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An investigation of the EPR zero-field splitting of Cr^{3+} ions at the tetragonal site and the Cd^{2+} vacancy in $\text{RbCdF}_3:\text{Cr}^{3+}$ crystals

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Abstract. The quantificational relationship between the EPR zero-field splitting parameter D and the structure parameters of the tetragonal Cr^{3+} centre in $\text{RbCdF}_3:\text{Cr}^{3+}$ crystals has been established according to the superposition model and third-order perturbation theory. The existence of the Cd^{2+} vacancy and the lattice distortion have been verified. Meanwhile, we obtain that the F^- ion moves toward the central Cr^{3+} ion by $X_1 = 0.0031$ nm, $X_2 = 0.00101$ nm, $X_3 = 0.00281$ nm. Good agreement between the theoretical results and the experimental values shows that the assumption of the Cd^{2+} vacancy and the lattice distortion is reasonable. Although the main source of the tetragonal crystal field comes from the Cd^{2+} vacancy caused by the charge compensation, the contribution of the lattice distortion cannot be neglected.

1. Introduction

$\text{RbCdF}_3:\text{Cr}^{3+}$ has attracted much attention because of its excellent optical qualities for laser applications. Perfect RbCdF_3 crystals have cubic structure; the local symmetry around the Cd^{2+} ion is O_h ; the Cd^{2+} ion is surrounded by six F^- ions. Trivalent Cr^{3+} ions replace divalent Cd^{2+} ions when doped into RbCdF_3 crystals. Nevertheless, the EPR experiment [1] shows that the Cr^{3+} ion is in a tetragonal axial symmetry environment at $T = 300$ K. This result implies that the local structure of the Cr^{3+} ion induces tetragonal lattice distortion and the local symmetry around the Cr^{3+} ion changes from O_h to C_{4v} . So far there is no satisfactory theoretical work explaining all of these experimental findings.

The present work suggests that the tetragonal crystal field of the Cr^{3+} ion in RbCdF_3 crystals comes from the following two origins:

- (a) The nearest-neighbour Cd^{2+} vacancy caused by the charge compensation in the [001]-axis direction.
- (b) The lattice distortions of the nearest-neighbour fluorine coordination caused by the Cd^{2+} vacancy and the differences in mass, charge and radius between the Cr^{3+} ion and Cd^{2+} ion.

Following the above idea, the relationship between the EPR zero-field splitting D and crystal structure for Cr^{3+} in RbCdF_3 crystals has been established according to the superposition model and third-order perturbation theory. The EPR zero-field splitting parameter D has been investigated, taking into account both the effect of lattice distortion and the Cd^{2+} vacancy itself; the calculated result ($D = -0.05693$ cm⁻¹) is in excellent agreement with the experimental result ($D = -0.05693(5)$ cm⁻¹).

2. Theory

Cr^{3+} is a $3d^3$ ion; the appropriate spin Hamiltonian is given as

$$H_s = \beta g \mathbf{H} \mathbf{S} + D[S_z^2 - \frac{1}{3}S(S+1)] \quad (1)$$

for C_{4v} symmetry, where the first term is the Zeeman interaction and D is the EPR zero-field splitting parameter. In cubic symmetry, $D = 0$. Under the combined influence of spin-orbit coupling and the tetragonal crystal field, the tetragonal 4A_2 ground state is split into two Kramers doublets of separation $2D$. It is known that the EPR zero-field splitting is very sensitive to variation of the crystal structure parameters. Thus one can determine approximatively displacement of all F^- ions surrounding the Cr^{3+} ion from the EPR zero-field splitting parameter and optical spectra.

With consideration of the combined effect of the tetragonal-field and spin-orbit coupling and utilization of the third-order perturbation theory given by Macfarlane [2], the EPR zero-field splitting parameter D of the Cr^{3+} cluster in the ground state is given by

$$D = \frac{1}{3}\xi^2\mu\left(\frac{1}{D_1^2} - \frac{1}{D_3^2}\right) - \frac{4}{9}\xi^2\delta\left(\frac{1}{D_3^2} - \frac{1}{D_1^2}\right) - \frac{B\xi^2}{D_2D_3^2}(3\mu - 4\delta) \quad (2)$$

where μ and δ denote the net tetragonal crystal parameters, and they vanish identically in cubic symmetry. ξ is the spin orbit coupling coefficient in crystal. By means of the cubic crystal field parameter Dq and Racah parameters B and C , energy D_i in the denominators are written as follows

$$\begin{aligned} D_1 &= E({}^4T_2) - E({}^4A_2) = 10Dq \\ D_2 &= E(a^2T_2) - E({}^4A_2) = 15B + 4C \\ D_3 &= E(b^2T_2) - E({}^4A_2) = 10Dq + 9B + 3C. \end{aligned} \quad (3)$$

It is convenient to define

$$\begin{aligned} \mu &= -\frac{4}{7}B_{20} - \frac{5}{21}B_{40} + \frac{10}{3\sqrt{70}}B_{44} \\ \delta &= -\frac{3}{7}B_{20} + \frac{5}{21}B_{40} - \frac{10}{3\sqrt{70}}B_{44} \end{aligned} \quad (4)$$

where B_{kq} are the crystal field parameters.

The Newman superposition model [3, 4] has proved to be a powerful tool in probing the local structure of the 4A_2 state ion in a variety of single crystals. In particular this method has been successfully applied to gain very detailed information on the lattice site and crystalline environment of Cr^{3+} ions in a crystal [5–8]. According to the superposition model the crystal field parameters B_{kq} are given as

$$B_{kq} = \sum_j \bar{A}_k(R_j) f_{kq} K_{kq}(\theta_j, \phi_j) \quad (5)$$

where (R_j, θ_j, ϕ_j) denotes the coordinates of the j th ligand; $f_{20} = 2$, $f_{40} = 8$, $f_{44} = 8/\sqrt{70}$ and K_{kq} are given as

$$\begin{aligned} K_{20} &= \frac{1}{2}(3\cos^2\theta - 1) \\ K_{40} &= \frac{1}{8}(35\cos^4\theta - 30\cos^2\theta + 3) \\ K_{44} &= \frac{35}{8}\sin^4\theta \cos 4\phi. \end{aligned} \quad (6)$$

The $\bar{A}_k(R_j)$ ($k = 2, 4$) are called intrinsic parameters and they are expressed as

$$\bar{A}_k(R_j) = \bar{A}_k(R_0) \left(\frac{R_0}{R_j}\right)^{t_k} \quad (7)$$

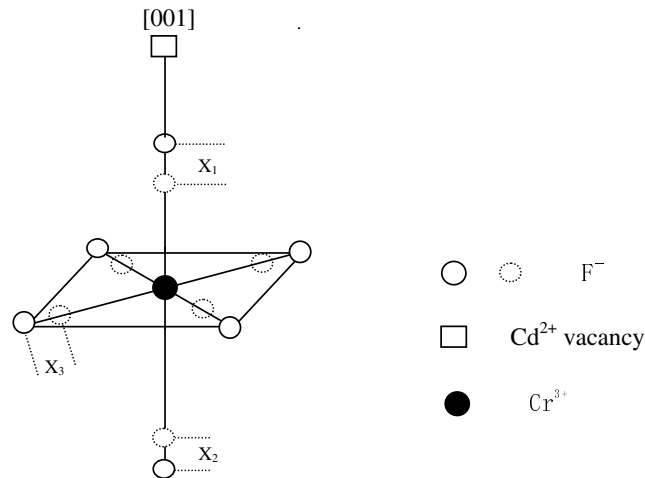


Figure 1. Local structure of Cr^{3+} in $\text{RbCdF}_3:\text{Cr}^{3+}$ crystals.

where the reference distance R_0 (0.22 nm) [1] is taken as the Cr–F distance in the cubic site. In the calculation, $t_2 = 4$ and $t_4 = 6$ are adopted [3].

According to the usual method [6, 7], the effect of the Cd^{2+} vacancy caused by the charge compensation is equivalent to a negative point charge $-2|e|$ located at the position of the vacancy (which is $2R_0$ from Cr^{3+}), namely, it is equivalent to two F^- ions at the Cd^{2+} position in the perfect lattice. Utilizing (5)–(7) the crystal field parameters induced by the Cd^{2+} vacancy are given as

$$\begin{aligned} B_{20} &= \bar{A}_2(2)^{1-t_2} \\ B_{40} &= \bar{A}_4(2)^{3-t_4} \\ B_{44} &= 0. \end{aligned} \quad (8)$$

Owing to the Cd^{2+} vacancy and the difference in mass, charge and radius between Cr^{3+} (0.063 nm) and Cd^{2+} (0.103 nm), the local structure of the Cr^{3+} will induce a tetragonal lattice distortion, namely, there is an inward displacement of all F^- ions surrounding the Cr^{3+} ion (see figure 1). By means of (5)–(7), the crystal field parameters due to the lattice distortion are given as

$$\begin{aligned} B_{20} &= 2\bar{A}_2(Q_1^{t_2} + Q_2^{t_2} - 2Q_3^{t_2}) \\ B_{40} &= 4\bar{A}_4(2Q_1^{t_4} + 2Q_2^{t_4} + 3Q_3^{t_4}) \\ B_{44} &= 2\sqrt{70}\bar{A}_4Q_3^{t_4} \end{aligned} \quad (9)$$

where $Q_1 = R_0/(R_0 - X_1)$, $Q_2 = R_0/(R_0 - X_2)$, $Q_3 = R_0/(R_0 - X_3)$. X_1 , X_2 and X_3 are the lattice distortion parameters (see figure 1).

It can be seen from the above discussions that the EPR zero-field splitting is related to the lattice distortion parameters X_1 , X_2 and X_3 for the defect centre in $\text{RbCdF}_3:\text{Cr}^{3+}$ crystals. However, before making calculations, we need values of the parameters B , C , Dq and ξ . The spin–orbit coupling parameter is taken as 217 cm^{-1} [10]. In order to determine the values of Dq , B and C , the optical spectra in cubic $\text{RbCdF}_3:\text{Cr}^{3+}$ crystals are calculated. A comparison of theory and experiment is given in table 1. It can be seen that the theoretical results are in agreement with experiments. The obtained values Dq , B and C will be used in the following calculation. According to the relationship $\bar{A}_4 = \frac{3}{4}Dq$ [11] and $\bar{A}_2 \approx 10.8\bar{A}_4$ [12], we obtain $\bar{A}_4 = 1065 \text{ cm}^{-1}$ and $\bar{A}_2 = 11502 \text{ cm}^{-1}$.

Table 1. The optical spectra of Cr³⁺ in cubic RbCdF₃:Cr³⁺ crystals (cm⁻¹).

Transition	Theoretical values	Experimental values [9]
⁴ A ₂ (⁴ F) → ⁴ T ₂ (⁴ F)	14 200	14 180
² E(² G)	15 550	15 550
² T ₁ (² G)	16 310	
⁴ T ₁ (⁴ F)	21 359	21 300
² T ₂ (² H)	22 716	
² A ₁ (² G)	27 270	
² T(² G)	29 667	
² T ₁ (² H)	30 286	
² E(² D)	32 116	
⁴ T ₁ (⁴ P)	33 241	33 300
$D_q = 1420 \text{ cm}^{-1}$	$B = 800 \text{ cm}^{-1}$	$C = 3290 \text{ cm}^{-1}$

Table 2. The EPR zero-field splitting parameter D of Cr³⁺ in RbCdF₃ crystals.

	$\mu \text{ (cm}^{-1}\text{)}$	$\delta \text{ (cm}^{-1}\text{)}$	$D \text{ (}10^{-4} \text{ cm}^{-1}\text{)}$
Cubic site	0	0	0
Cd ²⁺ vacancy	-853.3	-584.5	-1005.4
Distortion	463.5	193.2	436.1
Total	-389.8	-391.3	-569.3
Experiment [1]			-569.3(5)

3. Results and discussion

From the above, it is seen that the EPR zero-field splitting parameter D can be obtained utilizing (2) as long as the location of Cr³⁺ in RbCdF₃ (i.e. its coordinates (R_i, θ_i, Φ_i)) is known. The calculated results are listed in table 2.

The point symmetry around the Cr³⁺ ion reduces from O_h to C_{4v} when Cr³⁺ replaces the Cd²⁺ ion in RbCdF₃ crystals. The Cd²⁺ vacancy induced by the charge compensation gives rise to a contribution to tetragonal crystal field components with $\mu = -853.3 \text{ cm}^{-1}$ and $\delta = -584.5 \text{ cm}^{-1}$. By using these parameters and the values of Dq, B, C and ξ , we obtain $D = -1005.4 \times 10^{-4} \text{ cm}^{-1}$, which is remarkably greater in magnitude than the experimental findings ($-569.3 \times 10^{-4} \text{ cm}^{-1}$) despite the correct sign (see table 2). This shows that a lattice distortion must occur and play a significant role in contributing to the EPR zero-field splitting. Moreover, the radius of the Cr³⁺ (0.063 nm) ion is much smaller than that of the host Cd²⁺ (0.103 nm) ion, and the charge of the Cr³⁺ ion is more than that of the Cd²⁺ ion, so that the Coulomb interaction between the Cr³⁺ ion and F⁻ ion is greater than that between Cd²⁺ and the F⁻ ion. It is reasonable to assume the six F⁻ move towards the central magnetic Cr³⁺ ion in such an ionic crystal where the Coulomb interaction serves as the main crystallized source [3, 13].

Considering the combined contribution of the lattice distortion ($X_1 = 0.0031 \text{ nm}$, $X_2 = 0.00101 \text{ nm}$, $X_3 = 0.00281 \text{ nm}$) and the Cd²⁺ vacancy itself to the EPR zero-field splitting parameter D , it can easily be seen from table 2 that the theoretical result is in agreement with experiment. On the other hand, if we allowed $X_3 \gg X_1$, we would obtain another set of values, which would give an equally good fit. In fact, owing to the existence of the Cd²⁺ vacancy on the [001]-axis, X_1 must be greater than X_2 or X_3 . Because of this, Takeuchi *et al* [14] omitted X_2 and X_3 , and obtained $X_1 = 0.0104 \text{ nm}$ for RbCdF₃:Fe³⁺ crystals and

$X_1 = 0.0112$ nm for $\text{CsCdF}_3:\text{Fe}^{3+}$ crystals. In their calculations, the contribution of the Cd^{2+} vacancy itself to the EPR zero-field splitting parameter has been ignored. In our present case, we find that the contribution of X_1 (or X_2) to the EPR zero-field splitting parameter D is negative, and the contribution of X_3 to the EPR zero-field splitting parameter D is positive. If we consider only X_1 , we can also fit the D value which is in agreement with experiment. However, the contribution of the Cd^{2+} vacancy itself to the EPR zero-field splitting parameter D must be considered [7]. If we consider only X_1 and the Cd^{2+} vacancy itself, we obtain the value $D = -1898 \times 10^{-4} \text{ cm}^{-1}$, which is greater in magnitude than the $D = -1005.4 \times 10^{-4} \text{ cm}^{-1}$ induced by the Cd^{2+} vacancy itself, of course, which are remarkably greater in magnitude than experiment findings ($-569.3 \times 10^{-4} \text{ cm}^{-1}$). This shows that movements (X_3) of the four planar F^- ions have to be taken into account [13]. Because the final equilibrium positions of F^- ions around the Cr^{3+} ion depend on the whole crystal field when Cr^{3+} replaces the Cd^{2+} ion in RbCdF_3 crystals, the similarity of X_1 and X_3 is comprehensible.

It is worthwhile to point out that a tetragonal Fe^{3+} centre has been found by EPR experiment [15] in addition to a trigonal Fe^{3+} centre [16] in $\text{KZnF}_3:\text{Fe}^{3+}$ fluoroperovskite crystals. The tetragonal Fe^{3+} centre is ascribed to the nearest-neighbour Zn^{2+} vacancy caused by the charge compensation on the tetragonal axis [15]. The trigonal Fe^{3+} centre is ascribed to the nearest-neighbour K^+ vacancy caused by the charge compensation on the trigonal axis [16]. Meanwhile, information concerning trigonal lattice distortion in $\text{KZnF}_3:\text{Fe}^{3+}$ has been gained from electron-nuclear double-resonance (ENDOR) experiments by Krebs and Jeck [16]; they have found that the front three ligand F^- ions around the Fe^{3+} ion rotate 2.8° away from the [111]-axis while the back three ligand F^- ions around the Fe^{3+} ion rotate 1.1° toward it.

4. Conclusion

Cr^{3+} impurities substitute for Cd^{2+} when they are doped into RbCdF_3 crystals. Owing to the charge compensation, a Cd^{2+} site on the [001] axis will be vacant. Meanwhile, the Cd^{2+} vacancy and the differences in mass and radius between the Cr^{3+} ion and Cd^{2+} ion induce the lattice distortion: there is an inward displacement of all F^- ions surrounding the Cr^{3+} ion by $X_1 = 0.0031$ nm, $X_2 = 0.00101$ nm, $X_3 = 0.00281$ nm. The main source of the EPR zero-field splitting parameter D comes from the Cd^{2+} vacancy, but contribution arising from the lattice distortion to the parameter D cannot be neglected.

Acknowledgments

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