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# Zeeman Splitting between Nondegenerate Crystalline Stark Levels of $\mathrm{Tm}^3$ $(4f^{12})$ in Monoclinic Single Crystals*

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Optical Zeeman absorption and electron-paramagnetic-resonance experiments reveal that the ground crystalline Stark levels of $\mathrm{Tm}^{3+}$ in $\mathrm{YCl_3\cdot 6H_2O}$ and $\mathrm{TmCl_3\cdot 6H_2O}$ and $\mathrm{Tm}^{3+}$ in $\mathrm{Y_2(SO_4)_3\cdot 8H_2O}$ and $\mathrm{Tm_2(SO_4)_3\cdot 8H_2O}$ are nearly accidentally degenerate. Extrapolation of the data to zero magnetic field gives the lowest Stark levels of the $^3H_6$ state of $\mathrm{Tm}^{3+}$ as 0 and 1.12 $\mathrm{cm}^{-1}$ for the chloride salts; 0 and 0.61 $\mathrm{cm}^{-1}$ for the sulfate salts. It is also found from the EPR data that the sulfate has two magnetically inequivalent lattice sites.

## INTRODUCTION

Recent experiments and the subsequent interpretation of the pseudoquadrupole shift of recoilless nuclear-resonance spectra of tripositive thulium-169 in crystals of low cation-site symmetry by Clauser and Mössbauer[1] have suggested that one or more electronic crystalline Stark levels of $\mathrm{Tm}^{3+}$ may be nearly accidentally degenerate with the ground Stark level. A crystal field splitting calculation by Harrop[2] also predicts that the two lowest crystalline Stark levels of the $^3H_6$ ground state of $\mathrm{Tm}^{3+}$ in $\mathrm{TmCl_3\cdot 6H_2O}$ are nearly accidentally degenerate. Previously unpublished optical Zeeman spectra[3] of thulium in various salts have led us to the same conclusion. We wish to report here the results and interpretation of the electron-paramagnetic-resonance spectra together with the optical Zeeman spectra of $\mathrm{Tm}^{3+}$ in $\mathrm{YCl_3\cdot 6H_2O}$ and $\mathrm{TmCl_3\cdot 6H_2O}$ and $\mathrm{Tm}^{3+}$ in $\mathrm{Y_2(SO_4)_3\cdot 8H_2O}$ and $\mathrm{Tm_2(SO_4)_3\cdot 8H_2O}$ which confirm the supposition of a near accidental degeneracy in the ground state of $\mathrm{Tm}^{3+}$ in these salts. We also wish to report the zero magnetic field splitting of the nearly degenerate ground Stark levels for $\mathrm{Tm}^{3+}$ in these salts deduced from the EPR and optical Zeeman data.

## OPTICAL ABSORPTION STUDIES

Absorption spectra of the hydrated chloride and sulfate single crystals have been taken between 2500 and 8000 Å at liquid-nitrogen temperature and from zero magnetic field to nearly 24 kG in regular intervals and for specific crystal orientations. The spectrometer used was a 3.4-m Jarrel-Ash Ebert scanning spectrometer/spectrograph with a resolution of 0.07 Å in first order in the region of 5000 Å. An L-96 Magnion magnet with a power supply stable to 0.1% was used for the Zeeman studies. The magnetic field strength was measured with a Rawson rotating coil accurate to 0.1%.

The cation point-group symmetry of $\mathrm{Tm}^{3+}$ in the hydrated chloride and sulfate salts is reported as $C_2$ and $m$, respectively.[4,5] Both crystals have monoclinic unit-cell symmetry.[6,7] For a non-Kramer's ion such as $Tm^{3+}$ ($4f^{12}$), such low symmetry completely lifts the degeneracy of each (SL) $J$ level of the ion producing $2J+1$ crystalline Stark levels for each $J$ manifold. We observe $2J+1$ Stark levels for each possible $J$ manifold with the exception of the $^1S_0$ level, which is too high in energy to be observed, and the $^3H_4$ and $^3H_5$ levels whose spectra are obscured by the absorption spectrum due to the water molecules in the crystal.[8] We have observed very little vibronic spectra in thin crystals of $Tm^{3+}$ diluted into the yttrium chloride and sulfate salts. Studies were carried out using crystals containing 0.5, 1, and 2% $Tm^{3+}$ in the yttrium salts. The spectrum of the pure salts was studied as well. Although thicker crystals with increasing concentrations of $Tm^{3+}$ brought out vibronic transitions along with the pure electronic, we find that unless vibronic and crystalline Stark levels coincide within the limit of resolution, we can determine which levels are vibronic by the repetition of such vibrational levels coupled to various electronic states.[9] From our work on both thin and thick crystals, we have been able to identify the pure electronic transitions to the $2J+1$ Stark levels associated with each $J$ manifold in zero magnetic field.[3]

Zeeman splitting of the ground state has been seen spectroscopically for transitions to all excited $J$ manifolds that are possible to observe. All Stark components examined appear as doublets and quartets in the presence of the magnetic field for the chloride and sulfate, respectively. Since the degeneracy of the $J$ manifolds is completely lifted by the crystalline electric field, the observed splitting appears to be caused by a nearly accidentally degenerate ground state which separates in the presence of a magnetic field sufficiently so that transitions from both Stark levels can be resolved by the spectrometer. To support this supposition we carried out the following EPR studies.

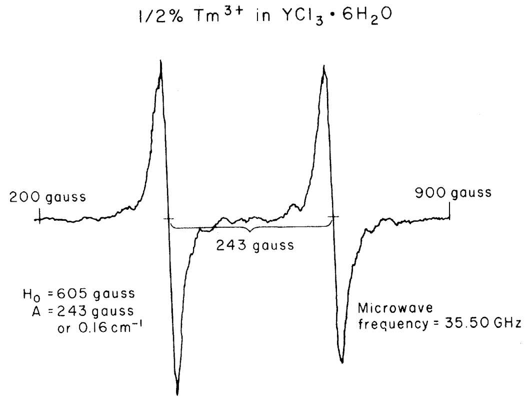


FIG. 1. EPR spectrum of 0.5% $Tm^{3+}$ in $YCl_3 \cdot 6H_2O$ taken at 4.2 °K with $H_{rf}$ parallel to, and $E_{rf}$ perpendicular to the local magnetic axis and the external magnetic field.

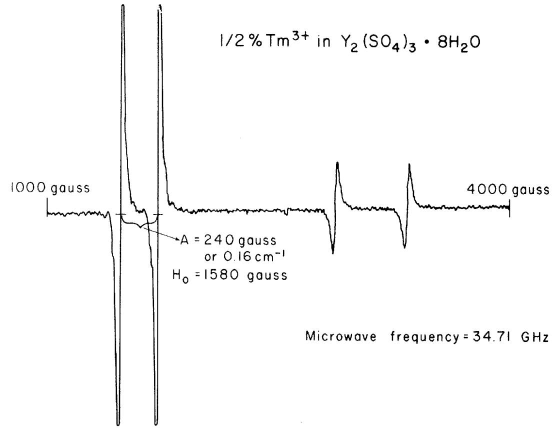


FIG. 2. EPR spectrum of 0.5% $Tm^{3+}$ in $Y_2(SO_4)_3 \cdot 8H_2O$ taken at 4.2 °K with $H_{rf}$ parallel to, and $E_{rf}$ perpendicular to the external magnetic field and *one* of the local magnetic axes.

## EPR STUDIES

The EPR spectrum of $Tm^{3+}$ in $YCl_3 \cdot 6H_2O$ and $Y_2(SO_4)_3 \cdot 8H_2O$ was investigated at 4.2 °K in the $K_a$ frequency range with magnetic fields ranging from 100 to 1000 G, and from 1000 to 5000 G, respectively. The transitions were induced over the frequency range of 33.7–36 GHz in a variable-frequency cavity. The spectrum is characteristic of a non-Kramer's doublet with $H_{rf}$ parallel to, and $E_{rf}$ perpendicular to the local magnetic axis and the external magnetic field.

The EPR spectrum of 0.5% $Tm^{3+}$ in $YCl_3 \cdot 6H_2O$ taken at 4.2 °K is shown in Fig. 1. The observed resonance spectrum at liquid-helium temperature confirms the supposition of near accidental degeneracy in the ground state as inferred from the optical data. The weak satellite structure observed on each of the two hyperfine resonances has not yet been analyzed.

From the optical Zeeman data for $Tm^{3+}$ in the sulfate crystals, we first thought that three crystalline Stark levels were nearly degenerate with the ground level. However, the results from the EPR studies indicate there are actually two magnetically inequivalent sites in the hydrated sulfate lattice.

Figure 2 shows a sample plot of the EPR spectrum of 0.5% $Tm^{3+}$ in the yttrium sulfate crystal with the characteristic hyperfine splitting of 240 G between resonances of the low-field doublet for Tm-169. The presence of the high-field doublet may be explained by the possibility of two magnetically inequivalent sites as illustrated in Fig. 3. As in the chloride, there are two nearly degenerate ground components in the sulfate for each magnetic site. Although the local symmetry is *m*, the direction of the crystalline electric field gradient at these sites may take one of two directions. The total magnetic moment $\vec{\mu}$ of the ions in these two kinds of sites will have different projections along the fixed axis provided by the external magnetic field $\vec{H}$. Optically one sees two overlapping spectra and hence the appearance of four transitions to each excited Stark level. One expects, therefore, that the magnetic behavior of the two hyperfine doublets (Fig. 2) should be different as the direction of the external magnetic field is changed. Such asymmetric behavior has indeed been observed by studying the spectrum as a function of magnetic field orientation. As a result we have found that the angle between the two magnetic axes in the hydrated sulfate is approximately 59°. The reasons for the existence of these two magnetically inequivalent sites are not yet clearly understood.

## ZERO-FIELD SPLITTING

To obtain the zero-field splitting from the optical data, one must be careful as the separation of the two Stark levels, $|E_2 - E_1| < V$, the Zeeman perturbation. Here, one may not use first-order nondegenerate perturbation theory, but must consider the two levels as "quasidegenerate."[10] In this scheme the near-degenerate levels are replaced by a single energy level $E$ intermediate between the original levels. This new level has degeneracy equal to the sum of the degeneracies of the original levels. The perturbation on the quasidegenerate level must also be modified so that the levels $E_1$ and $E_2$ are obtained when $V = 0$. The perturbation for the Zeeman interaction takes the form

$$V' = \vec{\mu}\cdot\vec{H} + (E_1 - E)|1\rangle\langle 1| + (E_2 - E)|2\rangle\langle 2|, \qquad (1)$$

where $|1\rangle\langle 1|$ and $|2\rangle\langle 2|$ are the projection operators onto the subspace with energy $E_1$ and $E_2$, respectively.

Now applying first-order degenerate perturbation theory to the quasidegenerate level we obtain

$$\begin{vmatrix} \langle 1|\vec{\mu}\cdot\vec{H}|1\rangle + (E_1 - E) & \langle 1|\vec{\mu}\cdot\vec{H}|2\rangle \\ \langle 2|\vec{\mu}\cdot\vec{H}|1\rangle & \langle 2|\vec{\mu}\cdot\vec{H}|2\rangle + (E_2 - E) \end{vmatrix} = 0\,. \qquad (2)$$

Second-order effects are negligible since the next higher Stark level is 211 and 250 $\mathrm{cm}^{-1}$ for the chloride and sulfate, respectively, as deduced from our temperature-dependent absorption studies.[3] It can be shown from symmetry considerations that

$$\langle 1|\vec{\mu}\cdot\vec{H}|1\rangle = \langle 2|\vec{\mu}\cdot\vec{H}|2\rangle = 0$$

for these low-symmetry crystals. The off-diagonal matrix elements are nonzero. We have as a solution of Eq. (2):

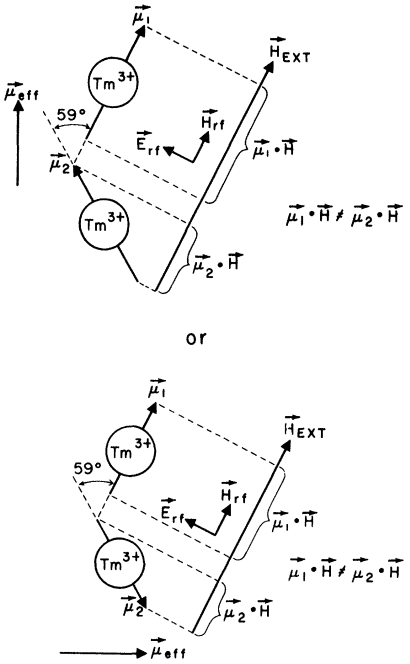


FIG. 3. Schematic illustrations showing the unequal projections of the local magnetic moments $\vec{\mu}_1$ and $\vec{\mu}_2$ onto the external magnetic field $\vec{H}_{ext}$ at each of the magnetically inequivalent sites in the hydrated sulfate lattice.

$$E^{(2),(1)} = \tfrac{1}{2}\{(E_2 + E_1) \pm [(E_2 - E_1)^2 + 4|\langle 1|\vec{\mu}\cdot\vec{H}|2\rangle|^2]^{1/2}\}. \qquad (3)$$

In large magnetic fields, which we observe optically, Eq. (3) becomes

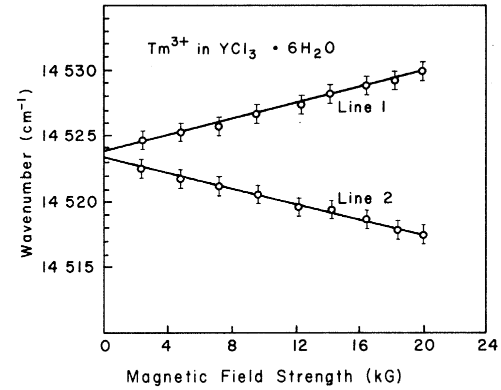
$$E^{(2),(1)} = \tfrac{1}{2}(E_2 + E_1) \pm |\langle 1|\vec{\mu}\cdot\vec{H}|2\rangle| \times\{1 + \tfrac{1}{2}[(E_2 - E_1)/2|\langle 1|\vec{\mu}\cdot\vec{H}|2\rangle|]^2 + \cdots\}\,. \qquad (4)$$

For magnetic fields above 4000 G, the quadratic term in the expansion amounts to less than one-tenth of a wave number. Therefore, at high fields, the Zeeman splitting appears linear as given by Eq. (5):

$$E^{(2),(1)} = \tfrac{1}{2}(E_2 + E_1) \pm |\langle 1|\vec{\mu}\cdot\vec{H}|2\rangle|\,. \qquad (5)$$

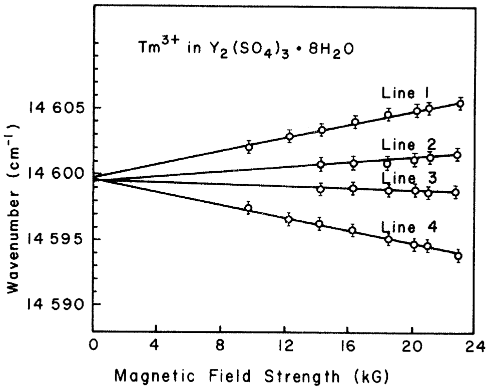
A plot of the optically observed Zeeman splitting for one of the crystalline Stark levels of the $^3F_3$ state as a function of magnetic field for the chloride and sulfate crystals, respectively, is given in Figs. 4 and 5. Within the experimental error a least-squares fit reveals that the Zeeman splitting depends linearly upon magnetic field as expected from Eq. (5). From extrapolation to zero magnetic field, we find a value for the zero-field splitting of 0.49 $\mathrm{cm}^{-1}$ for the chloride and an over-all value of 0.33 $\mathrm{cm}^{-1}$ for the sulfate.

A more accurate value of the zero-field splitting



| Line | Intercept | Standard Error |
|---|---|---|
| 1 | 14 523.76 | 0.077 |
| 2 | .27 | 0.070 |

FIG. 4. Least-squares fitting of the data obtained from Zeeman spectrum of the lowest crystalline Stark component of the $^3F_3$ level in pure $TmCl_3 \cdot 6H_2O$. In zero magnetic field this transition appears at 14 522 $cm^{-1}$. Error bars reflect the full linewidth of the Zeeman-split transitions. Spectrum was taken at 77 °K with the magnetic axis of the crystal at 25° to the external magnetic field. The magnetic axis is 65° from the major crystal habit axis and in the plane of the broad tabular face. The crystal structure and habit are discussed in Refs. 4 and 6.



| Line | Intercept | Standard Error |
|---|---|---|
| 1 | 14 599.57 | 0.031 |
| 2 | .27 | 0.054 |
| 3 | .50 | 0.031 |
| 4 | .60 | 0.063 |

FIG. 5. Least-squares fitting of the data obtained from the Zeeman spectrum of one crystalline Stark component of the $^3F_3$ level in 2% $Tm^{3+}$ in $Y_2(SO_4)_3 \cdot 8H_2O$. In zero magnetic field these transitions appear at 14 599 $cm^{-1}$. Error bars reflect the full linewidth of the Zeeman-split transitions. Spectrum was taken at 77 °K with the major axis of the crystal habit perpendicular to the external magnetic field.

should be obtained from

$$(E^{(2)} - E^{(1)})^2 = (E_2 - E_1)^2 + 4\left|\langle 1 | \vec{\mu} \cdot \vec{H} | 2 \rangle\right|^2 . \qquad (6)$$

If the experimental values of $(E^{(2)} - E^{(1)})^2$ are plotted against $H^2$ we obtain the zero magnetic field splitting from the intercept of the graph. The zero-field splittings obtained in this way are $1.3 \pm 0.3$ $cm^{-1}$ for the chloride and $0.9 \pm 0.3$ $cm^{-1}$ for the sulfate. Within experimental error, these values are in agreement with the following EPR results.

The theory of the EPR spectra of non-Kramer's ions has been treated by Baker and Bleaney[11] and other authors.[12] If the lowest energy levels of the paramagnetic ion in the crystal field are two close-lying singlets with the other levels much further away, this pair can be treated as a doublet of effective spin $S = \frac{1}{2}$ and initial splitting $\Delta$. The spin Hamiltonian for a non-Kramer's doublet is[11]

$$\mathcal{H} = g_{\parallel}\beta H S_z \cos\theta + A S_z I_z + \Delta(S_x I_x + S_y I_y) , \qquad (7)$$

where $g_{\parallel}$ is the $g$ factor for $H$ along the local magnetic axis, $S_z = \pm\frac{1}{2}$ are the two projections of $S$ on $H_z$, $A$ is the hyperfine splitting parameter, $\Delta$ is the zero-field splitting of the doublet, $I$ is the nuclear spin, and $\theta$ is the angle between $H$ and the magnetic axis.

The resulting expression for the EPR transitions is

$$hc\sigma = \left[(g_{\parallel}\beta H \cos\theta + Am)^2 + \Delta^2\right]^{1/2} , \qquad (8)$$

where $\sigma$ is the microwave frequency (in wave numbers) and $m$ represents the eigenvalues ($\pm\frac{1}{2}$) of the nuclear quadrupole moment of Tm-169. It is seen from Eq. (8) that a plot of $\sigma^2$ versus $H^2$ gives a straight line with a slope proportional to $g_{\parallel}^2$ and $\sigma^2 \times (H = 0) = \Delta^2$ when $A$ is small.

Figure 6 shows a plot of the rf frequency against magnetic field strength. Extrapolation to zero magnetic field for the chloride gives the zero-field

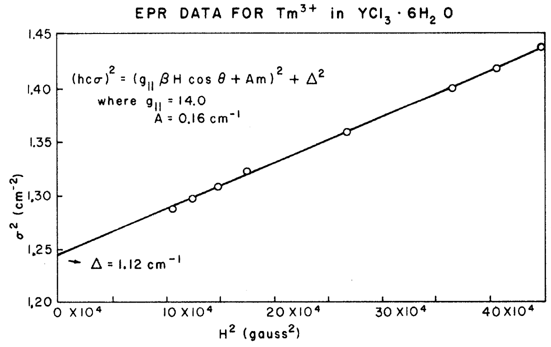


FIG. 6. Microwave frequency versus magnetic field strength for 0.5% $Tm^{3+}$ in $YCl_3 \cdot 6H_2O$ taken at 4.2 °K. Crystal orientation is specified in Fig. 1.

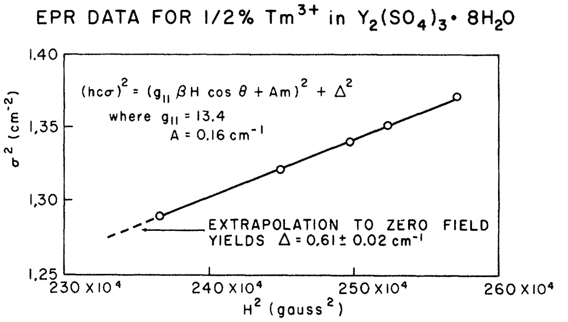


FIG. 7. Microwave frequency versus magnetic field strength for 0.5% $Tm^{3+}$ in $Y_2(SO_4)_3 \cdot 8H_2O$ taken at 4.2 °K. The data are from the low-field resonances only which correspond to the crystal orientation specified in Fig. 2.

splitting parameter $\Delta$ to be $1.12 \pm 0.01\ cm^{-1}$. From the slope we obtain $g_{\parallel} = 14.0 \pm 0.05$ LU (Lorentz units).[13] This value is in excellent agreement with Harrop's prediction of 13.7 LU for the thulium chloride hexahydrate.[2] A sample of the EPR spectrum for the chloride is shown in Fig. 1. The two resonances occur at $m = \pm\frac{1}{2}$, and enable us to deduce the hyperfine splitting factor $A = 243$ G or $0.16\ cm^{-1}$.

Figure 7 shows a plot of the EPR data for the sulfate crystal. Extrapolation to zero magnetic field yields $\Delta = 0.61 \pm 0.02\ cm^{-1}$, and $g_{\parallel} = 13.4$ LU.

In conclusion, we have deduced from the optical Zeeman and EPR spectra that the separation between the ground and first excited Stark levels for $Tm^{3+}$ in the chloride hydrate crystals is $1.12\ cm^{-1}$ and for the sulfate, $0.61\ cm^{-1}$.

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