD SPECTRUM

In a cubic crystal field, the $^6H_{15/2}$ free ion ground state of Dy^{3+} is split into a Γ_6 doublet, a Γ_7 doublet, and three Γ_8 quartets. The Hamiltonian describing this cubic field may be written as

$$\mathcal{H}=B_4(O_4^0+5O_4^4)+B_6(O_6^0-21O_6^4), \qquad (1)$$

where O_n^m are operators transforming as the corresponding spherical harmonics and B_4 and B_6 are parameters describing the fourth and sixth degree terms in the crystal field potential. In the notation of Elliott and Stevens,[4] $B_4=\beta A_4\langle r^4\rangle$ and $B_6=\gamma A_6\langle r^6\rangle$. Lea, Leask, and Wolf[5] have determined the eigenfunctions and eigenvalue solutions of Eq. (1) for various angular momenta J. Their diagram of the eigenvalues for $J=15/2$ is reproduced in Fig. 2. The levels are plotted as a function of the parameter x which is related to the ratio of B_4 and B_6 by

$$\frac{B_4}{B_6}=\frac{x}{1-|x|}\frac{F(6)}{F(4)}, \qquad (2)$$

where $-1\leq x\leq1$ and $F(4)=60$, $F(6)=13\,860$ for $J=15/2$. If a point charge model of Dy^{3+} in the eight-coordinated CaF_2 lattice is assumed, x is restricted to be positive. Thus, from Fig. 2, the ground state will be either a Γ_7 or a Γ_8 depending upon the ratio B_4/B_6.

An isotropic g value of $(17/3)\,\lambda=7.55$ is predicted for the Γ_7 doublet. Low[6] has reported an isotropic Dy^{3+}

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[1] See, for example, W. Low, J. Phys. Soc. Japan **17**, Suppl. B-I, 440 (1962) and references therein.

[2] R. W. Bierig and M. J. Weber, Bull. Am. Phys. Soc. **8**, 24 (1963).

[3] B. Bleaney, Proc. Phys. Soc. (London) **73**, 937 and 939 (1959).

[4] R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A215**, 437 (1952); and **A218**, 553 (1953).

[5] K. R. Lea, M. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids **23**, 1381 (1962).

[6] W. Low, Proc. Phys. Soc. (London) **76**, 307 (1960).

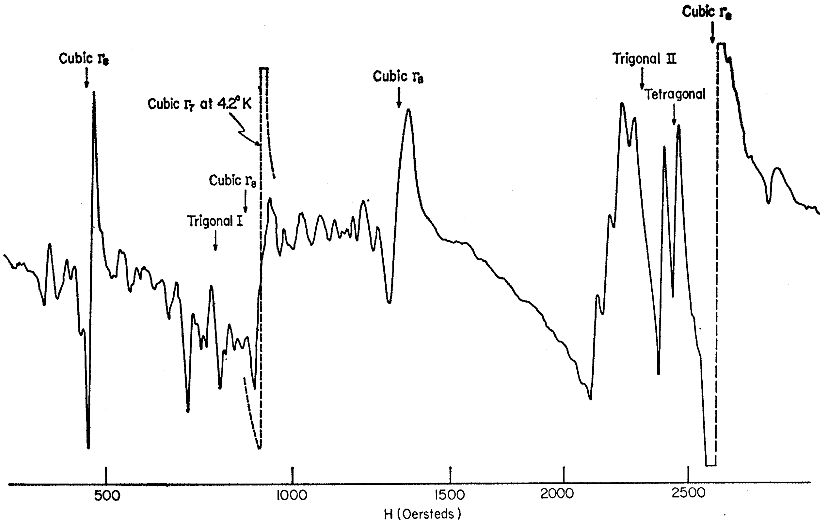

FIG. 1. Paramagnetic resonance spectrum of dysprosium-doped CaF_2 at 9.6 kMc/sec and 2°K with the magnetic field H applied slightly off a [100] axis.

resonance in CaF_2 at 8.8 kMc/sec and 20°K corresponding to the Γ_7 doublet with $g=7.47\pm0.03$. We also observe this line, $g=7.52\pm0.05$. However, from the temperature dependence of its intensity, we find that the Γ_7 is not the ground state but an excited state, the ground state being a Γ_8.

Bleaney[3] has formulated a spin Hamiltonian,

$$\mathcal{H}=g\beta(H_xS_x+H_yS_y+H_zS_z)+f\beta(H_xS_x^3+H_yS_y^3+H_zS_z^3),\quad(3)$$

to describe the Zeeman splitting and resonance properties of an isolated Γ_8 quartet in a magnetic field H. The four energy levels of the effective $S=\frac{3}{2}$ spin system derived from the solution of Eq. (3) are, in terms of the parameters g and f,

$$(W/\beta H)^2=\tfrac{1}{4}(5\gamma^2+3\delta^2)\pm\gamma[\gamma^2+\tfrac{1}{2}\delta^2\{9(l^4+m^4+n^4)-3\}]^{1/2},\quad(4)$$

where $\gamma=g+7f/4$, $\delta^2=f(g+5f/2)$, and (l,m,n) are direction cosines of H with respect to the cubic axes. For $H\|[100]$, three resonances are observed in $Dy^{3+}:CaF_2$ with g values of 2.63 ± 0.05, 5.48 ± 0.15, and 14 ± 1. These lines and their relative intensities correspond to the allowed transitions within a Γ_8 quartet for this orientation and are shown as solid arrows in Fig. 3. The relatively large experimental uncertainty associated with the $g=14$ line arose from the difficulty in accurately calibrating the low magnetic field at resonance.

The experimental and Bleaney's theoretical angular dependences for the Γ_8 resonances are shown in Fig. 4 for the magnetic field applied in both the (100) and (111) crystallographic planes. Note that the (111) plane is a convenient orientation in which to identify lines arising from a Γ_8 multiplet since the energy levels are independent of the direction of the applied magnetic field in this plane. Only a portion of the angular dependence of the $g=5.48$ resonance could be determined since its intensity decreases as H departs from a [100] direction. Calculations of the angular dependence of the transition probabilities predicted the measured decrease in intensity and that the resonance should not have been observable in our experiment for $H\|[110]$. The angular dependence of a fourth Γ_8 resonance whose transition probability is zero for $H\|[100]$ is also shown.

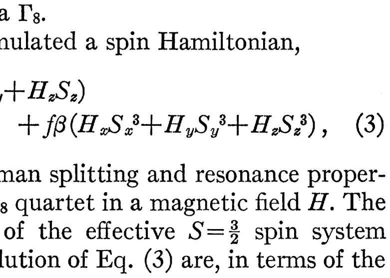

FIG. 2. Energy eigenvalues for $J=15/2$ in a cubic crystal field as a function of the parameter x [from Lea, Leask, and Wolf (Ref. 5)].

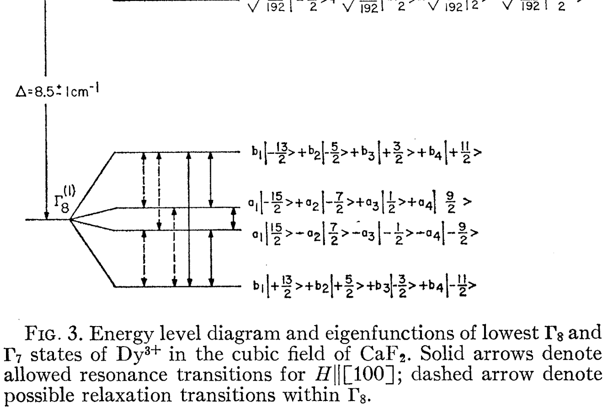

FIG. 3. Energy level diagram and eigenfunctions of lowest Γ_8 and Γ_7 states of Dy^{3+} in the cubic field of CaF_2. Solid arrows denote allowed resonance transitions for $H\|[100]$; dashed arrow denote possible relaxation transitions within Γ_8.

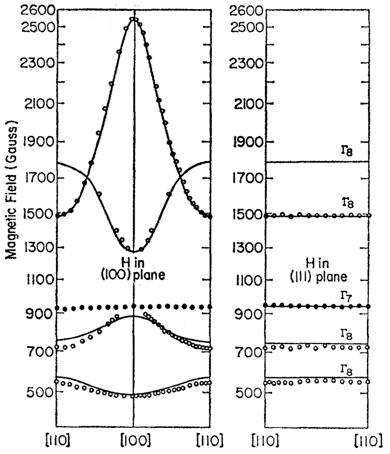

FIG. 4. Observed and predicted angular dependence for $x=0.6$ of the Γ_7 and Γ_8 state resonances for Dy^{3+} in the cubic field of CaF_2.

A good fit to the observed cubic field spectrum is obtained using Lea, Leask, and Wolf's eigenfunctions for $x=0.6$, where for $H\|[100]$, g values of 2.57, 5.36, and 13.3 are predicted. Of these, the g value of the high-field resonance is most sensitive to the parameter x, is the most accurately determined experimentally, and is not affected by Zeeman field admixing with the Γ_7 state at this orientation. The value $x=0.6$ is, indeed, fortuitous since explicit numbers are given in Ref. 5 for this x value. Although a slightly improved agreement, within experimental error, is obtained with a shade larger value of x, a value of 0.6 will suffice for the present discussion. From Fig. 2 it is seen that at $x=0.6$ the first excited state is a Γ_7 doublet, the remaining excited states being much higher in energy. The observed temperature dependence of the Γ_7 resonance from 2–18°K can be fitted to a Boltzmann population function in which only a Γ_8 ground state is included and with a $\Gamma_8-\Gamma_7$ energy separation of $\Delta=8.5\pm1$ cm^{-1}. In Bleaney's treatment the assumption is made that spin-orbit coupling$\gg$cubic field splitting$\gg$Zeeman energy, which, to a first approximation, is satisfied. We have also examined the angular dependence of the high-field cubic line at 16 kMc/sec. The observed g values agree, within experimental uncertainty, with the values derived above from the X-band data. This result lends credence to the assumption that the amount of Zeeman admixing between the Γ_7 and Γ_8 states is indeed small. The first excited state, $^6H_{13/2}$, of the Dy^{3+} ground term is $\sim$3300 cm^{-1} above the ground state and, hence, crystal field mixing introduces only a small perturbation of $\sim$1% on the g values of the ground level.

The approximate eigenvalues and eigenfunctions of the remaining cubic field Stark levels of the Dy^{3+} $^6H_{15/2}$ ground state can be determined using the above values of x and Δ and the results of Lea, Leask, and Wolf. From these, the cubic crystal field parameters are found to be

$$A_4\langle r^4\rangle\sim-200\ \mathrm{cm}^{-1},\quad A_6\langle r^6\rangle\sim30\ \mathrm{cm}^{-1}.$$

The value of x used above is very near the point at which the Γ_7 and Γ_8 levels cross and since we have used the measured $\Gamma_7-\Gamma_8$ energy separation as a scale factor, it is clear that any small change in x will produce rather large changes in an estimate of the total cubic crystal-field splitting. Hence, the overall uncertainty in the crystal-field parameters.

The hyperfine structure of the Γ_7 resonance due to nuclear isotopes Dy^{161} and Dy^{163} (nuclear spins $I=\frac{5}{2}$, natural abundance 18.9 and 25%, respectively) was studied. The relative spacing of the Dy^{163} and Dy^{161} hyperfine components was approximately 1.4 in agreement with Park's[7] more accurate determination of the dysprosium hfs in $La_2Mg_3(NO_3)_{12}\cdot24H_2O$. The measured hyperfine structure constant for the more intense Dy^{163} components is $(280\pm10)\times10^{-4}$ cm^{-1}. The hfs of the Γ_8 lines, which is expected to be anisotropic, could not be accurately determined due to an insufficient signal-to-noise ratio and the complexity of the overall spectrum.

AXIAL FIELD SPECTRUM

In a crystal field of axial symmetry, the $J=15/2$ ground state of Dy^{3+} is split into eight Kramer's doublets. Two groups of lines have been observed which exhibit trigonal crystal field symmetry about the four [111] body diagonals of the cubic CaF_2 lattice and have g values of (I) $g_{\parallel}=16\pm1$, $g_{\perp}<1$, and (II) $g_{\parallel}4.93\pm0.05$, $g_{\perp}=1.50\pm0.05$. Their angular dependence in the (100) plane is shown in Fig. 5. The symmetry has been confirmed by additional measurements in the (111) plane.

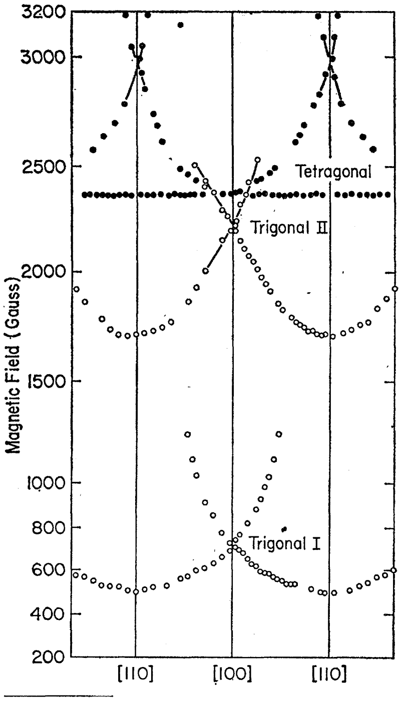

FIG. 5. Angular dependences of resonances from Dy-doped CaF_2 which exhibit tetragonal or trigonal crystal field symmetry.

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[7] J. G. Park, Proc. Roy. Soc. (London) **A245**, 118 (1958).

The eigenfunctions for a Kramers doublet in a crystal field of trigonal symmetry will be formed from linear combinations of basis vectors with J_z values ($\pm 15/2$, $\pm 9/2$, $\pm 3/2$) or ($\pm 13/2$, $\pm 7/2$, $\pm 1/2$, $\mp 5/2$, $\mp 11/2$). Resonance (I) above probably corresponds to the first set of eigenvectors for which $g_\perp = 0$. The g values of both sets of trigonal lines can be fitted by appropriate combinations of the above groups of eigenvectors, however an unambiguous determination of the coefficients is not possible since only two data are known. No distinct difference in the temperature dependence of the two groups of trigonal lines was observed down to 2°K, thus indicating that if one arises from a ground doublet and the other from an excited doublet, their separation is very small. The two trigonal resonances may be due to different types of trigonal sites in the lattice.[8] For example, the origin of a [111] trigonal field is usually ascribed to the replacement of one of the eight nearest neighbor F^- by an O^{2-}, however an F^- in a next-nearest neighbor interstitial site would also produce a crystal field of trigonal symmetry.

A set of lines exhibiting tetragonal symmetry about the [100] crystallographic directions was also found. The experimental g values are $g_\parallel = 1.78 \pm 0.05$, $g_\perp = 2.84 \pm 0.05$, and the observed angular dependence in a (100) plane is shown in Fig. 5. These resonances most probably derive from a physical configuration wherein a Dy^{3+} ion replaces a Ca^{2+} ion and an F^- ion occupies one of the six nearest neighbor interstitial lattice sites, thereby generating a local crystal field with axial symmetry about a [100] direction.

SPIN-LATTICE RELAXATION

An attempt was made to measure the spin-lattice relaxation time T_1 using pulse saturation techniques at temperatures 2–4°K. No measurable signals could be obtained from any of the Dy^{3+} lines reported above. Based upon the limiting time resolution of the apparatus and the results of other relaxation measurements, we estimate the effective relaxation time at these temperatures to be $\lesssim 3$ μsec. This time is much shorter than the observed T_1's of other rare-earth ions in CaF_2, which are typically in the order of 100 μsec and exhibit a T^{-1} dependence at liquid-helium temperatures.[9]

Although we have no direct measurements of the magnitude or temperature dependence of the relaxation times, it is nevertheless of interest to speculate about possible mechanisms which may account for the rapid relaxation times deduced above. In particular, we shall consider rare-earth relaxation processes arising from dynamic orbit-lattice coupling which have been treated by Orbach.[10]

The Dy^{3+} relaxation rates may be faster than those of other rare-earth ions in CaF_2 simply because of the existence of relatively low-lying excited states which tend to enhance the low-temperature relaxation rates. Relaxation times of the order of magnitude estimated above are predicted for the cubic field Γ_8 resonances at 4°K if a two-phonon Orbach process involving real transitions to and from the Γ_7 excited state is operative and the pertinent matrix elements of the dynamic crystal field are ~ 100 cm^{-1}. The rate of this process would decrease rapidly with decreasing temperature due to the exponential character of its temperature dependence. Order-of-magnitude estimates suggest that at low temperatures, $T \approx 2$°K, the dominant relaxation mechanism may be two-step relaxation processes involving states within the Γ_8 quartet. Although the orbit-lattice interaction does not connect time conjugate states, relaxation transitions between other states are allowed as shown by the dashed arrows in Fig. 3. If such processes are active, the relaxation would be expected, in general, to exhibit a time dependence characteristic of a linear combination of exponential terms. The relaxation modes of various pairs of states within the Γ_8 quartet will be discussed in more detail in a forthcoming paper.

The relaxation rate of the cubic field Γ_7 resonance would also be fast if the strength of the orbit-lattice interaction is as strong as required above. Since the principal Orbach process for the Γ_7 excited state at low temperatures would proceed via transitions to and from a lower state, the temperature dependence of $T_1(\Gamma_7)$ would change from a constant at low temperatures, $T \ll \Delta$, to a T^{-1} law at high temperatures. At temperatures $\gtrsim 15$°K, lifetime broadening of the Γ_7 resonance is observed which, due to the estimated magnitude and slow temperature variation of the Orbach process via the τ_8 ground state, probably arises from the dominance of Raman relaxation processes at these temperatures or an Orbach process via higher excited states.

ACKNOWLEDGMENTS

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[9] M. J. Weber and R. W. Bierig, Bull. Am. Phys. Soc. **8**, 259 (1963).

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