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Theoretical study of spin singlets contributions to zero-field splitting and local lattice structure of Cr^{2+} in $CdGa_2S_4$

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ABSTRACT

A theoretical method for investigating the inter-relation between electronic and the molecular structures of a d^4 ion in a tetragonal ligand-field has been established on the basis of 210×210 complete energy matrix within a weak-field-representation. Using the method, the local structure parameters of $CdGa_2S_4$:Cr^{2+} system are determined by the experimental EPR zero-field splitting (ZFS) spectra. Our results show that the local structure around Cr^{2+} is a compression distortion and the local lattice structure parameters $R = 2.46$ Å and $\theta = 57.63°$ are determined. Moreover, the contributions of the spin singlets to ZFS parameters of Cr^{2+} ions in $CdGa_2S_4$ crystals are investigated for the first time. The results indicate that the spin singlets contributions to ZFS parameter D are negligible, but the contributions to ZFS parameters a and F cannot be neglected.

1. Introduction

Impurities in semiconductors have attracted a great deal of attention for many years owing to their significance for practical applications, as in photoconductors, microwave detectors, and electroluminescent devices [1–8]. Among the impurities, particular attention has been focused on the transition metal ions because they are commonly associated with deep levels within the host crystal band gap. Cadmium thiogallate, $CdGa_2S_4$, belongs to a wide class of $A^{II}B_2{}^{III}C_4{}^{VI}$ ternary semiconductors, which has been extensively studied in recent years [9–12]. It is known that the introduction of transition metal ions, particularly Cr^{2+}, into II–VI materials such as ZnSe and ZnS, has made it possible to extend their capabilities and to produce broadly tunable lasers [13]. Recently investigations demonstrate that $CdGa_2S_4$ doped with Cr^{2+} may also be a laser-active material [12]. The EPR spectra of transition metal Cr^{2+} ions doped into $CdGa_2S_4$ have been experimentally observed by Avanesov et al. [11]. Their experimental results give important information about the ground state of the transition metal Cr^{2+} ions and form a useful starting point for understanding the interrelationships between electronic and molecular structure of Cr^{2+} ions in $(CrS_4)^{6-}$ coordination complex. Despite the large number of publications relating to Cr^{2+} ions in a $CdGa_2S_4$:Cr^{2+} system, as yet a comprehensive report of its zero-field splitting parameters is lacking.

Theoretically, the studies of the electronic structure of transition metal Cr^{2+} impurities in crystals have made remarkable progress in the past decades by the ^5D approximation [14–16]. However, we have not fully been able to understand the nature of transition metal Cr^{2+} ions within this approach because the contributions of spin triplet states ^3L (L = H, G, F, D, P) and the spin singlets states ^1L (L = I, G, F, D, S) have been neglected in them. To remedy these discrepancies between theory and experiments, the spin triplet states contributions to the zero-field splitting (ZFS) for a d^4 configuration ion in crystals were performed by Zhou et al. [17–19]. Unfortunately, these method are still insufficient to understand the detailed information and physical origin of transition metal Cr^{2+} ions in crystals because the spin singlets states ^1L (L = I, G, F, D, S) influence the fine structure splitting of the ground states, i.e., affect the ground zero-field splitting parameters.

It is well known that the Hamiltonian matrix of a d^4 configuration in crystals has 210×210 dimensions for all the spin states but only 25×25 for the ^5D state and 160×160 for both ^5D and ^3L states. So, to obtain more accurate ZFS, all ^{2S+1}L multiplets with $S = 2$, 1 and 0 should be considered, i.e., a complete calculation. In this paper, complete energy matrices (210×210) of a d^4 configuration ion in a tetragonal ligand-field are constructed and the ZFS parameters a, D and F of the $CdGa_2S_4$:Cr^{2+} system are investigated. By diagonalizing the complete energy matrices, the local structure distortion parameters ΔR and $\Delta\theta$ are determined. Moreover, the contributions of the spin singlets to ZFS parameters of Cr^{2+} ions in $CdGa_2S_4$ crystals are investigated for the first time.

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Table 1
Spin Hamiltonian matrix.

S,M_S	2,2	2,−2	2,0	2,1	2,−1
2,2	$2D+\frac{a}{10}+\frac{F}{15}$	$\frac{a}{2}$	0	0	0
2,−2	$\frac{a}{2}$	$2D+\frac{a}{10}+\frac{F}{15}$	0	0	0
2,0	0	0	$-2D+\frac{3a}{5}+\frac{2F}{5}$	0	0
2,1	0	0	0	$-D-\frac{2a}{5}-\frac{4F}{15}$	0
2,−1	0	0	0	0	$-D-\frac{2a}{5}-\frac{4F}{15}$

2. Theoretical model

For the $CdGa_2S_4$:Cr^{2+} system, the local symmetry of the centers is tetragonal. The EPR spectrum of the tetragonal Cr^{2+} may be described in terms of the following spin Hamiltonian [20]:

$$\hat{H}_S = D(S_Z^2-2)+\frac{a}{120}(35S_Z^4-155S_Z^2+72) + \frac{a}{48}(S_+^4+S_-^4)+\frac{F}{180}(35S_Z^4-155S_Z^2+72) \quad (1)$$

where a, D and F are the so-called zero-field splitting parameters. a is the cubic field splitting parameter, D and F correspond to axial component of the second-order and the fourth-order, respectively. By combing the effective spin function $|SM\rangle$ for $S=2$, we can construct a set of spin basis functions of the irreducible representations Γ'' (A_1, A_2, B_2, E) of the $^5B_2$ ground state for spin Hamiltonian as follows:

$$\begin{aligned}
|A_1\rangle &= \frac{i}{\sqrt{2}}(|2-2\rangle-|22\rangle)\\
|A_2\rangle &= \frac{1}{\sqrt{2}}(|2-2\rangle+|22\rangle)\\
|E_y\rangle &= \frac{i}{\sqrt{2}}(|21\rangle+|2-1\rangle)\\
|E_x\rangle &= \frac{1}{\sqrt{2}}(|21\rangle-|2-1\rangle)\\
|B_2\rangle &= |20\rangle
\end{aligned} \quad (2)$$

With such a set of spin basis functions, the ZFS Hamiltonian matrix reduces into diagonal blocks, shown in Table 1. From this, it is very easy to obtain the eigenvalues of Eq. (1),

$$\begin{aligned}
E(A_1) &= 2D-\frac{2a}{5}+\frac{F}{15}\\
E(A_2) &= 2D+\frac{3a}{5}+\frac{F}{15}\\
E(E_\gamma) &= -D-\frac{2a}{5}-\frac{4F}{15}\quad(\gamma=x,y)\\
E(B_2) &= -2D+\frac{3a}{5}+\frac{2F}{5}
\end{aligned} \quad (3)$$

Thus, we have

$$\begin{aligned}
a &= E(A_2)-E(A_1)\\
D &= -\frac{1}{7}(E(E_\gamma)-E(A_1)-E(A_2)+E(B_2))\\
F &= \frac{3}{7}(3E(B_2)-3E(A_2)-4E(E_\gamma)+4E(A_1))
\end{aligned} \quad (4)$$

The values of $E(\Gamma'')$ can be obtained by comparison with the eigenvalues of the d^4 matrix corresponding to the orbitally non-degenerate ground state. It is noteworthy to mention that the parameters a, D and F are related to the ZFS parameters b_k^q. The relationships are given by

$$b_2^0=D,\qquad b_4^0=\frac{a}{2}+\frac{F}{3},\qquad b_4^4=\frac{5a}{2} \quad (5)$$

The Hamiltonian for a $3d^4$ configuration ion in a tetragonal ligand-field can be written as:

$$\hat{H}=\hat{H}_{ee}+\hat{H}_{SO}+\hat{H}_{LF}=\sum_{i<j}\frac{e^2}{r_{ij}}+\zeta\sum_i l_i\cdot s_i+\sum_i V_i \quad (6)$$

where $\hat{H}_{ee}$ denotes the electrostatic energy, $\hat{H}_{SO}$ denotes the spin–orbit coupling energy and $\hat{H}_{LF}$ denotes the ligand-field energy. ς is the spin–orbit coupling coefficient, and V_i is the ligand-field potential:

$$V_i=\gamma_{00}Z_{00}+\gamma_{20}r_i^2Z_{20}(\theta_i,\phi_i)+\gamma_{40}r_i^4Z_{40}(\theta_i,\phi_i) + \gamma_{44}^c r_i^4 Z_{44}^c(\theta_i,\phi_i)+\gamma_{44}^s r_i^4 Z_{44}^S(\theta_i,\phi_i) \quad (7)$$

where r_i, θ_i and ϕ_i are spherical coordinates of the ith electron. Z_{lm}, Z_{lm}^c and Z_{lm}^s are defined as:

$$\begin{aligned}
Z_{l0} &= Y_{l0}\\
Z_{lm}^c &= \frac{1}{\sqrt{2}}[Y_{l,-m}+(-1)^m Y_{l,m}]\\
Z_{lm}^S &= \frac{i}{\sqrt{2}}[Y_{l,-m}-(-1)^m Y_{l,m}]
\end{aligned} \quad (8)$$

The Y_{lm} in Eq. (8) are the spherical harmonics. γ_{l0}, γ_{lm}^c and γ_{lm}^s are associated with the local lattice structure of the $3d^4$ ion by the relations:

$$\begin{aligned}
\gamma_{l0} &= -\frac{4\pi}{2l+1}\sum_{\tau=1}^{n}\frac{eq_\tau}{R_\tau^{l+1}}Z_{l0}(\theta_\tau,\phi_\tau)\\
\gamma_{lm}^c &= -\frac{4\pi}{2l+1}\sum_{\tau=1}^{n}\frac{eq_\tau}{R_\tau^{l+1}}Z_{lm}^c(\theta_\tau,\phi_\tau)\\
\gamma_{lm}^s &= -\frac{4\pi}{2l+1}\sum_{\tau=1}^{n}\frac{eq_\tau}{R_\tau^{l+1}}Z_{lm}^s(\theta_\tau,\phi_\tau)
\end{aligned} \quad (9)$$

where $(R_\tau,\theta_\tau,\phi_\tau)$ are the spherical coordinates of the τth ligand, q_τ is its effective charge.

The matrix elements of Hamiltonian (6) are functions of the Racah parameters B and C, the spin–orbit coupling coefficient ζ, and the ligand-field parameters which are generally expressed as follows [21]:

$$\begin{aligned}
B_{20} &= \left(\frac{5}{4\pi}\right)^{1/2}\gamma_{20}\langle r^2\rangle\\
B_{40} &= \left(\frac{9}{4\pi}\right)^{1/2}\gamma_{40}\langle r^4\rangle\\
B_{44}^c &= \left(\frac{9}{8\pi}\right)^{1/2}\gamma_{44}^c\langle r^4\rangle\\
B_{44}^s &= i\left(\frac{9}{8\pi}\right)^{1/2}\gamma_{44}^s\langle r^4\rangle
\end{aligned} \quad (10)$$

For the $CdGa_2S_4$:Cr^{2+} system, the local structure symmetry belongs to the group D_{2d}. Taking the superposition model, the