Theoretical investigations of the local distortion and electron paramagnetic resonance parameter for $CdCl_2$:V^{2+} and $CsMgX_3$:V^{2+} (X=Cl, Br) systems*

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(Received 24 October 2009; revised manuscript received 20 November 2009)

This paper systematically investigates the local distortion and electron paramagnetic resonance (EPR) parameter for $CdCl_2$:V^{2+} and $CsMgX_3$:V^{2+} (X=Cl, Br) systems on the basis of the complete energy matrix, in which not only the contributions due to the spin–orbit coupling of the central ions but also that of the ligands are considered. To describe the difference of overlapping between d-orbits and p orbit, two spin–orbit coupling coefficients are introduced. By simulating the crystal field parameter and EPR parameter, the local distortion parameters are studied and the relationships between the EPR parameter and the spin–orbit coupling coefficients as well as divergent parameter are discussed. These results show that the local structures exhibit compression distortion for $CdCl_2$:V^{2+} and elongation distortions for $CsMgX_3$:V^{2+} (X=Cl, Br), respectively. It notes that the empirical formula $R \approx R_{\rm H} + (r_{\rm i} - r_{\rm h})/2$ is not suitable for $CdCl_2$:V^{2+} and $CsMgX_3$:V^{2+} (X=Cl, Br) systems. The contributions of ligand to spin–orbit coupling interaction cannot be neglected for strong covalent systems, especially for V^{2+} doped in $CsMgBr_3$:V^{2+}.

Keywords: complete energy matrix, two spin–orbit coupling parameter model

PACC: 7170C, 7630, 7630F

1. Introduction

The transition-metal (TM) ions, especially the $3d^n$ configuration ions, are often regarded as impurity ions which are extensively applied in various promising systems such as laser crystal, catalyzers, photoelectric basic materials and high-temperature superconductive materials. As we know, the electromagnetic property of the TM ions in crystals is strongly influenced by both the TM ions and their ligand ions. In Van Vleck's simple crystal field theory, generally, only the d-orbit electrons of the TM ions are handled in terms of quantum theory, the surrounding of ligand ions, however, are regarded as the classical mechanical systems. The theory of Van Vleck, in which the spin–orbit (s.o.) coupling interaction is only related with the central ion, has been proved to be applicable only to the description of the electron paramagnetic resonance (EPR) and optical spectra for the typical ionic crystals.[1−3] However, since both the s.o. coupling and covalent effect increase with the increasing atomic number of the ligand ions, the contributions to EPR from the s.o. coupling of the ligand ions are expected to increase with increasing covalent effect (such as $\zeta_{\rm p}^0$ (F^-) = 220 cm^{-1}, $\zeta_{\rm p}^0$ (Cl^-) = 587 cm^{-1}, $\zeta_{\rm p}^0$ (Br^-) = 2460 cm^{-1} and $\zeta_{\rm p}^0$ (I^-) = 5060 cm^{-1}). Therefore, the one s.o. coupling parameter model will not be considered as a reasonable one when the atomic number of the ligand ions takes on a large value. A two-s.o. coupling parameter model (in which not only the contribution of s.o. coupling of central ions, but also that of ligands are included) should be used. So, with regard to the strong covalent system, just as that remarked by Sugano *et al,* [4], two s.o. coupling coefficients ζ and ζ' should be simultaneously introduced to describe the difference of overlapping between d-orbits $|t_{2g}\rangle$ and $|e_g\rangle$ of central ions with the p orbit of the ligands.

In view of this, on the basis of the theory of high order perturbation including two s.o. coupling coefficients ζ and ζ', there has been much interest in the theoretical investigation of EPR parameters (D, $g_\parallel$, $g_\perp$) for a covalent system. Vicaro *et al.*[5] gave a theory of the EPR parameter for d^4/d^6 TM clus-

*Project supported by the National Natural Science Foundation of China (Grant Nos. 10774103 and 10974138).

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ters with tetragonal symmetry and interpreted the EPR parameter of Cr^{2+} in GaAs. Du *et al.*[6,7] investigated the EPR parameters for RX:V^{2+} (R=Na, K, Rb; X=Cl, Br, I), Al_2O_3:Cr^{3+} and $CsMgX_3$:Cr^{3+} (X=Br, I) systems, etc., and established the formulae of EPR parameters for d^3 configuration ions in the trigonal ligand field. Furthermore, the local distortion parameters and EPR parameters are also analysed by Zheng and Wu *et al.*[8−11] based on these formulae for $CdCl_2$:V^{2+} and $CsMgX_3$:V^{2+} (X=Cl, Br, I) systems. These studies showed that the contributions from s.o. coupling of ligand ions to EPR parameters in a covalent system may not be negligible. Simultaneously, it is worth while noticing that the advantages of high order perturbation lie in the fact that the EPR parameters may be analysed by the expressions of crystal field and s.o. coupling parameter. It possesses an intuitive and simplified feature. However, the high order perturbation is just an approximation, and the empirical formula $R \approx R_{\rm H} + (r_{\rm i} - r_{\rm h})/2$, which has been employed in previous works, is not suitable for all the doped systems according to recent studies.[12,13] Therefore, it should be noted that some uncertainties may exist in previous conclusions,[8−11] and the local structure distortion of the TM complex needs to be determined by using other reliable methods.

Since the method of complete energy matrix is established in complete d^3 configuration space, and all interactions in Hamiltonian may be taken into account unambiguously, this method is obviously superior to the high order perturbation method. Based on the complete energy matrix (252×252), two-s.o. coupling parameter model for d^5 configuration ions are introduced, and it has been applied to study the ground state zero-field splitting (ΔE_1, ΔE_2) of Mn^{2+} and Fe^{3+} ions in ZnO ($\zeta_{\rm p}^0(O^{2-}) = 136$–$158$ cm^{-1}) and CdSe ($\zeta_{\rm p}^0$ (Se^{2+}) = 1868 cm^{-1}) crystals.[14,15] In the present work, by using the two-s.o. coupling parameter model, the complete energy matrix (120×120) for d^3 configuration ions in trigonal ligand field has been established. The local distortion parameters (ΔR, $\Delta\theta$) for $CdCl_2$:V^{2+} and $CsMgX_3$:V^{2+} (X=Cl, Br) systems are studied and the relationships between the EPR parameter D and s.o. coupling coefficients (ζ, ζ') as well as divergent parameter ζ_2 ($(\zeta - \zeta')/2$) are discussed. Our results show that the local structures exhibit compression distortion for $CdCl_2$:$V^{2+}$and elongation distortions for $CsMgX_3$:V^{2+} (X=Cl, Br), respectively. It is shown that the empirical formula $R \approx R_{\rm H} + (r_{\rm i} - r_{\rm h})/2$ is also not suitable for $CdCl_2$:V^{2+} and $CsMgX_3$:V^{2+} (X=Cl, Br) systems. The contributions of ligand to s.o. coupling interaction should be considered for the strong covalent systems, especially for V^{2+} in $CsMgBr_3$:V^{2+}.

2. Theoretical methods

2.1. Complete energy matrix for d^3 configuration ions

In Sugano *et al.*'s strong field covalent theory, two s.o. parameters ζ and ζ' are related to the s.o. coupling constants of the 3d electrons in a TM ion ($\zeta_{\rm d}^0$) and the p electrons in a ligand ($\zeta_{\rm p}^0$). In the linear combination of atomic orbitals (LCAO) method, the molecular-orbital basis can be written as[7]

$$|\gamma\rangle = \sqrt{N_\gamma}(|d_\gamma^0\rangle - \lambda_\gamma |p_\gamma\rangle), \tag{1}$$

where $|d^0\rangle$ is the d orbital of the central metal ion; $|p\rangle$ is the p orbital of the ligand ion; the subscript $\gamma = t_{2\rm g}$ or $e_{\rm g}$ are the irreducible representations of the cubic group; N_γ and λ_γ are the normalization factor and orbital mixing coefficients, respectively. The two s.o. coupling coefficients ζ and ζ', which are correlated with the s.o. coupling coefficients of central metal ion ($\zeta_{\rm d}^0$) and its ligand ($\zeta_{\rm p}^0$), can be expressed as[7]

$$\begin{aligned}\zeta &= N_t\left(\zeta_{\rm d}^0 + \frac{1}{2}\lambda_t^2\zeta_{\rm p}^0\right),\\ \zeta' &= \sqrt{N_t N_{\rm e}}\left(\zeta_{\rm d}^0 - \frac{1}{2}\lambda_t\lambda_{\rm e}\zeta_{\rm p}^0\right).\end{aligned} \tag{2}$$

The coefficients N_γ and λ_γ may be estimated by the approximate relationship[7]

$$f_\gamma = N_\gamma^2[1 - 2\lambda_\gamma S_{\rm dp}(\gamma) + \lambda_\gamma^2 S_{\rm dp}^2(\gamma)], \tag{3}$$

and the normalization correlation[7]

$$N_\gamma[1 - 2\lambda_\gamma S_{\rm dp}(\gamma) + \lambda_\gamma^2] = 1, \tag{4}$$

where $S_{\rm dp}(\gamma)$ is the group overlap integral and $f_\gamma \approx (B/B_0 + C/C_0)/2$. B, C are the Racah parameters of TM ion in studied crystal[16−18] and B_0, C_0 are the free ion parameters. For V^{2+} ion, $B_0 \approx 766$ cm^{-1} and $C_0 \approx 2855$ cm^{-1}.[19] From Eqs. (2), (3), (4), the values of N_γ, λ_γ, ζ and ζ' may be obtained and the results for V^{2+} ions in $CdCl_2$ and $CsMgX_3$ (X=Cl, Br) crystals are collected in Table 1.

Table 1. The impurity-ligand distances, group overlap integrals, the crystal field parameters, Racah parameters, LCAO coefficients, s.o. coupling coefficients, divergent parameter for V^{2+} in $CdCl_2$ and $CsMgX_3$ (X=Cl, Br) crystals, (1 Å=0.1 nm).

compounds	R/Å	$S_{\rm dpe}$	$S_{\rm dpt}$	Dq/cm^{-1}	B/cm^{-1}	C/cm^{-1}	f_γ	N_t
$CdCl_2$	2.5495	0.0688	0.0225	920	642	2430	0.8446	0.9254
$CsMgCl_3$	2.5216	0.0729	0.0243	975	613	2370	0.8152	0.9103
$CsMgBr_3$	2.6668	0.0698	0.0220	895	603	2320	0.7999	0.9014

$N_{\rm e}$	λ_t	$\lambda_{\rm e}$	ζ/cm^{-1}	ζ'/cm^{-1}	ζ_2/cm^{-1}
0.9403	0.3073	0.3298	180.19	128.03	26.0165
0.9273	0.3392	0.3623	182.76	120.29	31.235
0.9185	0.3535	0.3758	289.05	3.315	142.868

The perturbation Hamiltonian for d^n configuration ions in ligand field can be expressed as

$$\begin{aligned}\hat{H} &= \hat{H}_{\rm ee} + \hat{H}_{\rm LF} + \hat{H}_{\rm SO} \\ &= \sum_{i<j} \frac{e^2}{r_{i,j}} + \sum_i V_i + \sum_i \zeta_{\rm d}^0(r_i)\hat{l}_i \cdot \hat{s}_i \\ &\quad + \sum_j \zeta_{\rm p}^0(r_j)\hat{l}_j \cdot \hat{s}_j, \end{aligned} \tag{5}$$

where $\hat{H}_{\rm ee}$, $\hat{H}_{\rm LF}$ and $\hat{H}_{\rm SO}$ are the electron–electron repulsion interaction, the ligand field interaction and the s.o. coupling interaction, respectively. The corresponding 120×120 energy matrix for a d^3 configuration ion has been constructed. The matrix elements are the functions of the Racah parameters B, C, the s.o. coupling coefficients ζ and ζ', and the ligand field parameters B_{kq}. In the trigonal ligand field, the B_{20}, B_{40} and $B_{43}^{\rm c}$ may be expressed as:[20]

$$B_{20} = \frac{1}{2}\sum_\tau G_2(\tau)(3\cos^2\theta_\tau - 1), \tag{6}$$

$$B_{40} = \frac{1}{8}\sum_\tau G_4(\tau)(35\cos^4\theta_\tau - 30\cos^2\theta_\tau + 3), \tag{7}$$

$$B_{43}^c = \frac{\sqrt{35}}{4}\sum_\tau G_4(\tau)\sin^3\theta_\tau\cos\theta_\tau \tag{8}$$

with

$$\begin{aligned} G_2(\tau) &= -eq_\tau G^2(\tau), \quad G_4(\tau) = -eq_\tau G^4(\tau), \\ G^k(\tau) &= \int_0^{R_\tau} R_{3{\rm d}}^2(r) r^2 \frac{r^k}{R_\tau^{k+1}}{\rm d}r \\ &\quad + \int_{R_\tau}^{\infty} R_{3{\rm d}}^2(r) r^2 \frac{R_\tau^k}{r^{k+1}}{\rm d}r, \end{aligned} \tag{9}$$

where τ and q_τ represent the τ-th ligand and its effective charge respectively, the R_τ and θ_τ are the V–X (X=Cl, Br) distance and the angle between V–X and C_3 axis, respectively. By using the Van Vleck approximation[21] and taking the point-dipole model, the $G_2(\tau)$, $G_4(\tau)$ can be written as

$$G_2(\tau) = \frac{A_2}{R_\tau^3}, \quad G_4(\tau) = \frac{A_4}{R_\tau^5} \tag{10}$$

with

$$\begin{aligned} A_4 &= -eq_\tau\langle r^4\rangle\left(1 + \frac{5\mu}{eR_\tau}\right), \\ A_2 &= -eq_\tau\langle r^2\rangle\left(1 + \frac{3\mu}{eR_\tau}\right), \\ A_2/A_4 &= \langle r^2\rangle\left(1 + \frac{3\mu}{eR_\tau}\right)\Big/\langle r^4\rangle\left(1 + \frac{5\mu}{eR_\tau}\right), \end{aligned} \tag{11}$$

where μ is the electric dipole moment of a ligand ion. The values of $\langle r^2\rangle = 2.565$ a.u. and $\langle r^4\rangle = 13.1132$ a.u. for V^{2+} ion are obtained from the semi-empirical radial wave function.[22] According to the cell parameters: $a_0 = 3.60$ Å, $c_0 = 5.83$ Å for VCl_2, $a_0 = 3.768$ Å, $c_0 = 6.18$ Å for VBr_2 and atomic arrangement: $V = (0,0,0)$, $X = \pm(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$, the structure parameters can be determined, those are $R_0 = 2.55$ Å, $\theta_0 = 54.6°$ for VCl_2 and $R_0 = 2.688$ Å, $\theta_0 = 54.618°$ for VBr_2, respectively. Taking $q_\tau = -e$ for X^- (X=Cl, Br), then we can get the dipoles $\mu_{\rm Cl} = 0.796eR_\tau$ and $\mu_{\rm Br} = 0.9683eR_\tau$ on the basis of the structure parameters and optical spectra of pure VCl_2 and VBr_2 crystals,[23] and the results are listed in Table 2. The values of A_2 and A_4, which are associated with dipole μ, can also be obtained by Eq. (9). Those values will be employed in the following calculation.

Table 2. The calculated and observed optical spectra of VX_2 (X=Cl, Br), all units in cm^{-1}.

transition site	VCl_2		VBr_2	
	$\mu_{Cl} = 0.796eR_\tau$		$\mu_{Br} = 0.9683eR_\tau$	
	Calc.	Obs.[23]	Calc.	Obs.[23]
$^4A_2 \rightarrow {}^4E$	9173	9200	8583	8600
$^4A_1$	9234		8637	
^2E	11715	11700	11405	11400
^2E	12341	12200	12016	12000
$^2A_2$	12379		12049	
$^4A_2$	14365	14270	13537	13330
^4E	14439		13600	
$^2A_1$	16240	16100	16221	15800
^2E	16324		16294	
$^1A_1$	19029	18520	18193	17180
^2E	20880	20790	19990	
$^2A_1$	20950		20052	

2.2. EPR parameters for d^3 configuration ions

The EPR spectra of d^3 configuration ions V^{2+} in a trigonal ligand field can be analysed by employing the spin Hamiltonian:[24]

$$\hat{H}_S = \mu_B g_{\parallel} H_z S_z + \mu_B g_{\perp}(H_x S_x + H_y S_y) + D\left[S_z^2 - \frac{1}{3}S(S+1)\right]. \quad (12)$$

In the absence of the external magnetic field, the ground state $^4A_2$ is split into two spin doublets $\left|\pm\frac{1}{2}\right\rangle$ and $\left|\pm\frac{3}{2}\right\rangle$.

$$E\left(\pm\frac{3}{2}\right) = D, \quad E\left(\pm\frac{1}{2}\right) = -D. \quad (13)$$

The ground state splitting ΔE can be expressed as

$$\Delta E = E\left(\pm\frac{3}{2}\right) - E\left(\pm\frac{1}{2}\right) = 2D. \quad (14)$$

The value of ΔE, which is associated with the local structure of the TM complex, may be obtained by diagonalizing the complete energy matrix of the Hamiltonian in Eq. (5).

3. Calculation and analysis

3.1. Calculation of the local distortion parameters for trigonal V^{2+} centres

The $CsMgX_3$ (X=Cl, Br) and $CdCl_2$ are favourable and important ionic crystals. The perovskite $CsMgX_3$ (X=Cl, Br), which exhibits a linear array of $(MgX_6)^{4-}$ octahedra sharing opposite faces along the hexagonal c-axis, are important magnetic and luminescent materials.[11,25] The $CdCl_2$ is a typical layered ionic crystal in which a Cd^{2+} plane is sandwiched between two halogen–ion planes and has extensively practical applications in low-dimensional magnetism, spectroscopy, and fluorescence mechanisms.[26,27] When V^{2+} ions are doped into $CdCl_2$ and $CsMgX_3$ (X=Cl, Br) crystals, they will be coordinated by six halogen ions sitting at the vertices and the local symmetry of $(VX_6)^{4-}$ clusters belongs to the space group D_{3d}. Owing to the difference of ionic radius and mass between the impurity ion V^{2+} and the replaced ions, it is expected that the local structures of $(VX_6)^{4-}$ clusters will display compression or elongation distortions in the doped systems. For the $CdCl_2$:V^{2+} system, we can predict that the local lattice structure around V^{2+} ion will exhibit a compression distortion along C_3-axis because the radius of V^{2+} ion (r = 0.88 Å) is smaller than that of Cd^{2+} (r = 0.97 Å) ion.[28] Correspondingly, we can also assume that there is an elongation distortion for $CsMgX_3$:V^{2+} (X=Cl, Br) systems, since the radius of V^{2+} ion is distinctly larger than that of Mg^{2+} ion (r = 0.66 Å).[28] For quantitative calculation, we introduce two local distortion parameters ΔR and $\Delta\theta$ (see Fig. 1) to describe the trigonal distortion. Then the local structure parameters R and θ can be expressed as

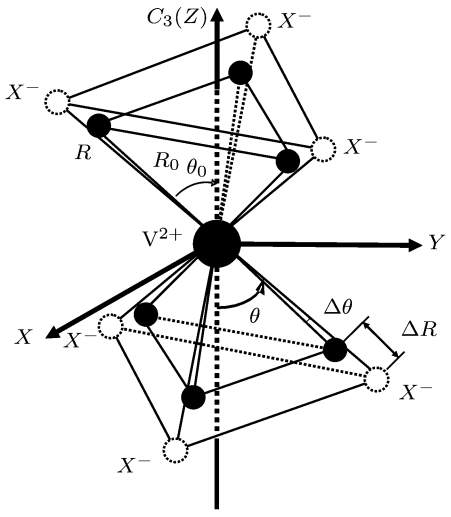


Fig. 1. The local distortion for $CdCl_2$:V^{2+} and $CsMgX_3$:V^{2+} (X=Cl, Br) systems with D_{3d} symmetry, R_0 and θ_0 are the structure parameters of host crystals. The ΔR and $\Delta\theta$ represent the local distortion parameters.

$$R = R_0 + \Delta R,$$
$$\theta = \theta_0 + \Delta\theta, \quad (15)$$

where $R_0 = 2.6567$ Å is the Cd–Cl bond length and $\theta_0 = 56.79°$ is the angle between Cd–Cl bond and C_3-axis for $CdCl_2$ crystal,[29] $R_0 = 2.496$ Å, $\theta_0 = 51.73°$ for $CsMgCl_3$ crystal and $R_0 = 2.662$ Å, $\theta_0 = 52.44°$ for $CsMgBr_3$ crystal.[30] In order to determine the local distortion parameters ΔR and $\Delta\theta$ of V^{2+} ions in different $(VX_6)^{4-}$ clusters, the corresponding Racah parameters B, C and the s.o. coupling coefficients ζ and ζ' listed in Table 1 are used. By diagonalizing the complete energy matrix, the crystal field parameter Dq ($10Dq$ corresponds to ${}^4T_2 \rightarrow {}^4A_2$) and EPR parameter D can be simulated as the functions of the local distortion parameters (ΔR, $\Delta\theta$). The theoretical values are listed in Tables 3 and 4.

Table 3. Comparison of optical spectra between the theoretical and experimental values for V^{2+} ions in $CdCl_2$ crystal, as well as the pure VX_2 (X=Cl, Br) crystals with $CdCl_2$:V^{2+} and $CsMgX_3$ (X=Cl, Br) systems, respectively, all units in cm^{-1}.

transition site	$CdCl_2$		$CsMgCl_3$		$CsMgBr_3$	
	Calc.	Obs.[31]	Calc.	VCl_2[23]	Calc.	VBr_2[23]
${}^4A_2 \rightarrow {}^4E$	9121	9000	9702	9200	8700	8600
${}^4A_1$	9265		9764		9126	
${}^2E$	11619	11530	11398	11700	10390	11400
${}^2E$	12124	11810	11983	12200	10801	12000
${}^2A_2$	12233		12020		12105	
${}^2A_1$	16491	16250	16458	16100	15929	15800
${}^2E$	16724		16540		16934	

Table 4. The local distortion parameters (ΔR, $\Delta\theta$) and EPR parameter D of the octahedral $(VX_6)^{4-}$ (X=Cl, Br) clusters for $CdCl_2$:V^{2+} and $CsMgX_3$:V^{2+} (X=Cl, Br) systems calculated from different methods.

compounds		ΔR/Å	$\Delta\theta$/(°)	D/m^{-1}	
				Calc.	Obs.[32,33]
$CsMgCl_3$:V^{2+}	[a]Calc.			–0.0850	±0.0961
	[b]Calc.			–0.0869	
	[c]Calc.	0.11	3.52	–0.0985	
	[d]Calc.	0.0296	3.09401	–0.0961	
	[e]Calc.	0.0256	2.8718	–0.0961	
$CsMgBr_3$:V^{2+}	[c]Calc.	0.11	5.43	0.1306	±0.1320
	[e]Calc.	0.0048	7.3955	0.1320	
$CdCl_2$:V^{2+}	[b]Calc.			–0.2086	–0.2077
	[c]Calc.	–0.045	–1.14	–0.2077	
	[d]Calc.	–0.1149	–1.3111	–0.2077	
	[e]Calc.	–0.1072	–1.6562	–0.2077	

[a] Calculated by using the crystal field theory.[8]
[b] Calculated from the high order perturbation based on the one-s.o. coupling parameter model.[34,35]
[c] Calculated from the high order perturbation based on the two-s.o. coupling parameter model.[9,10]
[d] Calculated from the complete energy matrix based on the one-s.o. coupling parameter model.
[e] Calculated from the complete energy matrix based on the two-s.o. coupling parameter model.

From Tables 3 and 4, we can clearly see that the experimental data of the crystal field parameter Dq and EPR parameter D can be satisfactorily simulated by using the local distortion parameters ΔR and $\Delta\theta$. It is found that the signs of the distortion parameters ΔR and $\Delta\theta$ of $CdCl_2$:V^{2+} system are negative, which implies a compression distortion. In contrast, the positive signs of ΔR and $\Delta\theta$ indicate an elongation distortion for $CsMgX_3$:V^{2+} (X=Cl, Br) systems. These two calculated results are in accordance with our above prediction. Although the optical spectra for $CsMgX_3$:V^{2+} (X=Cl, Br) systems have not

been reported so far, it can be predicted by our theoretical calculation. It will provide powerful help for the further experimental measurement. Besides, we also find that the calculated data of optical spectra for $CdCl_2$:$V^{2+}$and $CsMgX_3$:V^{2+} (X=Cl, Br) systems are approximately in agreement with the optical spectra of pure VX_2 (X=Cl, Br) crystals, respectively. It may be attributed to the fact that VCl_2 crystal and $CdCl_2$:V^{2+} and $CsMgCl_3$:V^{2+} systems have the similar $(VCl_6)^{4-}$ cluster, as well as VBr_2 crystal and $CsMgBr_3$:V^{2+} system. Of course, our theoretical results need to be verified by further experiments.

From Table 4, for $CdCl_2$:V^{2+} and $CsMgCl_3$:V^{2+} systems, we find that the local distortion parameters obtained with the one-s.o. coupling parameter model are close to those calculated by using the two-s.o. coupling parameter model. However, for $CsMgBr_3$:V^{2+} system, the local distortion parameters cannot be obtained by means of the one-s.o. coupling parameter model, it indicates that the one-s.o. coupling parameter model could not give reasonable interpretation. Furthermore, the comparison based on the methods of the complete energy matrix and high order perturbation is also shown, it is noted that the local distortion parameters ΔR and $\Delta\theta$ are different using the two different methods. On the basis of the EPR calculation, this difference may be ascribed to that of the empirical formula $R \approx R_{\rm H} + (r_{\rm i} - r_{\rm h})/2$ in previous calculations, which is induced from the given doped systems,[36] and is not suitable for the $CdCl_2$:V^{2+} and $CsMgX_3$:V^{2+} (X=Cl, Br) systems. Of course, in order to detailedly clarify the local distortion, more careful experiments especially electron nuclear double resonance (ENDOR) are required.

3.2. The relationships between the s.o. coupling coefficients ζ and ζ' and EPR parameter D

As mentioned above, the s.o. coupling coefficients ζ and ζ' are introduced by Sugano *et al.* for a strong covalent system. From Table 1, we note that the values of ζ and ζ' show the following order: $\zeta(Cl^-) < \zeta(Br^-)$, $\zeta'(Cl^-) > \zeta'(Br^-)$. Furthermore, by adjusting the corresponding parameters, the relationships of D vs. ζ and D vs. ζ' are shown in Fig. 2. It is remarked that according to the high order perturbation formula, D is directly linearly related to ζ[7] and directly proportional to the square of ζ',[7] respectively. But, our results show that the function of D vs. ζ is not a strictly linear relation, as well as D vs. ζ' is not a strictly quadratic relation. This difference may be due to the fact that the complete energy matrix method involves all microstates of the d^3 configuration, whereas the high order perturbation method is only considered as a part of the microstates of the d^3 configuration.

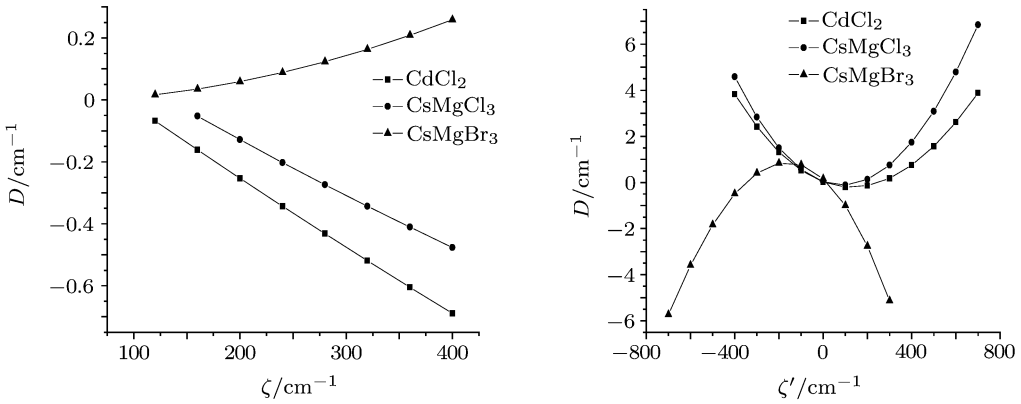


Fig. 2. The relationships between (ζ, ζ') and D for $CdCl_2$:V^{2+} and $CsMgX_3$:V^{2+} (X=Cl, Br) systems.

3.3. The influence of divergent parameter ζ_2 on EPR parameter D

In the classical crystal field theory, in general, the influence of the ligands on the central metal ion is simply treated as the reduction of the s.o. coupling coefficient ζ, $\zeta < \zeta_0$, where ζ_0 is the s.o. coupling coefficient of

the free TM ion. This method may be understood as the average covalent theory[4,37−39] and it is available only for the system with the negligible s.o. coupling contribution of the ligands. Usually, the splitting of the d-orbit in the ligand field and the different covalent effects between the sub-orbitals should be introduced in the calculation. To clarity in physics, two-s.o. parameters ζ_1 and ζ_2 are also introduced:

$$\zeta_1 = (\zeta + \zeta')/2, \quad \zeta_2 = (\zeta - \zeta')/2. \tag{16}$$

The physical meanings of ζ_1 and ζ_2 are the average and divergent contributions of the orbits $|t_{2g}\rangle$, $|e_g\rangle$ and p orbits to the s.o. coupling interaction, respectively. From Eqs. (2) and (16), we have

$$\begin{aligned}\zeta_1 &= \frac{1}{2}[N_t + \sqrt{N_t N_e}]\zeta_d^0 + \frac{1}{4}[N_t\lambda_t^2 - \sqrt{N_t N_e}\lambda_t\lambda_e]\zeta_p^0,\\ \zeta_2 &= \frac{1}{2}[N_t - \sqrt{N_t N_e}]\zeta_d^0 + \frac{1}{4}[N_t\lambda_t^2 + \sqrt{N_t N_e}\lambda_t\lambda_e]\zeta_p^0.\end{aligned} \tag{17}$$

From Eq. (17), we can clearly see that the divergent parameter ζ_2 is related to the s.o. coupling parameter ζ_p^0 of the ligand. Consequently, the strong covalent system ($CsMgBr_3$:V^{2+}) with the large value of the s.o. coefficient ($\zeta_p^0(Br^-) = 2460$ cm^{-1}) of the ligand induces the large value of the divergent parameter ζ_2 ($\zeta_2 = 142.868$ cm^{-1}). From Table 1, it is found that ζ_2 increases from Cl^- to Br^- since the covalence and s.o. coupling parameter ζ_p^0 of ligand ions increase from Cl^- to Br^-, and the ratio ζ_2/ζ =14.44%, 25.97%, 49.43% can be obtained for $CdCl_2$:V^{2+} and $CsMgX_3$:V^{2+} (X=Cl, Br) systems, respectively. So, the one-s.o. coupling parameter model is approximately effective to the studies of EPR parameter for $CdCl_2$:$V^{2+}$and $CsMgCl_3$:V^{2+} systems, and the two-s.o. coupling parameter model should be adopted for $CsMgBr_3$:V^{2+} system. Although the contributions of chlorine as ligand is less significant than that of bromine ligand, its contributions cannot also be neglected in rigorous calculation. So, the two-s.o. coupling parameter model should be preferred for those systems.

At last, the influence of the divergent parameter ζ_2 on EPR parameter D is studied, the detailed results are plotted in Fig. 3. We find that the curve of D vs. ζ_2 has an approximately linear relationship. The values of D will decrease with the increase of ζ_2 for $CdCl_2$:V^{2+} and $CsMgCl_3$:V^{2+} systems. In contrast, the values of D will increase with the increase of ζ_2 for $CsMgBr_3$:V^{2+} system.

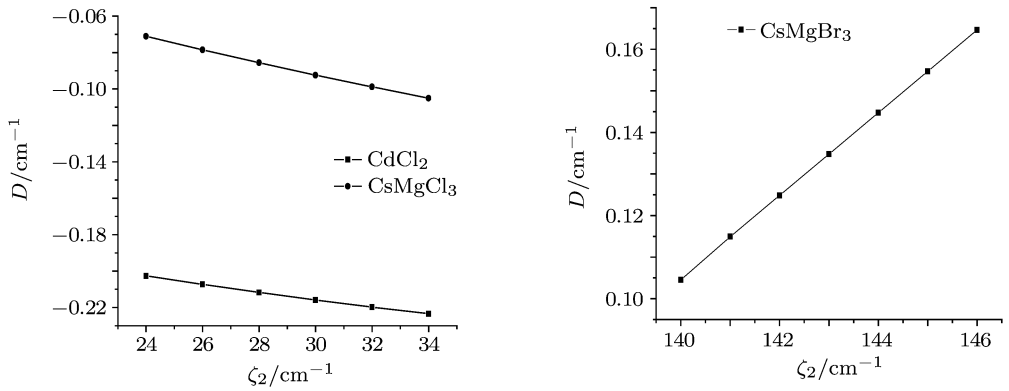


Fig. 3. The dependence of ζ_2 on D for $CdCl_2$:V^{2+} and $CsMgX_3$:V^{2+} (X=Cl, Br) systems.

4. Conclusion

By using the complete energy matrix method and taking into account the contributions from the s.o. coupling of the TM ions as well as those of the ligand ions, we systematically investigated the EPR parameter and local distortion for $CdCl_2$:V^{2+} and $CsMgX_3$:V^{2+} (X=Cl, Br) systems and draw the following conclusions.

(i) The local lattice structures for the $(VX_6)^{4-}$ (X=Cl, Br) clusters in $CdCl_2$:V^{2+} and $CsMgX_3$:V^{2+} (X=Cl, Br) systems are determined. There exists compression distortion ($\Delta R = -0.1072$ Å, $\Delta\theta = -1.6562°$)

for $CdCl_2$:V^{2+} system and the elongation distortions (ΔR = 0.0256 Å, 2.8718 Å, $\Delta\theta$ = 0.0048°, 7.3955°) for $CsMgX_3$:V^{2+} (X=Cl, Br) systems, respectively. Moreover, the results also show that the empirical formula $R \approx R_H + (r_i - r_h)/2$ is unsuitable for the V^{2+} in $CdCl_2$ and $CsMgX_3$ (X=Cl, Br) crystals.

(ii) The s.o. coupling coefficients ζ and ζ' have an important influence on the EPR parameter D. There is an approximately linear relation between ζ and D, and an approximately quadratic relation between ζ' and D.

(iii) It is worth while noting that there are approximately linear relations between the EPR parameter D and the divergent parameter ζ_2. The values of D will decrease with the increase of ζ_2 for $CdCl_2$:V^{2+} and $CsMgCl_3$:V^{2+} systems. Contrarily, D will increase with the increase of ζ_2 for $CsMgBr_3$:V^{2+} system.

(iv) For strong covalent systems, especially for V^{2+} doped in $CsMgBr_3$:V^{2+}, the contributions of ligand to s.o. coupling interaction should be included.

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