Investigations of the EPR Parameters and Defect Structures of Two Types of Trigonal Cr^{3+} Centers in CsMgCl_3 , CsMgBr_3 and CsCdBr_3 Crystals

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The EPR g factors $g_{\parallel}$, $g_{\perp}$ and zero-field splitting D of trigonal $\text{Cr}^{3+}\text{-M}^+$ ($\text{M}^+ = \text{Li}^+, \text{Cu}^+, \text{Na}^+$) and $\text{Cr}^{3+}\text{-V}_\text{B}\text{-M}^{3+}$ ($\text{M}^{3+} = \text{Cr}^{3+}, \text{In}^{3+}, \text{Sc}^{3+}, \text{Y}^{3+}, \text{Lu}^{3+}$; V_B denotes the B^{2+} vacancy) centers in some CsBX_3 ($\text{B} = \text{Mg}, \text{Cd}$; $\text{X} = \text{Cl}, \text{Br}$) crystals are calculated from high-order perturbation formulas based on the two-spin-orbit coupling parameter model of the $3d^3$ ion in trigonal symmetry. From the calculations, these EPR parameters are reasonably explained and the local lattice distortions caused by the charge compensators M^+ or V_B are estimated. The results are discussed.

Key words: Electron Paramagnetic Resonance; Crystal- and Ligand-field Theory; Defect Structure; Cr^{3+} ; CsMgCl_3 ; CsMgBr_3 ; CsCdBr_3 .

1. Introduction

The quasi-one-dimensional halides CsBX_3 ($\text{B} = \text{Mg}, \text{Cd}$; $\text{X} = \text{Cl}, \text{Br}$) adopt the hexagonal structure identical to that of CsNiCl_3 [1, 2]. The most prominent structural feature of these lattices is a system of linear arrays of $(\text{BX}_6)^{4-}$ octahedra sharing opposite faces. These arrays form infinite chairs along the crystallographic C -axis. The point symmetry at a B^{2+} site is D_{3d} and the surrounding X^- octahedron is slightly elongated along the trigonal C -axis. When a Cr^{3+} ion replaces a B^{2+} ion in CsMgCl_3 , CsMgBr_3 and CsCdBr_3 crystals, EPR measurements did show that there are two types of trigonal (C_{3v}) Cr^{3+} centers caused by charge compensation, and their EPR parameters (g factors $g_{\parallel}$, $g_{\perp}$ and zero-field splitting D) were reported [3]. One type of the trigonal Cr^{3+} center is assigned to Cr^{3+} at a B^{2+} site associated with a monovalent M^+ ($\text{M}^+ = \text{Li}^+, \text{Cu}^+$ or Na^+) at a nearest-neighboring B^{2+} site along the C -axis (so it is called $\text{Cr}^{3+}\text{-M}^+$ center), and another type of the trigonal Cr^{3+} center is $\text{Cr}^{3+}\text{-V}_\text{B}\text{-M}^{3+}$ ($\text{M}^{3+} = \text{Cr}^{3+}, \text{In}^{3+}, \text{Sc}^{3+}, \text{Y}^{3+}$ or Lu^{3+}) centers, where the Cr^{3+} ion is associated with a B^{2+} vacancy V_B at the nearest-neighboring B^{2+} site and a trivalent impurity M^{3+} at the next-neighboring B^{2+} site along the C -axis

(see Fig. 1 in [3]). Since the effective charge of M^+ (or V_B) at the B^{2+} site is negative, it can be expected that the Cr^{3+} ion shifts towards the M^+ (or V_B) by Δx_1 , and the three X^- ions in the plane between Cr^{3+} and M^+ (or V_B) shift away from M^+ (or V_B) by Δx_2 along the $\text{M}^+\text{-X}^-$ direction, because of the electrostatic interactions. No explanations for these EPR parameters have been given. Since the EPR parameters of a paramagnetic impurity center are sensitive to its local structure, some useful information on the defect structure of the impurity center can be obtained by studying the EPR data [4–7]. In this paper we calculate the EPR parameters $g_{\parallel}$, $g_{\perp}$ and D for the two types of trigonal Cr^{3+} centers in these CsBX_3 crystals. From the calculations, the displacements Δx_1 and Δx_2 and hence the defect structures of these Cr^{3+} centers are estimated.

2. Calculations

In $\text{CsBX}_3\text{:Cr}^{3+}$ crystals, since the spin-orbit (SO) coupling parameter ζ_p^0 ($\approx 587 \text{ cm}^{-1}$ for Cl^- and 2460 cm^{-1} for Br^- [8]) of the ligand ion X^- is greater than that ($\zeta_d^0 \approx 273 \text{ cm}^{-1}$ [9]) of the central metal ion Cr^{3+} , we should apply the high-order perturba-

tion formulas of EPR parameters based on the two-SO-parameter model [10, 11], where not only the contribution to EPR parameters due to the SO coupling

parameter of the central $3d^n$ ion, but also the contribution due to the SO coupling parameter of ligand are included. These formulas are [11]:

$$\begin{aligned} D &= (2/9)\zeta'^2\nu(1/D_1^2 - 1/D_3^2) - \sqrt{2}\zeta\zeta'\nu'(2/3D_1D_4 + 1/D_2D_3 + 1/3D_3D_4 + 1/D_2D_4 + 1/D_2D_4 \\ &\quad + 4/\sqrt{2}B/D_1D_4D_5) - \sqrt{2}\zeta'^2B\nu'(4/D_3D_4D_5 + 9/2D_2^2D_3), \\ g_{\parallel} &= g_s - 8\zeta'k'/3D_1 - 2\zeta(2k'\zeta - k\zeta' + 2g_s\zeta')/9D_1^2 + 4\zeta'^2(k - 2g_s)/9D_3^2 - 2\zeta^2(k + g_s)/3D_2^2 \\ &\quad - 4\zeta\zeta'k'/3D_1D_2 + 4\zeta\zeta'k'/9D_1D_3 + 4\zeta\zeta'k'/3D_2D_3 + 8\zeta'k'\nu/9D_1^2 - 4\sqrt{2}(k'\zeta + k\zeta')\nu'/3D_1D_4, \\ g_{\perp} &= g_{\parallel} - 4\zeta'k'\nu/3D_1^2 + 4\sqrt{2}(2k\zeta' + k'\zeta)\nu'/3D_1D_4 \end{aligned} \quad (1)$$

with

$$\begin{aligned} \zeta &= N_t(\zeta_d^0 + \lambda_t^2\zeta_p^0/2), \quad \zeta' = (N_tN_e)^{1/2}(\zeta_d^0 - \lambda_t\lambda_e\zeta_p^0/2), \\ k &= N_t[1 - 2\lambda_tS_{dp}(t_{2g}) + \lambda_t^2/2], \quad k' = (N_tN_e)^{1/2}[1 - \lambda_tS_{dp}(t_{2g}) - \lambda_eS_{dp}(e_g) - \lambda_t\lambda_e/2], \end{aligned} \quad (2)$$

in which g_s (≈ 2.0023) is the g factor of a free electron. D_i ($i = 1 - 5$) are the zero-order energy denominators defined in [12]. They can be calculated from the cubic field parameter Dq and Racah parameters B and C . ν and ν' are the trigonal field parameters. N_{γ} ($\gamma = t_g$ or e_g) is the normalization coefficient and λ_{γ} is the orbital mixing coefficient in the one-electron basis function. They can be estimated from the normalization relationship [10, 11]

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

and the approximate relationship [10, 11]

$$\begin{aligned} f_r &= 1/2(B/B_0 + C/C_0) \\ &\approx N_{\gamma}^2[1 + \lambda_{\gamma}^2S_{dp}^2(\gamma) - 2\lambda_rS_{dp}(\gamma)], \end{aligned} \quad (4)$$

in which B_0 and C_0 are the Racah parameters of the $3d^n$ ion in free state. For a free Cr^{3+} ion we have $B_0 \approx 1030 \text{ cm}^{-1}$ and $C_0 \approx 3850 \text{ cm}^{-1}$ [9]. The group overlap integral $S_{dp}(\gamma)$ can be calculated from the Slater-type SCF functions [13, 14] and the metal-ligand distance R_0 in the studied system. From $R_0 \approx 2.496, 2.662$ and $2.770 \text{ \AA}$ [2] for CsMgCl_3 , CsMgBr_3 , and CsCdBr_3 , respectively, we obtain the group overlap integrals for Cr^{3+} in the three crystals. They are shown in Table 1.

Table 1. The group overlap integrals, spin-orbit coupling parameters and orbital reduction factors for Cr^{3+} in CsMgCl_3 , CsMgBr_3 , and CsCdBr_3 crystals.

	$S_{dp}(e_g)$	$S_{dp}(t_{2g})$	ζ (cm^{-1})	ζ' (cm^{-1})	k	k'
$\text{CsMgCl}_3:\text{Cr}^{3+}$	0.0582	0.0189	282.5	138.9	0.8779	0.6201
$\text{CsMgBr}_3:\text{Cr}^{3+}$	0.0531	0.0161	524.4	-119.9	0.8707	0.5993
$\text{CsCdBr}_3:\text{Cr}^{3+}$	0.0418	0.0118	521.5	-116.4	0.8717	0.6048

From the optical spectra of $\text{CsMgCl}_3:\text{Cr}^{3+}$ [15], we have

$$B \approx 500 \text{ cm}^{-1}, C \approx 2625 \text{ cm}^{-1}, Dq \approx 1360 \text{ cm}^{-1}. \quad (5)$$

For CsBBr_3 crystals, from the method in [10], we obtain for $\text{CsMgBr}_3:\text{Cr}^{3+}$,

$$B \approx 480 \text{ cm}^{-1}, C \approx 2520 \text{ cm}^{-1}, Dq \approx 1250 \text{ cm}^{-1}, \quad (6)$$

and for $\text{CsCdBr}_3:\text{Cr}^{3+}$,

$$B \approx 480 \text{ cm}^{-1}, C \approx 2520 \text{ cm}^{-1}, Dq \approx 1200 \text{ cm}^{-1}. \quad (7)$$

Thus, from (3) and (4), N_{γ} and λ_{γ} can be calculated. From the parameters ζ_d^0 and ζ_p^0 given above, the parameters in (2) for Cr^{3+} in the three CsBX_3 crystals can be obtained. They are also shown in Table 1.

The trigonal field parameters ν and ν' for a C_{3v} center can be given in the superposition model [16] as

$$\begin{aligned} \nu &\approx \sum_{i=1}^2 \left[\frac{9}{7}\bar{A}_2(R_0) \left(\frac{R_0}{R_i} \right)^{t_2} (3\cos^2\theta_i - 1) + \frac{20}{21}\bar{A}_4(R_0) \left(\frac{R_0}{R_i} \right)^{t_4} (35\cos^4\theta_i - 20\cos^2\theta_i + 3) \right. \\ &\quad \left. + \frac{20\sqrt{2}}{3}\bar{A}_4(R_0) \left(\frac{R_0}{R_i} \right)^{t_4} \sin^3\theta_i \cos\theta_i \right], \end{aligned}$$

Table 2. EPR parameters ($g_{\parallel}$, $g_{\perp}$ and D) and the displacements Δx_1 and Δx_2 for two types of trigonal Cr^{3+} centers in CsMgCl_3 , CsMgBr_3 , and CsCdBr_3 crystals.

Center	Δx_1 (Å) ^a	Δx_2 (Å) ^b	Cal.	$g_{\parallel}$ Expt. [3]	Cal.	$g_{\perp}$ Expt. [3]	Cal.	D (cm ⁻¹) Expt. [3]
CsMgCl₃:								
$\text{Cr}^{3+}\text{-Li}^+$	0.08	0.270	1.985	1.991(4)	1.985	1.991(4)	0.0087	0.0088(2)
-Cu^+	0.08	0.264	1.985	1.987(3)	1.985	1.987(3)	0.0272	0.0272(8)
-Na^+	0.08	0.246	1.985	1.991(3)	1.985	1.991(3)	0.086	0.086(1)
$\text{Cr}^{3+}\text{-V}_\text{B}\text{-Cr}^{3+}$	0.10	0.196	1.986	1.984	1.984	1.984	0.221	0.221
-In^{3+}	0.10	0.196	1.986	1.984(4)	1.984	1.983(4)	0.221	0.220(1)
-Sc^{3+}	0.10	0.196	1.986	1.984(2)	1.984	1.983(2)	0.221	0.221(1)
-Y^{3+}	0.10	0.196	1.986	1.984(2)	1.984	1.983(2)	0.221	0.222(1)
-Lu^{3+}	0.10	0.196	1.986	1.984(2)	1.984	1.983(2)	0.221	0.224(1)
CsMgBr₃:								
$\text{Cr}^{3+}\text{-Li}^+$	0.05	0.233	2.016	2.012(6)	2.016	2.012(6)	0.0174	0.0171(5)
$\text{Cr}^{3+}\text{-V}_\text{B}\text{-Cr}^{3+}$	0.10	0.261	2.016	2.011	2.016	2.011	0.228	0.228
CsCdBr₃:								
$\text{Cr}^{3+}\text{-Li}^+$	0.09	0.206	2.016	2.014(6)	2.017	2.014(6)	0.0330	0.0329(8)
-Cu^+	0.09	0.209	2.016	2.014(3)	2.017	2.016(3)	0.426	0.0426(8)
-Na^+	0.09	0.221	2.016	2.014(3)	2.016	2.014(3)	0.0962	0.0964(8)
$\text{Cr}^{3+}\text{-V}_\text{B}\text{-Cr}^{3+}$	0.11	0.249	2.016	2.010(4)	2.016	2.010(4)	0.252	0.251
-In^{3+}	0.11	0.249	2.016	2.015(4)	2.016	2.010(4)	0.252	0.246(4)

^a The displacement of Cr^{3+} towards M^+ (or V_B). ^b The displacement of the three O^{2-} far away from M^+ (or V_B).

$$v' \approx \sum_{i=1}^2 \left[\frac{3\sqrt{2}}{7} \bar{A}_2(R_0) \left(\frac{R_0}{R_i} \right)^{t_2} (3 \cos^2 \theta_i - 1) + \frac{5\sqrt{2}}{21} \bar{A}_4(R_0) \left(\frac{R_0}{R_i} \right)^{t_4} (35 \cos^4 \theta_i - 30 \cos^2 \theta_i + 3) + \frac{10}{3} \bar{A}_4(R_0) \left(\frac{R_0}{R_i} \right)^{t_4} \sin^3 \theta_i \cos \theta_i \right], \quad (8)$$

where the power-law exponents are $t_2 \approx 3$ and $t_4 \approx 5$ [16–18]. $\bar{A}_2(R_0)$ and $\bar{A}_4(R_0)$ are the intrinsic parameters with the reference distance R_0 . For $3d^n$ ions in an octahedron, we have $\bar{A}_4(R_0) = 3/4Dq$ [17–19] and $\bar{A}_2(R_0) \approx (9 \sim 12)\bar{A}_4(R_0)$ [18–20]. We take the mean value $\bar{A}_2(R_0) \approx 10.5\bar{A}_4(R_0)$ here. R_i ($i = 1$ or 2) and θ_i are, respectively, the impurity-ligand distance and the angle between the directions of R_i and C_3 -axis. They can be calculated from the structural data R_0 and θ_0 in the host crystals, and the displacements Δx_1 and Δx_2 . The angles θ_0 are 51.7° , 52.4° , and 52.65° [2] in CsMgCl_3 , CsMgBr_3 , and CsCdBr_3 , respectively. Thus, from the above formulas and parameters, we obtain the displacements Δx_1 and Δx_2 (see Table 2) by fitting the calculated EPR parameters to the observed values for the $\text{Cr}^{3+}\text{-M}^+$ and $\text{Cr}^{3+}\text{-V}_\text{B}\text{-M}^{3+}$ centers in the three CsBX_3 crystals. The calculated EPR parameters are compared with the observed values in Table 2.

3. Discussion

a) From the above studies one can find that the EPR parameters $g_{\parallel}$, $g_{\perp}$ and D for the trigonal $\text{Cr}^{3+}\text{-M}^+$ and $\text{Cr}^{3+}\text{-V}_\text{B}\text{-M}^{3+}$ centers in CsMgCl_3 , CsMgBr_3 and CsCdBr_3 crystals can be reasonably explained by considering suitable displacements Δx_1 and Δx_2 (see Table 2). The displacement directions of Δx_1 and Δx_2 are consistent with the expectation based on the electrostatic interactions. So, the defect structures for both types of Cr^{3+} centers can be regarded as reasonable.

b) For the $\text{Cr}^{3+}\text{-V}_\text{B}\text{-M}^{3+}$ centers, the displacements Δx_1 of Cr^{3+} and Δx_2 of O^{2-} are mainly caused by the effective charge of the nearest-neighboring V_B . They are not sensitive to the size and nature of M^{3+} , because M^{3+} is in the next-neighboring site along the C_3 -axis. So the fact, that the EPR parameters and hence the displacements Δx_1 and Δx_2 for various $\text{Cr}^{3+}\text{-V}_\text{B}\text{-M}^{3+}$ centers in the same crystal are almost the same (see Table 2), can be understood.

c) For the $\text{Cr}^{3+}\text{-M}^+$ centers, since the M^+ ion is in the nearest-neighboring site, the size and nature of M^+ ion can influence the displacements Δx_1 and Δx_2 (and hence the EPR parameters). This point agrees with our calculations (see Table 2).

d) The effective charge ($\approx -2e$) of V_B is larger than that ($\approx -e$) of M^+ in the B^{2+} site. Thus it can be expected that the displacements Δx_1 and Δx_2 in $\text{Cr}^{3+}\text{-V}_\text{B}\text{-M}^{3+}$ centers are larger than those in $\text{Cr}^{3+}\text{-}$

M^+ centers. Our calculated results for $\text{CsMgBr}_3\text{:Cr}^{3+}$ and $\text{CsCdBr}_3\text{:Cr}^{3+}$ (see Table 2) support the expectation. However, for $\text{CsMgCl}_3\text{:Cr}^{3+}$, the calculated Δx_2 in $\text{Cr}^{3+}\text{-V}_\text{B}\text{-M}^{3+}$ centers are smaller than those in $\text{Cr}^{3+}\text{-M}^+$ centers. The reason is not known (it may, in our opinion, be due to the repulsive force caused by the overlap of electronic clouds, because the $\text{M}^+\text{-Cl}^-$ distances are smaller) and remains an open question.

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