

# Double Covalency Factors and Double Model in Study on Optical and Magnetic Properties of Diluted Magnetic Semiconductors $\text{ZnX} : \text{Co}^{2+}$

Shi Siqi, Lei Minsheng and Ouyang Chuying

(Department of Physics, Jiangxi Normal University, Nanchang 330027, China)

**Abstract:** The optical absorption spectra of the covalent crystals  $\text{ZnX}$  ( $X = \text{S}, \text{Se}$ ) doped with  $\text{Co}^{2+}$  are studied using the double covalency factors, which considers the anisotropic distortion of  $e_g$  and  $t_{2g}$  orbitals for d electron. When the paramagnetic  $g$  factor is calculated, the contributions of the spin-orbit coupling from the ligand ions are taken into account besides that from the central ion, which is the double  $\xi$  model. The calculated results indicate that the theoretical values coincide with the experimental values very well. This suggests that the method presented in this paper could be more valid to some strongly-covalent crystals.

**Key words:** diluted magnetic semiconductors; double covalency factors; double spin-orbit coupling

**PACC:** 7170C; 7170E; 7125J

**CLC number:** O734

**Document code:** A

**Article ID:** 0253-4177(2002)09-0897-05

## 1 Introduction

The II-VI compounds doped by the transition-metal impurities such as  $\text{ZnX} : \text{Co}^{2+}$  ( $X = \text{S}, \text{Se}$ ) are a group of important diluted magnetic semiconductors (DMS). Many researchers have experimentally and theoretically studied their optical absorption spectra, EPR spectra etc.<sup>[1~3]</sup>. Some valuable results have been gained. However, nearly no researches about the optical spectra differ the  $e_g$  orbit from the  $t_{2g}$  orbit. And the spin-orbit (S-O) coupling from the ligand ions was also neglected when the paramagnetic  $g$  factor was calculated. The above model is, in fact, a reducing classical crystal-field model. It describes the covalency only by the single orbital reduction factor (the average covalency factor), and considers simply the contribution of S-O coupling from the central transition-metal ion to  $g$  factor. Of course, for some crystals with strong ionic-

ty and small S-O coupling from ligand ions, such as N, O and F, this reducing model is surely a approximate way.

However, most of the II-VI compounds possess strong covalency, and the d-p electrons' orbital hybridization causes the anisotropic distortion for the  $e_g$  and  $t_{2g}$  orbitals of the d electron<sup>[4]</sup>. In the early 70's, Curie *et al.* had once dealt with the double covalency factors  $N_t, N_e$  for describing covalent bond though they neglected the contribution of Racah parameter  $A$ <sup>[5]</sup>. The value of  $N_e$  is a little smaller than that of  $N_t$  due to the greater bonding character of  $e_g$  orbitals<sup>[6]</sup>. Therefore, if we adopt the single average covalency factor  $N$  to describe the covalency effect, the contribution of Racah parameter  $A$  is actually offset, resulting in the difference between the theoretical values and the experimental ones. In order to consider the real effect of Racah parameter  $A$ , we have to use the double covalent factors ( $N_t \neq N_e$ ) to study the optical spectra of

\* Project supported by Natural Science Foundation of Jiangxi Province (Grant No. 981001)

the diluted magnetic semiconductors  $\text{HgS} : \text{Co}^{2+}$  crystals<sup>[7]</sup>. The calculated results are identical to the experimental values. Moreover, it is worthwhile to point out that the S-O coupling from ligand ions which was usually neglected in the previous works pertains to the paramagnetic g factor. In this paper, it is suggested that the S-O coupling from ligand ions may not be neglected for the strongly-covalent crystals, based on which a double  $\xi$  model was proposed to replace the single  $\xi$  model in the strong-field perturbation-loop method developed by Macfarlane<sup>[8,9]</sup>. The optical and magnetic properties of  $\text{ZnX} : \text{Co}^{2+}$  were also investigated and the calculated results coincide with the experimental data very well.

## 2 Theory

In the cubic strong field, the perturbation-Hamilton of  $3d^7$  configurations can be written as<sup>[10]</sup>:

$$H = H_e(A, B, C) + H_{so} + H_z \quad (1)$$

where  $H_e(A, B, C)$  is the off-diagonal electrostatic Coulomb interaction,  $H_{so}$  is the S-O coupling interaction, obviously, it should include both contributions from the d electron of central transition-metal ion and the p electron of ligand ions. Thus, this Hamilton may be given by

$$H_{so} = H_{so}(d) + H_{so}(p) \quad (2a)$$

$$\text{and } H_{so}(d) = \sum_i \xi_d(r_i) L_i S_i \quad (2b)$$

$$H_{so}(p) = \sum_n \xi_p(r_n) L_n S_n \quad (2c)$$

The third term of formula (1) is called Zeeman interaction. If the external magnetic field is  $H$ , according to the strong-field perturbation-loop method<sup>[8,9]</sup>, the  $H_z$  can be defined by the following form<sup>[3]</sup>

$$H_z = \sum_i \mu_B(L_i + g_e S_i) H \quad (3)$$

All symbols in Eqs. (2) ~ (3) have their usual meanings.

Considering the covalency effect and the S-O couplings, by means of the LCAO molecular or-

bits, the one-electron basic functions can be written as:

$$|\gamma\rangle = N_\gamma (|\mathcal{d}_\gamma\rangle - \lambda_\gamma |p_\gamma\rangle) \quad (4)$$

where  $\mathcal{Y} = e_g$  and  $t_{2g}$  are the irreducible representations of the cubic ( $T_d$ ) point group,  $N_\gamma$  and  $\lambda_\gamma$  are the normalization and mixture coefficients of molecular orbits, respectively.

Under the cubic strong-field scheme<sup>[10]</sup>, the zero-order wave functions may be obtained. Then, using Eqs. (1) ~ (4) and the strong-field perturbation-loop method, a perturbation-theory expression of the g factor in the ground state  ${}^4A_2(t_{2g}^3)$  can be obtained as follows

$$g = g_e + g(\xi) + g(\xi) + g(\xi, \xi) \quad (5a)$$

$$g(\xi) = -\frac{8k_2 \xi}{3E_1} - \frac{4k_2 \xi \xi + 2(2g_e - k_1) \xi}{9E_1^2} + \frac{4(k_1 - 2g_e) \xi}{9E_3^2} - \frac{2(k_1 + g_e) \xi}{3E_2^2} + \frac{4k_2 \xi \xi}{9E_1 E_3} - \frac{4k_2 \xi \xi}{3E_1 E_2} + \frac{4k_2 \xi \xi}{3E_2 E_3} \quad (5b)$$

$$g(\xi) = \frac{8k_2 \xi}{3E_1} + \frac{4k_2 \xi \xi - 2(2g_e - k_1) \xi}{9E_1^2} + \frac{4(k_1 - 2g_e) \xi}{9E_3^2} - \frac{2(k_1 + g_e) \xi}{3E_2^2} - \frac{4k_2 \xi \xi}{9E_1 E_3} + \frac{4k_2 \xi \xi}{3E_1 E_2} - \frac{4k_2 \xi \xi}{3E_2 E_3} \quad (5c)$$

$$g(\xi, \xi) = \frac{4(2g_e - k_1) \xi \xi}{9E_1^2} - \frac{8(k_1 - 2g_e) \xi \xi}{9E_3^2} - \frac{4(k_1 + g_e) \xi \xi}{3E_2^2} - (\xi \xi - \xi \xi) \times \left[ \frac{4k_2}{9E_1^2} - \frac{4k_2}{9E_1 E_3} + \frac{4k_2}{3E_1 E_2} - \frac{4k_2}{3E_2 E_3} \right] \quad (5d)$$

In Eqs. (5a) ~ (5d),  $g_e = 2.0023$ ,  $k_1 = N_e^2(1 + \frac{1}{2}\lambda)$ ,  $k_2 = N_t N_e(1 - \frac{1}{2}\lambda\lambda)$ ,  $\xi = N_t N_e \xi$ ,  $\xi = N_e^2 \xi$ ,  $\xi = \frac{1}{2} N_t N_e \lambda \lambda \xi$ ,  $\xi = \frac{1}{2} N_e^2 \lambda \xi$ , where  $\xi$  and  $\xi$  are the S-O coupling parameters of the d electron of the central free transition-metal ion and the p electron of the free ligand ions, respectively; the subscripts t and e denote  $t_{2g}$  and  $e_g$  orbits, and  $g_e (= 2.0023)$  is the spin-only value; the energy denominators  $E_i$  are energy of the excited states  ${}^4T_2(t_{2g}^2 e)$ ,  ${}^2T_2(t_{2g}^3)$ ,  ${}^2T_2(t_{2g}^2 e)$  and the ground state  ${}^4A_2(t_{2g}^3)$  which can be calculated from following equations:

$$\begin{aligned}
 E_1 &= E(^4T_2) - E(^4A_2) = (-2A + 10B)N_e^4 \\
 &\quad + (2A - 10B)N_t^2N_e^2 + 10D_q \\
 E_2 &= E(^2T_2) - E(^4A_2) = (5A + 15B)N_e^4 \\
 E_3 &= E(^2T_2) - E(^4A_2) = (-2A + 10B)N_e^4 \\
 &\quad + (2A - B + 3C)N_t^2N_e^2 + 10D_q
 \end{aligned}$$

Evidently, taking  $\lambda = \lambda = 0$  and  $N_t = N_e = N$ , then Eq. (5) will return to the classical expression<sup>[10]</sup>.

### 3 Applications

In this section, the expression of the  $g$  factor for the  $^4A_2(t_2^3)$  term developed in Section 2 is applied to  $Co^{2+}$  in  $ZnX$  ( $X=S, Se$ ). For the free  $Co^{2+}$  ion, the Racah parameters  $A = 16118\text{cm}^{-1}$ ,  $B = 1115\text{cm}^{-1}$  and  $C = 4366\text{cm}^{-1}$ <sup>[11]</sup>. Using energy matrix in the Ref. [8] (or referring to Appendix), we may obtain the double covalency factors  $N_t$  and  $N_e$ , and the crystal field parameter  $D_q$  with the least squares fit method. Thus, the theoretical values of the optical spectra of  $Co^{2+}$  in cubic  $ZnX$  ( $X=S, Se$ ) crystals can be easily calculated, and the results are shown in Table 1 and Table 2. It can be seen that our calculated values are in good agreement with the experimental values.

Table 1 Optical spectra of  $Co^{2+}$  in cubic ZnS crystals  $\text{cm}^{-1}$

Transition	Theoretical value	Experimental value <sup>[2]</sup>
ZnS : $Co^{2+}$	$N_t=0.9231, N_e=0.8465, D_q=378$	
$^4A_2(F) \rightarrow ^4T_1(F)$	6540	5924.2~7183.9
$^4A_2(F) \rightarrow ^2E(G)$	12535	12547
$^4A_2(F) \rightarrow ^2T_{1a}(G)$	12899	12804
$^4A_2(F) \rightarrow ^2T_{1b}(G)$	13200	13106
$^4A_2(F) \rightarrow ^4T_1(P)$	14512	14472
$^4A_2(F) \rightarrow ^2A_1(G)$	14986	15015

Table 2 Optical spectra of  $Co^{2+}$  in cubic ZnSe crystals  $\text{cm}^{-1}$

Transition	Theoretical value	Experimental value <sup>[2]</sup>
ZnSe : $Co^{2+}$	$N_t=0.9115, N_e=0.8249, D_q=391$	
$^4A_2(F) \rightarrow ^4T_1(F)$	6086	5887.2~6290.5
$^4A_2(F) \rightarrow ^2E(G)$	11670	11696
$^4A_2(F) \rightarrow ^2T_{1a}(G)$	12215	12106
$^4A_2(F) \rightarrow ^2T_{1b}(G)$	12305	12225
$^4A_2(F) \rightarrow ^4T_1(P)$	14000	13682~14265
$^4A_2(F) \rightarrow ^2A_1(G)$	14278	

To determine the mixture-coefficients  $\lambda$  of LCAO, the normalization condition of the orbits in Eq. (4) may be used. So we have

$$N^2(1 - 2\lambda S_{dp}(\gamma + \bar{\lambda})) = 1 \quad (6)$$

where  $S_{dp} = \langle d\gamma | p\gamma \rangle = \int d\gamma^*(1)p\gamma(2) d\tau d\tau$  is the group overlap integral of  $d\gamma$  and  $p\gamma$  orbits, it is related to the distance  $R$  between the impurity and its ligand. In general,  $R$  is not equal to the distance  $R_H$  between the positive ion and negative ion of the base material. However, the distance  $R$  can be determined by<sup>[12]</sup>:

$$R \approx R_H + \frac{1}{2}(r_i - r_h) \quad (7)$$

where  $r_i$  and  $r_h$  are the radiuses of the impurity-ion and the replaced ion, respectively. Their values are  $r_i(Co^{2+}) = 0.072\text{nm}$ ,  $r_i(Zn^{2+}) = 0.074\text{nm}$ ,  $R_H(ZnS) = 0.2369\text{nm}$  and  $R_H(ZnSe) = 0.289\text{nm}$  may be found from the crystallographic data<sup>[13]</sup>. Therefore,  $R(Co^{2+} \sim S^{2-}) = 0.2359\text{nm}$  and  $R(Co^{2+} \sim Se^{2-}) = 0.288\text{nm}$ .

As is well known that it is often convenient to use the Slater orbit in computation of the overlap integral, but a reasonable S-O coupling coefficient cannot be found from the orbits. On the contrary, the SCF (self-consistent field) orbit is capable of yielding a reasonable S-O coupling coefficient. We hence use the Slater-type SCF functions<sup>[14,15]</sup> to calculate the group overlap integral  $S_{dp}(\gamma)$ . Consequently, the LCAO coefficients  $\lambda$  can be determined by using Eq. (6) and the double covalency factors  $N_t$ . Finally, can be calculate the value of the  $g$  factor in  $ZnX : Co^{2+}$ . The results are given in Table 3 and Table 4.

Table 3 Group overlap integrals and coefficients in  $ZnX$  ( $X=S, Se$ ) crystals

samples	$\langle d_e   p_e \rangle$	$\langle d_t   p_t \rangle$	$N_t$	$N_e$	$\lambda$	$\bar{\lambda}$
ZnS : $Co^{2+}$	0.06980	0.02406	0.9231	0.8465	0.44135	-0.562991
ZnSe : $Co^{2+}$	0.06231	0.02278	0.9115	0.8249	0.47458	-0.625786
$\xi(Co^{2+}) = 533\text{cm}^{-1}$ , $\xi(S^{2-}) = 365\text{cm}^{-1}$ , $\xi(Se^{2-}) = 1659\text{cm}^{-1}$ <sup>[18,19]</sup>						

Table 4 Paramagnetic  $g$  factor value of  $\text{Co}^{2+}$  in  $\text{ZnX}$  ( $X=\text{S,Se}$ ) crystals

Samples	$g_{\text{cal}}$ (in the present work)					$g_{\text{cal}}$ (in the classical model) [17]	$g_{\text{obs}}$ (experiment) [16]
	$g_e$	$g(\xi_1)$	$g(\xi_2)$	$g(\xi_3, \xi_4)$	$g$		
$\text{ZnS} : \text{Co}^{2+}$	2.0023	0.2561	-0.0285	0.0081	2.238	2.215	2.248
$\text{ZnSe} : \text{Co}^{2+}$	2.0023	0.2901	-0.0419	0.0095	2.260	2.233	2.274

## 4 Discussion and conclusion

This work presents an approach to the calculation of the optical absorption spectrum and  $g$  factor in  $\text{ZnX} : \text{Co}^{2+}$  ( $X=\text{S,Se}$ ). With this model, the calculated results are found to agree with experimental data well. Thus, the puzzle that the  $g$  factor calculated by the classical model was always smaller than experimental data is explained. From this paper the following conclusions are drawn: (1) The approximate method in the paper is more reasonable for the more strongly-covalent crystals in which the S-O coupling from the ligand ions is notably large. (2) Although the theoretical formula in this paper deals with the seven-electron (three-hole) system in the cubic strong field, we think that the formula should be valid to the covalent crystals containing not only  $\text{Co}^{2+}$  ion but also  $\text{V}^{2+}$  ion or  $\text{Cr}^{3+}$  ion (three-electron). It means that the neglect of contributions of Racah parameter  $A$  and the S-O coupling from ligand ions is also not reasonable in strongly-covalent crystals containing  $\text{V}^{2+}$  ion or  $\text{Cr}^{3+}$  ion. (3) For other symmetrical systems, we infer that adopting this approximate method can also come to results fitting better to experimental data.

## References

[1] Vallin J T, Watkins G D. EPR of  $\text{Cr}^{2+}$  in  $\text{II-VI}$  lattice. *Phys Rev B*, 1974, 9(5):2051

[2] Chen Chenjia, Wang Xuezhong, Liu Guobin. Energy spectrum of new type diluted magnetic semiconductors  $\text{Zn}_{1-x}\text{Co}_x\text{Se}$  and  $\text{Zn}_{1-x}\text{Co}_x\text{S}$ . *Universitatis Pekinensis (Acta Scientiarum Naturalium)*, 1995, 31(5):586 (in Chinese) [陈辰嘉, 王学忠, 刘国彬. 新型稀磁半导体  $\text{Zn}_{1-x}\text{Co}_x\text{Se}$  和  $\text{Zn}_{1-x}\text{Co}_x\text{S}$  的能谱. 北京大学学报(自然科学版), 1995, 31(5):586]

[3] Li Fuzhen, Zhou Yiyang. Theoretic study of ground state fine split of  $\text{ZnSe} : \text{Fe}^{2+}$  and anisotropy's of carbon. *Acta Physica*

*Sinica*, 1998, 47(3):472 (in Chinese) [李福珍, 周一阳.  $\text{ZnSe} : \text{Fe}^{2+}$  的基态精细分裂和碳的各向异性理论研究. 物理学报. 1998, 47(3):472]

[4] Fazzio A, Galads M J, Zunger A. Many-electron multiplet effects in the spectra of  $3d$  impurities in heteropolar semiconductors. *Phys Rev B*, 1984, 30:3430

[5] Curie D, Barthou C, Canny B. Covalent bonding of  $\text{Mn}^{2+}$  ions in octahedral and tetrahedral coordination. *J Chem Phys*, 1974, 61(8):3048

[6] Zheng Wenchen, Wu Shaoyi, Ren Ping. Theoretical investigations of the zero-field splitting and  $g$  factors for  $\text{CdS} : \text{Ti}^{2+}$  and  $\text{CdSe} : \text{Ti}^{2+}$  crystals. *Physica B*, 1999, 269:314

[7] Shi Siqi, Lei Minsheng. The application of the double covalency factors in the optical spectra for the semimagnetic semiconductors  $\text{HgS} : \text{Co}^{2+}$ . *Acta Photonica Sinica*, 2000, 29(12):1096 (in Chinese) [施思齐, 雷敏生. 双共价因子在半磁半导体  $\text{HgS} : \text{Co}^{2+}$  光谱中的应用. 光子学报, 2000, 29(12):1096]

[8] Macfarlane R M. Zero field splitting of  $t_2^3$  cubic terms. *J Chem Phys*, 1967, 47:2066

[9] Macfarlane R M. Perturbation methods in the calculation of zeeman interactions and magnetic dipole line strengths for  $d$  trigonal-crystal spectra. *Phys Rev B*, 1970, 1:989

[10] Sugano S, Tanabe Y, Kaminura H. Multiplets of transition metal ions in crystals. London: Academic Press, 1970

[11] Skinner H A, Summer F H. The valence of the elements V, Cr, Mn, Ni, and Cu. *J Inorg Nucl Chem*, 1957, 4:245

[12] Hernández D, Rodríguez F, Moreno M, et al. Pressure dependence of the crystal field spectrum of the  $\text{NH}_4\text{MnCl}_3$  perovskite: correlation between  $^{10}\text{Dq}$ , Ne and Nt, and the Mn-Cl distance in  $\text{MnCl}_2$  complexes. *Physica B: Condensed Matter*, 1999, 265(1~4):186

[13] Weast R C. CRC handbook of chemistry and physics. Boca Baton: CRC Press, 1989

[14] Clementi E, Raimondi D L. Atomic screening constant SCF function. *J Chem Phys*, 1963, 38:2686

[15] Clementi E, Raimondi D L, Reinhardt W P. Atomic screening constant SCF functions(II): atomic with 37 to 86 Electrons. *J Chem Phys*, 1967, 47:1300

[16] Chen Chenjia, Gao Wei, Qin Zhifeng, et al. Magnetization and magnetic susceptibility of the diluted magnetic semiconductors  $\text{Zn}_{1-x}\text{Co}_x\text{S}$  and  $\text{Zn}_{1-x}\text{Co}_x\text{Se}$ . *J Appl Phys*, 1991, 70(10):6277

[17] Sugano S, Peter M. Effect of configuration mixing and covalency on the energy spectrum of ruby. *Phys Rev*, 1961, 122:381

[18] Viccaro de A M H, Sundaram S, Sharma R R. Electron paramagnetic resonance of substitutional  $\text{Cr}^{2+}$  impurity in  $\text{GaAs}$  by a cluster approach. *Phys Rev B*, 1982, 25:7731

[19] Fraga S, Saxena K M S, Karwowski J. Handbook of atomic data. New York: Elsevier Press, 1976

# 稀磁半导体 $\text{ZnX}:\text{Co}^{2+}$ 光磁性质的双共价因子和双 $\xi$ 模型\*

施思齐 雷敏生 欧阳楚英

(江西师范大学物理系, 南昌 330027)

**摘要:** 考虑到 d 电子  $t_{2g}$  轨道与  $e_g$  轨道局域性的差异, 用双共价因子研究了掺  $\text{Co}^{2+}$  的共价晶体  $\text{ZnX}$  ( $X=\text{S}, \text{Se}$ ) 的光学吸收谱. 在研究顺磁  $g$  因子时, 除考虑中心离子的旋-轨耦合贡献外, 还计及配体的旋-轨耦合贡献(双  $\xi$  模型). 研究表明, 计算结果与实验值吻合得很好, 对于一些共价性较强的化合物晶体, 该方法更加有效.

**关键词:** 稀磁半导体; 双共价因子; 双旋-轨耦合

**PACC:** 7170C; 7170E; 7125J

**中图分类号:** O734      **文献标识码:** A      **文章编号:** 0253-4177(2002)09-0897-05

\* 江西省自然科学基金资助项目(No. 981001)

2002-01-12 收到, 2002-04-15 定稿