ANALYSIS AND COMPARISON OF OPTICAL ENERGY LEVELS OF SOME ERBIUM AND NEODYMIUM COMPOUNDS

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Abstract: NdCl₃ and ErCl₃ both has hexagonal structure with site symmetry C₃₆ for trivalent rare earth ion and KNdF₁₀ has tetragonal structure with site symmetry C₄ᵥ for the same. The energy levels (all in cm⁻¹ units) of ground term, magnetic splitting factors i.e g-values and magnetic susceptibilities were calculated with the help of crystal field theory. Then using the corresponding crystal field parameters (CFP) energy levels of some excited states in visible and UV range of this compound has been calculated and compared with some other compounds from different references. As they belong to visible range so they are called optical energy levels. Possible Zeeman splitting was also shown for two states of ErCl₃.

Keywords: Crystal field effect, g-values, excited energy levels with spectroscopic notation, Zeeman effect.

1. Introduction

Studies on magnetic, EPR optical properties of Nd³⁺ [1, 8] and Er³⁺ [7, 9] compounds have been studied extensively. Both of the ions are strongly magnetic and high anisotropic. When Nd³⁺ ion (ground term symbol ⁴I₀₂) and Er³⁺ ion (ground term symbol ⁴I₁₂) sit in the neighborhood of 9 chloride ions its site symmetry becomes C₃₆. Again when Nd³⁺ ion sits in the surroundings of fluoride ions in KNdF₁₀ compound its site symmetry becomes C₄ᵥ. Then FI terms of Nd³⁺ ion and Er³⁺ ions splits into 5 and 8 Kramer’s doublets respectively. Then values of the crystal field parameters (CFP) were determined keeping in mind about the referred values of magnetic splitting factors, total splitting of the ground term with a particular lowest level etc. After that using the values of CFP the energy splitting of the levels belonging to the visible and UV region were calculated.

2. Theoretical considerations

The RE ion normally exists as tripositive ion in solid crystal with spherical symmetry and (2J+1) fold degenerate energy level. The ion embedded in a crystalline lattice is acted upon by a number of interaction forces which were not present in the free ion. The electrostatic crystal field (CF), produced by surrounding anions modifies the energy levels and eigen functions of the free ion which is the object of CF theory. Under the action of CF the symmetry becomes lower than that of the free ion and the degree to which (2J+1) degeneracy is removed will depend on the point symmetry of the RE ion called its site symmetry. The static crystal field acting on the free ion in terms of the spherical harmonics (since the unperturbed energy functions would have complete spherical symmetry) can be expressed as

\[
H_\psi = \sum_{k,q} B^q_k \psi^q_k \quad \text{(with condition } |q| \leq k \text{ and } 0 \leq k \leq \infty) \quad \text{……………….. (1)}
\]

Here \(B_k\) and \(V_k\) denote corresponding crystal field parameter (CFP) and CF potential respectively. The value of \(k\), \(q\) will be limited by the point symmetry of RE ion. For example for C₃₆ symmetry,

\[
H_\psi = B^0_2 V^0_2 + B^0_4 V^0_4 + B^0_6 V^0_6 + B^0_8 (V^0_8 + V^0_6) \quad \text{……………….. (2)}
\]

In C₄ᵥ symmetry (NdCl₃ and ErCl₃) there are three fold axis of rotational symmetry with a mirror plane perpendicular to the rotational axis. The electric field produced in this case is similar due to same symmetry. If a rotation of 120° is made followed by a reflection on the potential \(V\), the new potential may be equated with the original potential if and only if \(q = 0\) or \(q = \pm 6\). The term with \(q = 0\) do not mix the eigenstates with different quantum number and the others arise due to the rotational elements of finite symmetry. For C₄ᵥ symmetry

\[
H_\psi = B^0_2 V^2_2 + B^0_4 V^0_4 + B^0_6 V^0_6 + B^0_8 (V^0_8 + V^0_6) + B^4_6 (V^4_6 + V^6_4) \quad \text{……………….. (3)}
\]

Which has lower symmetry than the previous potential expressed in...
equation (2) . For the sample Potassium Neodymium Fluoride (PNF) the CF potential has the above form . \( H_v \) will act upon the
state vectors and give non-zero values when \( V_1, V_2, V_3, V_4 \) acts without any change in wave function and \( V_5, V_6 \) act upon
the ket states less or greater than the bra states by 6 . Similarly the potential \( V_4^4 \) and \( V_4^4 \) act upon the ket states less or greater than
the bra states by 4 .

The \( g \)-values for ground level along and perpendicular to the symmetry axis of the sample are obtained from the relations

\[
g_{\parallel} = 2 g_I \langle \psi_0 | J_z | \psi_0 \rangle \quad \text{and} \quad g_{\perp} = 2 g_I \langle \psi_0 | J_x | \psi_0 \rangle
\]

(4) Where \( g_I \) = Lande’ splitting factor and \( |\psi_0\rangle \) = ground state CF wave function .

For Zeeman splitting an electronic energy level with given \( n \) and \( l \) splits in a magnetic field into \( 2l+1 \) equidistant terms corresponding to \( 2l+1 \) settings , each with a slightly different energy determined by \( m_l \) . It can be shown that when the spin of the

Here optical energy levels for \( ^4F_{9/2}, ^4G_{7/2}, ^4G_{9/2}, ^2D_{5/2}, ^2D_{3/2} \) for the two Nd-compounds and \( ^4F_{9/2}, ^4S_{9/2}, ^2H_{11/2}, ^4F_{7/2}, ^4F_{5/2}, ^4F_{3/2} \) for ErCl3 were calculated after determining the values of CFP effective for \( g \) values for ground term.

### 3. Results and Discussion :-

#### 3.1

The obtained set of CF parameters ( in cm\(^{-1}\) ) are

\[
B_2^0 = 52, B_4^0 = -61, B_6^0 = -44, \text{ and } B_6^6 = 625 \quad \text{for NdCl}_3
\]

\[
B_2^0 = 96, B_4^0 = -270, B_6^0 = -1, B_4^4 = 5 \text{ and } B_6^6 = -240 \quad \text{for KNd}_3\text{F}_{10}
\]

\[
B_2^0 = 75, B_4^0 = -43, B_6^0 = -41, \text{ and } B_6^6 = 540 \quad \text{for ErCl}_3
\]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Symmetry</th>
<th>( g_{\parallel} )</th>
<th>( g_{\perp} )</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd(^{3+}):LaCl(_3)</td>
<td>C(_{3h})</td>
<td>3.996</td>
<td>1.763</td>
<td>[11]</td>
</tr>
<tr>
<td>Nd(^{3+}):Y(OH)(_3)</td>
<td>C(_{3h})</td>
<td>3.630</td>
<td>1.960</td>
<td>[12]</td>
</tr>
<tr>
<td>NdES</td>
<td>C(_{3h})</td>
<td>3.594</td>
<td>2.039</td>
<td>[10]</td>
</tr>
<tr>
<td>NdCl(_3)</td>
<td>C(_{3h})</td>
<td>3.444</td>
<td>2.277</td>
<td>[3]</td>
</tr>
<tr>
<td>KNd(<em>3\text{F}</em>{10})</td>
<td>C(_{4v})</td>
<td>3.594</td>
<td>1.132</td>
<td>[5]</td>
</tr>
<tr>
<td>ErES</td>
<td>C(_{3h})</td>
<td>1.47</td>
<td>8.85</td>
<td>[2]</td>
</tr>
<tr>
<td>Er(^{3+}):Y(OH)(_3)</td>
<td>C(_{3h})</td>
<td>1.70</td>
<td>8.75</td>
<td>[6]</td>
</tr>
<tr>
<td>Er(OH)(_3)</td>
<td>C(_{3h})</td>
<td>1.693</td>
<td>8.848</td>
<td>[9]</td>
</tr>
<tr>
<td>ErCl(_3)</td>
<td>C(_{3h})</td>
<td>2.079</td>
<td>8.832</td>
<td>[4]</td>
</tr>
</tbody>
</table>
### Table - 2
Optical level of different three Neodymium Compounds (in cm⁻¹ unit):

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>State (Fl energy)</th>
<th>Ref [8] for NdDG Splitting</th>
<th>NdCl₃ Splitting</th>
<th>KNd₅F₁₀ Splitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>⁴F₉/₂ (14762)</td>
<td>14670.3 14736.6 14753.7 14804.6 14853.0</td>
<td>182.7</td>
<td>14737.8 14745.3 14760.5 14771.9 14794.5</td>
</tr>
<tr>
<td>2</td>
<td>⁴G₉/₂ (17106)</td>
<td>17022.4 17162.7 17189.6</td>
<td>167.2</td>
<td>17082.5 17097.9 17137.5</td>
</tr>
<tr>
<td>3</td>
<td>⁴G₇/₂ (19027)</td>
<td>18962.1 19023.2 19067.4 19091.9</td>
<td>129.8</td>
<td>18989.5 19006.5 19024.2 19087.7</td>
</tr>
<tr>
<td>4</td>
<td>⁴G₉/₂ (19488)</td>
<td>19441.3 19483.1 19503.5 19528.9 19535.7</td>
<td>94.4</td>
<td>19477.5 19481.6 19495.6 19506.6</td>
</tr>
<tr>
<td>5</td>
<td>²G₉/₂ (21002)</td>
<td>20962.5 20986.8 21012.7 21019.0 21042.5</td>
<td>80.0</td>
<td>20972.6 20992.9 21009.6 21027.6</td>
</tr>
<tr>
<td>6</td>
<td>²D₃/₂ (21180)</td>
<td>21179.3 21180.7</td>
<td>1.4</td>
<td>21174.6 21185.4</td>
</tr>
</tbody>
</table>

### Table - 3
Optical level of two Erbium Compounds (in cm⁻¹ unit):

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>State (Fl energy)</th>
<th>Er(OH)₃ Splitting</th>
<th>ErCl₃ (Present work) Splitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>⁴F₉/₂ (15346)</td>
<td>15299.1 15335.9 15347.9 15387.4 15409.6</td>
<td>110.5</td>
</tr>
<tr>
<td>2</td>
<td>⁴S₃/₂ (18470)</td>
<td>18448.4 18491.9</td>
<td>43.5</td>
</tr>
<tr>
<td>3</td>
<td>²H₁₁/₂ (19221)</td>
<td>19145.6 19201.5 19213.5 19221.3 19257.6 19259.3</td>
<td>113.7</td>
</tr>
<tr>
<td>4</td>
<td>⁴F₇/₂ (20594)</td>
<td>20516.0 20564.5 20617.5 20650.8</td>
<td>134.8</td>
</tr>
<tr>
<td>5</td>
<td>⁴F₅/₂ (22250)</td>
<td>22240.4 22247.7 22269.8</td>
<td>29.4</td>
</tr>
<tr>
<td>6</td>
<td>⁴F₃/₂ (22590)</td>
<td>22559.9 22619.8</td>
<td>59.9</td>
</tr>
</tbody>
</table>
3.2 Zeeman Splitting of $^4S_{3/2}$ and $^4F_{3/2}$ for ErCl$_3$

4. Conclusions
For the three samples the CF parameters do not change generally with temperature or by someway. So using the obtained CFP the energy levels of the aforesaid states were calculated. It was shown that the splitting was stronger for KNd$_3$F$_{10}$ than NdCl$_3$ for the present work. But the splitting of NdDG is in between that of the two samples. For ErCl$_3$ the splitting is less than that of Er(OH)$_3$ but is of same pattern (Fig 1b).
For Zeeman splitting of $^{4}S_{3/2}$ and $^{4}F_{3/2}$ it can be said that after the first splitting due to crystal field effect, second one comes due to Zeeman effect in external magnetic field according to the formula $\Delta E=g\mu_BmJH$ where symbols have their usual meaning. It is observed that the Zeeman splitting for both $J = \pm 3/2$ and $J = \pm 1/2$ are lesser for $^{4}F_{3/2}$ than $^{4}S_{3/2}$ state. For both cases the Zeeman splitting of $J = \pm 3/2$ is three times than that of $J = \pm 1/2$. But the splitting of energy levels due to crystal field is in the reverse order.

REFERENCES