

Investigations of the EPR Parameters and Local Structures for Two Tetragonal Cr^{3+} Centers in NH_4Cl Crystal

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In this paper, the zero-field splittings D and g factors g_{\parallel} , g_{\perp} at room temperature for two tetragonal Cr^{3+} centers in $\text{NH}_4\text{Cl}:\text{Cr}^{3+}$ crystal have been investigated by a two-spin-orbit (S.O.)-parameter model, in which both the contribution due to the S.O. coupling of central d^3 ion and that of ligands are considered. From the investigations, the signs of zero-field splitting and the local structures of both centers are obtained. The electron paramagnetic resonance parameters D , g_{\parallel} and g_{\perp} of both centers are also explained.

Key words: Spin-orbit Coupling; Electron Paramagnetic Resonance (EPR); Crystal-field Theory; Cr^{3+} ; NH_4Cl_4 .

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1. Introduction

For crystal line $\text{NH}_4\text{Cl}:\text{Cr}^{3+}$ the electron paramagnetic resonance (EPR) and optical spectra [1, 2] indicate that the Cr^{3+} ion occupies an interstitial site in the plane of four CT (see Fig. 4 of [1]), and the original two NH_4^+ ions along the [001] axis (or C_4 axis) may be substituted for Cl^- ions or water molecules because of the charge compensation. Thus, two tetragonal Cr^{3+} centers are formed in $\text{NH}_4\text{Cl}:\text{Cr}^{3+}$ crystal. Center I is associated with an incorporated $[\text{CrCl}_4(\text{H}_2\text{O})_2]^-$ complex, and center II is a $(\text{CrCl}_6)^{3-}$ complex. The EPR parameters $|D|$, g_{\parallel} and g_{\perp} for both centers were measured [1], however the signs of the zero-field splittings D of both centers were not determined, and so these EPR parameters have not been explained. In addition, although the defect models for the two Cr^{3+} centers were given, the local structure data of these defect centers are not clear as yet. In this paper we study these problems by using the perturbation formulas of EPR parameters based on a two-spin-orbit (S.O.)-parameter model.

2. Calculation

Usually, for transition-metal ions in crystals, the theoretical investigation of EPR parameters is based on Macfarlane's high-order perturbation formulas in which only the contribution from the S.O. coupling co-

efficient of the central d^3 ion is considered [3, 4]. However, for $\text{NH}_4\text{Cl}:\text{Cr}^{3+}$, since the S.O. coupling coefficient ζ_p^0 ($\approx 587 \text{ cm}^{-1}$ [5]) of the Cl^- ligands is much greater than the coefficient ζ_d^0 ($\approx 273 \text{ cm}^{-1}$ [6]) of the central Cr^{3+} ion, the contribution from S.O. coupling of ligands cannot be neglected. So, the above conventional perturbation formulas of D , g_{\parallel} and g_{\perp} [3, 4] for a d^3 ion in axial symmetry should be substituted by the two-S.O.-parameter formulas containing the contributions from both the S.O. coupling of the central d^3 ion and the ligands [5, 7, 8]. For d^3 ions in tetragonal symmetry, the two-S.O.-parameter formulas of D , g_{\parallel} and g_{\perp} can be expressed as [8]

$$D = (35/9) D_t \zeta'^2 [1/E_1^2 - 1/E_3^2] - 35 B D_t \zeta \zeta' / E_2 E_3^2, \quad (1)$$

$$\begin{aligned} g_{\parallel} = & g_s - 8k' \zeta' / 3 E_1 - 2 \zeta' (2k' \zeta - k \zeta' + 2g_s \zeta') / 9 E_1^2 \\ & + 4 \zeta'^2 (k - 2g_s) / 9 E_3^2 - 2 \zeta^2 (k + g_s) / 3 E_2^2 \\ & + 4k' \zeta' \zeta / 9 E_1 E_3 - 4k' \zeta' \zeta / 3 E_1 E_2 \\ & + 4k' \zeta' \zeta / 3 E_2 E_3 + 140k' \zeta' D_t / 9 E_1^2, \\ g_{\perp} = & g_{\parallel} - 210k' \zeta' D_t / 9 E_1^2, \end{aligned} \quad (2)$$

where

$$\begin{aligned} \zeta = & N_t (\zeta_d^0 + \lambda_t^2 \zeta_p^0 / 2), \\ \zeta' = & (N_t N_e)^{1/2} (\zeta_d^0 - \lambda_t \lambda_e \zeta_p^0 / 2), \\ k = & N_t (1 + \lambda_t^2 / 2), \\ k' = & (N_t N_e)^{1/2} (1 - \lambda_t \lambda_e / 2), \end{aligned} \quad (3)$$

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and $g_s (= 2.0023)$ is the spin-only value and D_t the tetragonal field parameter. E_i are the zero-order energy separations [8]. N_γ and λ_γ are the LCAO coefficients, which can be obtained from the approximate relationship [7, 8]

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

and the normalization correlation

$$N_\gamma (1 - 2\lambda_\gamma S_{dp}(\gamma) + \lambda_\gamma^2) = 1, \quad (5)$$

where $S_{dp}(\gamma)$ is the group overlap integral and $f_\gamma [= (B/B_0 + C/C_0)/2]$ the ratio of the Racah parameters for an ion in a crystal to those for the free ion. From the optical spectra of a center II in $\text{NH}_4\text{Cl}:\text{Cr}^{3+}$ at room temperature [2], we have $D_q \approx 1350 \text{ cm}^{-1}$, $B \approx 650 \text{ cm}^{-1}$ and $C \approx 3100 \text{ cm}^{-1}$. For a free Cr^{3+} ion [6], $B_0 \approx 1030 \text{ cm}^{-1}$ and $C_0 \approx 3850 \text{ cm}^{-1}$; then we have $f_\gamma \approx 0.718$.

From the superposition model [9], the tetragonal field parameter for center II is

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

where R_\parallel and R_\perp are the $\text{Cr}^{3+}-\text{Cl}^-$ distances parallel with and perpendicular to the C_4 axis, respectively. The reference distance $R_0 \approx \bar{R} \approx (R_\parallel + 2R_\perp)/3$. For an ionic crystal, similar to the point-charge model, we take the power-law exponent $t_4 \approx 5$ [9]. The intrinsic parameter $\bar{A}_4(\text{Cl}^-) \approx (3/4) D_q$ [10]. Since the Cr^{3+} ion occupies the interstitial site, if the Cl^- ions along the C_4 axis is considered to be in the exact site of the NH_4^+ ion it replaces, the $\text{Cr}^{3+}-\text{Cl}^-$ distance ($\approx a_0/2 \approx 1.94 \text{ \AA}$ [11]) is too small to be regarded as reasonable when compared with the normal $\text{Cr}^{3+}-\text{Cl}^-$ distance ($\approx r_{\text{Cr}^{3+}} + r_{\text{Cl}^-} \approx 0.63 + 1.81 \approx 2.44 \text{ \AA}$, where r_i denotes the ionic radius [12]). So, we assume that the two Cl^- ions do not occupy the exact NH_4^+ site, but are shifted away from the Cr^{3+} ion along the C_4 axis, which results in a normal $\text{Cr}^{3+}-\text{Cl}^-$ distance $R_\parallel \approx 2.44 \text{ \AA}$. Thus, in the above formulas only the distance R_\perp is not known. By fitting the calculated optical spectral parameters D_t and the EPR parameters to the observed values, we obtain $R_\perp \approx 2.465 \text{ \AA}$. The calculated optical and EPR parameters are compared with the observed values in Table 1. In the above calculation, the overlap integrals $S_{dp}(t_{2g}) \approx 0.02121$ and $S_{dp}(e_g) \approx 0.06346$ are calculated from the Slater-type SCF functions [13, 14] and the average distance $\bar{R} \approx 2.456 \text{ \AA}$. Thus, from (3)–(5), we have $N_t \approx 0.855$, $N_e \approx 0.872$, $\lambda_t \approx 0.433$, $\lambda_e \approx 0.451$, $k \approx 0.935$, $k' \approx 0.779$, $\zeta \approx 281 \text{ cm}^{-1}$ and $\zeta' \approx 186 \text{ cm}^{-1}$.

Table 1. The tetragonal field parameter D_t and EPR parameters D , g_\parallel and g_\perp for two tetragonal Cr^{3+} centers in NH_4Cl crystal.

	Center I [$\text{CrCl}_4(\text{H}_2\text{O})_2$] [−]				Center II [CrCl_6] ^{3−}			
	D_t (cm^{-1})	D (cm^{-1})	g_\parallel	g_\perp	D_t (cm^{-1})	D (cm^{-1})	g_\parallel	g_\perp
Cal.	−277	−0.108	1.973	1.980	−40	−0.0207	1.978	1.982
Expt.		−0.111 ^a	1.988 ^a	1.985 ^a	−30 ^b	−0.0210 ^a	1.985 ^a	1.987 ^a

^a [1], in which the signs of D for the two centers were not given.

^b [2].

For center I, according to the superposition model [9], we have

$$D_t \approx (16/21) [\bar{A}_4(\text{Cl}^-) - \bar{A}_4(\text{H}_2\text{O})], \quad (7)$$

where the intrinsic parameter $\bar{A}_4(\text{Cl}^-) \approx \bar{A}_4(\text{Cl}^-) (R_0/R_\perp)^4 \approx 1013 \text{ cm}^{-1}$ and $\bar{A}_4(\text{H}_2\text{O}) \approx (3/4) D_q(\text{H}_2\text{O})$. The normal value of $D_q(\text{H}_2\text{O})$ is 1740 cm^{-1} [15]. Since the S.O. coupling coefficient of O^{2-} ($\approx 150 \text{ cm}^{-1}$ [16]) in molecular water is much smaller than that of Cl^- , the contribution due to the coefficient $\zeta_p^0(\text{O}^{2-})$ may be ignored. Thus, we can approximately calculate the integrals $S_{dp}(\gamma)$ by considering only the overlaps among Cr^{3+} and four coplanar Cl^- ions with $\bar{R} \approx R_\perp$. The results and hence the parameters in (3)–(5) are $S_{dp}(t_{2g}) \approx 0.02067$, $S_{dp}(e_g) \approx 0.06224$, $N_t \approx 0.855$, $N_e \approx 0.872$, $\lambda_t \approx 0.432$, $\lambda_e \approx 0.450$, $k \approx 0.935$, $k' \approx 0.779$, $\zeta \approx 281 \text{ cm}^{-1}$ and $\zeta' \approx 186 \text{ cm}^{-1}$. Substituting all these parameters into (1) and (2), we calculate the EPR parameters for center I. The results show good agreement with the observed values (see Table 1).

3. Discussions

From the above studies, two points should be discussed here:

- The signs of the zero-field splittings D for both Cr^{3+} centers in NH_4Cl are negative. The reasons are due to the facts that for the center II the observed value of D_t is negative and that for center I the cubic field parameter $D_q(\text{H}_2\text{O})$ is larger than $D_q(\text{Cl}^-)$. Thus, the EPR parameters D , g_\parallel and g_\perp can be explained reasonably by the two-S.O.-parameter model.
- The $\text{Cr}^{3+}-\text{Cl}^-$ distances R_\perp in center II and also center I is 2.465 \AA . The value is also close to the sum ($\approx 2.44 \text{ \AA}$) of the ionic radii of Cr^{3+} and Cl^- . Considering that the cubic field parameter

D_q ($\approx 1350 \text{ cm}^{-1}$ [2]) for center II in $\text{NH}_4\text{Cl}:\text{Cr}^{3+}$ is close to that ($\approx 1380 \text{ cm}^{-1}$ [15]) of the normal value, the result that the above distances R_{\parallel} and R_{\perp} are close to the normal $\text{Cr}^{3+}-\text{Cl}^-$ distance (i.e., the sum of ionic radii of Cr^{3+} and Cl^-) can be regarded as reasonable. The distance ($\approx a_0/\sqrt{2} \approx 2.737 \text{ \AA}$ [11]) between the interstitial site, in the plane of four Cl^- , and the Cl^- ion is greater than the distance R_{\perp} , so, when the Cr^{3+} ion occupies the interstitial site, the four Cl^- ions should be displaced towards the Cr^{3+} ion by about 0.27 \AA owing to the electrostatic attraction between Cr^{3+} and Cl^- . For center I, the use of the normal value of D_q for the $\text{Cr}(\text{H}_2\text{O})_6$ group

suggests that the $\text{Cr}^{3+}-\text{H}_2\text{O}$ distance (characterized by the $\text{Cr}^{3+}-\text{O}^{2-}$ distance in this group) should be close to the normal distance ($\approx r_{\text{Cr}^{3+}} + r_{\text{O}^{2-}} \approx 1.95 \text{ \AA}$ [12]). Since the $\text{Cr}^{3+}-\text{H}_2\text{O}$ distance is close to the $\text{Cr}^{3+}-\text{NH}_4^+$ distance ($\approx 1.94 \text{ \AA}$ [11]), the substitutional H_2O molecules are almost in the sites of NH_4^+ . Thus, the local structural parameters for both defect centers in $\text{NH}_4\text{Cl}:\text{Cr}^{3+}$ crystal are obtained by analyzing the EPR and optical data. It appears that the effect of ionic radius or size is dominant for the local structures around the Cr^{3+} ion in NH_4Cl . This point should be checked for other similar cases.

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