EPR Parameters and Local Atom-position Parameters for Co$^{2+}$ Ions in CdS and CdSe Semiconductors

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Z. Naturforsch. 59a, 783 – 786 (2004); received July 9, 2004

The EPR parameters (zero-field splitting $D$ and $g$ factors $g_{\|}$, $g_{\perp}$) of Co$^{2+}$ ions in CdS and CdSe semiconductors are calculated from the high-order perturbation formulas based on the cluster approach for a 3d$^7$ ion in trigonal symmetry. These formulas include the contribution to the EPR parameters from both the spin-orbit coupling parameter of the 3d$^7$ ion and that of the ligand. From the calculations, the local atom-position parameters $u$ (which are different from the corresponding values in the host crystals) for the Co$^{2+}$ impurity centers in both semiconductors are estimated. The results are discussed.

Key words: Electron Paramagnetic Resonance; Local Atom-Position Parameter; Crystal- and Ligand- Field Theory; Co$^{2+}$; CdS; CdSe.

1. Introduction

Transition metal impurities strongly influence the optical, electric and magnetic properties of semiconductor devices [1, 2]. Therefore it is important to get information about the local structure of these impurity centers in semiconductors. As is known, the EPR parameters (zero-field splitting and $g$ factors) of a paramagnetic impurity in crystals are sensitive to its immediate environment. Therefore one can obtain useful information on the local or defect structures of transition metal impurity centers in semiconductors. The zero-field splitting $D$ and $g$ factors $g_{\|}$, $g_{\perp}$ of Co$^{2+}$ in CdS and CdSe crystals were reported [3, 4], however the defect structures of these Co$^{2+}$ impurity centers in both crystals have not been estimated by analyzing these EPR parameters. Co$^{2+}$ ions in CdS and CdSe replace the Cd$^{2+}$ ions and occupy the trigonal symmetry sites [3, 4]. The trigonal distortion of the tetrahedral MX$_4$ clusters in the wurtzite structure is sensitive to the atom-position parameter $u$. Since the nature and size of the Co$^{2+}$ impurity are unlike those of the replaced Cd$^{2+}$ ion, the local trigonal distortion and hence the local atom-position parameter $u_{loc}$ may be different from the corresponding values in the host or pure crystals. In this paper, we study the local atom-position parameters $u_{loc}$ and hence the local structures for Co$^{2+}$ in CdS and CdSe semiconductors by calculating their EPR parameters. The results are discussed.

2. Calculation

For 3d$^n$ ions in semiconductors, such as Co$^{2+}$ in CdS, and CdSe, the conventional one spin-orbit (SO) parameter model (where only the contribution of the SO coupling parameter $\zeta_d$ of the central 3d$^n$ ion is included) based on the classical crystal-field theory is not suitable, because of the strong covalence of these semiconductors, and the admixture of the SO coupling parameters between the d electrons of the 3d$^n$ ion and the p electrons of the ligands via the covalence effects should be considered [5, 6]. Therefore, a two-SO-parameter model (where the contributions of both the SO coupling parameter of 3d$^n$ ion and that of the ligand are included) based on the cluster approach must be used here [6 – 8]. According to this model, the one-electron basis functions of a 3d$^n$ MX$_4$ cluster can be expressed as

$$\begin{align*}
\Psi_t &= N_t (|d_t\rangle + \lambda_\sigma |\sigma_t\rangle + \lambda_\pi |\pi_t\rangle), \\
\Psi_e &= N_e (|d_e\rangle + \sqrt{3} \lambda_\pi |\pi_e\rangle),
\end{align*}$$

(1)
where the subscript $e$ or $t$ stands for the irreducible representation of the $T_d$ group, $|d_e\rangle$ and $|d_t\rangle$ are the d orbitals of the 3$d^9$ ion, $|\pi_e\rangle$, $|\pi_t\rangle$ and $|\pi_\sigma\rangle$ are the p orbitals of the ligands, $N_i$ and $N_c$ are the normalization coefficients, and $\lambda_\sigma$ and $\lambda_\pi$ are the orbital mixing coefficients.

\[
D = 2\zeta^2 \left( \frac{1}{E_1^2} - \frac{1}{E_2^2} \right) v/9 - \sqrt{2v'} \zeta' \left( \frac{2}{3E_1 E_3} + \frac{1}{(E_2 E_3)} + \frac{1}{(E_2 E_4)} + \frac{\sqrt{2v}{v'}}{(E_1 E_4 E_5)} \right)
- \frac{\sqrt{2v'} B_4 \zeta'^2}{4/(E_1 E_4 E_5)} + \frac{9}{(E_2^2 E_3)},
\]

\[
g_1 = g_s + 8 \zeta'/\left(3E_1\right) - 2 \zeta'/\left(2k'\zeta - k'\zeta' + 2g_s\zeta'\right)/\left(9E_1^2\right) + 4 \zeta'^2 (k - 2g_s)/\left(9E_1^2\right) - 2 \zeta^2 (k + g_s)/\left(3E_1^2\right)
+ 4k' \zeta' \left(1/(9E_1 E_3) - 1/(3E_1 E_2) + 1/(3E_2 E_3)\right) - 8k' \zeta'/\left(9E_1^2\right) + 4 \sqrt{2v'} (k' \zeta + k' \zeta' + \zeta '/\left(6E_1 E_4\right)),
\]

where $E_1$, $E_2$, $E_3$, $E_4$ and $E_5$ are the zero-order energy separations between the ground state $^4A_2(t^2_e e^6)$ and the excited states $^2T_2(t^2_e e^6)$, $^2T_{1g}(t^2_e e^6)$, $^2T_{2g}(t^2_e e^6)$, $^2T_{1u}(t^2_e e^6)$ and $^4T_{1u}(t^2_e e^6)$, respectively. $g_s \approx 2.0023$ is the free-ion value, $B_4 = N_i^4 N_c^4 B_0$ [B_0 and \( C_0 \)] are the Racah parameters of a free 3$d^9$ ion. $v$ and $v'$ are the trigonal field parameters. The SO coupling parameters $\zeta$, $\zeta'$ and the orbital reduction factors $k$, $k'$ are

\[
\zeta = (N_i)^2 \left\{ \zeta_0' + [\sqrt{2} \lambda_\pi \lambda_\sigma - (\lambda_\sigma)^2/2] \zeta_0' \right\},
\]

\[
\zeta' = N_i \cdot N_c \left\{ \zeta_0' + [\lambda_\pi \lambda_\sigma / \sqrt{2} + (\lambda_\sigma)^2/2] \zeta_0' \right\},
\]

\[
k = (N_i)^2 \left\{ 1 - (\lambda_\sigma)^2/2 + \sqrt{2} \lambda_\sigma \lambda_\pi + 2 \lambda_\pi S_{dp}(\sigma) \right\} + 2 \lambda_\pi S_{dp}(\sigma),
\]

\[
k' = N_i \cdot N_c \left\{ 1 + (\lambda_\sigma)^2/2 + \lambda_\pi \lambda_\sigma / \sqrt{2} + 4 \lambda_\pi S_{dp}(\pi) + \lambda_\sigma S_{dp}(\sigma) \right\},
\]

where $\zeta_0'$ and $\zeta_0''$ are, respectively, the SO coupling parameter of the 3$d^9$ ion and that of the ligands in free state. $S_{dp}(\pi) = \langle d_\pi | r_\pi \rangle = \langle d_\pi | r_\pi \rangle / \sqrt{3}$ and $S_{dp}(\sigma) = \langle d_\pi | r_\pi \rangle$ are the group overlap integrals. From the Slater-type SCF functions [11, 12] and the average metal-ligand distances in CdS and CdSe [13], we calculate $S_{dp}(\pi) \approx 0.0054$ and $S_{dp}(\sigma) \approx 0.0226$ for CdS; Co$^{2+}$ and $S_{dp}(\pi) \approx 0.0053$ and $S_{dp}(\sigma) \approx 0.0230$ for CdSe: Co$^{2+}$.

According to the one-electron basis functions, we have the normalization relationships

\[
N_i = \left[ 1 + (\lambda_\sigma)^2 + (\lambda_\pi)^2 + 2 \lambda_\sigma S_{dp}(\sigma) + 2 \lambda_\pi S_{dp}(\pi) \right]^{-1/2},
\]

\[
N_c = \left[ 1 + 3(\lambda_\sigma)^2 + 6 \lambda_\sigma S_{dp}(\pi) \right]^{-1/2}.
\]

From these basis functions and Macfarlane’s perturbation-loop method [9, 10], the high-order perturbation formulas of the EPR parameters $D$, $g_1$ and $g_{1u}$, based on the cluster approach for the 3$d^7$ ion in a trigonal MX$_4$ cluster can be derived as

\[
v = \frac{3}{7} \tilde{A}_2(R_0) \left[ 2(R_0/R_1)^2 \right] + 3(\cos^2 \theta - 1)(R_0/R_1)^2 \left[ 8(R_0/R_1)^4 \right] + 3(15 \cos^2 \theta - 3 \cos^2 \theta - 1)(R_0/R_1)^4 + 20 \sqrt{2}/3 \tilde{A}_4(R_0) \sin \theta \cos \theta (R_0/R_1)^4,
\]
\[ v' = -\sqrt{2}/7A_2(R_0) (2(R_0/R_1)^2 + 3(3\cos^2 \theta - 1)(R_0/R_2)^2) + 5\sqrt{2}/63A_4(R_0) (8(R_0/R_1)^4 + 3(35\cos^2 \theta - 30\cos^2 \theta + 3)(R_0/R_2)^4) + 10/3A_4(R_0) \sin^3 \theta \cos (R_0/R_2)^4, \]

where \( t_2 \) and \( t_4 \) are the power-law exponents. For the 3d\( ^n \) ions in many crystals we take \( t_2 \approx 3 \) and \( t_4 \approx 5 \) [8, 22, 23]. \( \tilde{A}_2(R_0) \) and \( \tilde{A}_4(R_0) \) are the intrinsic parameters with the reference distance \( R_0 \approx (R_1 + 3R_2)/4 \). For 3d\( ^n \) MX\(_4\) clusters, \( \tilde{A}_4(R_0) = 27D_q/16 \) [8, 21, 23]. The ratio \( \tilde{A}_2(R_0)/\tilde{A}_4(R_0) \approx 9 \sim 12 \) [8, 22 – 24] is obtained for 3d\( ^n \) ions in many crystals. We take the average value \( \tilde{A}_2(R_0)/\tilde{A}_4(R_0) \approx 10.5 \) here. \( R_1 \) is the bonding length along \( C_3 \) axis, and \( \theta \) is the angle between the directions of \( R_1 \) and \( R_2 \). The structural parameters \( R_1, R_2 \) and \( \theta \) in wurtzite structure can be calculated from the lattice constants \( a, c \) and the atom-position parameter \( u \) (note: the trigonal distortion of the MX\(_4\) cluster is sensitive to the parameter \( u \)). For CdS [3], \( a \approx 4.137 \) \( \text{Å} \), \( c \approx 6.7144 \) \( \text{Å} \), \( u \approx 0.378 \), and for CdSe [13], \( a \approx 4.30 \) \( \text{Å} \), \( c \approx 7.0133 \) \( \text{Å} \), \( u \approx 0.377 \). Applying the structure data of the host crystals to the above formulas, the EPR parameters of CdS: Co\(^{2+}\) and CdSe: Co\(^{2+}\) have been calculated. The calculated zero-field splittings \( D \) agree poorly in sign and magnitude with the observed values (see Table 1), suggesting that the local structural parameters in the vicinity of the Co\(^{2+}\) ions in CdS and CdSe are unlike the corresponding structural parameters in the pure host crystals. Since the zero-field splitting \( D \) is very sensitive to the trigonal distortion of impurity centers and hence to the local atom-position parameter \( u_{\text{loc}} \), we mainly study the change of the atom-position parameter \( u \) caused by the impurity (i.e., the local parameter \( u_{\text{loc}} \)) for Co\(^{2+}\) in both crystals. By fitting the calculated EPR parameters (in particular, the zero-fields splitting \( D \)) to the observed values, we obtain for CdS: Co\(^{2+}\) and for CdSe: Co\(^{2+}\)

\[ u_{\text{loc}} \approx 0.3747, \]

The comparisons between the calculated and experimental EPR parameters are shown in Table 1.

### Table 1. EPR parameters (zero-field splitting and \( g \) factors) for Co\(^{2+}\) in CdS and CdSe semiconductors.

<table>
<thead>
<tr>
<th></th>
<th>CdS: Co(^{2+})</th>
<th>CdSe: Co(^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D ) (cm(^{-1}))</td>
<td>Cal.</td>
<td>Expt.</td>
</tr>
<tr>
<td>( g_{|} )</td>
<td>1.2255</td>
<td>0.6637</td>
</tr>
<tr>
<td>( g_{\perp} )</td>
<td>2.2691</td>
<td>2.2580</td>
</tr>
</tbody>
</table>

*Calculated by using the atom-position parameter \( u \) in the pure crystals.*

*Calculated by using the local atom-position parameter \( u_{\text{loc}} \) in the impurity center.*

3. Discussion

From Table 1 it can be seen that by applying suitable local atom-position parameters \( u_{\text{loc}} \), the calculated EPR parameters for CdS: Co\(^{2+}\) and CdSe: Co\(^{2+}\) are consistent with the observed values. The local parameter \( u_{\text{loc}} \), differing from the host parameter \( u \), suggests that the impurity ions Co\(^{2+}\) in CdS and CdSe do not occupy the exact Cd\(^{2+}\) sites, but are displaced by \( \Delta R = (u - u_{\text{loc}}) \approx 0.022 \) \( \text{Å} \) along the \( C_3 \) axis for CdS: Co\(^{2+}\) and \( \Delta R \approx 0.020 \) \( \text{Å} \) for CdSe: Co\(^{2+}\). Similar displacements of 3d\( ^n \) impurities in wurtzite-type semiconductors have also been found for Ti\(^{2+}\) and V\(^{3+}\) in CdS [8] and Fe\(^{3+}\), Mn\(^{2+}\) and Ni\(^{3+}\) in GaN [23]. So, the local atom-position parameters \( u_{\text{loc}} \) can be regarded as reasonable. Evidently the local structure of 3d\( ^n \) impurity centers in crystals can be estimated by studying their EPR parameters.

Acknowledgements

This project was supported by the National Natural Science Foundation of China (Grant No. 10274054), the Doctor Training Program in Universities and Colleges in China (Grant No.20010610008), and the Science Foundation of CAFUC.


