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# Optical-Absorption Spectrum of $GdCl_3 \cdot 6H_2O$

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An analysis is performed on the spectroscopic properties of the levels $^6P_{5/2}$ and $^6P_{7/2}$ of $Gd^{3+}$ $4f^7$ in $GdCl_3 \cdot 6H_2O$. It is supposed that the crystal field can be represented by a cylindrically symmetric part on which a small distortion is superposed. Very good agreement is obtained for the Zeeman splittings of the components of the levels. The crystal splittings are discussed, as well as the intensities of the magnetic-dipole transitions from the ground level $^8S_{7/2}$ to the $^6P$ multiplet.

## I. INTRODUCTION

The optical spectra of $Gd^{3+}$ in crystalline environments have long been popular with spectroscopists.[1–8] The absorption spectra, unlike those of many rare-earth ions, are comparatively free from vibronic structure, and so are well suited to a study of the purely electronic properties of the gadolinium ion. The ground level of $Gd^{3+}$ is $^8S_{7/2}$, of the configuration $4f^7$. The crystal-field splitting of $^8S_{7/2}$ is so small ($\sim 1$ cm$^{-1}$) that it can usually be ignored in optical work. The first two excited levels, lying some 32 000 cm$^{-1}$ above the ground level, are $^6P_{7/2}$ and $^6P_{5/2}$. Although no crystal-field splittings are expected for a pure $f^7$ configuration in Russell-Saunders coupling, both levels exhibit splittings of about 100 cm$^{-1}$. Several calculations of eigenfunctions and energy levels in intermediate coupling have been carried out.[9–12]

We are concerned with the spectrum of $Gd^{3+}$ in $GdCl_3 \cdot 6H_2O$. Although the point symmetry at a rare-earth ion site is only $C_2$,[13] there is evidence[3,14] of an effective high-symmetry axis perpendicular to the $C_2$ axis for $Gd^{3+}$ and $Yb^{3+}$. Eisenstein[15] has given an interpretation of the crystal-field and Zeeman splittings for $YbCl_3 \cdot 6H_2O$ in terms of a cylindrical crystal field. Some description of the corresponding properties of $GdCl_3 \cdot 6H_2O$ has been given by Harrop,[16] but the original data of Dieke and Leopold[3] remain largely unaccounted for. It is the purpose of this article to show that, with only one parameter, representing the deviation from perfect cylindrical symmetry about the high-symmetry axis, most of the Zeeman data can be well understood. Within this simple approach, other spectroscopic properties can be described.

## II. CRYSTAL FIELD AND SYMMETRY

To treat the effect of a crystal lattice on a free ion, it is customary to expand the crystal-field Hamiltonian in a series of spherical harmonics of even rank $k$.[17] The fact that our interest lies in the $^6P$ multiplet leads to a simplification in crystal-field theory. Because of the selection rules on $k$ with respect to orbital angular momenta, no terms beyond $k=2$ are required. This is rigorously true if $^6D$ states are permitted to mix with $^6P$, but breaks down if admixtures of $^6F$ states are admitted as well. Fortunately, the latter appear to be quite small.[12] Taking the $C_2$ axis as the $x$ axis, we can write

$$H = A_2^0 \sum_i (3x_i^2 - r_i^2) + A_2^2 \sum_i (y_i^2 - z_i^2),$$

the sums running over the electrons $i$. The existence of a cylindrical axis (the $z$ axis) perpendicular to the $C_2$ axis is easy to understand for we can put $H$ in the form

$$H = B_2^0 \sum_i (3z_i^2 - r_i^2) + B_2^2 \sum_i (x_i^2 - y_i^2),$$

in which

$$B_2^0 = -\tfrac{1}{2}(A_2^0 + A_2^2), \quad B_2^2 = \tfrac{1}{2}(3A_2^0 - A_2^2).$$

If it should happen – perhaps accidentally – that $3A_2^0 = A_2^2$, then the second term vanishes and only the cylindrically symmetric term survives. Of course, we do not wish to be so restrictive as to insist that $B_2^2 = 0$. Instead, we prefer to consider the cylindrically symmetric term first and then treat the term involving $B_2^2$ as a perturbation. To this end, we define

$$\delta = B_2^2 / 3B_2^0,$$

which thus measures the deviation from perfect cylindrical symmetry.

In a cylindrical crystal field, the level $^6P_J$ splits up into $J + \frac{1}{2}$ doublets. The energy of a doublet $\pm M$, relative to the center of gravity of the level, is given by

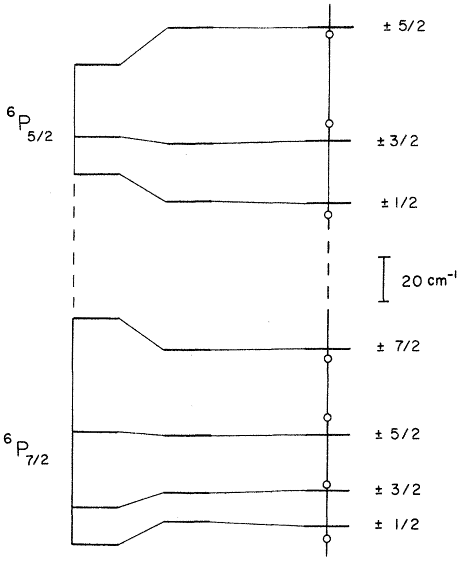

FIG. 1. The splittings of $^6P_{5/2}$ and $^6P_{7/2}$ of Gd$^{3+}$ $4f^7$ produced by a nearly cylindrically symmetric crystal field. On the left are shown the splittings produced by a perfectly cylindrical crystal field, assuming a pure $4f^7$ configuration very near the Russell-Saunders limit. To the immediate right of this structure are shown the displacements produced by configuration interaction, assuming perfect Russell-Saunders coupling. The relative strength of the splittings on the left increases slightly if intermediate coupling is assumed. The effect of a small distortion to the cylindrical symmetry produces the structure on the right, on which are superposed the energies (small circles) of the experimentally determined levels.

$$\alpha_J B_2^0 \langle r^2\rangle [3M^2 - J(J+1)],$$

where $\alpha_J$ is the operator-equivalent factor.[17] A straightforward calculation shows that, if we assume $4f^7$ is pure, but subject it to very slight deviations from Russell-Saunders coupling, then

$$\alpha_{7/2}/\alpha_{5/2} = \tfrac{25}{24}.$$

On the other hand, if configuration interaction is present but the Russell-Saunders limit still applies, then

$$\alpha_{7/2}/\alpha_{5/2} = -\tfrac{5}{12}.$$

The requisite relative strengths of these two mechanisms is illustrated in Fig. 1, which shows that the first dominates. However, to be sure that the experimental levels have been correctly identified, the effect of an external magnetic field must be examined.

## III. ZEEMAN EFFECT

The properties most sensitive to $\delta$ are the Zeeman splittings of the doublets. The spin Hamiltonian for one of them can be written as

$$g_x \beta H_x S_x + g_y \beta H_y S_y + g_z \beta H_z S_z,$$

where the effective spin $S$ is $\frac{1}{2}$, and where $\beta$ is the Bohr magneton. In terms of the splittings $s_u$, given, in Lorentz units, by Dieke and Leopold,[3]

$$s_1 = g_y, \quad s_2 = g_z, \quad s_3 = g_x.$$

Algebraic expressions are set out in Table I for the various $g_u$. Caspers *et al.*[12] find that in intermediate coupling the Landé $g$ value of $^6P_{5/2}$ is given by $g = 1.840$, while that of $^6P_{7/2}$ (denoted by $g'$) is given by $g' = 1.678$. A fitting procedure in which the crystal-field splittings and Zeeman splittings are given roughly equal weight yields $\delta = 0.089\,25$. As can be seen from Table I, the 28 calculated values of $g_u$ are in excellent over-all agreement with the observed values. The good fit ensures that the doublets have been correctly identified.

In Fig. 1, the calculated crystal-field splittings are broken down into (a) the contribution from $4f^7$, (b) the contribution from configuration interaction, and (c) the effect of the deviations from perfect cylindrical symmetry. The details are set out in Table II. Since no Zeeman data are apparently available

TABLE I. Zeeman splittings for $^6P_{5/2}$ and $^6P_{7/2}$.

| State[a] | Nominal $M$ | $g_u$ | Algebraic $g_u$ | Calculated $g_u$ | Observed[b] $g_u$ |
|---|---|---|---|---|---|
| $B_3$ | $\pm\frac{5}{2}$ | $g_x$ | $\frac{10}{3}\delta^2 g$ | 0.05 | 0.3 |
| | | $g_y$ | $\frac{10}{3}\delta^2 g$ | 0.05 | 0 |
| | | $g_z$ | $g(5-\frac{10}{9}\delta^2)$ | 9.18 | 9.08 |
| $B_2$ | $\pm\frac{3}{2}$ | $g_x$ | $6g\delta(2+\delta)$ | 2.06 | 1.34 |
| | | $g_y$ | $6g\delta(2-\delta)$ | 1.88 | 1.32 |
| | | $g_z$ | $g(3-18\delta^2)$ | 5.26 | 5.56 |
| $B_1$ | $\pm\frac{1}{2}$ | $g_x$ | $g(3-12\delta-\frac{28}{3}\delta^2)$ | 3.41 | 3.94 |
| | | $g_y$ | $g(3+12\delta-\frac{28}{3}\delta^2)$ | 7.35 | 6.83 |
| | | $g_z$ | $g(1-\frac{152}{9}\delta^2)$ | 1.59 | 1.69 |
| $A_4$ | $\pm\frac{7}{2}$ | $g_x$ | 0 | 0 | 0 |
| | | $g_y$ | 0 | 0 | 0 |
| | | $g_z$ | $g'(7-\frac{21}{25}\delta^2)$ | 11.73 | 11.45 |
| $A_3$ | $\pm\frac{5}{2}$ | $g_x$ | $20\delta^2 g'$ | 0.27 | 0.58 |
| | | $g_y$ | $20\delta^2 g'$ | 0.27 | 0.39 |
| | | $g_z$ | $g'(5-5\delta^2)$ | 8.32 | 7.88 |
| $A_2$ | $\pm\frac{3}{2}$ | $g_x$ | $15g'\delta(2+\delta)$ | 4.69 | 3.98 |
| | | $g_y$ | $15g'\delta(2-\delta)$ | 4.29 | 4.26 |
| | | $g_z$ | $g'(3-59.16\delta^2)$ | 4.24 | 4.05 |
| $A_1$ | $\pm\frac{1}{2}$ | $g_x$ | $g'(4-30\delta-35\delta^2)$ | 1.75 | 1.91 |
| | | $g_y$ | $g'(4+30\delta-35\delta^2)$ | 10.73 | 10.52 |
| | | $g_z$ | $g'(1-55\delta^2)$ | 0.94 | 0.92 |

[a] In the notation of Ref. 3. The symbol $A$ refers to $^6P_{7/2}$, and $B$ to $^6P_{5/2}$.

[b] From Ref. 3.

TABLE II. Doublet energies for $^6P$. Calculated energies ($cm^{-1}$).

| Level | $M$ | Within $f^7$ [a] | Configuration interaction [b] | Distorting term [c] | Total | Adjusted total [d] | Expt [e] |
|---|---|---|---|---|---|---|---|
| $^6P_{3/2}$ | $\pm\frac{1}{2}$ | 16.3 | 2.8 | 0.2 | 19.3 | 33 292 | (33 290) |
| | $\pm\frac{3}{2}$ | −16.3 | −2.8 | −0.2 | −19.3 | 33 253 | (33 255) |
| $^6P_{5/2}$ | $\pm\frac{5}{2}$ | 26.7 | 15.8 | 0.2 | 42.7 | 32 742 | 32 739 |
| | $\pm\frac{3}{2}$ | −5.3 | −3.2 | 0.9 | −7.6 | 32 692 | 32 699 |
| | $\pm\frac{1}{2}$ | −21.4 | −12.6 | −1.1 | −35.1 | 32 664 | 32 659 |
| $^6P_{7/2}$ | $\pm\frac{7}{2}$ | 58.4 | −13.9 | 0.1 | 44.6 | 32 150 | 32 145 |
| | $\pm\frac{5}{2}$ | 8.3 | −2.0 | 0.4 | 6.7 | 32 112 | 32 121 |
| | $\pm\frac{3}{2}$ | −25.0 | 5.9 | 1.4 | −17.7 | 32 088 | 32 091 |
| | $\pm\frac{1}{2}$ | −41.7 | 9.9 | −1.9 | −33.7 | 32 072 | 32 066 |

[a] Calculated very near the Russell-Saunders limit, for which $\alpha_{3/2}:\alpha_{5/2}:\alpha_{7/2}::-49:24:25$.

[b] Calculated for an arbitrary superposition of configurations, assuming a pure $^6P$ multiplet. For this, $\alpha_{3/2}:\alpha_{5/2}:\alpha_{7/2}::7:-12:5$.

[c] Produced by deviations from pure cylindrical symmetry.

[d] Adjusted to bring the center of gravity of the components of each $J$ level into coincidence with the experimental figure.

[e] From Dieke and Leopold (Ref. 3) except for numbers in parentheses, which are taken from Hellwege, Hüfner, and Schmidt (Ref. 4). The numbers represent the energies (in $cm^{-1}$) of the $^6P$ multiplet above the ground level $^8S_{7/2}$.

for $^6P_{3/2}$, the two components of this level cannot be assigned quantum numbers $M$, and they were not included in the fitting procedure. However, it is clear from Table I that their predicted separation is in very good agreement with experiment.

To estimate the crystal-field parameters, the extent of the admixture of $^6D$ states into the $^6P$ multiplet must be known. If the eigenfunctions of Caspers *et al.* are used, the relative contribution of the $4f^7$ configuration to the splitting increases slightly, and we find, in $cm^{-1}$,

$$B_2^0\langle r^2\rangle = -306, \quad B_2^2\langle r^2\rangle = -82.$$

These numbers are slightly larger in magnitude than would be anticipated from the data of Hellwege and Kahle[18] on $EuCl_3 \cdot 6H_2O$. If the entire splitting of $^7F_1$ is assumed to arise from a pure $f^7$ configuration (a hypothesis that cannot easily be tested in the case of $Eu^{3+}$), then we obtain, in $cm^{-1}$,

$$B_2^0\langle r^2\rangle = -177, \quad |B_2^2\langle r^2\rangle| = 69.$$

Analogous (though smaller) differences between corresponding parameters $B_2^0\langle r^2\rangle$ for $^7F$ of $Eu^{3+}$ and $^6P$ of $Gd^{3+}$ occur for other crystals. This effect may be due in part to the larger value of $\langle r^2\rangle$ for the excited $^6P$ multiplet.

## IV. LINE STRENGTHS

It seems clear now that the transitions $^8S_{7/2} \rightarrow {}^6P_{5/2}$ and $^8S_{7/2} \rightarrow {}^6P_{7/2}$ are largely magnetic dipole in character. As evidence for this, we may cite the extreme weakness of $^8S_{7/2} \rightarrow {}^6P_{3/2}$ and the fact that, near the Russell-Saunders limit, forced electric-dipole radiation would yield relative total strengths for $^8S_{7/2} \rightarrow {}^6P_J$ in the proportions 28: 27: 15 for $J = \frac{3}{2}$, $\frac{5}{2}$, and $\frac{7}{2}$, respectively. On the other hand, magnetic-dipole radiation is forbidden for $\Delta J > 1$. Having made the assumption that we are dealing with magnetic-dipole transitions, it is a simple matter for us to calculate the relative strengths of the lines, since the relevant eigenfunctions have been calculated in the process of constructing Table I. The results are listed in Table III. For simplicity, we have assumed that the total strength of all transitions $^8S_{7/2} \rightarrow {}^6P_{7/2}$, compared to the total strength of all transitions $^8S_{7/2} \rightarrow {}^6P_{5/2}$, is in the proportion 9: 5. This corresponds to a close approach to the Russell-Saunders limit. Detrio[8] has calculated this proportion in intermediate coupling, and finds it to be 1.77: 1. Somewhat surprisingly, this is virtually identical to the former proportion.

In spite of the fact that Dieke and Leopold[3] state that very little evidence of polarization is found in the lines of $GdCl_3 \cdot 6H_2O$, it is clear from Table III that some lines should show appreciable anisotropy. Presumably the photographic recording used by the experimentalists was not sufficiently sensitive to make precise observations practicable. However, it is apparent from the photograph given in Fig. 4 of their article[3] that the line labeled $A_1$ is much weaker than $A_2$, $A_3$, and $A_4$. That this is possible can be confirmed from Table III, though the absence of a detailed description of the experimental conditions obtaining at the time the photograph was taken makes it impossible to comment further.

TABLE III. Relative line strengths for ${}^6P_{5/2}$ and ${}^6P_{7/2}$.

| State | Nominal $M$ | Axis[a] | Algebraic strength[b] | Numerical strength[b] |
|---|---|---|---|---|
| $B_3$ | $\pm\frac{5}{2}$ | $x$ | $55-\frac{25}{3}\delta-\frac{25}{6}\delta^2$ | 54 |
| | | $y$ | $55+\frac{25}{3}\delta-\frac{25}{6}\delta^2$ | 56 |
| | | $z$ | $30+\frac{25}{3}\delta^2$ | 30 |
| $B_2$ | $\pm\frac{3}{2}$ | $x$ | $45-45\delta-\frac{45}{2}\delta^2$ | 41 |
| | | $y$ | $45+45\delta-\frac{45}{2}\delta^2$ | 49 |
| | | $z$ | $50+45\delta^2$ | 50 |
| $B_1$ | $\pm\frac{1}{2}$ | $x$ | $40+\frac{160}{3}\delta+\frac{80}{3}\delta^2$ | 45 |
| | | $y$ | $40-\frac{160}{3}\delta+\frac{80}{3}\delta^2$ | 35 |
| | | $z$ | $60-\frac{160}{3}\delta^2$ | 60 |
| $A_4$ | $\pm\frac{7}{2}$ | $x$ | $21+\frac{126}{5}\delta+\frac{63}{5}\delta^2$ | 23 |
| | | $y$ | $21-\frac{126}{5}\delta+\frac{63}{5}\delta^2$ | 19 |
| | | $z$ | $147-25.2\delta^2$ | 147 |
| $A_3$ | $\pm\frac{5}{2}$ | $x$ | $57+90\delta+45\delta^2$ | 65 |
| | | $y$ | $57-90\delta+45\delta^2$ | 49 |
| | | $z$ | $75-90\delta^2$ | 74 |
| $A_2$ | $\pm\frac{3}{2}$ | $x$ | $81+\frac{1674}{5}\delta+\frac{837}{5}\delta^2$ | 112 |
| | | $y$ | $81-\frac{1674}{5}\delta+\frac{837}{5}\delta^2$ | 53 |
| | | $z$ | $27-334.8\delta^2$ | 24 |
| $A_1$ | $\pm\frac{1}{2}$ | $x$ | $93-450\delta-225\delta^2$ | 51 |
| | | $y$ | $93+450\delta-225\delta^2$ | 131 |
| | | $z$ | $3+450\delta^2$ | 7 |

[a] Axis parallel to which the magnetic vector of the electromagnetic radiation lies. This axis is thus perpendicular to the direction of propagation of the radiation and to the latter's electric vector.

[b] Figures given for a coupling near the Russell-Saunders limit.

## V. CONCLUSION

It has been shown that many of the spectroscopic properties of $GdCl_3 \cdot 6H_2O$ can be reasonably well understood in terms of a slightly distorted cylindrically symmetric crystal field. The Zeeman splittings of the doublets belonging to ${}^6P_{5/2}$ and ${}^6P_{7/2}$ have been particularly well accounted for. The crystal-field splittings could certainly be brought into closer accord with experiment if detailed intermediate-coupling eigenfunctions were used, since it would then be possible to introduce new parameters of the type $B_4^m\langle r^4\rangle$. Indeed, it is perhaps worth mentioning that of these parameters only $B_4^0\langle r^4\rangle$ would contribute within the approximation of cylindrical symmetry: and a straightforward calculation, in which the reduced matrix elements of Wybourne[10] are used, reveals that every one of the seven doublets of ${}^6P_{5/2}$ and ${}^6P_{7/2}$ would be brought nearer its experimental energy if $B_4^0\langle r^4\rangle$ were positive. Rather than develop these ideas in detail, we have preferred to keep the calculations as simple as possible, thereby making such agreement as we have obtained all the more striking.

## ACKNOWLEDGMENT

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