

Optically Induced Tm^{2+} Ions in Trigonal Sites in BaF_2

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Some γ -irradiated crystals of thulium-doped BaF_2 exhibit spectra associated with Tm^{2+} ions in both cubic and trigonal sites. The centers with trigonal symmetry are generated by irradiating the crystal at or below 77°K with light around 4000 Å. Irradiating the crystal with 7000 Å radiation or cycling to room temperature eliminates the trigonal centers and increases the number of Tm^{2+} cubic centers. The noncubic spectrum can be fitted using $g_{\parallel} = 2.23 \pm 0.01$, $g_{\perp} = 3.98 \pm 0.02$, $A = 0.0248 \pm 0.0003 \text{ cm}^{-1}$, and $B = 0.0432 \pm 0.0004 \text{ cm}^{-1}$. Two optical fluorescence lines were also identified with the noncubic centers. An approximate value for the second-degree crystal-field parameter $A_2^0 \langle r^2 \rangle$ is $+140 \text{ cm}^{-1}$.

I. INTRODUCTION

WITH the exception of Eu^{2+} and Sm^{2+} , the valence state of the rare-earth ions in doped crystals of the alkaline-earth fluorides is trivalent. Exposing the doped crystal to ionizing radiation¹ was the first technique employed for reduction to the divalent state. This method reduces only a fraction of the rare-earth ions, and in addition, the divalent ions are unstable. The details of this mechanism are still not very well understood, the most widely used explanation being that only those trivalent ions in cubic sites could be reduced by trapping an electron which has been ejected from distant ions. The major evidence for this explanation is that the optical and EPR spectra of the divalent species formed are found only in cubic sites. Recently, Forrester and McLaughlan² have indicated the presence of Tm^{2+} in noncubic sites in irradiated crystals of CaF_2 doped with Tm_2O_3 . We have found that in CaF_2 , SrF_2 , and BaF_2 crystals doped with TmF_3 and reduced by vapor baking³ approximately 1% of the divalent thulium ions are in noncubic sites for thulium concentrations of 0.02%. But in some γ -irradiated $\text{BaF}_2:\text{Tm}$ crystals, it was found that about 30% of the Tm^{2+} ions in cubic sites could be switched, using optical illumination around 4000 Å, to Tm^{2+} ions in noncubic sites. Optical radiation at lower energy had the effect of decreasing the number of ions in noncubic sites while increasing the number in cubic sites. This paper describes the use of paramagnetic resonance and optical measurements to give details of the light-generated Tm^{2+} spectra.

II. CRYSTALS

The BaF_2 samples used in the experiments discussed in this paper were grown by H. Temple of RCA Laboratories using the Czochralski method with an atmosphere of purified helium and a pulling speed of about 1 in./h. The dopant was added to the melt in the form of TmF_3

and the thulium concentration was 0.1%. Part of the Tm ions were reduced to the divalent state by γ irradiation at room temperature. Other crystals of thulium-doped BaF_2 , SrF_2 , and CaF_2 were grown by a gradient-freeze technique using a HF atmosphere. The Tm ions in these crystals were reduced by vapor baking.

III. SPIN-RESONANCE SPECTRA

The lowest configuration of the Tm^{2+} ion is shown in Fig. 1 along with the measured energy values of

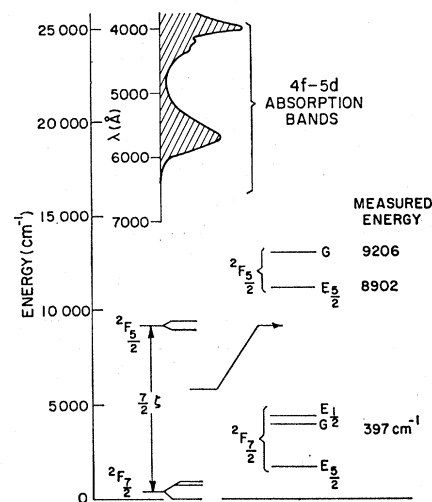


FIG. 1. Energy levels of $\text{BaF}_2:\text{Tm}^{2+}$. Measured values are those of H. Weakliem [Ref. 4].

Weakliem⁴ for Tm^{2+} in BaF_2 . The ground-state doublet $E_{5/2}$ is split by a magnetic field into four levels because of the nuclear spin $I = \frac{1}{2}$ of the 100% abundant Tm^{169} isotope. After subjecting the $\text{BaF}_2:\text{Tm}$ crystals to γ rays at room temperature and going to liquid-helium temperatures, the observed paramagnetic spectrum consisted of two strong isotropic lines [see Fig. 2(a)] with some much weaker lines which were not investigated in detail. The fluorine superhyperfine structure was resolved when the magnetic field was directed along the [100] direction. The isotropic spectrum can be in-

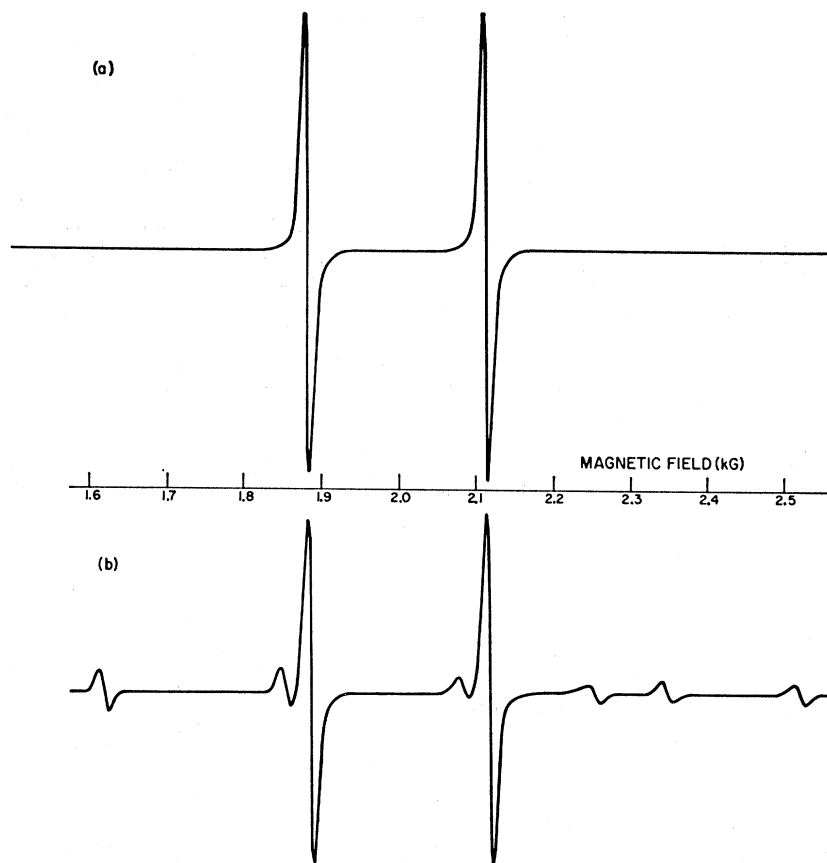
¹ W. Hayes and J. W. Twidell, *J. Chem. Phys.* **35**, 1521 (1961).

² P. A. Forrester and S. D. McLaughlan, *Phys. Rev.* **138**, A1682 (1965); S. D. McLaughlan, P. A. Forrester, and A. F. Fray, *ibid.* **146**, 344 (1966).

³ Z. J. Kiss and P. N. Yocom, *J. Chem. Phys.* **41**, 1511 (1964).

⁴ H. Weakliem (private communication).

FIG. 2. First derivative of EPR lines for crystal in (a) nonswitched and (b) switched conditions at equivalent gain. Data are for 9.4 GHz and $\pm 1.4^\circ\text{K}$ about 5° from [110] direction.



terpreted in terms of the usual spin Hamiltonian

$$\mathcal{H} = g\beta\mathbf{H} \cdot \mathbf{S} + A\mathbf{I} \cdot \mathbf{S},$$

where $S = \frac{1}{2}$ is the effective spin and $I = \frac{1}{2}$ is the nuclear spin. The experimental data taken at frequencies around 9 GHz and helium temperatures can be fitted using $g = 3.431 \pm 0.005$ and $A = 0.0369 \pm 0.003 \text{ cm}^{-1}$. As expected these results are very similar to the results⁵ for Tm²⁺ in CaF₂ where a g value of 3.452 ± 0.003 was reported. The g difference for Tm²⁺ in the different alkaline-earth fluorides will be discussed in another paper.

After irradiating the crystal with light around 4000 \AA at liquid-helium temperatures, the intensity of the cubic spectrum decreased and a new spectrum appeared [see Fig. 2(b)]. When light around 7000 \AA was applied to the crystal, the light-generated (LG) spectrum could be made to disappear while the intensity of the cubic spectrum increased. The LG spectrum had an angular variation characteristic for a distortion along the [111] directions. In addition, the resonance lines occurred in pairs in which the splitting of the pair of lines was approximately equal to the hyperfine splitting of the

Tm²⁺ cubic lines. The LG spectrum can be interpreted using a spin Hamiltonian for axial symmetry. That is,

$$\mathcal{H} = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + A S_z I_z + B(S_x I_x + S_y I_y),$$

where $S = \frac{1}{2}$ and $I = \frac{1}{2}$. The experimental results can be fitted using

$$g_{\parallel} = 2.23 \pm 0.01, \quad g_{\perp} = 3.98 \pm 0.02, \\ A = 0.0248 \pm 0.0003 \text{ cm}^{-1}, \quad B = 0.0432 \pm 0.0004 \text{ cm}^{-1}.$$

Figure 3 shows the angular variation of the LG spectrum in the (110) plane. The data in Fig. 3 along with the angular variation in the (111) plane were used to establish the distortion as along the [111] directions. The data clearly show that the hyperfine structure splitting is practically isotropic when measured at constant frequency, or quantitatively, A/g_{\parallel} differs from B/g_{\perp} by 2%; they differ by $\pm 1\%$ from A/g_0 for Tm²⁺ in the cubic site. Also, the trace of the g tensor for the noncubic spectrum is $\frac{1}{3}(g_{\parallel} + 2g_{\perp}) = 3.43$, which can be compared to the measured g value for Tm²⁺ in cubic sites of 3.431 ± 0.005 . From the hyperfine splitting and the trace of the g tensor, the LG spectrum is attributed to Tm²⁺ ions in a site of trigonal symmetry.

⁵ R. G. Bessent and W. Hayes, Proc. Roy. Soc. (London) A285, 430 (1965).

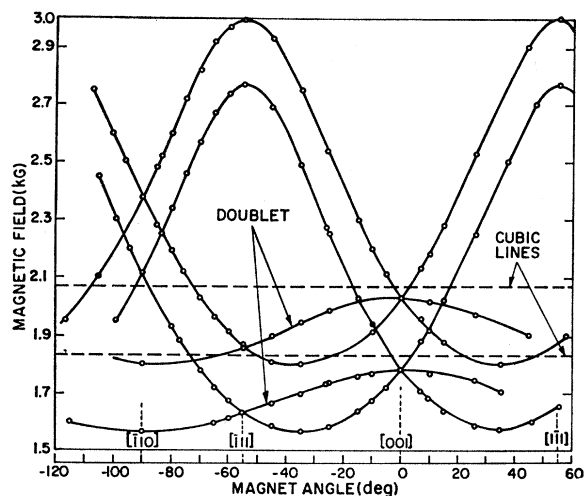


FIG. 3. Angular variation for Tm^{2+} spectrum in BaF_2 in (110) plane. Data taken at 9402 MHz and $1.4^\circ K$.

IV. DYNAMICS OF SWITCHING

The lamp used in these experiments was a 500-W dc mercury arc, which has the majority of its power output concentrated in the mercury lines rather than a continuum. The most efficient conversion from the cubic site to the noncubic site took place when the pump radiation was filtered to remove all wavelengths longer than 5000 \AA (light appears blue). Reconversion was most efficient when all wavelengths shorter than 5500 \AA were filtered out (light appears red). While pumping with about 30 mW of blue radiation, the spin-resonance signal intensity for Tm^{2+} in cubic sites decayed exponentially at the rate of $7 \times 10^{-2} \text{ sec}^{-1}$ (see Table I) to a value of approximately 70% of its initial value. Under identical optical conditions, the noncubic spin-resonance lines grew in intensity at the same rate. The integrated intensity of the noncubic spectra was equivalent to that lost by the cubic lines. Under optical conditions

TABLE I. The decay and generation rate for Tm^{2+} ions under optical excitation at $1.4^\circ K$.

| Light | Optical atten. dB | Monitor noncubic site | | Monitor cubic site |
|-------|-------------------|-----------------------------------|--|-----------------------------------|
| | | $P_e \text{ sec}^{-1}$ Decay rate | $P_e \text{ sec}^{-1}$ Generation rate | $P_e \text{ sec}^{-1}$ Decay rate |
| Red | 3 | 3.7×10^{-2} | | |
| Red | 6 | 1.9×10^{-2} | | |
| Red | 9 ^a | 1.0×10^{-2} | | |
| Blue | 6 | | 14×10^{-2} | |
| Blue | 9 ^a | | 6.5×10^{-2} | 7×10^{-2} |
| Blue | 12 | | 2.6×10^{-2} | 2.5×10^{-2} |

^a For this condition, a flux of about 30 mW was incident on the crystal over an area of 0.15 cm^2 .

appropriate for reconversion, it was found that the reconversion takes place exponentially but at a much slower rate of $1 \times 10^{-2} \text{ sec}^{-1}$.

To within our experimental accuracy, no loss in the total number of divalent thulium centers was observed after switching back and forth a number of times at helium temperatures. Although initially there are no measurable ions in the noncubic site, it was not possible to completely return to this condition at helium temperatures after generation of the noncubic centers. Cycling the crystals up to nitrogen temperatures had no significant effect on the noncubic centers while cycling the crystals to room temperature eliminates the noncubic centers entirely. Optical pumping with linearly polarized light directed along a distortion axis did not have the effect of preferentially populating or bleaching the noncubic centers.

V. OPTICAL SPECTRA

The fluorescence spectrum of $BaF_2:Tm^{2+}$ in cubic sites consists of two narrow lines between 11 200 and

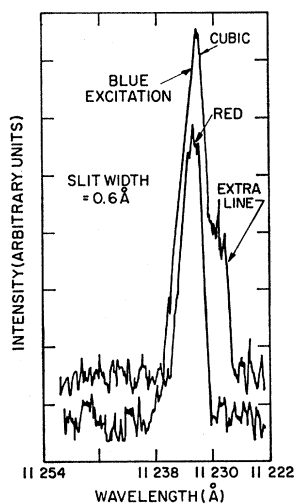


FIG. 4. $|\frac{5}{2}, E_{5/2}\rangle \rightarrow |\frac{7}{2}, E_{5/2}\rangle$ transition for Tm^{2+} in BaF_2 at $4.2^\circ K$ under red and blue excitation.

$12\ 000 \text{ \AA}$ at low temperatures. The fluorescence spectrum using crystals which exhibited the trigonal EPR spectra was examined in this region using blue and red excitation. Figures 4 and 5 show the data of interest. In Fig. 4, an extra line is clearly visible using blue excitation on the higher-energy side of the cubic line. This extra line was not resolved at $77^\circ K$ because of linewidth broadening. However, a change in the line shape of the cubic line was observed at $77^\circ K$. Figure 5 also shows the presence of an extra line for blue excitation and it is located at 61 cm^{-1} in lower energy from a cubic resonance line, which also was observed at $4.2^\circ K$.

The Hamiltonian describing the crystal-field potential of trigonal symmetry contains six crystal-field param-

eters and can be written as

$$\mathcal{H}_{\text{trig}} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^3 O_4^3 + B_6^0 O_6^0 + B_6^6 O_6^6.$$

The parameters B_n^m are related to the strength of the crystal-field components, and in the notation of Elliott and Stevens,⁶ are equal to $\langle J \parallel \zeta_n \parallel J \rangle A_n^m \langle r^n \rangle$, where $\langle J \parallel \zeta_n \parallel J \rangle$ is a reduced matrix element. O_n^m are the angular momentum operators transforming as corresponding spherical harmonics. Since only two optical transitions were observed for the LG center, the data are insufficient for evaluating the parameters. However, since the distortion is small as evidenced by the EPR data, one might hope that a reasonable approximation to the distorted site could be obtained by adding the second-order term $B_2^0 O_2^0 = \alpha A_2^0 \langle r^2 \rangle O_2^0$ to the Hamiltonian for cubic symmetry. If this is done (see Appendix), a relationship between the g factors and the unknown parameter $A_2^0 \langle r^2 \rangle$ is found to be

$$g_{\perp} - g_{\parallel} = (16/7)^2 \frac{A_2^0 \langle r^2 \rangle}{E(G) - E(E_{5/2}) + (2/7)(A_2^0 \langle r^2 \rangle)}.$$

From the experimental values of g_{\perp} , g_{\parallel} , and $E(G) - E(E_{5/2})$, a value of 140 cm⁻¹ for $A_2^0 \langle r^2 \rangle$ is obtained. Using this value for $A_2^0 \langle r^2 \rangle$, the optical transition, $|^2F_{5/2}, E_{5/2}\rangle \rightarrow |^2F_{7/2}, E_{5/2}\rangle$, for the LG center is expected to be found about 2.5 cm⁻¹ lower in energy from the cubic line. Experimentally a line of the correct intensity is found at 1.1 cm⁻¹ from the cubic line, but higher in energy. For the transition $|^2F_{5/2}, E_{5/2}\rangle \rightarrow |^2F_{7/2}, G\rangle$, one expects to see two lines for the LG center and they should occur at -65 and +24 cm⁻¹ with respect to the cubic line. Experimentally an extra

line is seen at -61 cm⁻¹ with an intensity of about 15% of the cubic line, while an intensity of 20% is expected. No observation of the expected line at +24 cm⁻¹ may be explained by noting that this line would fall in the wing of the strong cubic line. Lower temperatures did not cause a significant narrowing of the cubic line. It should be noted that the $|^2F_{5/2}, E_{5/2}\rangle \rightarrow |^2F_{7/2}, E_{1/2}\rangle$ transition for the LG center should occur at about -60 cm⁻¹ or just about the region where the extra line is observed. However, this transition is eliminated on the basis of intensity. From the above arguments, we tentatively conclude that the two extra optical lines observed under blue excitation are the $|^2F_{5/2}, E_{5/2}\rangle \rightarrow |^2F_{7/2}, E_{5/2}\rangle$ and $|^2F_{5/2}, E_{5/2}\rangle \rightarrow |^2F_{7/2}, G, \pm \frac{1}{2}\rangle$ transitions of divalent thulium in trigonal sites.

VI. SUMMARY

γ -irradiated BaF₂ crystals doped with TmF₃ generally exhibit EPR spectra associated with Tm²⁺ ions in cubic sites. However, some crystals upon irradiation with light around 4000 Å at temperatures of 77°K and below exhibit EPR spectra of both Tm²⁺ ions in cubic and trigonal sites. In addition, irradiation with light around 7000 Å at 77°K and below or cycling to room temperature has the effect of converting all the trigonal sites to cubic sites. Assuming the distortion can be taken into account by adding the second-order term $B_2^0 O_2^0$ to the cubic potential, a value for $A_2^0 \langle r^2 \rangle$ of 140 cm⁻¹ was obtained. To verify this assumption, an attempt was made to correlate optical data with the trigonal site. This met with only fair success since the optical lines of the trigonal centers were found to be in very close proximity to the optical lines of the dominant cubic center and only two optical transitions could be identified with the trigonal centers.

Since $\Delta g = g_{\perp} - g_{\parallel}$ for the trigonal centers is positive, this implies that the distortion is caused by a negative charge. This is in agreement with the results of Ranan and Yaniv⁷ on the isoelectronic Yb³⁺ ion in various sites in the fluorides. Since Δg is small and the trace of the g tensor is in good agreement with the g value for the cubic centers, the distortion is attributed to a negative ion occupying interstitial body centers of the nearest cube along the [111] directions. We find a Δg of +1.66 while a value of +1.0 was reported for Yb³⁺ in BaF₂ for a trigonal distortion attributed to interstitial F⁻ ions. The experimental results⁸ on Ho³⁺ and Er³⁺ have suggested that the crystal-field parameters increase in going from the divalent ion to the isoelectronic trivalent ion. This implies Tm²⁺ would have a smaller value for B_2^0 or Δg than Yb³⁺. On this basis, one can assume that the distorting ion for Tm²⁺ in these crystals of BaF₂ are not interstitial F⁻ ions. At present, data are insufficient to justify a specific

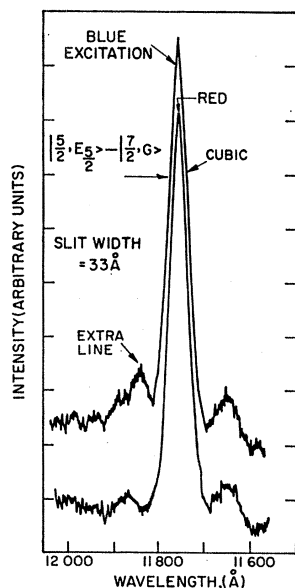


FIG. 5. Fluorescence of Tm²⁺ in BaF₂ at 77°K under red and blue excitation.

⁶ R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A218**, 553 (1953).

⁷ U. Ranan and A. Yaniv, Phys. Letters **9**, 17 (1964).

⁸ H. R. Lewis and E. S. Sabisky, Phys. Rev. **130**, 1370 (1963).

model for the switching centers. However, the experimental results do suggest that reduction by γ irradiation can produce divalent ions with a nearby defect and that the defect can be ionized (un-ionized) upon application of light at temperatures below 77°K. This is contrary to the generally accepted concept that only those trivalent ions with distant or nonlocal compensators can be reduced to the divalent state in these crystals.

ACKNOWLEDGMENTS

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APPENDIX: THE PERTURBATION OF THE $E_{5/2}$ GROUND DOUBLET FOR Tm^{2+} BY AN AXIAL DISTORTION AND A MAGNETIC FIELD

We will apply the approach used by Lewis and Sabisky⁸ to a particular case of a small axial distortion for Tm^{2+} in BaF_2 , the assumption being that the total perturbation energy is small compared to the separation of the doublet from the nearby quartet. This is a very good approximation in this case since the ground doublet is separated from the quartet by 400 cm^{-1} . We use basis functions appropriate to a cubic crystalline field with the axes: z axis $[1, 1, 1]$, x axis $[1, -2, 1]$, and y axis $[1, 0, -1]$. The wave functions given by Polo⁹ for the $E_{5/2}$, $E_{1/2}$, and G states for Tm^{2+} are unique since only one of a kind occur within a single J state. The Hamiltonian which must be diagonalized is given by

$$\mathcal{H} = \Lambda\beta H \cos\theta J_z + \Lambda\beta H \sin\theta J_x + V,$$

where θ is the angle between the magnetic field and the z axis (z axis is taken as $[1, 1, 1]$), and the magnetic field is taken in the zx plane. In general, the axial potential V is of the form $C_1 J_z^2 + C_2 J_z^4 + C_3 J_z^6$. However, for the purpose of getting a number for the distortion, we will in the end use the assumption that the distortion only adds a second-order term to the crystal field which in operator-equivalent form can be written⁶ as $V = B_2^0 O_2^0$, where $O_2^0 = [3J_z^2 - J(J+1)]$ and $B_2^0 = \alpha A_2^0 \langle r^2 \rangle$.

The required matrix elements of J connecting the

⁹ S. Polo (private communication).

doublet and quartet are

$$\begin{aligned} \langle G | J_x | E_{5/2} \rangle = & \begin{matrix} & +\frac{1}{2} & -\frac{1}{2} \\ & \frac{3}{2} & \\ & \frac{1}{2} & -\sqrt{3} \\ -\frac{1}{2} & & +\sqrt{3} \\ & -\frac{3}{2} & \end{matrix} \\ & \begin{matrix} & +\frac{1}{2} & -\frac{1}{2} \\ & \frac{3}{2} & -\frac{1}{2} & -\sqrt{2} \\ & \frac{1}{2} & 0 & \frac{1}{2}\sqrt{3} \\ -\frac{1}{2} & \frac{1}{2}\sqrt{3} & & 0 \\ & -\frac{3}{2} & \sqrt{2} & -\frac{1}{2} \end{matrix} \end{aligned}$$

To apply perturbation theory, it is necessary to use linear combinations of $|E_{5/2}, +\frac{1}{2}\rangle$ and $|E_{5/2}, -\frac{1}{2}\rangle$ that diagonalize the $E_{5/2}$ or Γ_7 doublet in the presence of the magnetic field. When this is done a second-order calculation gives the following equation:

$$\begin{aligned} E(E_{5/2}, +) - E(E_{5/2}, -) \\ = 3\Lambda\beta H + \frac{2\sqrt{3}\Lambda\beta H \langle G, +\frac{1}{2} | V | E_{5/2}, + \rangle}{E(G) - E(E_{5/2}) + \langle G, \frac{1}{2} | V | G, \frac{1}{2} \rangle} \\ \times (2 \cos^2\theta - \sin^2\theta). \end{aligned}$$

As it should, the above equation gives the expected result that $g_{||} + 2g_{\perp} = 3g_0 =$ three times the g value for the ion in a cubic field. From the above equation, one can relate the matrix element to the observed axial spectrum. That is

$$g_{||} - g_{\perp} = \frac{6\sqrt{3}\Lambda \langle G, +\frac{1}{2} | V | E_{5/2}, + \rangle}{E(G) - E(E_{5/2}) + \langle G, +\frac{1}{2} | V | G, \frac{1}{2} \rangle},$$

and since

$$\begin{aligned} \langle G, +\frac{1}{2} | V | E_{5/2}, + \rangle &= -(16/63)\sqrt{3}A_2^0 \langle r^2 \rangle, \\ \langle G, +\frac{1}{2} | V | G, +\frac{1}{2} \rangle &= (2/7)A_2^0 \langle r^2 \rangle, \end{aligned}$$

we find that for Tm^{2+} ,

$$g_{\perp} - g_{||} = \left(\frac{16}{7}\right)^2 \frac{A_2^0 \langle r^2 \rangle}{E(G) - E(E_{5/2}) + (2/7)A_2^0 \langle r^2 \rangle}.$$