

## Zero-field splitting and local structure for $V^{2+}$ ions in $CsMgX_3$ ( $X=Cl, Br, I$ ) crystals

Q WEI<sup>1,2,\*</sup>, Q M XU<sup>1</sup>, Z Y YANG<sup>2</sup>, D Y ZHANG<sup>1,3</sup> and J G ZHANG<sup>1</sup>

<sup>1</sup>College of Material Science & Engineering, Xi'an University of Architecture & Technology, Xi'an 710055, China

<sup>2</sup>Department of Physics, Baoji University of Arts and Science, Baoji 721007, Shaanxi, China

<sup>3</sup>School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530 004, Guangxi, China

\*Corresponding author. E-mail: weiaqun@tom.com

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**Abstract.** The zero-field splitting and local structure for  $V^{2+}$  ions in  $CsMgX_3$  ( $X = Cl, Br, I$ ) crystals are theoretically investigated using complete diagonalization method (CDM) for a  $3d^3$  ion in trigonal symmetry. Spin–spin (SS) and spin–other-orbit (SOO) interactions are taken into account in addition to the general spin–orbit (SO) interaction. On this basis, using ligand ion displacement model, we find that the ligand ions move away from  $C_3$ -axis, and therefore the local angles in the  $V^{2+}$  centres are larger than the angles in the hosts. The results show good agreement with the observed values.

**Keywords.** Zero-field splitting; local structure;  $V^{2+}$  ions.

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### 1. Introduction

Transition-metal (TM) ions and rare-earth ions are active ions in solid state laser materials, non-linear optical materials and superconductors [1–7]. These impurity ions in the materials play a major role because they can be responsible for the modification of optical properties. Thus, microscopic study of TM ions in various crystals has attracted much attention. Since the microscopic spin-Hamiltonian (MSH) theory enables correlation of the optical spectroscopy and structural data with the spin-Hamiltonian (SH) parameters extracted from the electron paramagnetic resonance (EPR) spectra, the studies of the transition-metal ions in crystals can provide a great deal of microscopic insight into the crystal structure, structural disorder, phase transitions and pressure behaviour as well as the observed magnetic and spectroscopic properties. EPR spectra and optic spectra of  $CsMgX_3$  ( $X = Cl,$

Br, I) crystals doped with TM ions have been extensively investigated experimentally and theoretically [2–15]. In the area of the EPR of transition ions, MSH theory has been extensively used [16–19]. Wu *et al* [12–14] studied the EPR parameters of  $V^{2+}$  ions in  $CsMgX_3$  crystals using the perturbation formulas. The perturbation formulas are deduced by taking into account spin-orbit (SO) interaction only. Recently, a more complete diagonalization method has been developed by Yang *et al* [20]. In this developed CDM, some slight magnetic interactions omitted in previous work, including spin-spin (SS) and spin-other-orbit (SOO) interactions, are considered. In this paper, by taking into account SS and SOO interactions, the local structure and zero-field splitting for  $V^{2+}$  ions in  $CsMgX_3$  ( $X = Cl, Br, I$ ) are investigated.

## 2. Calculations

In the crystal field (CF) framework, the total Hamiltonian is written as [21,22]

$$H = H_{ee}(B, C) + H_{CF}(B_{kq}) + H_M(\zeta, M_0, M_2), \quad (1)$$

where  $H_{ee}$  represents the Coulomb interactions,  $H_{CF}$  represents the CF interactions and  $H_M$  represents the magnetic interactions. In addition to the magnetic spin-orbit interaction parametrized by  $\zeta$ , slight magnetic interactions, including SS and SOO interactions being parametrized by the Marvin integrals [23,24]  $M_0$  and  $M_2$ , are included [25–27]:

$$H_M = H_{SO}(\zeta) + H_{SS}(M_0, M_2) + H_{SOO}(M_0, M_2). \quad (2)$$

The CF Hamiltonian for trigonal symmetry in the Wybourne notation is given as [21,22,28]

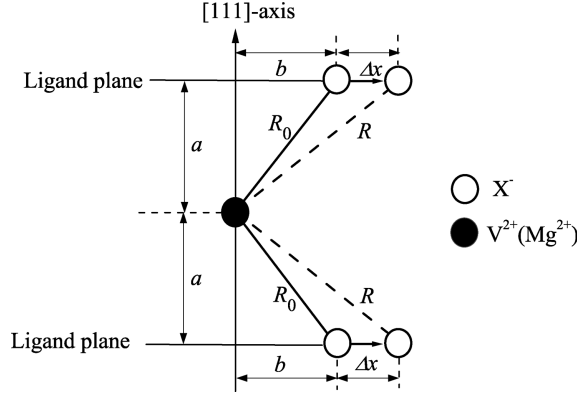
$$H_{CF} = B_{20}C_0^{(2)} + B_{40}C_0^{(4)} + B_{43}C_3^{(4)} + B_{4-3}C_{-3}^{(4)}, \quad (3)$$

where  $B_{kq}$  are the CF parameters and  $B_{43} = -B_{4-3}$  for trigonal symmetry ( $C_{3v}$ ,  $D_3$ ,  $D_{3d}$ ), and they are real. The methods of calculation of the matrix elements for  $H_{ee}$ ,  $H_{SO}$  and  $H_{CF}$  have been described in refs [29,30], whereas those of  $H_{SS}$  and  $H_{SOO}$  in refs [20,21,25].

For  $3d^3$  ions with the trigonal ( $C_{3v}$ ,  $D_3$ ,  $D_{3d}$ ) symmetry, the matrices of Hamiltonian in eq. (1) are of the dimension  $120 \times 120$  and can be partitioned into three smaller matrices, i.e.  $42 \times 42$  ( $E''$ ),  $39 \times 39$  ( $E'_+$ ) and  $39 \times 39$  ( $E'_-$ ) for the double group  $C_{3v}^*$  ( $3d^3$ ), where  $E'_+$  and  $E'_-$  denote Kramers doublets. Diagonalization of the full Hamiltonian matrices yields the energy levels and eigenvectors as functions of the Racah parameters  $B$  and  $C$ , CF parameters  $B_{kq}$ , SO coupling constant  $\zeta$ , and the Marvin's radial parameters  $M_0$ ,  $M_2$  used for representing the SS and SOO interactions. The ground state eigenvectors will be used for calculating the spectroscopic splitting  $g$  factors. For  $3d^3$  ions at trigonal symmetry, the effective spin-Hamiltonian, taking into account the ZFS terms, can be written as

$$H_S = D \left[ S_z^2 - \frac{1}{3}S(S+1) \right] \quad (4)$$

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**Figure 1.** Local structure around  $V^{2+}$  ions in  $\text{CsMgX}_3$  crystals and the moving model of ligand ions.

with the  $z$ -axis along the  $[1\ 1\ 1]$  direction. By means of the matrix element equivalence between the effective spin-Hamiltonian and actual physical Hamiltonian, the ZFS parameter  $D$  for  $3d^3$  ions at trigonal symmetry sites are expressed in terms of the quantities pertinent for the actual physical Hamiltonian as [22]

$$D = \frac{1}{2} \{ \varepsilon(|E''(^4F \downarrow^4 A_{2g} \downarrow^4 A_2)) - \varepsilon(|E'(^4F \downarrow^4 A_{2g} \downarrow^4 A_2)) \}. \quad (5)$$

For taking into account the SS and SOO interactions, the CDM program can provide more accurate determination of the EPR parameters. When  $V^{2+}$  ions are doped in  $\text{CsMgX}_3$  crystals,  $V^{2+}$  ions occupy the site of  $\text{Mg}^{2+}$  ions, which is in the local symmetry of  $D_{3d}$  with the three-fold symmetry axis coincident with the crystallographic  $c$ -axis [3,4]. The Mg–X bonding length  $R_0 = 2.496 \text{ \AA}$ ,  $2.662 \text{ \AA}$  and  $2.899 \text{ \AA}$  and bonding angle  $\theta_0 = 51.73^\circ$ ,  $52.44^\circ$  and  $52.89^\circ$  for  $X = \text{Cl}$ ,  $\text{Br}$  and  $\text{I}$ , respectively. On account of the difference between the ionic radius of impurities  $V^{2+}$  ( $0.88 \text{ \AA}$ ) and host  $\text{Mg}^{2+}$  ( $0.66 \text{ \AA}$ ), the local structure will be changed. Usually, the mass of impurity ions is larger than the ligand ions. So, with local structure distorted, the displacement of ligand ions should be easier. On this basis, we assume that, the  $V^{2+}$  ions are located at trigonal symmetry site, whereas ligand ions are displaced in ligand plane. The local distortion can be described by the displacement parameter  $\Delta x$  (see figure 1). Thus, using superposition model [31,32], the CF parameter  $B_{kq}$  can be expressed as

$$B_{20} = 6\bar{A}_2 \left( \frac{3a^2}{a^2 + (b + \Delta x)^2} - 1 \right), \quad (6)$$

$$B_{40} = 6\bar{A}_4 \left( \frac{35a^4}{[a^2 + (b + \Delta x)^2]^2} - \frac{30a^2}{a^2 + (b + \Delta x)^2} + 3 \right), \quad (7)$$

$$B_{43} = -12\sqrt{35}\bar{A}_4 \frac{a(b + \Delta x)^2}{[a^2 + (b + \Delta x)^2]^2}, \quad (8)$$

**Table 1.** Zero-field splitting parameter  $D$  (in  $\text{cm}^{-1}$ ) for  $\text{V}^{2+}$  ions in  $\text{CsMgX}_3$  ( $X = \text{Cl, Br, I}$ ) crystals.

$X$	$R$ (Å)	$\theta$ (°)	$\Delta\theta$ (°)	$\Delta x$ (Å)	$D_{\text{SO}}$	$D_{\text{Total}}$	$D_{\text{Expt.}}$ [3,4]	$\delta$ (%)
Cl	2.688	55.93	4.20	0.2359	-0.0826	-0.0860	-0.0858(7)	3.95
Br	2.823	55.33	2.89	0.1989	-0.1240	-0.1282	-0.1280(15)	3.28
I	3.010	54.48	1.59	0.1380	0.2032	0.2082	0.2080(30)	2.40

where  $\bar{A}_2$  and  $\bar{A}_4$  are intrinsic parameters [22,32], and following the relationship  $\bar{A}_4 = \frac{3}{4}Dq$  [31,33],  $\bar{A}_2 = 10.8\bar{A}_4$  [33].  $a = R_0 \cos \theta_0$ ,  $b = R_0 \sin \theta_0$ ,  $\Delta x$  describes the local distortion.

In our calculations, we take the spectral parameters of  $\text{V}^{2+}$  ions in  $\text{CsMgX}_3$ ,  $X = \text{Cl, Br, I}$ , respectively,  $B = 613, 603, 590 \text{ cm}^{-1}$  and  $C = 2370, 2320, 2230 \text{ cm}^{-1}$  for Racah parameters,  $Dq = 975, 895, 795 \text{ cm}^{-1}$  for cubic CF parameters [13], and the spin-orbit coupling parameter  $\zeta = k\zeta_0$ , with  $\zeta_0 = 167 \text{ cm}^{-1}$ . Here,  $k$  is the orbital reduction factor, and can be calculated by  $k = (\sqrt{B/B_0} + \sqrt{C/C_0})/2$  [34,35]. The Marvin's radial integrals  $M_0$  and  $M_2$  can be obtained by the relation  $M_0 = k^2 M_{0F}$  and  $M_2 = k^2 M_{2F}$ . Here  $M_{0F} = 0.1317 \text{ cm}^{-1}$ ,  $M_{2F} = 0.0103 \text{ cm}^{-1}$  are for free  $\text{V}^{2+}$  ions. Substituting the related parameters into the above equations, and diagonalizing the obtained complete energy matrices, the ZFS parameters of ground state can be calculated. By fitting the calculated  $D$  to the observed values, one can obtain the displacement of ligand ions  $\Delta x = 0.2359, 0.1989, 0.1380 \text{ Å}$ , as well as the local  $\text{V-X}$  bonding length  $R = 2.688, 2.823$  and  $3.010 \text{ Å}$ , and bonding angles  $\theta = 55.93^\circ, 55.33^\circ, 54.48^\circ$  for  $X = \text{Cl, Br, I}$ , respectively. In order to illustrate the contribution to  $D$  from SS and SOO interactions, we calculate the ZFS parameter  $D$  with SO interaction only (denoted as  $D_{\text{SO}}$ ) and ones with SO, SS and SOO interactions (denoted as  $D_{\text{Total}}$ ). The calculated results and experimental values are shown in table 1.

### 3. Discussion

From table 1, one can see that the theoretical data are consistent with experimental data. The agreement of the theoretical data and experimental data indicate that the model we adopted is reasonable. The displacement of ligands  $\Delta x$  is positive (accordingly, the angular distortion  $\Delta\theta$  is positive). This means the ligand ions move away from  $C_3$ -axis. Thus, the bonding length become longer than those in host crystals. An approximate empirical formula  $R = R_0 + (r_i - r_h)/2$  is used in [13,36], where  $R_0$  is the bonding length in host crystals,  $r_i$  is the radius of impurity ions,  $r_h$  is the radius of host ions. From this formula, one can see that if the radius of impurity ions is larger than the host ions, then the bonding length should become longer, and this is coincident with our results. We found that, the displacement of ligands  $\Delta x$  (or the angular distortion  $\Delta\theta$ ) decreases with the order of  $X = \text{Cl, Br}$  and  $\text{I}$  and the mass of ligand ions increases with this order. So the results we calculated is reliable in physical meanings.

In order to illustrate the contributions to ZFS parameter  $D$  from slight magnetic interactions, including SO, SS and SOO interactions, we use the percentage ratio defined in ref. [21] as

$$\delta = 100 \left| \frac{D_{\text{Total}} - D_{\text{SO}}}{D_{\text{Total}}} \right| \%, \quad (9)$$

and the calculated percentage ratio of  $\text{CsMgX}_3 : V^{2+}$  systems are also listed in table 1. The calculated results show that, the contribution to ZFS parameter  $D$  from SS and SOO interactions is less than 4% in  $\text{CsMgX}_3 : V^{2+}$  systems. It is found that the contributions to ZFS parameter  $D$  from slight magnetic interactions follow the order:  $\text{CsMgCl}_3 : V^{2+} > \text{CsMgBr}_3 : V^{2+} > \text{CsMgI}_3 : V^{2+}$ .

In summary, the local structure for  $V^{2+}$  ions in  $\text{CsMgX}_3$  crystals has been studied. It is shown that, the ligand ions move away from  $C_3$ -axis, and the contributions to ZFS from SS and SOO interactions are discussed.

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