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1998 J. Phys.: Condens. Matter 10 7545

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Theoretical investigations of the zero-field splittings and g factors for the Cr^{3+} ion at the rhombic defect site in the AgCl crystal

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Received 7 November 1997, in final form 18 May 1998

Abstract. In this paper we establish the high-order perturbation formulas of zero-field splittings D and E and g factors g_x , g_y and g_z for $3d^3$ ions in rhombic symmetry by using a two-spin-orbit (SO) coupling parameter model, in which not only the contribution due to the SO coupling of the central $3d^3$ ion but also that of the ligands are included. Based on these formulas, all five EPR parameters for the Cr^{3+} ion at the rhombic defect site in the cubic AgCl crystal are satisfactorily explained by considering suitable defect-induced lattice distortion. The relative importance among the various contributions to the EPR parameters from the SO couplings of the central $3d^3$ ion, the ligand ions and the mixed ones is discussed. It can be seen that for the $3d^3$ ions in crystals with ligands having large SO coupling parameter, the contribution due to the SO coupling of ligands cannot be neglected and we should apply the two-SO parameter model in studies of EPR parameters.

1. Introduction

The theoretical calculations of EPR parameters for $3d^3$ ions in low symmetry are often based on high-order perturbation formulas. These formulas can be derived from different theoretical models. For the sake of simplicity, in classical crystal-field theory, only the contribution from the spin-orbit (SO) coupling of the central $3d^3$ ions is considered in these perturbation formulas, as done by Macfarlane [1, 2] and He and Du [3, 4]. This is the conventional one-SO-parameter model which is suitable for $3d^3$ ions in crystals with ligand ions (such as F^- and O^{2-} ions) having small SO coupling parameter. However, if the SO coupling parameter of ligand electrons is large, we should employ a two-SO-parameter model where not only the contribution due to the SO coupling of the central $3d^3$ ions but also that of ligands is included. In previous papers [5–7], the high-order perturbation formulas of EPR parameters based on the two-SO-parameter model for $3d^3$ ions in cubic, trigonal and tetragonal symmetries were established. However, for $3d^3$ ions in the more complex rhombic symmetry, no perturbation formulas of EPR parameters based on the two-SO-parameter model have been reported. In this paper, we first of all establish the high-order perturbation formulas of EPR parameters based on the two-SO-parameter model for $3d^3$ ions in rhombic symmetry. According to these formulas, we can explain the EPR parameters for $3d^3$ ions in rhombic symmetry, or, conversely, study the local structure of some rhombic $3d^3$ clusters in crystals from their EPR data. Since the transition-metal impurities can play an important role in the properties of inorganic compounds, the studies of the local structural

parameters of defect site are of significance. As an example, we apply the above formulas to the studies of the EPR parameters D , E and g_i ($i = x, y, z$) for the Cr^{3+} ion at the rhombic defect site in the cubic AgCl crystal by considering suitable defect-induced lattice distortion. The calculated results show good agreement with the observed values. The local lattice distortion and the relative importance among the various contributions to the EPR parameters are discussed.

2. Theoretical formulas

In the two-SO-parameter model, the contributions from the SO coupling of the central $3d^3$ ions and that of ligands should be included, so we take the LCAO orbital

$$|\Psi_\gamma\rangle = N_\gamma^{1/2}(|d_\gamma\rangle - \lambda_\gamma |p_\gamma\rangle) \quad (1)$$

as the one-electron basis function, where $|d\rangle$ is the d orbital of the central $3d^3$ ion and $|p\rangle$ is the p orbital of the ligands; the subscript $\gamma = t_g$ or e_g is the irreducible representation of the O_h group. N_γ and λ_γ are the normalization factors and the orbital mixing coefficients.

For $3d^3$ ions in a rhombic symmetry (where the symmetry axes and hence the principal axes of EPR parameters lie along $\langle 110\rangle$, $\langle \bar{1}10\rangle$ and $\langle 001\rangle$ axes), the Hamiltonian can be written as

$$H = H_{cryst} + H_a(B, C) + H_b(B, C) + H_{so}(\zeta_d, \zeta_p) + H_z \quad (2)$$

with [3, 4]

$$\begin{aligned} H_{cryst} = H_{cub} + H_{rhomb} = & [\bar{\gamma}_{00}Z_{00} + \bar{\gamma}_{40}r^4Z_{40} + \bar{\gamma}_{44}^c r^4Z_{44}^c] \\ & + [(\gamma_{00} - \bar{\gamma}_{00})Z_{00} + \gamma_{20}r^2Z_{20} + \gamma_{22}^c r^2Z_{22}^c + (\gamma_{40} - \bar{\gamma}_{40})r^4Z_{40} \\ & + \gamma_{42}^c r^4Z_{42}^c + (\gamma_{44} - \bar{\gamma}_{44}^c)r^4Z_{44}^c] \end{aligned} \quad (3)$$

where H_{cub} , H_{rhomb} , $H_a(B, C)$ and $H_b(B, C)$, respectively, are the cubic and rhombic parts of crystal field and the diagonal and the off-diagonal terms of the electrostatic Coulomb interaction which appear in the d-d transition energy matrices. The SO coupling Hamiltonian $H_{so}(\zeta_d, \zeta_p)$ (where ζ_d and ζ_p are the SO coupling parameters of the $3d^3$ ion and ligand, respectively) can be written as [5, 7]

$$H_{so}(\zeta_d, \zeta_p) = \sum \zeta_d(r_{id}) \mathbf{I}_{id} \cdot \mathbf{s} + \sum \zeta_p(r_{ip}) \mathbf{I}_{ip} \cdot \mathbf{s} \quad (4)$$

and the Zeeman term H_z is [5, 7]

$$H_z = \beta H(\mathbf{L} + g_s \mathbf{s}). \quad (5)$$

Similar to Macfarlane's perturbation-loop method [1, 2], we choose a strong-field cubic basis for the perturbation calculations. The perturbation Hamiltonian for $3d^3$ ions in rhombic symmetry is

$$H' = H_{rhomb} + H_b(B, C) + H_{so}(\zeta_d, \zeta_p) + H_z. \quad (6)$$

Thus, the high-order perturbation formulas of EPR parameters based on the two-SO-parameter model can be derived. They are

$$D = D(\zeta_d) + D(\zeta_p) + D(\zeta_d, \zeta_p)$$

$$\begin{aligned} D(\zeta_d) = & (1/9)(\zeta_d^{te})^2(35D_t + 7D_\eta)(1/E_1^2 - 1/E_3^2) + (\zeta_d^{te})^2\zeta_d^t(35D_t + 7D_\eta) \\ & \times [(1/E_1^3 + 1/E_3^3 - 1/E_1^2E_3)/27 + 5/(108E_1E_3^2)] \\ & + (\zeta_d^{te})^3(35D_t + 7D_\eta)[4/(E_1^2E_2) - 1/(E_3^2E_2)]/36 \\ & + (1/72)(\zeta_d^{te})^2\{-72B/(E_2E_3^2)(35D_t + 7D_\eta) \end{aligned}$$

$$\begin{aligned}
& + (1/E_1^3 - 1/E_3^3)[(7D_t + 7D_\xi + 3D_\eta)^2 + (7D_t - 7D_\xi + 3D_\eta)^2 \\
& + 112(5D_t + D_\eta)(7D_t - D_\eta) - 32(7D_t + D_\eta)^2] \} \\
D(\zeta_p) = & (1/9)(\zeta_p^{te})^2(35D_t + 7D_\eta)(1/E_1^2 - 1/E_3^2) + (\zeta_p^{te})^2\zeta_p^t(35D_t + 7D_\eta) \\
& \times [(1/E_1^3 + 1/E_3^3 - 1/E_1^2E_3)/27 + 5/(108E_1E_3^2)] \\
& - (\zeta_p^{te})^3(35D_t + 7D_\eta)[4/(E_1^2E_2) - 1/(E_3^2E_2)]/36 \\
& + (1/72)(\zeta_p^{te})^2\{-72B/(E_2E_3^2)(35D_t + 7D_\eta) \\
& + (1/E_1^3 - 1/E_3^3)[(7D_t + 7D_\xi + 3D_\eta)^2 + (7D_t - 7D_\xi + 3D_\eta)^2 \\
& + 112(5D_t + D_\eta)(7D_t - D_\eta) - 32(7D_t + D_\eta)^2]\} \quad (7) \\
D(\zeta_d, \zeta_p) = & -(2/9)\zeta_d^{te}\zeta_p^{te}(35D_t + 7D_\eta)(1/E_1^2 - 1/E_3^2) \\
& + [(\zeta_d^{te})^2\zeta_p^t + (\zeta_p^{te})^2\zeta_d^t - 2\zeta_d^t\zeta_p^{te}\zeta_d^{te} - 2\zeta_p^t\zeta_p^{te}\zeta_d^{te}]/(35D_t + 7D_\eta) \\
& \times [(1/E_1^3 + 1/E_3^3 - 1/E_1^2E_3)/27 + 5/(108E_1E_3^2)] \\
& + [3(\zeta_d^{te})^2\zeta_p^{te} - 3(\zeta_p^{te})^2\zeta_d^{te}]/(35D_t + 7D_\eta)[4/(E_1^2E_2) - 1/(E_3^2E_2)]/36 \\
& - (1/36)\zeta_d^{te}\zeta_p^{te}\{-72B/(E_2E_3^2)(35D_t + 7D_\eta) \\
& + (1/E_1^3 - 1/E_3^3)[(7D_t + 7D_\xi + 3D_\eta)^2 + (7D_t - 7D_\xi + 3D_\eta)^2 \\
& + 112(5D_t + D_\eta)(7D_t - D_\eta) - 32(7D_t + D_\eta)^2]\}
\end{aligned}$$

$$E = E(\zeta_d) + E(\zeta_p) + E(\zeta_d, \zeta_p)$$

$$\begin{aligned}
E(\zeta_d) = & [7(\zeta_d^{te})^2/9]D_\xi(1/E_1^2 + 1/E_3^2) + [7(\zeta_d^{te})^2/18]D_\xi \\
& \times [(1/E_1^3 + 1/E_3^3)(35D_t - 7D_\eta) + 18B/(E_2E_3^2)] \\
& + [7(\zeta_d^{te})^2\zeta_d^t/54]D_\xi[1/E_1^3 - 1/E_3^3 - 1/(E_1^2E_3) - 5/(4E_1E_3^2)] \\
& + [7(\zeta_d^{te})^3/18]D_\xi[1/E_1^2E_2 + 1/(4E_2E_3^2)] \\
E(\zeta_p) = & [7(\zeta_p^{te})^2/9]D_\xi(1/E_1^2 + 1/E_3^2) + [7(\zeta_p^{te})^2/18]D_\xi \\
& \times [(1/E_1^3 + 1/E_3^3)(35D_t - 7D_\eta) + 18B/(E_2E_3^2)] \\
& + [7(\zeta_p^{te})^2\zeta_p^t/54]D_\xi[1/E_1^3 - 1/E_3^3 - 1/(E_1^2E_3) - 5/(4E_1E_3^2)] \\
& - [7(\zeta_p^{te})^3/18]D_\xi[1/E_1^2E_2 + 1/(4E_2E_3^2)] \quad (8)
\end{aligned}$$

$$\begin{aligned}
E(\zeta_d, \zeta_p) = & (-14\zeta_d^{te}\zeta_p^{te}/9)D_\xi(1/E_1^2 + 1/E_3^2) - (7\zeta_d^{te}\zeta_p^{te}/9)D_\xi \\
& \times [(1/E_1^3 + 1/E_3^3)(35D_t - 7D_\eta) + 18B/(E_2E_3^2)] \\
& + \{7[(\zeta_d^{te})^2\zeta_p^t + (\zeta_p^{te})^2\zeta_d^t - 2\zeta_d^t\zeta_p^{te}\zeta_d^{te} - 2\zeta_p^t\zeta_p^{te}\zeta_d^{te}]/54\}D_\xi \\
& \times [1/E_1^3 - 1/E_3^3 - 1/(E_1^2E_3) - 5/(4E_1E_3^2)] \\
& + \{7[(\zeta_d^{te})^2\zeta_p^{te} - (\zeta_p^{te})^2\zeta_d^{te}]/6\}D_\xi[1/E_1^2E_2 + 1/(4E_2E_3^2)]
\end{aligned}$$

$$\Delta g_z = g_z - g_s = \Delta g_z(\zeta_d) + \Delta g_z(\zeta_p) + \Delta g_z(\zeta_d, \zeta_p)$$

$$\begin{aligned}
\Delta g_z(\zeta_d) = & -8k'\zeta_d^{te}/3E_1 + [2(k - 2g_s)(\zeta_d^{te})^2 - 4k'\zeta_d^{te}\zeta_d^t]/9E_1^2 + 4(\zeta_d^{te})^2(k - 2g_s)/9E_3^2 \\
& - 2(\zeta_d^t)^2(k + g_s)/3E_2^2 + 4k'\zeta_d^{te}\zeta_d^t[1/9E_1E_3 - 1/3E_1E_2 + 1/3E_2E_3] \\
& + 16k'D_\eta\zeta_d^{te}/9E_1^2 \\
\Delta g_z(\zeta_p) = & 8k'\zeta_p^{te}/3E_1 + [2(k - 2g_s)(\zeta_p^{te})^2 + 4k'\zeta_p^{te}\zeta_p^t]/9E_1^2 + 4(\zeta_p^{te})^2(k - 2g_s)/9E_3^2 \\
& - 2(\zeta_p^t)^2(k + g_s)/3E_2^2 - 4k'\zeta_p^{te}\zeta_p^t[1/9E_1E_3 - 1/3E_1E_2 + 1/3E_2E_3] \\
& - 16k'D_\eta\zeta_p^{te}/9E_1^2 \quad (9)
\end{aligned}$$

$$\Delta g_z(\zeta_d, \zeta_p) = -[4k'(\zeta_p^t\zeta_d^{te} - \zeta_d^t\zeta_p^{te}) + 4(k - 2g_s)\zeta_d^{te}/\zeta_p^{te}]/9E_1^2 - 8\zeta_d^{te}\zeta_p^{te}(k - 2g_s)/9E_3^2$$

$$-4\zeta_p^t \zeta_d^t (k + g_s) / 3E_2^2 + 4k' (\zeta_p^t \zeta_d^{te} - \zeta_d^t \zeta_p^{te}) \\ \times [1/9E_1E_3 - 1/3E_1E_2 + 1/3E_2E_3]$$

$$\Delta g_x = g_x - g_s = \Delta g_x(\zeta_d) + \Delta g_x(\zeta_p) + \Delta g_x(\zeta_d, \zeta_p) \\ \Delta g_x(\zeta_d) = \Delta g_z(\zeta_d) - 2k' \zeta_d^{te} (35D_t + 7D_\xi + 7D_\eta) / 9E_1^2 \\ \Delta g_x(\zeta_p) = \Delta g_z(\zeta_p) + 2k' \zeta_p^{te} (35D_t + 7D_\xi + 7D_\eta) / 9E_1^2 \quad (10)$$

$$\Delta g_x(\zeta_d, \zeta_p) = \Delta g_z(\zeta_d, \zeta_p) \\ \Delta g_y = g_y - g_s = \Delta g_y(\zeta_d) + \Delta g_y(\zeta_p) + \Delta g_y(\zeta_d, \zeta_p) \\ \Delta g_y(\zeta_d) = \Delta g_z(\zeta_d) - 2k' \zeta_d^{te} (35D_t - 7D_\xi + 7D_\eta) / 9E_1^2 \\ \Delta g_y(\zeta_p) = \Delta g_z(\zeta_p) + 2k' \zeta_p^{te} (35D_t - 7D_\xi + 7D_\eta) / 9E_1^2 \quad (11)$$

$$\Delta g_y(\zeta_d, \zeta_p) = \Delta g_z(\zeta_d, \zeta_p)$$

with

$$\zeta_d^t = N_t \zeta_d^0 \quad \zeta_p^t = N_t \lambda_t^2 \zeta_p^0 / 2 \quad \zeta_d^{te} = (N_t N_e)^{1/2} \zeta_d^0 \quad \zeta_p^{te} = (N_t N_e)^{1/2} \lambda_t \lambda_e \zeta_p^0 / 2 \\ k = N_t (1 + \lambda_t^2 / 2) \quad k' = (N_t N_e)^{1/2} (1 - \lambda_t \lambda_e / 2). \quad (12)$$

In the above EPR parameters P ($P = D, E, \Delta g_i$), $P(\zeta_d)$, $P(\zeta_p)$ and $P(\zeta_d, \zeta_p)$ denote the contributions from the $3d^3$ ion, the ligand ions and the mixed ones, respectively. B and C are the Racah parameters. g_s ($= 2.0023$) is the spin-only value. E_i ($i = 1, 2, 3$) in (7)–(11) are the zero-order energy denominators defined in [1, 2]. The rhombic field parameters D_t , D_ξ and D_η are defined by

$$D_t = -\frac{1}{7\sqrt{4\pi}} \langle (\gamma_{40} - \bar{\gamma}_{40}) r^4 \rangle \\ D_\xi = -\frac{2\sqrt{5}}{7\sqrt{4\pi}} \langle \gamma_{42}^c r^4 \rangle \quad (13) \\ D_\eta = \sqrt{\frac{5}{7}} \frac{1}{\sqrt{4\pi}} \langle (\gamma_{44}^c - \bar{\gamma}_{44}^c) r^4 \rangle.$$

Noteworthy, the above perturbation calculations show that, in this kind of rhombic symmetry, the contributions to the EPR parameters from the rhombic distortion are described by the rhombic field parameters D_t , D_ξ and D_η , corresponding to the terms $(\gamma_{40} - \bar{\gamma}_{40})$, γ_{42}^c and $(\gamma_{44}^c - \bar{\gamma}_{44}^c)$, respectively, and the contributions due to the terms including γ_{22}^c and γ_{20} are cancelled. This point is also held in the conventional single-SO formulas for d^3 ions in rhombic symmetry [3, 4].

Obviously, in the conventional one-SO-parameter model, $D = D(\zeta_d)$, $E = E(\zeta_d)$ and $\Delta g_i = \Delta g_i(\zeta_d)$.

3. Calculations

Now, we apply the above formulas to study the local structure of the rhombic Cr^{3+} centre in the AgCl crystal (where the SO coupling parameter ($\zeta_p^0 \approx 587 \text{ cm}^{-1}$ [8]) of the free ligand ion Cl^- is much larger than that ($\zeta_d^0 \approx 273 \text{ cm}^{-1}$ [9]) of the free Cr^{3+} ion) by calculating its EPR parameters. AgCl is an ionic conductor. The knowledge of local structure for Cr^{3+} in AgCl is helpful to the understanding of the ionic conductivity and optical absorption [10, 11]. So, the studies are of interest. The experimental x , y and z axes of the spin Hamiltonian and hence of the rhombic coordination for the rhombic centre are $\langle 110 \rangle$, $\langle \bar{1}10 \rangle$ and $\langle 001 \rangle$,

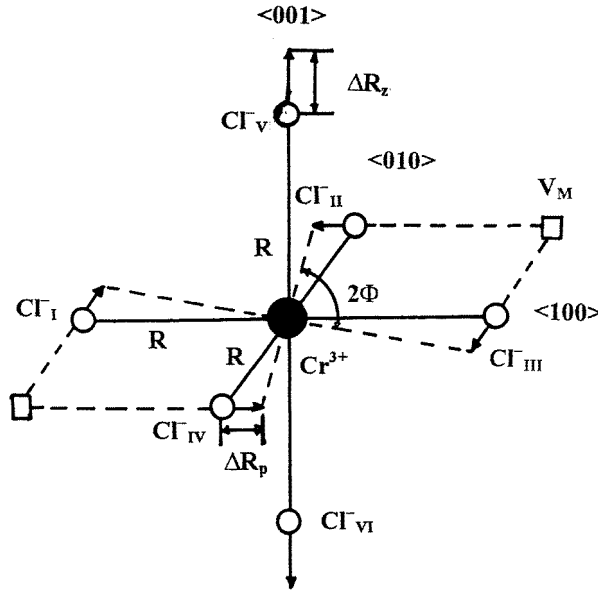


Figure 1. The defect-induced lattice distortion for the rhombic $V_M-Cr^{3+}-V_M$ centre in AgCl expected from the electrostatic interaction. The ions Cl_{v}^{-} and Cl_{vi}^{-} are repulsed by both V_M and each planar Cl^{-} ion is repulsed by the neighbouring V_M . The displacement of the Cl_{v}^{-} and Cl_{vi}^{-} is ΔR_z and that of the four planar Cl^{-} ions is ΔR_p .

respectively [12], suggesting that the rhombic Cr^{3+} centre in cubic AgCl is formed by a Cr^{3+} ion associated with two nearest Ag^{+} vacancies (V_M) along the $\langle 110 \rangle$ and $\langle \bar{1}\bar{1}0 \rangle$ axes (see figure 1) due to charge compensation, and so we call it the rhombic $V_M-Cr^{3+}-V_M$ centre. The effective charge of V_M is negative; it can be expected that the six Cl^{-} ions around the Cr^{3+} ion should be displaced owing to the electrostatic repulsive forces between the Cl^{-} ions and the two V_M . The displacement directions and amounts ΔR_p and ΔR_z are shown in figure 1. The cubic field parameter $Dq \propto R^{-n}$. The pressure experiment for NiO [13] and the theoretical studies based on molecular orbital calculations for $3d^3$ ions in many crystals [14, 15] show that $n \approx 5$, the value obtained from the point-charge model, is approximately valid. So, we apply this model to estimate the rhombic field parameters. Thus, we have

$$\begin{aligned} D_t &= eq \langle r^4 \rangle [1/(28R_{\perp}^5) + 1/(21R_{\parallel}^5) - 1/(12R^5)] \\ D_{\xi} &= eq \langle r^4 \rangle \cos 2\Phi / (21R_{\perp}^5) \\ D_{\eta} &= (5/6)eq \langle r^4 \rangle (\cos 4\Phi / R_{\perp}^5 + 1/R^5) \end{aligned} \quad (14)$$

where

$$R_{\perp} = (R^2 + \Delta R_p^2)^{1/2} \quad R_{\parallel} = R + \Delta R_z \quad \Phi = \pi/4 + \tan^{-1}(\Delta R_p/R) \quad (15)$$

and R is the impurity–ligand distance in the cubic centre. It can be expected that $R < R_H$ (where R_H is the cation–anion distance in the host crystal) in the AgCl: Cr^{3+} crystal owing to the smaller ionic radius and the extra charge of Cr^{3+} compared with those of the Ag^{+} ion. We can estimate R from the approximate formula [16, 17]

$$R \approx R_H + (r_i - r_h)/2 \quad (16)$$

where r_i and r_h are the ionic radii of the impurity and that of the replaced host ion, respectively. For the $\text{AgCl}:\text{Cr}^{3+}$ crystal, $r_i \approx 0.755 \text{ \AA}$, $r_h \approx 1.29 \text{ \AA}$ [18] and $R_H \approx 2.77 \text{ \AA}$ [19]. So we have $R \approx 2.503 \text{ \AA}$. The value of $eq\langle r^4 \rangle$ can be obtained from the observed Dq by using the formula $Dq = -eq\langle r^4 \rangle/6R^5$ based on the point-charge model. For the studied $\text{AgCl}:\text{Cr}^{3+}$, $Dq \approx 1310 \text{ cm}^{-1}$, $B \approx 600 \text{ cm}^{-1}$ and $C \approx 2400 \text{ cm}^{-1}$ are obtained from the optical spectra [10] and the value $eq\langle r^4 \rangle$ can be calculated.

Here, a semiempirical method [5] is employed to determine the LCAO coefficients N_γ and λ_γ . We have the approximate relationship [5]

$$f_\gamma = N_\gamma^2[1 + \lambda_\gamma^2 S_{dp}^2(\gamma) - 2\lambda_\gamma S_{dp}(\gamma)] \quad (17)$$

and the normalization correlation

$$N_\gamma(1 - 2\lambda_\gamma S_{dp}(\gamma) + \lambda_\gamma^2) = 1 \quad (18)$$

where $S_{dp}(\gamma)$ is the group overlap integral. $f_\gamma \approx f \approx (B/B_0 + C/C_0)/2$, where B_0 ($\approx 1030 \text{ cm}^{-1}$) and C_0 ($\approx 3850 \text{ cm}^{-1}$) are the Racah parameters of the free Cr^{3+} ion [9]. From the above parameters B and C in $\text{AgCl}:\text{Cr}^{3+}$, we obtain $f_\gamma \approx 0.6$ here. Since the rhombic distortion of the impurity centre is small, we obtain $S_{dp}(t_g) \approx 0.01854$ and $S_{dp}(e_g) \approx 0.05729$ by using the Slater-type SCF function [20, 21] and the distance R in $\text{AgCl}:\text{Cr}^{3+}$. Thus, from (17) and (18), we have $N_t \approx 0.7825$, $\lambda_t \approx 0.5461$, $N_e \approx 0.8003$ and $\lambda_e \approx 0.5601$. Substituting all these parameters related to the rhombic Cr^{3+} centre in the AgCl crystal into (7)–(11), we find that when $\Delta R_p \approx 0.044 \text{ \AA}$ and $\Delta R_z \approx 0.145 \text{ \AA}$, the five calculated EPR parameters D , E and Δg_i show very good agreement with the observed values (within the experimental errors) [12]. The comparisons between the calculated and observed EPR parameters are shown in table 1.

Table 1. The EPR parameters P ($P = D, E, g_x, g_y, g_z$) of the rhombic Cr^{3+} centre in AgCl .

P	D (10^{-4} cm^{-1})	E (10^{-4} cm^{-1})	Δg_x	Δg_y	Δg_z
$P(\zeta_d)$	696	409	-0.0309	-0.0305	-0.0301
$P(\zeta_p)$	74	44	0.0099	0.0098	0.0097
$P(\zeta_d, \zeta_p)$	-457	-269	6×10^{-5}	6×10^{-5}	6×10^{-5}
$P(\text{total})$	313	184	-0.0209	-0.0207	-0.0204
$P(\text{expt.})$ [12]	313(5)	184(1)	-0.0223(50)	-0.0223(50)	-0.0223(50)

4. Discussions

From the above studies, one can find that $\Delta R_p > 0$ and $\Delta R_z > 0$, suggesting that the displacement directions of Cl^- ions in figure 1 are consistent with the expectations based on the electrostatic interactions. Since the expectations of ion displacement directions based on the electrostatic interactions in similar cases, e.g., the tetragonal $\text{Cr}^{3+}-V_M$ centre in MgO , are supported by the embedded-quantum-cluster calculations [22] and EXAFS experiment [23], the displacement directions obtained in this paper can be regarded as physically reasonable. The larger displacement ΔR_z of the two ions Cl_V^- and Cl_{VI}^- than that of the four planar Cl^- ions may be because (i) the ions Cl_V^- and Cl_{VI}^- are repulsed by both V_M , and (ii) the repulsive force between Cl_I^- and Cl_{II}^- (and also that between Cl_{III}^- and Cl_{IV}^-) increases with decreasing distance between the two Cl^- ions caused by the V_M (see figure 1), which should limit the displacement ΔR_p . So, the above impurity-induced lattice distortions are understandable.

Table 1 shows that if only the contribution from the SO coupling of Cr³⁺ ions is considered, all the calculated EPR parameters $D(\zeta_d)$, $E(\zeta_d)$ and $\Delta g_i(\zeta_d)$ are in poor agreement with the observed values. Therefore, although the contributions to EPR parameters from the SO coupling of the central ion Cr³⁺ are the largest, the contributions from the terms related to the SO coupling of ligand cannot be neglected. In fact, one can find that for the zero-field splittings D and E in AgCl:Cr³⁺, the contributions from the mixing terms $D(\zeta_d, \zeta_p)$ and $E(\zeta_d, \zeta_p)$ are opposite in sign and about 65% in magnitude compared to the corresponding $D(\zeta_d)$ and $E(\zeta_d)$, and the contributions of $D(\zeta_p)$ and $E(\zeta_p)$ are also about 10% those of $D(\zeta_d)$ and $E(\zeta_d)$. For the g shifts Δg_i , the relative importance between the contributions from the SO coupling of ligand and mixing term is opposite to that for the zero-field splittings, i.e., the absolute values of $\Delta g_i(\zeta_p)$ are about 32% those of $\Delta g_i(\zeta_d)$ and the values of $\Delta g_i(\zeta_d, \zeta_p)$ are very small. According to (7)–(11), the main contribution to D (or E) arises from the third-order terms in $D(\zeta_d)$ and $D(\zeta_d, \zeta_p)$ (or $E(\zeta_d)$ and $E(\zeta_d, \zeta_p)$), thus the ratio $|D(\zeta_d, \zeta_p)/D(\zeta_d)|$ (or $|E(\zeta_d, \zeta_p)/E(\zeta_d)|$) is approximately $2(\zeta_p^{te}/\zeta_d^{te})$. However, the main contribution to Δg_i arises from the second-order terms in $\Delta g_i(\zeta_d)$ and $\Delta g_i(\zeta_p)$, thus the ratio $|\Delta g_i(\zeta_p)/\Delta g_i(\zeta_d)|$ is approximately $(\zeta_p^{te}/\zeta_d^{te})$. Therefore, the conclusion that the inclusion of the ligands gives larger contribution to the parameter D (or E) than that to the g factors (i.e., $|D(\zeta_d, \zeta_p)/D(\zeta_d)| \approx |E(\zeta_d, \zeta_p)/E(\zeta_d)| \approx 2|\Delta g_i(\zeta_p)/\Delta g_i(\zeta_d)|$) can be understood.

In summary, for all the EPR parameters D , E and Δg_i of the rhombic V_M -Cr³⁺- V_M centre in AgCl, since the SO coupling parameter of the ligand is larger than that of the central metal ion, the contributions from the terms related to the SO coupling of ligand are important and should be taken into account. Noteworthily, the contributions to EPR parameters from the SO coupling of ligand increase with the increasing SO coupling parameter. Therefore, in the studies of EPR parameters for 3d³ ions in crystals with ligands having large SO coupling parameter, the conventional one-SO-parameter model is not suitable and hence the two-SO-parameter model should be applied.

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