

Theoretical Investigations of the EPR Parameters for Three Tetragonal Centers in CsCl:Cr³⁺ Crystal

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Z. Naturforsch. **58a**, 93–96 (2003); received November 25, 2002

The electron paramagnetic resonance parameters zero-field splitting D and g factors g_{\parallel} and g_{\perp} of three tetragonal centers in CsCl: Cr³⁺ crystal at room temperature have been investigated by a two-spin-orbit (S.O.)-coupling parameter model. In this model, the contributions arising from the S.O. coupling of the central d^3 ion and the ligands are included. For center III, the very small D of the [CrCl₆]³⁻ cluster may be due to the displacement ($\approx 0.506 \text{ \AA}$) of the two substitutional Cl⁻ ions along the tetragonal (C_4) axis. For the centers I and II, the relatively larger D results from the contribution of two or one water molecules, i. e., corresponding to [CrCl_{6-n}(H₂O)_n]ⁿ⁻³ with, $n = 2$ or 1 along the C_4 axis, respectively. The reasonableness of the theoretical results is discussed.

Key words: Electron Paramagnetic Resonance (EPR); Crystal and Ligand-Field Theory; Cr³⁺; CsCl.

1. Introduction

Electron paramagnetic resonance (EPR) and optical studies [1, 2] on CsCl:Cr³⁺ crystals at room temperature have shown that Cr³⁺ occupies an interstitial site in the plane of four Cl⁻ (see Fig. 4 of [1]), and that the two host Cs⁺ along the [001] (or C_4) axis may be substituted by Cl⁻ ions or water molecules due to charge compensation, and so the local symmetry of Cr³⁺ is tetragonal. In fact three tetragonal Cr³⁺ centers, named I, II and III, were found in the EPR measurements [1]. For center III, the very small zero-field splitting D ($|D| \approx 25 \times 10^{-4} \text{ cm}^{-1}$) is attributed to an incorporated [CrCl₆]³⁻ cluster, as supported by the optical studies in Refs. [2–5]. In contrast, associated with the [CrCl_{6-n}(H₂O)_n]ⁿ⁻³ cluster for $n = 2$ or 1, the relatively larger D is attributed to the center I ($|D| \approx 2170 \times 10^{-4} \text{ cm}^{-1}$ [1]) or II ($|D| \approx 1400 \times 10^{-4} \text{ cm}^{-1}$ [1]), respectively. However, until now no satisfactory theoretical analysis has been made on the above three centers. In this paper, the EPR parameters D , g_{\parallel} and g_{\perp} for the three tetragonal Cr³⁺ centers are reasonably explained based on a two-spin-orbit-coupling parameter model.

2. Theory and Calculation

For transition-metal ($3d^n$) ions in crystals, theoretical investigations of the EPR parameters can be made

by using Macfarlane's high-order perturbation methods [6,7] when the S.O. coupling parameter of ligands is smaller than that of central metal ions. However for CsCl:Cr³⁺ crystal, where the S.O. coupling parameter ($\approx 587 \text{ cm}^{-1}$ [8]) of the ligands is much larger than that ($\approx 240 \text{ cm}^{-1}$ [9]) of the central Cr³⁺ ion, the contribution from S.O. coupling of the ligands cannot be neglected. So, in the study of the EPR parameters of the CsCl:Cr³⁺ crystal made in this paper the conventional perturbation formulas of D , g_{\parallel} and g_{\perp} for the $3d^3$ ion in tetragonal symmetry including only the contribution of the central d^3 ion should be replaced by two-S.O.-parameter formulas containing the contributions from both the central $3d^3$ ion and that of the ligands. This point has been supported by some authors [10, 11].

For $3d^3$ ions in tetragonal symmetry, the two-S.O.-coupling parameter formulas of D , g_{\parallel} and g_{\perp} can be expressed as [12]

$$D = \frac{35}{9} D_t \zeta'^2 [1/E_1^2 - 1/E_3^2] - 35 B D_t \zeta \zeta' / E_2 E_3^2,$$

$$g_{\parallel} = g_s \frac{8k' \zeta'}{3E_1} - \frac{2\zeta'}{9E_1^2} (2k' \zeta - k\zeta' + 2g_s \zeta') \\ + \frac{4\zeta'^2}{9E_3^2} (k - 2g_s) - \frac{2\zeta^2}{3E_2^2} (k + g_s)$$

$$+ \frac{4k'\zeta'\zeta}{9E_1E_3} - \frac{4k'\zeta'\zeta}{3E_1E_2} \\ + \frac{4k'\zeta'\zeta}{3E_2E_3} + \frac{140k'\zeta'D_t}{9E_1^2},$$

$$g_{\perp} = g_{\parallel} - 210k'\zeta'D_t/9E_1^2, \quad (1)$$

where

$$\zeta = N_t(\zeta_d^0 + \lambda_t^2\zeta_p^0/2),$$

$$\zeta' = (N_tN_e)^{1/2}(\zeta_d^0 - \lambda_t\lambda_e^2\zeta_p^0/2),$$

$$k = N_t(1 + \lambda_t^2/2),$$

$$k' = (N_tN_e)^{1/2}(1 - \lambda_t\lambda_e/2), \quad (2)$$

and $g_s (= 2.0023)$ is the spin-only value. ζ_d^0 and ζ_p^0 are, respectively, the S.O. coupling parameters of the d electron of the central ion and that of the p electron of the ligand in free state. For CsCl:Cr³⁺ crystal under study, $\zeta_d^0 \approx 240 \text{ cm}^{-1}$ [9] and $\zeta_p^0 \approx 587 \text{ cm}^{-1}$ [8]. D_t is the tetragonal field parameter. E_i are the zero-order energy separations between the ground 4A_2 and the excited 4T_2 , $^2T_{2a}$, and $^2T_{2b}$ states [12]. N_{γ} and λ_{γ} are the normalization factor and the orbital mixing parameter, which can be obtained from the approximate relationship [12]

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

and the normalization relationship [12]

$$N_{\gamma}(1 - 2\lambda_{\gamma}S_{dp}(\gamma) + \lambda_{\gamma}^2) = 1, \quad (4)$$

where $S_{dp}(\gamma)$ is the group overlap integral and $f_{\gamma} [\approx (B/B_0 + C/C_0)/2]$ the ratio of the Racah parameters for an ion in a crystal to that in free state.

2.1. Center III

From the optical spectra of CsCl:Cr³⁺ crystals at room temperature [2], one can obtain the cubic field parameter Dq and the Racah parameters B and C for center III (or $[\text{CrCl}_6]^{3-}$ cluster):

$$Dq \approx Dq(\text{Cl}^-) \approx 1370 \text{ cm}^{-1},$$

$$B \approx 645 \text{ cm}^{-1}, C \approx 2920 \text{ cm}^{-1}. \quad (5)$$

According to the Racah parameters $B_0 \approx 920 \text{ cm}^{-1}$ and $C_0 \approx 3331 \text{ cm}^{-1}$ [9] for a free Cr³⁺ ion, we have $f_{\gamma} \approx 0.7899$.

By using the superposition model [14], the tetragonal field parameter for center III can be written as

$$D_t \approx \frac{16}{21}\bar{A}_4(\text{Cl}^-)[(R_0/R_{\perp})^4 - (R_0/R_{\parallel})^4], \quad (6)$$

where R_{\parallel} and R_{\perp} are the Cr³⁺-Cl⁻ distances parallel and perpendicular to the C_4 axis, respectively. The reference bonding distance $R_0 \approx \bar{R} = (R_{\parallel} + 2R_{\perp})/3$. For the ionic crystal, similar to the point-charge model, we take the power law exponent $t_4 \approx 5$ [14, 15]. The intrinsic parameter $\bar{A}_4(\text{Cl}^-)$ for the hexachloro-complex can be obtained from the relationship $\bar{A}_4(\text{Cl}^-) \approx (3/4)D_q$ [15]. For simplicity we consider R_{\perp} to be the sum of the ionic radii of Cr³⁺ ($r \approx 0.755 \text{ \AA}$ [16]) and the coplanar Cl⁻ ($r \approx 1.81 \text{ \AA}$ [17]), i. e., $R_{\perp} \approx 2.565 \text{ \AA}$. As for R_{\parallel} , if the two substitutional Cl⁻ ions occupy exactly the host Cs⁺ sites, the sum of the ionic radii of Cr³⁺ and the substitutional Cl⁻ is 2.565 \AA , even larger than half of the lattice constant ($a \approx 4.11 \text{ \AA}$ [1]) of CsCl. So, the two substitutional Cl⁻ ions may be expected to be displaced away from the central interstitial Cr³⁺ ion by about an amount ΔZ due to the spacial size effect along the C_4 axis, in spite of the electrostatic attraction between the central Cr³⁺ and the two Cl⁻ along C_4 axis. By fitting the observed of D , we find that for center III

$$\Delta Z \approx 0.506 \text{ \AA} \quad \text{or} \quad R_{\parallel} \approx 2.561 \text{ \AA}. \quad (7)$$

Thus, we have the average metal-ligand distance $\bar{R} = (R_{\parallel} + 2R_{\perp})/3 \approx 2.564 \text{ \AA}$. By using the Slater-type SCF function [18,19] and the value of \bar{R} , the group overlap integrals $S_{dp}(t_{2g}) \approx 0.01555$ and $S_{dp}(e_g) \approx 0.05$ can be obtained, and the parameters N_{γ} and λ_{γ} can be also calculated. In consideration of the tetragonal field parameter $D_t (\approx -6.1 \text{ cm}^{-1})$, from (6), one may reasonably suggest that for center III the tetragonal distortion is very small, which also agrees with its experimental D value. The related theoretical D , g_{\parallel} and g_{\perp} are shown in Table 1.

2.2. Centers I and II

According to the larger values of centers I and II [1], and the superposition studies for the $[\text{CrCl}_n(\text{H}_2\text{O})_{6-n}]^{3-n}$ and $[\text{Mn}^{2+}\text{Cl}_n(\text{H}_2\text{O})_{6-n}]^{2-n}$ clusters [20,21], molecular water contributes more to D than to the Cl⁻ ion. It can be shown that the centers I and II are clusters of $[\text{CrCl}_{6-n}(\text{H}_2\text{O})_n]^{n-3}$ with $n = 2$

	Center I [CrCl ₄ (H ₂ O) ₂] ⁻			Center II [CrCl ₅ (H ₂ O)] ²⁻			Center III [CrCl ₆] ³⁻		
	D	g	g _⊥	D	g	g _⊥	D	g	g _⊥
Cal.	-216	1.970	1.981	-110	1.973	1.979	-26	1.976	1.977
Expt ^a	-217	1.970	1.982	-140	1.965	1.979	-25	1.982	1.981

^a The signs of D for the three tetragonal centers were not given in [1]. However, we can reasonably assume that for all the centers the sign of D is negative, based on the empirical relationship $D \approx \zeta (g_{||} - g_{\perp}) / (6k)$ [23,24].

and 1, respectively [1, 2]. Similar to (6), the tetragonal field parameter can be expressed as

$$D_t \approx \frac{16}{21} [\bar{A}_4(\text{Cl}^-) - \bar{A}_4(\text{H}_2\text{O})] \quad (8)$$

for center I and

$$D_t \approx \frac{8}{21} \left\{ \bar{A}_4(\text{Cl}^-) [2(R'_0/R'_\perp)^{t_4} - (R_0/R'_\parallel)^{t_4}] - \bar{A}_4(\text{H}_2\text{O}) \right\} \quad (9)$$

for center II.

In the above formulas, the reference bonding distance for center II can be written as $R_0' \approx (R_{||}' + 4R_{\perp}')/5$. Considering that the only difference between center III and center I (or II) arises from two (or one) water molecules substituting the host Cs⁺ ion(s) along the C₄ axis, the metal-ligand distances $R_{||}$ and R_{\perp} in center III can be approximately adopted for the center II (i. e., $R_{||}' \approx R_{||}$ and $R_{\perp}' \approx R_{\perp}$). The intrinsic parameter $\bar{A}_4(\text{H}_2\text{O})$ equals about $(3/4)D_q(\text{H}_2\text{O})$ [15], with the cubic field splitting $D_q(\text{H}_2\text{O})$ ($\approx 1740 \text{ cm}^{-1}$) for the [Cr(H₂O)₆]³⁺ cluster [22]. Since there are no optical spectra available for the centers I and II, we can reasonably take the mean cubic field parameters $D_q(\text{I})$ and $D_q(\text{II})$ for the centers I and II in terms of D_q in (5) for center III, i. e.,

$$D_q(\text{I}) \approx [2D_q(\text{Cl}^-) + D_q(\text{H}_2\text{O})]/3, \\ D_q(\text{II}) \approx [5D_q(\text{Cl}^-) + D_q(\text{H}_2\text{O})]/6 \quad (10)$$

For simplicity, the values B and C in (5) are approximately adopted for the centers I and II.

Since the S. O. coupling parameter of O²⁻ ($\zeta_p^0 \approx 150 \text{ cm}^{-1}$ [22]) in molecular water is much smaller than that of Cl⁻, the contribution to the EPR parameters from the S. O. coupling parameter of molec-

ular(s) water in centers I and II may be much smaller than that from the S. O. coupling parameter of Cl⁻ ligands and can be ignored. So, only the five and four Cl⁻ ions are included in the calculation of metal-ligand overlap for center I and II, respectively. Thus, we have the average group overlap integrals $S_{\text{dp}}(t_{2g}) \approx 0.01293$ and $S_{\text{dp}}(e_g) \approx 0.04158$ for the center I and $S_{\text{dp}}(t_{2g}) \approx 0.01034$ and $S_{\text{dp}}(e_g) \approx 0.03327$ for center II.

By applying the above parameters in (1), the theoretical values of D , $g_{||}$ and g_{\perp} for centers I and II are calculated and shown in Table 1.

3. Results and Discussion

From Table 1, one finds that the calculated values of D , $g_{||}$ and g_{\perp} for the three centers agree reasonably with the observed data. By analyzing its EPR data, the local structure of center III is also determined, i. e., the two substitutional Cl⁻ ions do not occupy exactly the host Cs⁺ sites, but shift away from the central interstitial Cr³⁺ ion by about 0.506 Å due to the spacial size effect along the C₄ axis. Thus, the little difference between $R_{||}$ and R_{\perp} ($\approx 2.565 \text{ \AA}$) and hence the very small D_t ($\approx -6.1 \text{ cm}^{-1}$) can be understood for the [CrCl₆]³⁻ cluster. Interestingly, if we still assume that the two substitutional Cl⁻ ions occupy exactly the host Cs⁺ sites ($\Delta Z = 0$, $R_{||} \approx a/2 \approx 2.055 \text{ \AA}$, and so $\bar{R} \approx 2.395 \text{ \AA}$), the calculated D ($\approx 4680 \times 10^{-4} \text{ cm}^{-1}$) would be about 180 times larger than the experimental value.

Compared with center III, the relatively larger D values for centers I and II may be due to the larger tetragonal distortions arising from the substitution of Cl⁻ ion(s) with molecular H₂O having a stronger crystal field [$D_q(\text{H}_2\text{O}) \approx 1740 \text{ cm}^{-1}$] than that [$D_q(\text{Cl}^-) \approx 1370 \text{ cm}^{-1}$] of the Cl⁻ ligand.

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Table 1. EPR parameters D (in units of 10^{-4} cm^{-1}), $g_{||}$ and g_{\perp} for the three tetragonal centers I, II and III in CsCl:Cr³⁺ crystal at room temperature.

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