Study on the Absorption Spectra of Ga_2Se_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_2Se_3:Co^{2+} single crystal were calculated and assigned. The calculated and assigned results are consistent with the experimental data.

Key words: Ga_2Se_3:Co^{2+} Crystal; Fine Structure; Average Covalent Factor; Spin-Orbit Coupling
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1. Introduction

Ga_2Se_3 is a typical representative of $A_2{}^{III}B_3{}^{VI}$ semiconducting material with cubic zinc blende structure [1]. It is widely investigated for potential applications in optical and electronic devices. Ga_2Se_3 and Ga_2Se_3:Yb crystals have been grown by the Bridgman method to investigate thermal and electronic properties [2]. The susceptibility of Ga_2Se_3 and Ga_2Se_3: ^{57}Fe crystals has been studied by Tagiev et al. [3], also the Mössbauer effect in Ga_2Se_3: Fe and the optical absorption properties of Ga_2Se_3:Co^{2+} [3, 4].

Using the chemical transport reaction method Yoon et al. obtained Ga_2Se_3 and Ga_2Se_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_2Se_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_2Se_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_2Se_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 $^4A_2(^4F)$ 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

$$^4T_1 : \begin{bmatrix} 3A-3B-2D_q & 6B \\ 6B & 3A-12B+8D_q \end{bmatrix}, \quad (1)$$

$$^4T_2(^4F): \quad 3A-15B-2D_q, \quad (2)$$

$$^4A_2(^4F): \quad 3A-15B-12D_q. \quad (3)$$

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

$$A = N^4A_0, \quad B = N^4B_0. \quad (4)$$

The Racah parameters in a free Co^{2+} ion are [6]

$$A_0 = 16118\ \mathrm{cm}^{-1}, \quad B_0 = 1115\ \mathrm{cm}^{-1}. \quad (5)$$

Table 1. Energy levels of Ga_2Se_3:Co^{2+} single crystal (cm^{-1}).

Transition	Experimental [5]	$N = 0.87$, $D_q = 345$ cm^{-1}
$^4A_2(^4F) \rightarrow {}^4T_2(^4F)$	3451	3451
$^4A_2(^4F) \rightarrow {}^4T_1(^4F)$	6285	5964
$^4A_2(^4F) \rightarrow {}^4T_1(^4P)$	13825	13967

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 $^4A_2(^4F) \rightarrow {}^4T_2(^4F)$, $^4A_2(^4F) \rightarrow {}^4T_1(^4F)$, and $^4A_2(^4F) \rightarrow {}^4T_1(^4P)$. 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

$$D_q = -\frac{4}{9}\frac{eq\langle r^4\rangle}{6R^5}, \tag{6}$$

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

$$\langle r^4\rangle = N^2\langle r^4\rangle_0. \tag{7}$$

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_2Se_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 a of Ga_2Se_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.

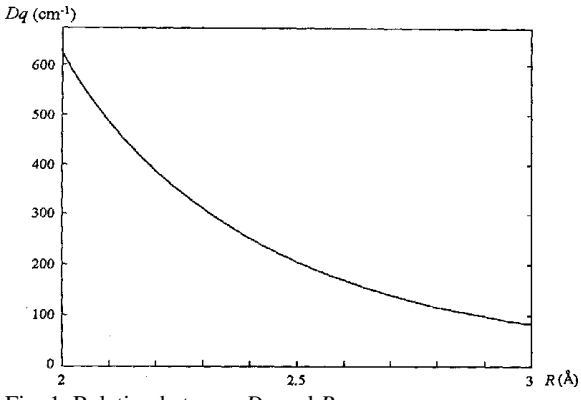

Fig. 1. Relation between D_q and R.

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

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

$$B_{40} = -e\sum_{m=1}^{4}\frac{q_m}{R_m^5}\langle r^4\rangle_0 N^2\left(\frac{4\pi}{9}\right)^{\frac{1}{2}}Y_{40}(\Theta_m,\Phi_m), \tag{8}$$

$$B_{44} = B_{4-4} = -e\sum_{m=1}^{4}\frac{q_m}{R_m^5}\langle r^4\rangle_0 N^2\left(\frac{4\pi}{9}\right)^{\frac{1}{2}}Y_{44}(\Theta_m,\Phi_m), \tag{9}$$

where Θ_m is the angle between ligand and the z-axis. Φ_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

$$\frac{B_{40}}{D_q} = -21, \quad \frac{B_{40}}{B_{44}} = \sqrt{\frac{14}{5}}. \tag{10}$$

Considering the spin-orbit coupling and the Tree's correction effects, the spin-orbit coupling coefficient ζ, Tree's correction α, and the Racah parameters B and C in the crystal can be defined as

$$B = N^4B_0,\ C = N^4C_0,\ \zeta = N^2\zeta_0,\ \alpha = N^4\alpha_0. \tag{11}$$

Table 2. Results of calculation and assignment.

$^4A_2(^4F)$ →	Calculated (cm^{-1})	Experimental (cm^{-1})	Assignment [5]	Assignment This paper
$^4T_2(^4F)$	3351	3184	Γ^8	Γ^6
	3431	3280	Γ^6	Γ^8
	3534	3392	Γ^8	Γ^8
	3622	3660	Γ^7	Γ^7
$^4T_1(^4F)$	5763	5605	Γ^6	Γ^6
	5895	5969	Γ^8	Γ^8
	6264	6553	Γ^7	Γ^8
	6497	6833	Γ^8	Γ^7
$^4T_1(^4P)$	13336	12937	Γ^8	Γ^7
	13436	13465	Γ^7	Γ^8
	13837	13926	Γ^8	Γ^8
	13836			Γ^6
$^2T_1(^2G)$	14460	14865	Γ^6 ($^4A_2(^4F)\rightarrow{}^4T_1(^4P)$)	Γ^8 ($^2U(^2G)$)

The values of the parameters B_0, C_0, ζ_0, and α_0 in the free Co^{2+} ion are 1115 cm^{-1}, 4366 cm^{-1}, 533 cm^{-1}, and 70 cm^{-1}, respectively [8]. According to the above formulas, these parameters can be calculated for $N = 0.87$ and $D_q = 345$ cm^{-1}. The results are shown in the following expressions:

$$\begin{aligned} &B_{40} = -7245\ \mathrm{cm}^{-1}, \\ &B_{44} = B_{4-4} = -4329.72\ \mathrm{cm}^{-1}, \\ &B = 638.78\ \mathrm{cm}^{-1}, \quad C = 2501\ \mathrm{cm}^{-1}, \\ &\zeta = 403\ \mathrm{cm}^{-1}, \quad \alpha = 40\ \mathrm{cm}^{-1}. \end{aligned} \tag{12}$$

Using a computer program [9], the energy levels of the Ga_2Se_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 Γ^6 (14865 cm^{-1}), Γ^8 (13926 cm^{-1}), Γ^7 (13465 cm^{-1}), and Γ^8 (12937 cm^{-1}) due to the first- and second-order spin-orbit coupling effects [5]. In our opinion, the assignment of Γ^6 (14865 cm^{-1}) was wrong. Because the difference between Γ^6 (14865 cm^{-1}) and Γ^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 $\Gamma^8(^2G)$ is 14460 cm^{-1}. As a result, the sublevel in 14865 cm^{-1} should be assigned as $\Gamma^2U(^2G)$). (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 Γ^8 and Γ^6 split from $^4T_2(^4F)$ should be Γ^6 and Γ^8. The sublevels Γ^7 and Γ^8 split from $^4T_1(^4F)$ should be Γ^8 and Γ^7. The sublevels Γ^7 and Γ^8 split from $^4T_1(^4P)$ should be Γ^8 and Γ^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_2Se_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_2Se_3:Co^{2+} single crystal are corrected, too.

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