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 Cr^{3+}-M^+ ($M^+ = Li^+, Cu^+, Na^+$) and Cr^{3+}-V_B-M^{3+} (M^{3+} = Cr^{3+}, In^{3+}, Sc^{3+}, Y^{3+}, Lu^{3+}; V_B denotes the B^{2+} vacancy) centers in some $CsBX_3$ (B = Mg, Cd; X = Cl, 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 $CsBX_3$ (B = Mg, Cd; X = Cl, 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 $(BX_6)^{4-}$ 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^+ ($M^+ = Li^+$, Cu^+ or Na^+) at a nearest-neighboring B^{2+} site along the C-axis (so it is called Cr^{3+}-M^+ center), and another type of the trigonal Cr^{3+} center is Cr^{3+}-V_B-M^{3+} ($M^{3+} = Cr^{3+}$, In^{3+}, Sc^{3+}, 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 M^+-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 $CsBX_3$:Cr^{3+} crystals, since the spin-orbit (SO) coupling parameter ζ_p^0 ($\approx 587\ cm^{-1}$ for Cl^- and $2460\ cm^{-1}$ for Br^- [8]) of the ligand ion X^- is greater than that ($\zeta_d^0 \approx 273\ cm^{-1}$ [9]) of the central metal ion Cr^{3+}, we should apply the high-order perturba-

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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]:

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

with

$$\begin{aligned}
&\zeta = N_\mathrm{t}(\zeta_\mathrm{d}^0 + \lambda_\mathrm{t}^2\zeta_\mathrm{p}^0/2), \quad \zeta' = (N_\mathrm{t}N_\mathrm{e})^{1/2}(\zeta_\mathrm{d}^0 - \lambda_\mathrm{t}\lambda_\mathrm{e}\zeta_\mathrm{p}^0/2), \\
&k = N_\mathrm{t}[1 - 2\lambda_\mathrm{t}S_\mathrm{dp}(\mathrm{t_{2g}}) + \lambda_\mathrm{t}^2/2], \quad k' = (N_\mathrm{t}N_\mathrm{e})^{1/2}[1 - \lambda_\mathrm{t}S_\mathrm{dp}(\mathrm{t_{2g}}) - \lambda_\mathrm{e}S_\mathrm{dp}(\mathrm{e_g}) - \lambda_\mathrm{t}\lambda_\mathrm{e}/2)],
\end{aligned} \tag{2}$$

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. v and v' are the trigonal field parameters. N_γ ($\gamma = \mathrm{t_g}$ or $\mathrm{e_g}$) 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]

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

and the approximate relationship [10, 11]

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

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 $B_0 \approx 1030$ cm^{-1} and $C_0 \approx 3850$ cm^{-1} [9]. The group overlap integral $S_\mathrm{dp}(\gamma)$ 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 Å [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.

	$S_\mathrm{dp}(\mathrm{e_g})$	$S_\mathrm{dp}(\mathrm{t_{2g}})$	ζ (cm^{-1})	ζ' (cm^{-1})	k	k'
$CsMgCl_3$:Cr^{3+}	0.0582	0.0189	282.5	138.9	0.8779	0.6201
$CsMgBr_3$:Cr^{3+}	0.0531	0.0161	524.4	−119.9	0.8707	0.5993
$CsCdBr_3$:Cr^{3+}	0.0418	0.0118	521.5	−116.4	0.8717	0.6048

From the optical spectra of $CsMgCl_3$:Cr^{3+} [15], we have

$$B \approx 500\ \mathrm{cm^{-1}},\ C \approx 2625\ \mathrm{cm^{-1}},\ Dq \approx 1360\ \mathrm{cm^{-1}}. \tag{5}$$

For $CsBBr_3$ crystals, from the method in [10], we obtain for $CsMgBr_3$:Cr^{3+},

$$B \approx 480\ \mathrm{cm^{-1}},\ C \approx 2520\ \mathrm{cm^{-1}},\ Dq \approx 1250\ \mathrm{cm^{-1}}, \tag{6}$$

and for $CsCdBr_3$:Cr^{3+},

$$B \approx 480\ \mathrm{cm^{-1}},\ C \approx 2520\ \mathrm{cm^{-1}},\ Dq \approx 1200\ \mathrm{cm^{-1}}. \tag{7}$$

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

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

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.

			$g_\parallel$		$g_\perp$		D (cm^{-1})	
Center	Δx_1 (Å)[a]	Δx_2 (Å)[b]	Cal.	Expt. [3]	Cal.	Expt. [3]	Cal.	Expt. [3]
$CsMgCl_3$:								
Cr^{3+}-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)
Cr^{3+}-V_B-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)
$CsMgBr_3$:								
Cr^{3+}-Li^+	0.05	0.233	2.016	2.012(6)	2.016	2.012(6)	0.0174	0.0171(5)
Cr^{3+}-V_B-Cr^{3+}	0.10	0.261	2.016	2.011	2.016	2.011	0.228	0.228
$CsCdBr_3$:								
Cr^{3+}-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)
Cr^{3+}-V_B-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).

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

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 Cr^{3+}-M^+ and Cr^{3+}-V_B-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 Cr^{3+}-M^+ and Cr^{3+}-V_B-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 Cr^{3+}-V_B-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 Cr^{3+}-V_B-M^{3+} centers in the same crystal are almost the same (see Table 2), can be understood.

c) For the Cr^{3+}-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 Cr^{3+}-V_B-M^{3+} centers are larger than those in Cr^{3+}-M^+ centers. Our calculated results for $CsMgBr_3$:Cr^{3+} and $CsCdBr_3$:Cr^{3+} (see Table 2) support the expectation. However, for $CsMgCl_3$:Cr^{3+}, the calculated Δx_2 in Cr^{3+}-V_B-M^{3+} centers are smaller than those in Cr^{3+}-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 M^+-Cl^- distances are smaller) and remains an open question.

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