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CRYSTAL FIELD SPLITTING OF ENERGY LEVELS OF THULIUM ETHYLSULFATE

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OF THULIUM ETHYLSULFATE

John B. Gruber and John G. Conway
August 1959

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ABSTRACT

The "operator-equivalence" method was employed to calculate the splitting of electronic energy levels in Tm \((\text{C}_2\text{H}_5\text{SO}_4)_3\cdot9\text{H}_2\text{O}\). The first-order perturbation treatment predicts the position of the crystal quantum states in reasonable agreement with experiment.
CRYSTAL FIELD SPLITTING OF ENERGY LEVELS
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THEORY

In a Tm\((\ce{C_{2}H_{5}SO_{4}})_{3}\cdot9\ce{H_{2}O}\) single crystal, the perturbing influence of the water and ethylsulfate ligands on the energy-level system of the free ion can be shown by expanding the crystal-field electric potential in a series of spherical harmonics. In addition, it has been shown that the point symmetry at the metal-ion site in rare earth ethylsulfates is predominately \(C_{3h}\). Johnsen and the authors have found this to be consistent in the interpretation of the Tm\((\ce{C_{2}H_{5}SO_{4}})_{3}\cdot9\ce{H_{2}O}\) absorption spectra. 4,5

Stevens has used "operator equivalences" to find the matrix elements of \(V_{k}\) between states with the same value of \(J\). 6 Tables of calculated matrix elements for \(V_{2}, V_{4}, V_{6},\) and \(V_{8}\), the nonzero terms for the \(C_{3h}\) calculation, are given in papers by Elliott and Stevens and by Judd. 2,7 Judd has calculated the crystal-field splitting for energy levels of \(\text{Pr}^{3+}\) in \(\text{LaCl}_{3}\) and has given operator-equivalent values for \(3_{H_{4}}, 3P_{2,1,0}, 1P_{2},\) and \(1G_{4}.\) 8 Additional values were calculated by the authors for the intermediate-coupling case for \(3P_{2,3,4}\) (see Table I). Because of the breakdown of L-S coupling it is convenient to label a hybrid level with LSJ values of its principal components. Corrections have been made to the L-S operator-equivalent factors following Judd, and Elliott and Stevens. 8,3 A pure L-S calculation was made for the ground state \(3_{H_{6}}.\)

Once the operator-equivalent factors are known, the crystal-field splittings of the levels can be expressed in terms of four products, \(A_{2}^{0} < r^{2} >,\)

*This work was done under the auspices of the U. S. Atomic Energy Commission.
$A_4^0 < r^4 >$, $A_6^0 < r^6 >$, and $A_6^6 < r^6 >$. For Tm $(C_2H_{5}SO_4)_3 \cdot 9H_2O$, the authors used:

$$A_2^0 < r^2 > = 0 \pm 10 \text{ cm}^{-1} \quad A_6^0 < r^6 > = 40 \pm 10 \text{ cm}^{-1}$$

$$A_4^0 < r^4 > = -40 \pm 10 \text{ cm}^{-1} \quad A_6^6 < r^6 > = 570 \pm 30 \text{ cm}^{-1}.$$

**Table I**

<table>
<thead>
<tr>
<th>Operator Equivalents for Tm $(C_2H_{5}SO_4)_3 \cdot 9H_2O$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy level&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>---------------------------</td>
</tr>
<tr>
<td>$^3H_6$</td>
</tr>
<tr>
<td>$^1G_4$</td>
</tr>
<tr>
<td>$^3F_4$</td>
</tr>
<tr>
<td>$^3F_3$</td>
</tr>
<tr>
<td>$^3F_2$</td>
</tr>
<tr>
<td>$^1P_2$</td>
</tr>
<tr>
<td>$^3P_2$</td>
</tr>
</tbody>
</table>

<sup>a</sup>Since $A_2^0 < r^2 > = 0$, all terms involving $\alpha$ in the matrix elements will be zero.

<sup>b</sup>Pure L-S operator equivalent values.
LIMITATIONS

The uncertainty in the $A_2^0 < r^2 >$ term could allow a small splitting of the $3P_1$ term. However, the experimental results do not seem to indicate a splitting within experimental error. All the splittings have been calculated according to first-order perturbation theory. The strong points of such a treatment are that the crystal quantum states appear in correct order, and in many cases reasonable agreement with experiment has been obtained. Just how rigorous is the assumption concerning the point symmetry $C_{3h}$, may be open to some question.

Interactions between nearby crystal quantum states of another multiplet of different $J$ have been ignored. The $J \pm 1$ multiplets should be important in the cases of $3P_{2,1,0}$ and $3F_{4,3,2}$, since the spread of crystal quantum states is significant compared to the spin-orbit splitting. Interactions between the $3H_4$ and $3H_5$ on the $3H_6$ may explain some of the disagreement found between experiment and theory for the ground-state multiplet.

Intermediate-field correction was ignored for the $3H_6$ multiplet since the $1I_6$ is some 35,000 cm$^{-1}$ to the ultraviolet. A second-order treatment which would take into account $J \pm N$ terms, and a revised fitting of crystal-field splitting parameters should yield better harmony between theory and experiment.
REFERENCES


<table>
<thead>
<tr>
<th></th>
<th>$^3P_2$</th>
<th></th>
<th>$^1D_2$</th>
<th></th>
<th>$^3F_2$</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
<td>obs.</td>
<td>calc.</td>
<td>obs.</td>
<td>calc.</td>
</tr>
<tr>
<td>(cm$^{-1}$)</td>
<td>(cm$^{-1}$)</td>
<td>(cm$^{-1}$)</td>
<td>(cm$^{-1}$)</td>
<td>(cm$^{-1}$)</td>
<td>(cm$^{-1}$)</td>
</tr>
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<td>±1</td>
<td>27971</td>
<td>24</td>
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<tr>
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<td>38140</td>
<td>±1</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>±2</td>
<td></td>
<td>±2</td>
</tr>
</tbody>
</table>

Fig. 1. The $^3P_2$, $^1D_2$, $^3F_2$ levels. The theoretical splitting of a particular J level is given on the left; the observed energy-level scheme on the right. Here $\mu$ is the crystal-quantum number.
<table>
<thead>
<tr>
<th>calc. (cm(^{-1}))</th>
<th>(\mu)</th>
<th>obs. (cm(^{-1}))</th>
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</thead>
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<tr>
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<tr>
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<td>14487</td>
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<td>14466</td>
</tr>
<tr>
<td>-86</td>
<td>3</td>
<td>14407</td>
</tr>
</tbody>
</table>

Fig. 2. The \(3F_3\) level.
\[ \begin{array}{c|c|c|c|c|c}
\text{calc.} & \text{obs.} & \text{calc.} & \text{obs.} \\
\text{(cm}^{-1}\text{)} & \mu & \text{(cm}^{-1}\text{)} & \mu & \text{(cm}^{-1}\text{)} \\
\hline
1_g^4 & 21379 & \pm 2 & 12763 & \pm 2 \\
97 & 3 & 21341 & \pm 1 & 12720 & 3 \\
63 & 3 & 21279 & \pm 1 & 12704 & 1 \\
14 & \pm 2 & 21255 & \pm 2 & 12649 & \\
-5 & 0 & 21191 & -32 & 3 & 12586 \\
-23 & & & -35 & \pm 2 & \\
-41 & \pm 1 & & -51 & 3 & 3 \\
\hline
\end{array} \]

\[ \begin{array}{c|c|c|c|c|c}
\text{3} \;\text{F}^+_4 & & & & & \\
\text{obs.} & \text{calc.} & \text{obs.} & \text{calc.} & \text{obs.} \\
\text{(cm}^{-1}\text{)} & \mu & \text{(cm}^{-1}\text{)} & \mu & \text{(cm}^{-1}\text{)} \\
\hline
-23 & \pm 1 & 21168 & & & \\
\end{array} \]

Fig. 3. The \(1_g^4\) and \(3\;\text{F}^+_4\) levels.
<table>
<thead>
<tr>
<th>calc. ((\text{cm}^{-1}))</th>
<th>(\mu)</th>
<th>obs. ((\text{cm}^{-1}))</th>
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<tr>
<td>122</td>
<td>±2</td>
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<tr>
<td>38</td>
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<tr>
<td>-18</td>
<td>±2</td>
<td>3 17 231</td>
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<tr>
<td>-23</td>
<td>±2</td>
<td>3 233</td>
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<tr>
<td>-113</td>
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<td>±1 33</td>
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<tr>
<td>-146</td>
<td>0</td>
<td>0 0</td>
</tr>
</tbody>
</table>

Fig. 4. The ground state, \(^3\text{H}_6\) level.
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