Study on the Absorption Spectra of Ga$_2$Se$_3$:Co$^{2+}$ Single Crystals

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Introducing the average covalent factor $N$ and considering the interaction of the cubic crystal field, the spin-orbit coupling and Tree’s correction effects, the crystal field parameter $D_q$ was calculated. Also the varying tendency of $D_q$ with the bond length $R$ was investigated. Using the complete diagonalizing method the energy levels of the fine structure of Ga$_2$Se$_3$:Co$^{2+}$ single crystal were calculated and assigned. The calculated and assigned results are consistent with the experimental data.

**Key words:** Ga$_2$Se$_3$:Co$^{2+}$ Crystal; Fine Structure; Average Covalent Factor; Spin-Orbit Coupling

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1. Introduction

Ga$_2$Se$_3$ is a typical representative of A$_2$IIIB$_3$VI semi-conducting material with cubic zinc blende structure [1]. It is widely investigated for potential applications in optical and electronic devices. Ga$_2$Se$_3$ and Ga$_2$Se$_3$:Yb crystals have been grown by the Bridgman method to investigate thermal and electronic properties [2]. The susceptibility of Ga$_2$Se$_3$ and Ga$_2$Se$_3$:Yb crystals has been studied by Tagiev et al. [3], also the Mössbauer effect in Ga$_2$Se$_3$:Fe and the optical absorption properties of Ga$_2$Se$_3$:Co$^{2+}$ [3, 4].

Using the chemical transport reaction method Yoon et al. obtained Ga$_2$Se$_3$ and Ga$_2$Se$_3$:Co$^{2+}$ single crystals and measured their optical absorption spectra to reveal the impurity optical absorption mechanism of the Co$^{2+}$ ion [5]. They assigned those absorption peaks according to the crystal field theory but there were some errors in the assigned results. In this paper, considering the electrostatic and spin-orbit coupling effect, the fine structure of the absorption spectra of the Ga$_2$Se$_3$:Co$^{2+}$ crystal has been recalculated and reassigned correctly. The relationship between the crystal field parameter and the Co-Se bond length has been studied, too.

2. Theory and Calculations

The Ga$_2$Se$_3$ crystal has a space group $F\bar{4}3m$, where the cation Ga$^{3+}$ ion is surrounded by four Se$^{2-}$ ions and all ions are situated in the $T_d$ symmetry point. The Ga$^{3+}$ ions lie in the center of the symmetry structure. In the Ga$_2$Se$_3$:Co$^{2+}$ single crystal the Ga$^{3+}$ ion is replaced by a Co$^{2+}$ ion. It is known that Co$^{2+}$ belongs to the electron system 3d$^7$. In $T_d$ symmetry crystal field the $^4A_2^{(4)F}$ state of Co$^{2+}$ ion is the ground state.

2.1. Crystal Field Parameter $D_q$

Applying the Sugano-Tanabe strong field theory, the energy matrix formula of a Co$^{2+}$ ion in the cubic crystal field can be shown as

\[
4T_1 : \begin{bmatrix} 3A - 3B - 2D_q & 6B \\ 6B & 3A - 12B + 8D_q \end{bmatrix},
\]

\[
4T_2^{(4)F} : 3A - 15B - 2D_q,
\]

\[
4A_2^{(4)F} : 3A - 15B - 12D_q.
\]

Introducing the average covalent factor $N$, the relationships between the Racah parameters ($A$, $B$) in the crystal and those ($A_0$, $B_0$) in the free ion obey the relation

\[
A = N^4A_0, \quad B = N^4B_0.
\]
Table 1. Energy levels of Ga$_2$Se$_3$:Co$^{2+}$ single crystal (cm$^{-1}$).

<table>
<thead>
<tr>
<th>Transition</th>
<th>Experimental [5]</th>
<th>$N = 0.87$, $D_q = 345$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4A_2(^4F)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table><p>ightarrow ^4T_2(^4F)$ | 3451             | 3451                             |
| $^4A_2(^4F)ightarrow ^4T_1(^4F)$ | 6285             | 5964                             |
| $^4A_2(^4F)ightarrow ^4T_1(^4P)$ | 13825            | 13967                            |</p>

In the experiment, the transition value from the ground state $^4T_2(^4F)$ to the excited state $^4T_2(^4F)$ was 3451 cm$^{-1}$ [5]. The crystal field parameter $D_q$ calculated from (2)–(3) amounts to 345 cm$^{-1}$. Varying the average covalent factor $N$, the transition values can be calculated to fit the experimental values. The results are listed in Table 1.

As shown in Table 1, when the average covalent factor $N$ is 0.87 and the crystal field parameter $D_q$ is 345 cm$^{-1}$, the calculated values of the energy level transition are in good agreement with the experimental data. But in [5], different values of crystal field parameter $D_q$, such as 345 cm$^{-1}$, 349 cm$^{-1}$, and 642 cm$^{-1}$, respectively, were used to assign the transitions $^4A_2(^4F) ightarrow ^4T_2(^4F)$, $^4A_2(^4F) ightarrow ^4T_1(^4F)$, and $^4A_2(^4F) ightarrow ^4T_1(^4P)$. In theory that method is not in accordance with the physical meanings of crystal field parameter $D_q$. In our work, using the same crystal field parameter $D_q$ (345 cm$^{-1}$), the calculated energy level transitions can be good fitted to the experimental values.

2.2. Relationship between $D_q$ and the Bond Length $R$

In the cubic crystal field, the crystal field parameter $D_q$ can be described as

$$D_q = -\frac{4 eq(r^4)}{96R^5},$$

where $R$ is the bond length between the Se$^{2-}$ ion and Co$^{2+}$. Considering the average covalent factor $N$, the relations between the expectation value $\langle r^4 \rangle$ in the crystal and $\langle r^4 \rangle_0$ in the free ion is

$$\langle r^4 \rangle = N^2 \langle r^4 \rangle_0.$$  \hspace{1cm} (7)

It is shown by some research, especially research on the optical spectrum in high pressure, that $D_q \propto R^{-5}$ is the suitable fitting result [7]. For Ga$_2$Se$_3$:Co$^{2+}$ single crystal, when $N = 0.87$, the calculated values can be in good agreement with the experimental values. As a result, the varying tendency of $D_q$ with the bond length $R$ is shown in Figure 1. When the ligand bond length $R$ increases, $D_q$ decreases. It can be calculated from (6) that the bond length $R$ (Co-Se bond length) is 2.256 Å for $D_q = 345$ cm$^{-1}$ and $N = 0.87$. The lattice constant of Ga$_2$Se$_3$ single crystal is 5.442 Å [5] and the Ga-Se bond length calculated is 2.356 Å. It is interesting that the Co-Se bond length is about 0.1 Å shorter than the Ga-Se bond length.

2.3. Considering Spin-Orbit Coupling and Tree’s Correction

In a $T_d$ symmetry crystal field the crystal parameter $B_{40}$ can be obtained from the expressions

$$B_{40} = -e \sum_{m=1}^4 \frac{q_m(r^4)}{R_m^5} N^2 \left(\frac{4\pi}{9}\right)^{\frac{1}{2}} Y_{40}(\Theta_m, \Phi_m), \hspace{1cm} (8)$$

$$B_{44} = B_{4-4} = -e \sum_{m=1}^4 \frac{q_m(r^4)}{R_m^5} N^2 \left(\frac{4\pi}{9}\right)^{\frac{1}{2}} Y_{44}(\Theta_m, \Phi_m), \hspace{1cm} (9)$$

where $\Theta_m$ is the angle between ligand and the z-axis, $\Phi_m$ is the angle between the projection of the ligand in the $x,y$-plane and the $x$-axis. The relations among the crystal parameters $B_{40}$, $B_{44}$, and $D_q$ are calculated as

$$\frac{B_{40}}{D_q} = -21, \hspace{0.5cm} \frac{B_{40}}{B_{44}} = \frac{14}{5}. \hspace{1cm} (10)$$

Considering the spin-orbit coupling and the Tree’s correction effects, the spin-orbit coupling coefficient $\zeta$, Tree’s correction $\alpha$, and the Racah parameters $B$ and $C$ in the crystal can be defined as

$$B = N^4B_0, \hspace{0.5cm} C = N^4C_0, \hspace{0.5cm} \zeta = N^2\zeta_0, \hspace{0.5cm} \alpha = N^4\alpha_0. \hspace{1cm} (11)$$
Table 2. Results of calculation and assignment.

<table>
<thead>
<tr>
<th>$^4A_2(4F)$ Calculated</th>
<th>Experimental</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(cm$^{-1}$)</td>
<td>(cm$^{-1}$)</td>
<td></td>
</tr>
<tr>
<td>$^2T_2(4F)$</td>
<td>3351</td>
<td>3184</td>
</tr>
<tr>
<td>$^4T_1(4F)$</td>
<td>4341</td>
<td>3280</td>
</tr>
<tr>
<td>$^4T_1(4P)$</td>
<td>3534</td>
<td>3392</td>
</tr>
<tr>
<td>$^2U(2G)$</td>
<td>3622</td>
<td>3660</td>
</tr>
<tr>
<td>$^4T_1(4P)$</td>
<td>5763</td>
<td>5605</td>
</tr>
<tr>
<td>$^4T_1(4F)$</td>
<td>5895</td>
<td>5996</td>
</tr>
<tr>
<td>$^2T_1(2G)$</td>
<td>6264</td>
<td>6553</td>
</tr>
<tr>
<td>$^4T_1(4F)$</td>
<td>6497</td>
<td>6833</td>
</tr>
<tr>
<td>$^2T_1(2G)$</td>
<td>13336</td>
<td>12937</td>
</tr>
<tr>
<td>$^4T_1(4F)$</td>
<td>13436</td>
<td>13465</td>
</tr>
<tr>
<td>$^2T_1(2G)$</td>
<td>13837</td>
<td>13926</td>
</tr>
<tr>
<td>$^4T_1(4F)$</td>
<td>13836</td>
<td>$^8\Gamma$</td>
</tr>
</tbody>
</table>

The values of the parameters $B_{40} = -7245$ cm$^{-1}$, $B_{44} = B_{4-4} = -4329.72$ cm$^{-1}$, $B = 638.78$ cm$^{-1}$, $C = 2501$ cm$^{-1}$, $\zeta = 403$ cm$^{-1}$, and $\alpha = 40$ cm$^{-1}$.

Using a computer program [9], the energy levels of the Ga$_2$Se$_3$:Co$^{2+}$ single crystal are recalculated and reassigned. All results are listed in Table 2. From this table, it can be seen that the calculated values are consistent with the experimental data.

But there are some differences between the reassigned results and the results [5] mentioned in (i) Yoon et al. drew the conclusion that the $^4T_1(4P)$ state of the Co$^{2+}$ ion sited in a T$_d$ symmetry split into four sublevels $^6\Gamma_6$ (14865 cm$^{-1}$), $^8\Gamma_8$ (13926 cm$^{-1}$), $^7\Gamma_7$ (13465 cm$^{-1}$), and $^6\Gamma_6$ (12937 cm$^{-1}$) due to the first- and second-order spin-orbit coupling effects [5]. In our opinion, the assignment of $^6\Gamma_6$ (14865 cm$^{-1}$) was wrong. Because the difference between $^6\Gamma_6$ (14865 cm$^{-1}$) and $^8\Gamma_8$ (13926 cm$^{-1}$) is 939 cm$^{-1}$ and considering only the spin-orbit coupling effects cannot explain the big difference. During calculation, when the interaction of two states is considered, the sublevel $^8\Gamma_8(2G)$ is 14460 cm$^{-1}$. As a result, the sublevel in 14865 cm$^{-1}$ should be assigned as $^2U(2G)$. (ii) The first- and second-order perturbation were adopted to calculate and assign the sublevels in [5]. But using this method there were some errors in the assigned results. In our work, the sublevels $^8\Gamma_8$ and $^6\Gamma_6$ split from $^4T_1(4F)$ should be $^6\Gamma_6$ and $^8\Gamma_8$. The sublevels $^7\Gamma_7$ and $^8\Gamma_8$ split from $^4T_1(4F)$ should be $^8\Gamma_8$ and $^7\Gamma_7$. The sublevels $^7\Gamma_7$ and $^8\Gamma_8$ split from $^4T_1(4F)$ should be $^8\Gamma_8$ and $^7\Gamma_7$.

3. Conclusion

In this paper, introducing the average covalent factor $N$, the calculated value of crystal field parameter $D_q$ was 345 cm$^{-1}$. Using the same crystal field parameter $D_q$ (345 cm$^{-1}$), the energy level transitions calculated can be in good agreement with the experimental values. The varying tendency of $D_q$ with the bond length $R$ is investigated. The calculated value of Co-Se bond length is 2.256 Å which is about 0.1 Å shorter than the Ga-Se bond length. Considering spin-orbit coupling and Tree’s correction effects, the energy levels of Ga$_2$Se$_3$:Co$^{2+}$ single crystal are recalculated and reassigned. The calculated values are consistent with the experimental data. The error in the assignments of the fine structure of Ga$_2$Se$_3$:Co$^{2+}$ single crystal are corrected, too.