

A Unified Calculation of the Optical and EPR Spectral Data for the Trigonal Cr^{3+} Center in Cr^{3+} -Doped $\alpha\text{-RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ Alum Crystal

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The optical band positions and the spin-Hamiltonian parameters (g factors g_{\parallel} , g_{\perp} , and zero-field splitting parameter D) of alum $\alpha\text{-RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}:\text{Cr}^{3+}$ are calculated by diagonalizing the 120×120 complete energy matrix based on the two-spin-orbit-coupling-parameter model. The model takes into account not only the contributions due to the spin-orbit-coupling parameter of central d^n ion in the conventional crystal field theory, but also those due to ligands via covalence effect. The calculation indicates that the fourteen observed spectral data (eleven optical band positions and three spin-Hamiltonian parameters) can be reasonably and uniformly explained with four adjustable parameters (the Racah parameters B , C , intrinsic parameter $A_4(R)$ in the superposition model, and the trigonal distortion angle β). The calculations also suggest that contrary to the previous findings, the trigonal distortion of Cr^{3+} (entering the Al^{3+} site in the host crystal) center in $\alpha\text{-RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ is induced mainly by the oxygen (or water) octahedron around the Cr^{3+} ion rather than the more distant neighbors.

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1. Introduction

Alums form a large group of salt hydrates with the formula $\text{M}^{\text{I}}\text{M}^{\text{III}}(\text{XO}_4)_2 \cdot 12\text{H}_2\text{O}$ (where M^{I} and M^{III} denote the monovalent and trivalent cations, respectively, $\text{X} = \text{S}, \text{Se}$). They exhibit the cubic crystal symmetry with the space group $T_h^6 (Pa\bar{3})$ and have three structure types, α , β , γ (the most common being the α and β types) [1–3]. Therefore, alums are the proper materials for studying the phase transition [4–7]. Recently, considerable interest has been focused on the development of materials suitable for storing the energy absorbed by solar collectors. Some inorganic hydrate complexes are among the promising materials because of the proper melting temperatures and high enthalpies of fusion [4, 5, 8]. Therefore, salt hydrates alums have attracted attention [4, 5, 8]. In addition, alums are suitable host materials for the studies of optical and electron paramagnetic resonance (EPR) spectra of doped transition metal (d^n) ions. A number of investigations of optical and EPR spectra for the d^n ion-doped alums have been performed [9–17]. The optical [17] and EPR [15, 16] studies of Cr^{3+} ($3d^3$)-doped $\alpha\text{-RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ alum determined eleven optical bands and three spin-Hamiltonian (SH) parameters (g factors g_{\parallel} , g_{\perp} and zero-field splitting (ZFS) parameter D) and indicated that Cr^{3+} ion replaces Al^{3+} ion. Since in $\alpha\text{-RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ alum the site symme-

try of Al^{3+} seems to be predominantly cubic, the slight trigonal distortion of Al^{3+} (or Cr^{3+} in the doped alum) center was regarded as induced by the distant neighbors rather than the surrounding oxygen (or water) octahedron [13–15]. The theoretical interpretation has been carried out [17] only for the crystal field (CF) energy levels of Cr^{3+} -doped $\alpha\text{-RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ based on diagonalization of energy matrix without the spin-orbit coupling and the CF parameters treating as adjustable parameters. However, no unified theoretical calculation for the optical and EPR data has been done as yet. The structural data of Cr^{3+} center in Cr^{3+} -doped $\alpha\text{-RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ were also not given. In order to explain the optical and EPR data of Cr^{3+} -doped $\alpha\text{-RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ in a unified way and to clarify the origin of trigonal distortion of Cr^{3+} (or Al^{3+}) center [13–15], we provide theoretical interpretation of the available optical and EPR data. The complete diagonalization of energy matrix method based on the two-spin-orbit coupling (SOC)-parameter model is employed. In the model, not only the contributions due to the SOC parameter of central d^n ions in the conventional CF theory, but also those of ligands via covalence effect [18–20] are considered. The input CF parameters are estimated using the superposition model (SPM) [21, 22] and the local structural data of Cr^{3+} center in Cr^{3+} -doped $\alpha\text{-RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ crystal.

2. Calculation

In the two-SOC-parameter model, the one-electron basis functions of a d^n octahedral cluster change from the d orbitals $|d_{\gamma}\rangle$ of central d^n ion to the molecular orbitals

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(MO) including the $|d_\gamma\rangle$ and the p orbitals $|p_\gamma\rangle$ of ligand ion, namely [18–20]:

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

where the subscript $\gamma = t$ or e indicates the irreducible representation of O_h group, N_γ and λ_γ are the MO coefficients. The basis functions can give rise to two spin-orbit parameters ζ , ζ' and two orbit reduction factors k , k' [18–20]:

$$\begin{aligned} \zeta &= N_t \left(\zeta_d^0 + \frac{1}{2} \lambda_t^2 \zeta_p^0 \right), \quad \zeta' = (N_t N_e)^{\frac{1}{2}} (\zeta_d^0 - \frac{1}{2} \lambda_t \lambda_e \zeta_p^0), \\ k &= N_t \left[1 - 2\lambda_t S_{dp}(t) + \frac{1}{2} \lambda_t^2 \right], \\ k' &= (N_t N_e)^{\frac{1}{2}} \left[1 - 2\lambda_t S_{dp}(t) - \lambda_e S_{dp}(e) - \frac{1}{2} \lambda_t \lambda_e \right], \end{aligned} \quad (2)$$

where ζ_d^0 and ζ_p^0 are the SOC parameters of free d^n ion and ligand ion in free state, whereas $S_{dp}(\gamma)$ are the group overlap integrals. For the studied α -RbAl(SO₄)₂ · 12H₂O:Cr³⁺, we have $\zeta_d^0(\text{Cr}^{3+}) \approx 273 \text{ cm}^{-1}$ [23] and $\zeta_p^0(\text{O}^{2-}) \approx 150 \text{ cm}^{-1}$ [18, 24].

The Hamiltonian of a d^3 ion in trigonal symmetry contains the free ion term H_f , the CF term H_{CF} and the two SOC parameter term H_{SO} [19, 20]:

$$H = H_f(B, C) + H_{\text{CF}}(B_{20}, B_{40}, B_{43}) + H_{\text{SO}}(\zeta, \zeta'), \quad (3)$$

where B and C are the Racah parameters, B_{kl} are the CF parameters in the Wybourne notation [25, 26] (the relationships between the Wybourne notation and Ballhausen's conventional notation in Ref. [17] for CF parameters are given in Ref. [22]). The 120×120 energy matrix of Eq. (3) is established using the strong CF basis functions [27]. The eigenvalues of this energy matrix can obtain the CF energy levels and hence the optical band positions. The eigenvalues $E(^4A_2, M_s)$ and the eigenfunctions $|^4A_2, M_s\rangle$ of the ground state 4A_2 enable calculation of SH parameters by the formulae given in Refs. [19, 20].

The energy matrix depends upon the Racah parameters B , C , which are treated as adjustable parameters, the parameters in Eq. (2) and the crystal field parameters B_{kl} . The MO coefficients used in the calculations of the parameters in Eq. (2) are estimated from the normalization relationships [18–20]:

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

and the approximate correlations [18–20]:

$$\begin{aligned} f_\gamma &= \frac{1}{2}(B/B_0 + C/C_0) = \\ &N_\gamma^2 [1 - 2\lambda_\gamma S_{dp}(\gamma) + \lambda_\gamma^2 S_{dp}^2(\gamma)], \end{aligned} \quad (5)$$

where B_0 ($\approx 1030 \text{ cm}^{-1}$ [23]) and C_0 ($\approx 3850 \text{ cm}^{-1}$ [23]) are the Racah parameters of free Cr³⁺ ion. The group overlap integrals $S_{dp}(\gamma)$ in Eqs. (2) and (5) can be calculated from the Slater-type self-consistent field (SCF) functions [28, 29] with the metal–ligand distance R . The metal–ligand distance R in an impurity center differs from that R_h in the host crystal because the ionic radius r_i of impurity differs from the radius r_h of the replaced host ion [30]. Here an approximate formula

$R \approx R_h + \frac{1}{2}(r_i - r_h)$ [30] is used to estimate the distance R . From $R_h \approx 0.1923 \text{ nm}$ of the host RbAl(SO₄)₂ · 12H₂O crystal [31], $r_i(\text{Cr}^{3+}) \approx 0.063 \text{ nm}$ and $r_h(\text{Al}^{3+}) \approx 0.051 \text{ nm}$ [32], we have $R \approx 0.1983 \text{ nm}$ for the Cr³⁺ center in RbAl(SO₄)₂ · 12H₂O:Cr³⁺ crystal, thus, we obtain $S_{dp}(t) \approx 0.0334$ and $S_{dp}(e) \approx 0.0932$.

The CF parameters B_{kl} are estimated from the SPM [21, 22]. The effectiveness of this model in predicting CF parameters gains the support of angular overlap model [21] and the exchange charge model [33, 34]. For d^n ions in trigonal (approximately D_{3d}) octahedral cluster, the SPM expressions of B_{kl} are [19, 20]:

$$B_{20} = 6\bar{A}_2(R)(3 \cos^2 \beta - 1),$$

$$B_{40} = 6\bar{A}_4(R)(35 \cos^4 \beta - 30 \cos^2 \beta + 3),$$

$$B_{43} = -12\sqrt{35}\bar{A}_4(R) \sin^3 \beta \cos \beta, \quad (6)$$

where $\bar{A}_k(R)$ ($k = 2, 4$) are the intrinsic parameters and β is the angle between the direction of metal–ligand distance R and C_3 axis. Since the ratio $\bar{A}_2(R)/\bar{A}_4(R) \approx 8\text{--}12$ was found for $3d^n$ ions in many crystals by studying the optical and EPR spectra [20, 23, 33–39], we take the value $\bar{A}_2(R)/\bar{A}_4(R) \approx 10$ here. The parameter $\bar{A}_4(R)$ and angle β are also treated as adjustable parameters. The four adjustable parameters B , C , $\bar{A}_4(R)$ and β in the energy matrix are determined by matching the calculated optical and EPR data using the diagonalization of energy matrix method with the observed values of Cr³⁺-doped α -RbAl(SO₄)₂ · 12H₂O crystal at low temperature. The best matched values for the four parameters are

$$B \approx 728 \text{ cm}^{-1}, \quad C \approx 3100 \text{ cm}^{-1},$$

$$\bar{A}_4(R) \approx 1330 \text{ cm}^{-1}, \quad \beta \approx 54.65^\circ. \quad (7)$$

The MO coefficients and hence the parameters in Eq. (2) obtained from the value of f_γ are tabulated in Table I. The CF parameters obtained from the SPM with values of $\bar{A}_4(R)$ and β are compared with those estimated in Ref. [17] in Table II. The calculated optical and EPR data are compared with the experimental values in Table III and Table IV, respectively.

TABLE I

Molecular orbital coefficients, spin-orbit parameters and orbit reduction factors for the Cr³⁺ center in α -RbAl(SO₄)₂ · 12H₂O crystal.

N_t	N_e	λ_t	λ_e	ζ [cm ⁻¹]	ζ' [cm ⁻¹]	k	k'
0.8260	0.8565	0.5615	0.4441	245	214	0.8698	0.6797

TABLE II

Crystal field parameters B_{kl} (in cm⁻¹) for the Cr³⁺ center in α -RbAl(SO₄)₂ · 12H₂O crystal.

B_{20}		B_{40}		B_{43}	
This work	Ref. [17]	This work	Ref. [17]	This work	Ref. [17]
337	-980 ^a	-24901	-28700 ^a	-29642	-30789 ^a

^aCalculated from the relationships [22] between the conventional and Wybourne CF notations and with the values of CF parameters in the conventional notations Dq , $D\sigma$ and $D\tau$ [17].

TABLE III

Optical band positions (or crystal field energy levels, in cm^{-1}) of the trigonal Cr^{3+} center in Cr^{3+} -doped α - $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ crystal at low temperature.

Irreducible representation		Calculation	Experiment [17]	
O_h group	D_{3d} group			
${}^4A_{2g}({}^4F)$	${}^4A_{2g}$	0	0	
		0.0702	0.0698(10) [16]	
${}^2E_g({}^2G)$	2E_g	14362	14261	
		14366		
${}^2T_{1g}({}^2G)$	2E_g	15077	15102	
		15092		
${}^4T_{2g}({}^4F)$	${}^2A_{1g}$	15157	15147	
		4E_g	17631	17570
			17680	
			17703	
${}^2T_{2g}({}^2G)$	${}^4A_{1g}$	17793		
		17825	18310	
		17831		
		21664	21271	
${}^4T_{1g}({}^4F)$	${}^2A_{1g}$	21713		
		21807		
${}^2T_{1g}({}^2H)$	2E_g	25294	24624	
		25298		
		25332		
		25361		
${}^2A_{1g}({}^2G)$	${}^4A_{2g}$	25372	25568	
		25381		
${}^2T_{1g}({}^2H)$	${}^2A_{1g}$	29592		
		31969	31636	
${}^2T_{2g}({}^2H)$	2E_g	32005		
		32053		
		32371	32564	
		32556		
${}^2E_g({}^2H)$	${}^2A_{2g}$	32591		
		34176		
${}^2T_{2g}({}^2H)$	2E_g	34178		
		37803		
		37833		
		37835		
${}^4T_{1g}({}^4P)$	4E_g	39457	38899	
		39489		
		39508		
		39551		
	${}^4A_{2g}$	39724		
		39735		

TABLE IV

Spin-Hamiltonian parameters of the trigonal Cr^{3+} center in Cr^{3+} -doped α - $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ crystal at low temperature.

g_{\parallel}		g_{\perp}		D [cm^{-1}]	
Calc.	Expt. [16]	Calc.	Expt. [16]	Calc.	Expt. [16]
1.9798	1.9759(25)	1.9797	1.9759(25)	0.0351	0.0349(5)

3. Discussion

The trigonal distortion of an octahedron can be characterized by the value of $|\beta - \beta_0|$, where $\beta_0 \approx 54.74^\circ$, the same angle in the cubic symmetry [40]. The above calculations show that the trigonal distortion $|\beta - \beta_0|$ ($\approx 0.09^\circ$) of Cr^{3+} octahedral center in α - $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}:\text{Cr}^{3+}$ crystal is very small. The angle β and hence the trigonal distortion $|\beta - \beta_0|$ in the Cr^{3+} center are in good agreement with those (where $\beta_h \approx 54.53(35)^\circ$ and hence $|\beta_h - \beta_0| \approx 0.21(35)^\circ$ [31]) of the Al^{3+} center in the host α - $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ crystal within the experimental error. This finding that the very small trigonal distortion of Cr^{3+} (or Al^{3+}) site in α - $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}:\text{Cr}^{3+}$ is induced mainly by the surrounding oxygen octahedron rather than the distant neighbors differs from the opinion in [13–15]. This point is also supported by the recent ${}^{27}\text{Al}$ NMR spectrum of $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ where oxygen atoms surrounding Al^{3+} form a trigonally distorted octahedron at low and room temperatures [5].

Table II shows that the values of CF parameters obtained in present work differ slightly from those estimated in Ref. [17]. Since the present work can explain not only the optical band positions, but also the SH parameters, and contains the contributions of SOC parameters, the present values of CF parameters seem to be more suitable.

Table III and Table IV indicate that by using the complete diagonalization of energy matrix method based on the two-SOC-parameter model with only four adjustable parameters, the calculated fourteen optical and EPR data are in rational agreement with the experimental values.

4. Conclusion

The experimentally determined optical and EPR data of Cr^{3+} -doped α - $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ crystal can be well explained in a unified way through the complete diagonalization of energy matrix method based on the two-SOC-parameter model with only four adjustable parameters. This suggests that this method is able to explain both the optical and EPR data of d^3 ions in crystals. The local structural data estimated from the calculation indicate that the trigonal distortion of Cr^{3+} (or Al^{3+} in the host crystal) center in α - $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ is induced mainly by the oxygen (or water) octahedron around the Cr^{3+} ion rather than the distant neighbors.

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