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Nephelauxetic-Effect in DMS $Zn_{1-x}Co_xSe$ and Effect of Pressure on Nephelauxetic-Effect*

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Abstract: Based on the 3D electron's radial wave function of Co^{2+} free ion, a Nephelauxetic-effect modifying factor to modify the radial wave function is introduced when Co^{2+} cations are put into the crystal field of $Zn_{1-x}Co_xSe$. With the modified wave functions, the optical transitions for $Zn_{1-x}Co_xSe$ crystals are calculated. Moreover, based on the first principle of physics, the influences of high-pressure to the Nephelauxetic-effect modifying factor is considered, and the high-pressure blue shift for the $Zn_{1-x}Co_xSe$ crystal absorption spectra are calculated and a shift rate of $dE/dp = 0.45$meV/GPa is obtained.

Key words: diluted magnetic semiconductors; Nephelauxetic-effect; radial wave functions; high-pressure effect
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1 Introduction

Diluted magnetic semiconductors (DMS), which are also called semi-magnetic semi-conductors (SMSC), are a class of semiconducting materials formed by randomly replacing some of the cations in II-VI compounds (like CdTe, ZnSe, CdSe, CdS, etc.) with transition metal ions (e.g. Mn, Fe or Co). From the beginning, it attracted attention of many investigators because of its remarkable magnetic and optic properties[1~4]. In the past years, a lot of works have been done, such as introducing the spin-orbit (S-O) interaction influences and considering the Jahn-Teller effect[5,6], to get the fine structure spectra. In the same time, high-pressure and high temperature optical properties of DMS have also been investigated[7~9]. But most of the previous works are only experimental results with quite brief explanations. We can not find an approach that comes from the first principle of physics. So a general theory is needed to explain those optical and magnetic phenomena. Dreyhsig[10] had proposed the charge-transfer concept to explain the optical transitions of some DMS, but his explanations were on the basis of photon theory.

At the beginning of the 20th century, crystal field theory was established to explain the bonding characters of the metal complexes. But when we use the crystal field theory, the electrons wave function of the ions in crystal must be obtained firstly. Slater[11] had proposed a d-orbit wave function (STO) and had successfully calculated the values of the Racah electrostatic parameters B and C with this function, but the spin-orbit coupling coefficient ξ_{3d} variated much from experimental values.

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Later, by studying the experimental spectra of the first transition metal free ions or by SCF method, some more precise 3D electron's radial wave functions were obtained[12,13]. Based on these radial wave functions, considering the influences of the Nephelauxetic-effect in the DMS complexes, in this paper we introduced a Nephelauxetic-effect modifying factor κ to modify these functions, and then get the optimal 3D electrons' radial wave functions of the ions in the DMS complexes. With these functions and a point charge-dipole model of the crystal field theory, it is easy to calculate the absorption spectra of $Zn_{1-x}Co_xSe$ crystal, and quantitatively describe the Nephelauxetic-effect. Considered the influences of high-pressure to the Nephelauxetic-effect, the form of Nephelauxetic-effect factor κ was modified, and the high-pressure shifts of the spectra was obtained conveniently.

2 Nephelauxetic-effect in $Zn_{1-x}Co_xSe$ crystal

Nephelauxetic-effect was first proposed by Jørgensen[14]. Jørgensen's point is that: if free ions are put into the crystals, their electron cloud will "expand", which leads to an energy level shift comparing with the free ion state. This effect is called as Nephelauxetic-effect. Obviously the essence of the Nephelauxetic-effect is due to the partly shift of the electrons from the complex to the center ion. From Reference[11] we know that the physical meaning of the parameter ζ in Slater's d-orbit wave function STO represents the effective nuclear charge number of the center ion. Later, though the double parameters ζ_1 and ζ_2 in Zhao's[13] and Mei's[12] double STO type radial wave functions are not directly represent the effective nuclear charge number of the center ion, the two parameters are directly controlled by the quantity of the charge of the center ion. Since the essence of the Nephelauxetic-effect is due to the partly shift of the electrons from the complex to the ion, which makes a reduction of the effective nuclear charge, we may introduce a Nephelauxetic-effect modifying factor κ($0 \leqslant \kappa \leqslant 1$) in the wave function to lower the effective nuclear charge number.

The double STO type 3D electrons' radial wave functions are written as[12]:

$$R_{3d}(r) = \sum_{i=1,2} a_i N_i r^2 \exp(-\zeta r) \qquad (1)$$

where

$$N_i = \left[\frac{(2\zeta)^7}{6!}\right]^{1/2} \qquad i = 1, 2 \qquad (2)$$

and

$$a_1^2 + a_2^2 + 2a_1a_2\left[\frac{2\sqrt{\zeta_1\zeta_2}}{\zeta_1 + \zeta_2}\right]^7 = 1 \qquad (3)$$

Based on the experimental spectra of the first transition metal free ions, Mei *et al.*[12] had already come up with a series of optimal double STO type 3D electrons' radial wave functions, as for Co^{2+}:

$a_1 = 0.5850, a_2 = 0.6179, \zeta_1 = 5.85, \zeta_2 = 2.00$

Considering the influences of the Nephelauxetic-effect to the wave function, this paper introduced a Nephelauxetic-effect modifying factor for the functions, and then the radial wave function of Co^{2+} in $Zn_{1-x}Co_xSe$ crystal can be expressed as:

$$R_{3d}(r) = \sum_{i=1,2} a_i N_i r^2 \exp(-\kappa\zeta r) \qquad (4)$$

where

$$N_i = \left[\frac{(2\kappa\zeta)^7}{6!}\right]^{1/2} \qquad i = 1, 2 \qquad (5)$$

a_1, a_2 in formula (4) also satisfy equation (3).

Since x is very small ($x \leqslant 0.01$) in $Zn_{1-x}Co_xSe$, it is assumed that the Co^{2+} cations replace the Zn^{2+} cations without altering the crystal symmetry. So, we may approximately take it as a T_d symmetry. From the crystal field theory, using the point charge-dipole model, the cubic crystal field parameter is:

$$D_q = -\frac{2}{27}\left(1 + \frac{5\mu}{eR}\right)\frac{qe\langle r^4\rangle}{R^5} \qquad (6)$$

where μ refers to the dipole moment of Se^{2-} ion, q is the charge of Se^{2-} ion, so $q = -2e$. By fitting the experimental results, we set $\kappa = 0.8863$, $\mu = 0.117eR$, e is the charge of the electron, R is the average bond length of Se^{2-} to Co^{2+}. Here R is not equal to the distance R_H between Zn^{2+} ion and Se^{2-}

ion. But it may be approximately equal to the following[15]:

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

where r_i and r_h are the radiuses of the impurity-ion and the replaced ion, respectively. Their values r_i= 0.072nm, r_h = 0.074nm, R_H = 0.289nm can be found from the crystallographic data[16]. Then we have R= 0.288nm.

From the wave function expressed by formula (4), we can have the values of the Racah electrostatic parameters B, C, and spin-orbit coupling coefficient ξ_{3d} as the following:

$$B = \frac{F^2}{49} - \frac{5F^4}{441} = 602.8(cm^{-1}) \tag{8}$$

$$C = \frac{35F^4}{441} = 2655.3(cm^{-1}) \tag{9}$$

where

$$F^k = e^2 \int_0^\infty \int_0^\infty r_1^2 r_2^2 \frac{r_<^k}{r_>^{k+1}} R_{3d}^2(r_1) R_{3d}^2(r_2)\, dr_1 dr_2 \tag{10}$$

ξ_{3d}= 389cm^{-1}. With these results, we calculated the absorption spectra of the $Zn_{1-x}Co_xSe$ crystal as shown in Table 1 in which the experimental values are from Reference[17]. From Table 1 we know that the calculated values are in very good agreement with the experimental values.

Table 1　Optical spectra of Co^{2+} in cubic ZnSe crystals

Transition	Theoretical value		Experimental value[17]	
	v/cm^{-1}	Energy/eV	v/cm^{-1}	Energy/eV
$^4A_2(F) \rightarrow {}^4T_1(F)$	6007	0.745	5887	0.73
$^4A_2(F) \rightarrow {}^2E(G)$	11673	1.447	11696	1.45
$^4A_2(F) \rightarrow {}^2T_1(G)$	12156	1.507	12106	1.50
$^4A_2(F) \rightarrow {}^4T_1(P)$	14260	1.767	14265	1.77
$^4A_2(F) \rightarrow {}^2A_1(G)$	14775	1.831	14688	1.82
$^4A_2(F) \rightarrow {}^2T_2(G)$	16893	2.094	16948	2.10
$^4A_2(F) \rightarrow {}^2H$	19007	2.356	18965	2.35
$^4A_2(F) \rightarrow {}^2P$	19921	2.469	19934	2.47
$^4A_2(F) \rightarrow {}^2D_1$	20954	2.597	21064	2.61

From Reference[12] we know that as for Co^{2+} free ion, B_0 = 1115cm^{-1}, ξ_{3d}^0 = 562cm^{-1}, the Jφrgensen factors are[14]:

$$\beta = \frac{B}{B_0} = 0.541, \quad \beta^* = \frac{\xi_{3d}}{\xi_{3d}^0} = 0.693$$

Thus the Nephelauxetic-effect of Co^{2+} in $Zn_{1-x}Co_xSe$ crystal can be quantitatively described.

3　Influences of high-pressure to the Nephelauxetic-effect of $Zn_{1-x}Co_xSe$ crystal

When the crystal is under high pressure, the bond length will be compressed, which leads to a declension for Racah electrostatic parameter B, C and the cubic crystal field parameter D_q and the spin-orbit coefficient ξ_{3d}. References[18, 19] have already reported this kind of changes. Now we set the point beginning from the Nephelauxetic-effect, and try to reveal the physical essence of this phenomenon.

Reference[18] have defined the liner compression ratio X as:

$$X = R/R_0 \tag{11}$$

where R_0 and R refer to the bond length under normal pressure and high-pressure condition respectively. While the X ratio we use here just bases on three assumptions:

(1) The crystal is isotropy to pressure.

(2) There are no phase transformation.

(3) The symmetry of crystal will not be changed under high-pressure.

Reference[20] had reported the relationship between the volume of the crystal and pressure as:

$$\frac{V_0 - V}{V_0} = ap - bp^2 \tag{12}$$

where V_0 and V refer to the volume of the crystal at normal pressure and high-pressure condition respectively, then:

$$X = R/R_0 = (1 - ap + bp^2)^{1/3} \tag{13}$$

Because of the influences of pressure, the Nephelauxetic-effect modifying factor κ will be a function of the pressure p.

$$\kappa = \kappa'(p) \tag{14}$$

When the bond length changes with the pressure, it consequently influences the κ factor, and the bond length change can be described by X; thus we can get the relationship between κ and X as the following:

$$\kappa = \kappa(X) \tag{15}$$

and spread out formula(15) by Taylor series expansion:

$$\kappa = \sum_{i=0}^{\infty} k_i (1 - X)^i \qquad (16)$$

Normally, the compression is very small, which means $X \approx 1$, so $(1 - X)$ is very small. Thus we may take the first two items $i = 0, 1$ from the right hand side of formula(16), therefore:

$$\kappa = \kappa_0 + \kappa_1 (1 - X) \qquad (17)$$

where κ_0 refers to the modifying factor at normal pressure condition. As for $Zn_{1-x}Co_xSe$ crystal, from the previous discussion we know that $\kappa = 0.8863$.

Reference[9] has reported the blue shifts for the absorption spectra of the $Zn_{1-x}Co_xSe$($x = 0.01$) crystal, now we choose the 1.767eV line [transition: $^4A_2(F) \rightarrow {}^4T_1(P)$] to test our theory. Comparing with the experimental results, fitting the values of κ_1, a, b, we set $k_1 = 0.531$, $a = 0.0076$, $b = 0.0018$, thus we calculated the high-pressure blue shift of the $Zn_{1-x}Co_xSe$ absorption spectra. The results are shown in Fig. 1. From the figure, we know that the theoretical values are in good agreement with the experimental values, and yielding the positive value of $dE/dp = 0.45$meV/GPa.

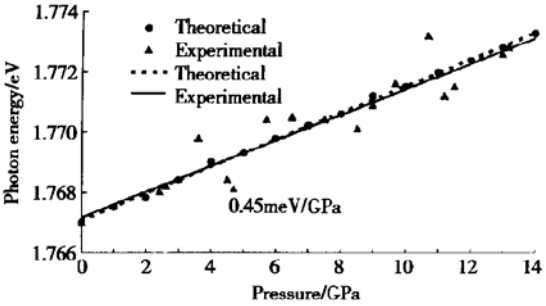

Fig. 1 High-pressure blue shift

4 Conclusion

From the previous discussion, it can be concluded that the method of introducing a Nephelauxetic-effect modifying factor to modify the free ions radial wave function is effective to handle the problems of DMS absorption spectra, and it is especially convenient when high-pressure problems are concerned.

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稀磁半导体 $Zn_{1-x}Co_xSe$ 中的电子云延伸效应及压力对电子云延伸效应的影响*

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摘要: 通过对 Co^{2+} 自由离子的 3D 电子径向波函数进行分析, 引入了一个电子云延伸效应修正因子 κ 来修正这一波函数, 从而得到了稀磁半导体 $Zn_{1-x}Co_xSe$ 晶体中 Co^{2+} 受到了晶体场作用的 3D 电子径向波函数. 应用这一修正后的波函数, 计算了 $Zn_{1-x}Co_xSe$ 晶体的光谱跃迁. 从物理学的本质出发, 考虑了高压力对电子云延伸效应修正因子 κ 的影响, 并且计算了 $Zn_{1-x}Co_xSe$ 晶体吸收谱的压力蓝移谱, 得到的蓝移率为 $dE/dp = 0.45 meV/GPa$.

关键词: 稀磁半导体; 电子云延伸效应; 径向波函数; 高压效应

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