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Theoretical Study of Local Structure for Cr^{3+} Ions in CsCl Crystal

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A theoretical method for studying the local lattice structure of $3d^3$ ions in tetragonal ligand-field is presented. The formulas relating the crystal structure parameters with optical spectrum and electron paramagnetic resonance have been derived by using Zhao's Semi-SCF d-orbit Wave Functions model, Point-charge Crystal Field model, and Perturbation Loop Method. This theoretical system is applied to calculate the local distortion structure of CsCl: Cr^{3+} crystal at 293 and 77 K. The calculated results are accorded well with the experimental values.

Keywords CsCl: Cr^{3+} crystal; EPR parameter; local structure; optical spectrum

1. Introduction

When a transition metal ion enters a crystal, the local environment of impurity ion may be unlike than that of the host crystal. A good characterization of the local structure around impurity is a prerequisite for gaining a better insight into the microscopic origin of such properties [1]. Many methods, such as Extended X-ray Absorption Fine Structure (EXAFS), magnetic resource (EPR or ENDOR), and optical spectra, have been performed to study the properties of transition metal ions doped in crystals. Among them, using optical and EPR spectra is an effective measurement.

The CsCl crystal has fascinated many material scientists due to its nuclear medicine applications such as treatment of cancer and diagnosis of myocardial infarction [2,3]. The optical and EPR experimental data on CsCl: Cr^{3+} crystals [4–6] have shown that there are three tetragonal centers in a CsCl crystal. They are $(\text{CrCl}_4(\text{H}_2\text{O})_2)$ (center I), $(\text{CsCl}_5\text{H}_2\text{O})$ (center II), and (CsCl_6) (center III). For center III, each Cr^{3+} ion surrounded by six Cl^- substitutes Cs^+ ion, and the local symmetry is tetragonal. Because both the radius and charge of Cr^{3+} are different from that of Cs^+ , the local lattice distortion should be taken into account. However, up to now, despite a tremendous effort in developing adaptable physics and chemistries [7,8], the local molecular structures near Cr^{3+} ions in this crystal have not been determined satisfactorily.

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In the present work, the Hamiltonian energy matrices for a $3d^3$ configuration ion in a tetragonal ligand-field are constructed in a strong field scheme on the basis of Zhao's semi-SCF d-orbit wave functions model [9], and the relationship between the low-symmetry EPR parameters and local lattice structure is established based on the Hamiltonian energy matrices, point-charge crystal field model [10], and Macfarlane's perturbation loop method [11]. By this method, the local lattice structures for the tetragonal symmetry (centre III) in CsCl: Cr^{3+} crystal at 77 and 297 K are determined.

2. Theoretical Methods

2.1. The Hamiltonian Energy Matrices of the $3d^3$ Configuration in Tetragonal Ligand-Field

In Sugano-Tanabe scheme [12], the Hamiltonian for transition metal ion in crystal can be written as

$$\hat{H} = \hat{H}_a(A, B, C) + \hat{H}_b(B, C) + \hat{H}_{CF}(D_q) + \hat{H}_{CF}(\delta, \mu) + \hat{H}_{SO}(\zeta) + \hat{H}_{Trees}(\alpha) + \hat{H}_{Racah}(\beta), \quad (1)$$

where $\hat{H}_a(A, B, C)$, $\hat{H}_b(B, C)$, $\hat{H}_{CF}(10D_q)$, $\hat{H}_{CF}(\delta, \mu)$, $\hat{H}_{SO}(\zeta)$, $\hat{H}_{Trees}(\alpha)$, and $\hat{H}_{Racah}(\beta)$ are the diagonal and off-diagonal term of electronic coulomb interaction, the octahedral crystal field (CF), the tetragonal part of crystal field, the spin-orbit Hamiltonian, the Trees correction term, and Racah correction term, respectively.

According to Zhao's Semi-SCF d-orbit Wave Functions model, the parameterization radial $3d^3$ wave function of Cr^{3+} reads [13]

$$R_d(r) = 0.5915 \left[\frac{9.32327}{6!} \right]^{1/2} r^2 \exp(-4.6616r) + 0.6015 \left[\frac{3.30527}{6!} \right]^{1/2} r^2 \exp(-4.6616r). \quad (2)$$

Which leads to

$$A_0 = 150848 \text{ cm}^{-1}, B_0 = 920.47 \text{ cm}^{-1}, C_0 = 3330.71 \text{ cm}^{-1}, \zeta_0 = 240 \text{ cm}^{-1}, \alpha_0 = 65 \text{ cm}^{-1}, \beta_0 = -131 \text{ cm}^{-1}, \langle r^2 \rangle = 2.4843 \text{ amu}, \langle r^4 \rangle = 16.4276 \text{ amu}. \quad (3)$$

Here, A_0 , B_0 , C_0 are the Racah electrostatic parameters; α_0 is the Trees correction; β_0 is the Racah correction; and $\langle r^n \rangle_0$ are the expectation value of r^n of the free Cr^{3+} , respectively.

In cubic crystal field, the orbit degeneracy of $3d^l$ electron is split into two parts which can be represented by t_{2g} and e_g irreducible representations. The zeroth order wave functions of a $3d^n$ can be described by the combination of t_{2g} and e_g wave functions; the subscripts t and e denote the t_{2g} and e_g irreducible representations of the cubic group, respectively. Consideration of the covalency effect [14], the functions are of the form

$$|t_{2g}\rangle = N_t |t_{2g}\rangle, \quad (4a)$$

$$|e_g\rangle = N_e |e_g\rangle. \quad (4b)$$

Following the works by Richardson and Jassen [15], Ballhausen and Gray et al. [16], the electrostatic parameters $a, b, c, d, e, f, g, h, i$, and j can be approximately written as

$$\begin{aligned} a &= N_t^4(A_o + 4B_o + 3C_o), \quad b = N_t^4(A_o - 2B_o + C_o), \quad c = N_e^2(3)1/2N_t2B_o, \\ d &= N_t^2N_e^2(A_o - 2B_o + C_o), \quad e = N_e^4(A_o + 4B_o + 3C_o), \quad f = N_e^4(4B_o + C_o), \\ g &= N_t^2N_e^2(B_o + C_o), \quad h = N_t^2N_e^2(3)1/2B_o, \quad i = N_eN_e^3(3)1/2B_o, \\ j &= N_t^4(3B_o + C_o). \end{aligned} \quad (5)$$

Similarly for the spin-orbit coupling constant, Tress correction constant and Racah correction constant, we obtained

$$\zeta = [(N_t + N_e)/2]^2 \zeta_0 \quad (6)$$

$$\alpha = [(N_t + N_e)/2]^4 \alpha_0 \quad (7)$$

$$\beta = [(N_t + N_e)/2]^4 \beta_0 \quad (8)$$

Here, we take $N_e = 0.915$ and $N_t = 0.894$ for $\text{CsCl: } Cr^{3+}$ crystal.

According to the point-charge crystal model [10], the tetragonal field parameters δ and μ can be written as

$$D_q = -\frac{1}{6}eq(1/R_0^5) < r^4 >_0. \quad (8)$$

$$\delta = \frac{6}{7}eq(1/R_{//}^3 - 1/R_{\perp}^3) < r^2 >_0 - \frac{10}{21}eq(1/R_{//}^5 - 1/R_{\perp}^5) < r^4 >_0. \quad (9)$$

$$\mu = \frac{6}{7}eq(1/R_{//}^3 - 1/R_{\perp}^3) < r^2 >_0 + \frac{10}{21}eq(1/R_{//}^5 - 1/R_{\perp}^5) < r^4 >_0. \quad (10)$$

Where R_{\perp} stands for the bond length in the plane, which perpendicular to the chosen C_4 axis; $R_{//}$ is the bond length along the C_4 axis; and R_0 is taken as the average $Cr-Cl$ distance of $Cr-Cl$ for $\text{CsCl: } Cr^{3+}$ crystal

$${}^{\prime}R_0 = ({}^{\prime}2R_{\perp} + {}^{\prime}R_{//})/3' \quad (11)$$

The Hamiltonian matrix elements of $3d^3$ configuration can be obtained by using the theorem of the calculation of single- or double-electron operator.

2.2. The EPR Parameters in a Tetragonal Ligand-Field

For Cr^{3+} ions in a tetragonal crystal field, the ground state is ${}^4A_2(F)$. With a strong-field tetragonal basis, the perturbation Hamiltonian appropriate to axial symmetry being

$$\hat{H}' = \hat{H}_b(B, C) + \hat{H}_{CF}(\delta, \mu) + \hat{H}_{SO}(\zeta) + H_{Tress} + H_{Racah}. \quad (12)$$

From Macfarlane's perturbation loop method [17], the third order perturbation expression of the EPR parameters can be used [18]

$$D = \zeta^2 \left(-\frac{2\mu}{3D_1^2} + \frac{2\mu}{3D_3^2} - \frac{8\delta}{9D_1^2} + \frac{8\delta}{9D_3^2} + \frac{6B\mu}{D_2D_3^2} - \frac{8B\delta}{D_2D_3^2} \right). \quad (13a)$$

$$g_{//} = g_s - \frac{8k\zeta}{3D_1} - \frac{(4k\zeta^2 - 2k\zeta^2 + 4g_s\zeta^2)}{9D_1^2} + \frac{4\zeta^2k - 8\zeta^2g_s}{9D_3^2} - \frac{2\zeta^2k + 4\zeta^2g_s}{9D_2^2} + \frac{4\zeta^2k}{9D_1D_3} - \frac{4\zeta^2k}{3D_1D_2} + \frac{4\zeta^2k}{3D_2D_3} - \frac{560k\delta\zeta}{315D_1^2} + \frac{420k\mu\zeta}{315D_1^2}. \quad (13b)$$

$$g_{\perp} = g_{//} + \frac{840k\delta\zeta}{315D_1^2} - \frac{630\mu k\zeta}{315D_1^2}. \quad (13c)$$

Where the zero-order energy separations are

$$D_1 = D(^4T_2) - D(^4A_2). \quad (14a)$$

$$D_2 = D(^2T_{2a}) - D(^4A_2). \quad (14b)$$

$$D_3 = D(^2T_{2b}) - D(^4A_2). \quad (14c)$$

Thus, using the Semi-SCF d-orbit model, all of the parameters in the calculation formulas of D , $g_{//}$ and g_{\perp} can be determined from the optical spectra parameters (A , B , C , Dq , ζ , α , β , μ , and δ) and local distortion parameters ($R_{//}$ and R_{\perp}).

3. Determination of Local Lattice Structure Parameters

When the Cr³⁺ ion is doped in CsCl crystal, because the radius and charge of both ions are not the same, the local lattice distortions in the vicinity of the Cr³⁺ impurity can be described by use of ΔR_{\perp} and $\Delta R_{//}$, respectively. Of these six chlorines, the four Cl⁻-Cr³⁺ distances which perpendicular to C_4 axis are equivalent, and the two axial ligands are equivalent,

Table 1. The d-d transition (cm⁻¹), EPR parameters (D , $g_{//}$ and g_{\perp}), and local structure parameters (R_{\perp} and $R_{//}$) for CsCl: Cr³⁺ crystal at 293 and 77 K

	293 K		77 K	
	Observed	Calculated values ($R_{\perp} = 0.1982$ nm, $R_{//} = 0.1979$ nm)	Observed	Calculated values ($R_{\perp} = 0.1982$ nm, $R_{//} = 0.1974$ nm)
⁴ A ₂ (⁴ T ₁ (F), e ² t ₂ ¹)→				
⁴ E (⁴ T ₂ , e ¹ t ₂ ²)	13,400 ^a	13,387	13,600 ^a	13,622
⁴ B ₂ (⁴ T ₂ , e ¹ t ₂ ²)	14,600 ^a	14,609	14,800 ^a	14,793
² A ₁ (² E, t ¹ t ₂ ²)	15,300 ^a	15,306	15,350 ^a	15,357
² E(² T ₁ , t ¹ e ²)		17,678	17,800 ^a	17,808
⁴ A ₂ (² T ₁ , e ² t ₂ ¹)	19,800 ^a	19,804	19,900 ^a	19,886
⁴ E(⁴ T ₁ , e ² t ₂ ¹)	23,400 ^a	23,391		
² A ₁ (² E, e ³)		25,677	25,800 ^a	25,813
D (cm ⁻¹)	25 ^b	-28		-46
$g_{//}$	1.982 ^b	1.983		1.986
g_{\perp}	1.981 ^b	1.979		1.982

^aRef. [4].

^bRef. [5].

too. The wave function is known, so there are only two local distortion parameters to be determined from experimental data [19].

The d–d transition, EPR parameters (D , g_{\parallel} and g_{\perp}), and local structure parameters (R_{\perp} and R_{\parallel}) for CsCl: Cr^{3+} crystal have been calculated and the results are given in Table 1. From the calculation, the local lattice parameters of CsCl: Cr^{3+} are determined as $R_{\perp} = 0.1985$ nm, $R_{\parallel} = 0.1979$ nm at 293 K and $R'_{\perp} = 0.1982$ nm, $R'_{\parallel} = 0.1974$ nm at 77 K, respectively.

In normal temperature, the $\Delta R_{\perp} = -0.0070$ nm and $\Delta R_{\parallel} = -0.0076$ shows that the tetragonal distortion of the chlorine octahedron surrounding the impurity ion may be smaller than that of un-doped CsCl. The theoretical zero-field splitting D was negative, which suggested that the displacement direction of Cl^{-} ions was compressed. The distortion may be caused by that the Cr ions radii $r_{\text{Cr}^{3+}} \approx 0.076$ is smaller than that of Cs ions radii $r_{\text{Cs}^{+}} \approx 0.167$ nm [20]; moreover, the electrostatic interaction of Cr^{3+} - Cl^{-} is stronger than that of Cs^{+} - Cl^{-} . The calculated energy levels and average value agree with the experimental finding, so the estimated local structural parameters may be reasonable in physics. Then for CsCl: Cr^{3+} at 77 K, the optical spectrum has been explained and EPR parameters have been theoretically reported.

4. Summary

In this paper, a theoretical method for studying the local lattice structure of $3d^3$ ions in tetragonal ligand-field was investigated by analyzing the optical spectrum and EPR parameters (D , g_{\parallel} and g_{\perp}). In these formulas, the local structure parameters related to the contributions from the configuration interaction and covalency effect can be estimated from the optical spectra and the structural data. The local distortion structure parameters (R_{\perp} and R_{\parallel}) of Cr^{3+} ions in CsCl at 293 and 77 K have been investigated. The calculated results agree well with experimental data.

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