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The covalence effect of energy levels of ZnS:Mn^{2+}

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ABSTRACT

The contribution of the different covalence for t_2 and e orbitals must be considered in the investigation of the optical and magnetic properties of the transition metal ion in II–VI and III–V semiconductors. In present paper, two covalent parameters N_t and N_e associated with t_2 and e orbitals have been adopted to describe the covalence. The energy matrices considering the different covalence for t_2 and e orbitals have been provided for d^5 ions in crystal. These matrices show that the contribution from the Racah parameter A cannot be neglected in calculation of energy-level of d^5 ions in covalent crystal. The calculated results using the matrix show that the energy levels of ^4E and $^4A_1$ states split, and the energy-level difference between ^4E and $^4A_1$ states increases with increase of the different covalence between t_2 and e orbitals. These energy levels are always degenerate, when the different covalence for t_2 and e orbitals is neglected. By using the energy matrices, the energy-level of ZnS:Mn^{2+} has been calculated. The calculated energy levels of ZnS:Mn^{2+} are in good agreement with the experiments.

1. Introduction

The average covalent factor model plays a major role on studies for the optical and magnetic properties of transition metal impurity in crystal. The average covalent factor model is used for describing the covalence for transition metal ion in crystal [1–3]. However, it has been found to be unsuitable for the prediction of optical and magnetic properties of the transition metal ion in II–VI and III–V semiconductors. One way to improve the average covalent factor model is to consider the different covalence of t_2 and e orbitals for the transition metal ion in II–VI and III–V semiconductors by introducing two covalent parameters N_t and N_e [4] associated with t_2 and e orbitals, respectively. The magnetic properties for the transition metal ion in II–VI and III–V semiconductors were investigated by the two spin–orbit coupling parameter model [5–9] considering the different covalence for t_2 and e orbitals. This model implies that it is necessary for a strong covalent crystal to take the different covalence for t_2 and e orbitals, when EPR are studied. The optical properties for the transition metal ion in II–VI and III–V semiconductors were investigated by establishing the energy matrices considering the different covalence for t_2 and e orbitals. For example, for $d^{2,8}$ ions, Du and Yeom [10] have provided the complete energy matrices considering the different covalence for t_2 and e orbitals, and calculated the energy levels of Ni^{2+}in ZnS and ZnSe compounds. For $d^{3,7}$ ions, Chen and Du [11] have provided the complete energy matrices, and calculated the energy levels of Co^{2+}in ZnSe compound. For $d^{4,6}$ ions, Zhou and Li [12] have provided the complete energy matrices, and calculated the energy levels of Cr^{2+}in ZnSe compound. These studies implied that it is necessary to take the different covalence for t_2 and e orbitals into account, when the optical properties for a strong covalent crystal are studied. To date, however, little attention has been paid to the energy matrix considering the different covalence for t_2 and e orbitals for d^5 ions.

ZnS:Mn^{2+} material, a typical II–VI semiconductor, has a stronger covalence than an ionic compound. For ZnS:Mn^{2+}, obviously, the influence of the different covalence of t_2 and e orbitals should not be neglected in the study of the optical properties. Many works [13–24] have been devoted to the study of the optical spectra and magnetic properties of ZnS:Mn^{2+}. However, the different covalence for t_2 and e orbitals has not yet been considered.

This work presents the complete energy matrix for d^5 ion in semiconductors by considering the contributions of the different covalence for t_2 and e orbitals, and provides variety of energy levels of varying covalence for d^5 ion in semiconductors. By using the energy matrix, the energy levels for ZnS:Mn^{2+} semiconductor are calculated, and the results show that the theoretical predictions are in excellent agreement with experimental data.

2. The energy matrix considering the different covalence for t_2 and e orbitals

For the transition metal in crystal, the pure d-orbital of the transition metal ion must mix with the ligand orbitals due

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to the covalence. In a cubic crystal-field, the five-fold degenerate d-orbital is split into three-fold degenerate t_2 orbital and two-fold degenerate e orbital, where t_2 and e are the irreducible representation of O_h or T_d point group. For the covalent semiconductors, the irreducible representation basic function for t_2 and e orbitals can be written as

$$\begin{aligned} |t_2\rangle &= N_t[|d_{0t}\rangle + \lambda_t|L_t\rangle], \\ |e\rangle &= N_e[|d_{0e}\rangle + \lambda_e|L_e\rangle], \end{aligned} \tag{1}$$

where N_t and N_e are covalent factors, λ_t and λ_e are orbital mixing coefficients, d_{0t} and d_{0e} are pure d-orbitals, L_t and L_e are the ligand–ion orbitals. When the electrostatic repulsions of two electrons are calculated by using the irreducible representation orbitals of Eq. (1), the matrix element for ligand–ion orbital can be neglected since the d-orbital is dominant; thus the matrix element can be written as

$$\begin{aligned} &\langle t_2t_2\|t_2t_2\rangle = N_t^4\langle d_{0t}d_{0t}||d_{0t}d_{0t}\rangle, \quad \langle t_2t_2||t_2e\rangle = N_t^3N_e\langle d_{0t}d_{0t}||d_{0t}d_{0e}\rangle, \\ &\langle t_2e\|t_2e\rangle = N_t^2N_e^2\langle d_{0t}d_{0e}||d_{0t}d_{0e}\rangle, \quad \langle ee||ee\rangle = N_e^4\langle d_{0e}d_{0e}||d_{0e}d_{0e}\rangle, \end{aligned} \tag{2}$$

where $\langle d_{0i}d_{0i}||d_{0i}d_{0i}\rangle (i=t,e)$ is electrostatic repulsion of two pure d-orbital, and $\langle t_2t_2||t_2t_2\rangle$, $\langle t_2t_2||t_2e\rangle$, $\langle t_2e||t_2e\rangle$, $\langle ee||ee\rangle$ are electrostatic repulsions of irreducible representation orbital in crystal. The correlation between the Racah parameters of crystal and free-ion can be written as

$$\begin{aligned} &A_1 = N_t^4A_0, \quad A_2 = N_t^2N_e^2A_0, \quad A_3 = N_t^2N_e^2A_0, \quad A_4 = N_e^4A_0, \\ &B_1 = N_t^4B_0, \quad B_2 = N_t^2N_e^2B_0, \quad B_3 = N_t^2N_e^2B_0, \quad B_4 = N_e^4B_0, \\ &C_1 = N_t^4C_0, \quad C_2 = N_t^2N_e^2C_0, \quad C_3 = N_t^2N_e^2C_0, \quad C_4 = N_e^4C_0, \end{aligned} \tag{3}$$

where A_i, B_i, $C_i (i=1, 2, 3, 4)$ and A_0, B_0, C_0 denote the Racah parameters of crystal and of the free-ion, respectively. By using Eqs. (2) and (3), the complete energy matrix of the d^5 electron system in the Sugano–Tanabe scheme can be obtained. The energy matrix, as shown in Appendix, will yield results that differ from the classical crystal-field. The striking difference is that the

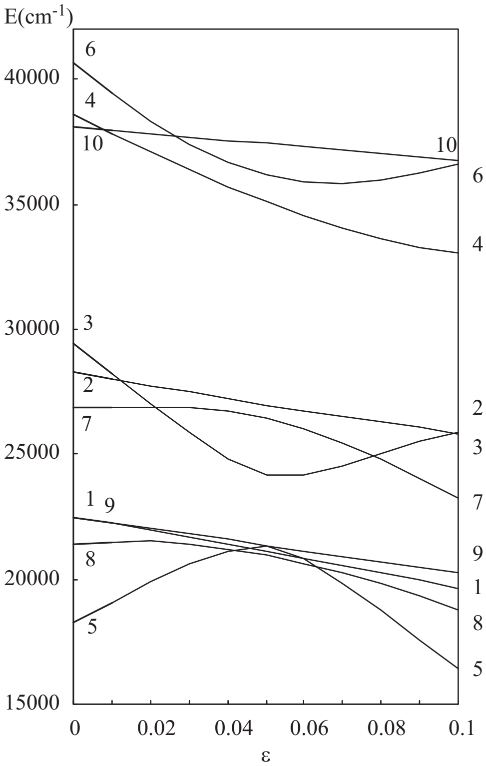

Fig. 1. Variation of the energy levels of Mn^{2+} for spin four-level system with the covalent parameter ε. The energy E is the difference between the state $^{2s+1}\Gamma$ term and the ground state $^6A_1$ term. The states 1–10 are ^4E_a,^4E_b,$^4T_{1a}$,$^4T_{1b}$, $^4T_{1c}$,$^4T_{2a}$,$^4T_{2b}$,$^4T_{2c}$,$^4A_1$,$^4A_2$. The fixed values of $Dq=-600\ cm^{-1}$, and $Ne=0.967$ are used in the calculation.

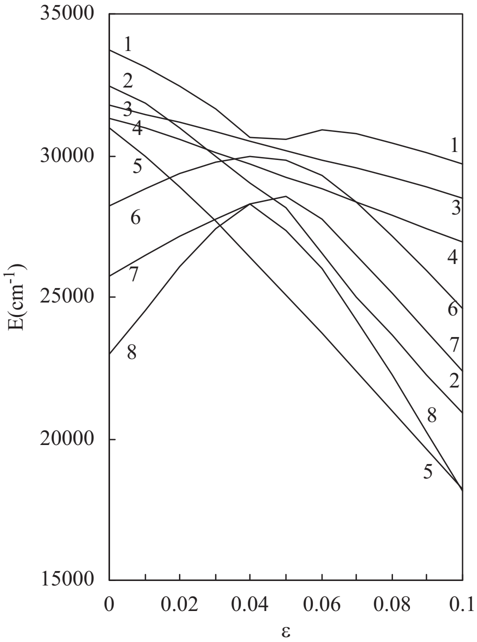

Fig. 2. Variation of the energy levels of Mn^{2+} for spin four-level system with the covalent parameter ε. The energy E is the difference between the state $^{2s+1}\Gamma$ term and the ground state $^6A_1$ term. The states 1–8 are $^2T_{2e}$,$^2T_{2c}$,$^2A_{1c}$,^2E_e, ^2E_d,$^2A_{2c}$,$^2T_{1h}$,$^2T_{2j}$. The fixed values of $Dq=-600\ cm^{-1}$, and $Ne=0.967$ are used in the calculation.

Table 1
Energy levels of Mn^{2+} in ZnS (in cm^{-1}).

	Calculation 1	Experiment [27]	Calculation 2
$^4T_{2a}$	36,235		35,905
$^2T_{2d}$	36,171		36,674
$^4A_2$	35,778		37,300
^2E_e	35,432		36,449
$^2T_{1f}$	35,207		35,978
$^2A_{2a}$	34,898	34,000	34,054
$^4T_{1b}$	34,482		34,585
$^2T_{2a}$	32,681		26,918
$^2T_{2e}$	29,910	30,800	32,113
$^2A_{1c}$	29,140		29,896
$^2T_{1a}$	28,825		27,380
^2E_d	28,575		29,047
$^2T_{2c}$	27,892		26,169
$^2A_{2c}$	26,849		29,312
^4E_b	26,003	25,297	26,751
$^4T_{1a}$	25,675	26,500	24,195
$^4T_{2b}$	24,810	22,638	20,647
^2E_b	24,300		22,661
$^2T_{1h}$	23,583		26,716
$^2T_{2j}$	21,547		28,176
^4E_a	20,474	21,237	20,846
$^4A_1$	20,631	21,237	21,152
$^4T_{2c}$	19,891	19,684	26,081
$^4T_{1c}$	18,048	17,891	20,814

$Dq=-800\ cm^{-1}$
Calculation 1: $N_e=0.955$, $N_t=0.938$ Calculation 2: $N_e=0.967$, $b=0.938$