Zeeman Effect in the $4f \rightarrow 5d$ Spectrum of Ce^{3+} in CaF_2

M. H. CROZIER
National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts*
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The Zeeman effect of the Ce^{3+} ion with tetragonal charge compensation in CaF_2 has been studied at 4.2°K. An absorption line at 3131.6 Å has been split with fields of 60 kG, and although all the components cannot be resolved, there is good agreement with epr results for the ground state. Axial stress results identify the upper state as having crystal quantum number $\mu=\pm\frac{1}{2}$. The occurrence of $4f^n \rightarrow 4f^{n-1}5d$ spectra in the trivalent rare earths is discussed. In an appendix, a result is established concerning the use of the Zeeman effect to identify the $\mu=\pm\frac{1}{2}$ and $\mu=\pm\frac{3}{2}$ components of a cubic Γ_8 level split by a tetragonal distortion.

INTRODUCTION

THE spectra of trivalent rare-earth ions as added impurities in solids are usually studied with concentrations near 1 to 0.1%, and under these conditions calcium fluoride containing cerium shows a very strong broad absorption band around 3000 Å. However, when concentrations near 1 part of CeF_3 in 10^6 of CaF_2 are used and the absorption is examined at low temperatures, it is found that there is in this region a series of absorption lines having the appearance of pure electronic plus vibrational transitions. These have already[1] been assigned as transitions between the $4f$ ground state of the Ce^{3+} ion and excited states belonging to the $5d$ configuration. It is interesting to consider whether these lines really are due to cerium, and if so why they are more easily observed here than for other rare-earth ions, and why there should be sharp zero-phonon lines at all. In this paper, we use the Zeeman effect to prove that the spectrum is due to trivalent cerium and we discuss the occurrence of $4f^n \rightarrow 4f^{n-1}5d$ spectra in the trivalent rare earths.

THE ZEEMAN EFFECT

The crystals studied were grown by Optovac Inc. in conditions under which the Ce^{3+} ions in CaF_2 occupy almost exclusively substitutional sites of tetragonal symmetry C_{4v}, with charge compensation by an additional F^- ion in the nearest interstitial site. Because the symmetry axes of such centers are randomly distributed among the three possible directions [100], [010], and [001], the observed Zeeman effect is complicated by the fact that except when the magnetic field is applied along a [111] direction, some of the centers must be at different angles to the field from others. Paramagnetic resonance studies[2] have shown that the ground state of Ce^{3+}, which belongs to the $^2F_{5/2}$ level in the $4f$ configuration of the free ion, may be derived from a Γ_{8u} state in O_h symmetry which is split by a tetragonal perturbation of the crystal field to give a lowest Kramer's doublet which is approximated by

$$|4f(\tfrac{5}{2})\pm\tfrac{3}{2}\rangle = \sqrt{\tfrac{1}{6}}\,|4f\,J=\tfrac{5}{2}\,M=\pm\tfrac{3}{2}\rangle + \sqrt{\tfrac{5}{6}}\,|4f\,J=\tfrac{5}{2}\,M=\mp\tfrac{5}{2}\rangle,$$

where the crystal quantum number $\mu=\pm\frac{3}{2}$ is used on the left. The splittings of this level by a magnetic field parallel or perpendicular to the tetragonal axis are observed to be $3.038\,\beta B$ and $1.396\,\beta B$, where βB is the Bohr magneton times the field intensity.

In the $5d$ configuration, we expect to have a Γ_{8g} state lowest in the O_h approximation since in cubal coordination the $5d(e_g)$ orbital has less energy than $5d(t_{2g})$, and the tetragonal field will split this Γ_{8g} into two Kramer's doublets which we may denote by $|5d(e_g)\pm\frac{1}{2}\rangle$ and $|5d(e_g)\pm\frac{3}{2}\rangle$. As e orbitals are not split by a magnetic field, we may expect an isotropic spin-only splitting of $\sim 2\beta B$ for these levels, with possible small anisotropic corrections due to the admixture of other states.

For special orientations of the crystal in a magnetic field, selection rules govern the number and polarization of the lines in the Zeeman effect. Consider a center whose fourfold symmetry axis lies along the [001] direction. When the magnetic field is applied in the [001] direction, the ion in this center is in C_4 symmetry. The selection rules which can thus be derived for the absorption of light polarized parallel (π) or perpendicular (σ) to **B** are given in Table I(a). When the field is applied along either the [100] or [110] or equivalent directions, only mirror symmetry remains, and each Kramer's doublet splits into two

TABLE I. Selection rules for a [001] center.

(a) **B**‖[001]

		$5d(e_g)$ $+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{3}{2}$	$-\frac{3}{2}$
$4f(\frac{5}{2})$	$+\frac{3}{2}$	σ	···	π	σ
	$-\frac{3}{2}$	···	σ	σ	π

(b) **B**‖[100] or [110]

		$5d(e_g)\pm\frac{1}{2}$ $(+\frac{1}{2})$	$(-\frac{1}{2})$	$5d(e_g)\pm\frac{3}{2}$ $(+\frac{1}{2})$	$(-\frac{1}{2})$
$4f(\frac{5}{2})$	$(+\frac{1}{2})$	π	σ	π	σ
	$(-\frac{1}{2})$	σ	π	σ	π

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[1] A. A. Kaplyanskii, V. N. Medvedev, and P. P. Feofilov, Opt. i Spektroskopia **14**, 664 (1963) [English transl.: Opt. Spectry. **14**, 351 (1963)].

[2] M. Dvir and W. Low, Proc. Phys. Soc. (London) **75**, 136 (1960); M. J. Weber and R. W. Bierig, Phys. Rev. **134**, A1492 (1964).

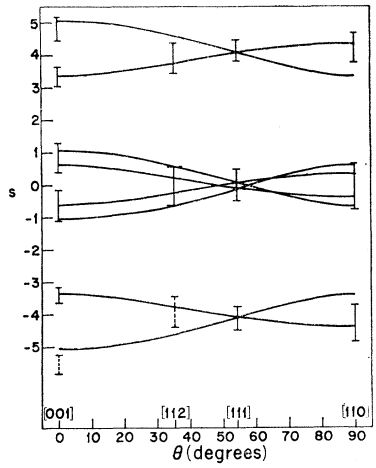

FIG. 1. Calculated and observed variation of the Zeeman splitting with angle in the plane normal to [1$\bar{1}$0].

levels which we may label by crystal quantum numbers $(+\frac{1}{2})$ or $(-\frac{1}{2})$, where parentheses are used to denote that this is with reference to the mirror normal. The selection rules for this orientation, again referred to the field direction, are given in Table I(b). For other orientations, no valid symmetry remains, and although it is possible to investigate the intensity of polarized absorption by more detailed arguments, we shall not discuss this further.

EXPERIMENTAL RESULTS

The absorption spectra were photographed at liquid helium temperature using a 2-m Bausch and Lomb spectrograph in second order, with an inverse dispersion of 1.9 Å/mm. The samples were oriented so that light could be propagated along the [1$\bar{1}$0] direction, and the magnetic field was applied at right angles along the [001], [112], [111], or [110] directions. A strong pure electronic absorption line was observed at an air wavelength of 3131.6 Å, and at shorter wavelengths there were several vibronic lines which were too broad to show a resolvable Zeeman effect. In addition to broad lines which were almost certainly vibronic, our samples also showed weaker relatively sharp lines at 3084.7, 3092.5, 3098.3, and 3112.7 Å. The line at 3092.5 Å showed a Zeeman effect which appeared to be similar to that of the line at 3131.6 Å, but it was not possible to obtain satisfactory measurements of this owing to the low intensity of the absorption.

In Fig. 1 we plot the expected splitting factors s given by $\nu=\nu_0+\frac{1}{2}s(\beta B/hc)$, with ν measured in cm^{-1}, against the angle θ between **B** and the [001] direction. Also shown are the values observed at 60 kG ($\beta B/hc=2.80$ cm^{-1}). It can be seen that there is sufficient general agreement to identify the Ce^{3+} ion, but that the linewidth prevents the resolution of the complete patterns. Thermal depopulation in the ground state also makes a few of the components very weak. In principle, the Zeeman effect can be used to decide whether the upper state is $|5d(e_g)\pm\frac{1}{2}\rangle$ or $|5d(e_g)\pm\frac{3}{2}\rangle$, but since the predicted polarized spectra, shown in Fig. 2 for **B**$\|$[001], are very similar, our present Zeeman results are not conclusive.

However, by applying an axial stress along the [001] direction, we find that the upper state involved is $|5d(e_g)\pm\frac{1}{2}\rangle$. The stress cannot lift the Kramer's degeneracy of the levels, but it does affect the centers oriented along [001] differently from those along [100] or [010] so that a Kaplyanskii splitting[3] appears in the spectrum. Two lines are observed, one of which is σ polarized (**E**$\perp$ stress direction), as would be expected for $|5d(e_g)\pm\frac{1}{2}\rangle$. For $|5d(e_g)\pm\frac{3}{2}\rangle$, two lines are likewise expected, but they should be completely unpolarized.

$4f^n \rightarrow 4f^{n-1}5d$ SPECTRA

For a sharp line to be observed in a transition between two electronic energy levels of an impurity ion in a crystal, it is necessary that the lattice states associated with the upper and lower levels are those in which no vibrations are excited. If there is very little overlap between these two unexcited vibrational states, the transition probability will be much greater when vibrations are involved, and no sharp spectrum will be observable. Hence, when we observe sharp $4f^n \rightarrow 4f^{n-1}5d$ lines in the divalent or trivalent rare earths, there must be considerable overlap between the appropriate zero-phonon states, which implies that in this respect there is no great difference between the contribution of the $4f$ or $5d$ orbitals to the interaction of the ion with its neighbors.

A simple calculation may be carried out to determine the variation of the energy separation of the lowest levels of $4f^n$ and $4f^{n-1}5d$ through the rare-earth series.[4,5] The electrostatic interaction between $4f$ and $5d$ electrons is not large, so that we may consider uncoupled states for which the energy may be approximated as

$$E(4f^{n-1}5d)=E(4f^{n-1})+E(5d).$$

Hence, apart from slow variations in $E(5d)$ and the center of gravity of the $4f^n$ configurations, we have the

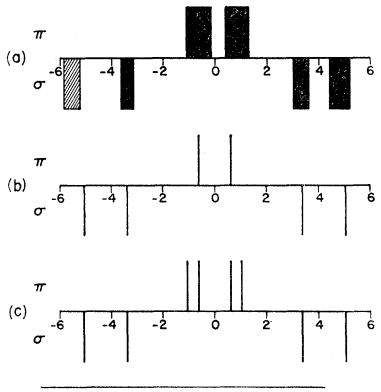

FIG. 2. Zeeman splittings s with polarization for **B**$\|$[001] (a) observed, (b) calculated for $\mu=\pm\frac{1}{2}$ upper state, (c) calculated for $\mu=\pm\frac{3}{2}$ upper state.

[3] A. A. Kaplyanskii, Opt. Spectry. **7**, 406, 409 (1959).
[4] C. K. Jørgensen, Mol. Phys. **5**, 271 (1962).
[5] D. S. McClure and Z. Kiss, J. Chem. Phys. **39**, 3251 (1963).

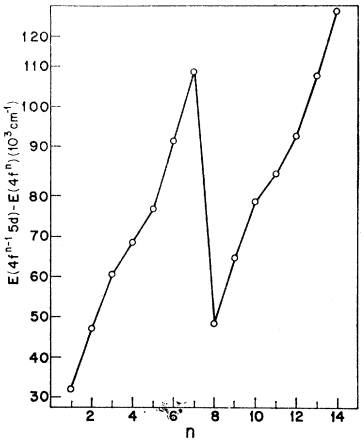

FIG. 3. Calculated variation of the separation of the lowest levels of $4f^{n-1}5d$ and $4f^n$ in the trivalent rare earths.

result that

$$E(4^{n-1}5d)-E(4f^n)$$

is determined by the energy of the lowest SL multiplet of each $4f^n$, which depends primarily on the Racah parameter[6] E^3.

The coefficient of E^3 in $E(4f^n)$ varies rather like $-S(S+1)$, where $S=\frac{1}{2}n$ for $n\leq 7$ and $S=\frac{1}{2}(14-n)$ for $n<7$, so that the general trend of the energy difference is to increase, with a sharp discontinuity between $n=7$ and $n=8$. This can be seen in Fig. 3, which shows the results of a calculation including a linearly varying background and some other minor corrections.

It is apparent that in addition to Ce^{3+}, ions in which $4f^n \rightarrow 4f^{n-1}5d$ transitions might occur at a low enough energy to be observable are Pr^{3+} or Tb^{3+}. We have already observed such lines[7] in $CaF_2(Pr^{3+})$, near 2200 Å, but there appear to be no Tb^{3+} lines out to 2100 Å.

CONCLUSION

It has been shown that the sharp absorption line at 3131.6 Å (31 923 cm^{-1}) in CaF_2 is due to Ce^{3+} ions at a tetragonal site. This line is so intense that we have used it to identify 1 part of Ce^{3+} in 10^7 of CaF_2. The optical Zeeman effect is in agreement with epr studies, but linewidth prevents complete resolution of the splitting at 60 kG, and significantly higher fields would be needed to acheive this. Axial stress gives good evidence that this line is due to an upper state with $\mu=\pm\frac{1}{2}$, and it is possible that a second weak line at 3092.5 Å (32 327 cm^{-1}) is due to the remaining $\mu=\pm\frac{3}{2}$ component of the $5d(e_g)\Gamma_{8g}$ cubic level.

In other trivalent rare-earth ions, the $4f^n \rightarrow 4f^{n-1}5d$ transitions should also give sharp lines, but with the exception of Pr^{3+} and possibly Tb^{3+}, they are expected to occur at wavelengths too short to be easily observable.

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APPENDIX

In the course of considering how the $|5d(e_g)\pm\frac{3}{2}\rangle$ and $|5d(e_g)\pm\frac{1}{2}\rangle$ centers could be distinguished, an interesting general result was noted. When a Γ_8 level in cubic symmetry is split by a tetragonal distortion, the first-order Zeeman splitting in each of the two components must always be the same when $\mathbf{B}$ is applied along the [111] direction. Note that this is the direction which is simplest to study, in which the three possible center orientations are equivalent.

To prove this we apply the Wigner-Eckart theorem to the calculations of the matrix elements of the operator $\mathbf{L}+2\mathbf{S}$ which transforms like a T_1 irreducible representation of whatever cubic point group is appropriate. Since the direct product of $\Gamma_8\times\Gamma_8$ contains T_1 twice, we must include two arbitrary (imaginary) reduced matrix elements iA and iB in the general expression

$$\langle\Gamma_{8\mu}|L_\gamma+2S_\gamma|\Gamma_{8\mu'}\rangle = iA\langle\alpha\Gamma_{8\mu}|T_{1\gamma}\Gamma_{8\mu'}\rangle+iB\langle\beta\Gamma_{8\mu}|T_{1\gamma}\Gamma_{8\mu'}\rangle,$$

where tabulated values of the coupling coefficients for μ, $\mu'=\pm\frac{1}{2}$, $\pm\frac{3}{2}$, and $\gamma=x$, y, z are available,[8] and α, β are used to distinguish the two independent sets of coefficients.

A tetragonal distortion along the z axis separates the two Kramer's doublets $|\Gamma_{8\mu}=\pm\frac{1}{2}\rangle$ and $|\Gamma_{8\mu}=\pm\frac{3}{2}\rangle$. We now need to calculate and diagonalize the matrices of

$$M=(L_x+L_y+L_z)+2(S_x+S_y+S_z)$$

for each doublet to obtain the splitting factors for the [111] direction. Since each matrix is Hermitian and has zero trace, the following elements between states with crystal quantum numbers μ, μ' determine the eigenvalues:

$$M(+\tfrac{1}{2},+\tfrac{1}{2})=-A(1/15)^{1/2}-B(3/5)^{1/2},$$
$$M(+\tfrac{1}{2},-\tfrac{1}{2})=-A(1+i)(4/15)^{1/2}+B(1+i)(3/20)^{1/2},$$

and

$$M(+\tfrac{3}{2},+\tfrac{3}{2})=-A\sqrt{\tfrac{3}{5}}+B(1/15)^{1/2}$$
$$M(+\tfrac{3}{2},-\tfrac{3}{2})=B(1+i)(5/12)^{1/2}.$$

In each case the splitting factors are then found to have the same value,

$$s=2[\tfrac{3}{5}A^2+(9/10)B^2-\tfrac{2}{5}AB]^{1/2}.$$

[6] G. Racah, Phys. Rev. **76**, 1352 (1959).
[7] M. H. Crozier, Bull. Am. Phys. Soc. **9**, 631 (1964).
[8] G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-Two Point Groups* (MIT Press, Cambridge, Massachusetts, 1963).