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

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(Received June 22, 2015; in final form February 22, 2016)

The optical band positions and the spin-Hamiltonian parameters (g factors $g_{||}$, $g_{\perp}$, and zero-field splitting parameter $D$) of alum α-RbAl(SO$_4$)$_2$ · 12H$_2$O-Cr$^{3+}$ are calculated by diagonalizing the $120 \times 120$ 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$^0$ 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 $A_0(R)$ in the superposition model, and the trigonal distortion angle $\beta$). 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 α-RbAl(SO$_4$)$_2$ · 12H$_2$O is induced mainly by the oxygen (or water) octahedron around the Cr$^{3+}$ ion rather than the more distant neighbors.

DOI: 10.12693/APhysPolA.129.340
PACS/topics: 71.70.Ch, 76.30.Fc, 78.40.Ha, 78.55.Hx

1. Introduction

Alums form a large group of salt hydrates with the formula $M^+M^{III}(XO_4)_{n} \cdot 12H_2O$ (where $M^+$ and $M^{III}$ denote the monovalent and trivalent cations, respectively, $X = S, Se$). They exhibit the cubic crystal symmetry with the space group $T_h^6$ ($Pa3$) 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$^0$) ions. A number of investigations of optical and EPR spectra for the d$^0$ ion-doped alums have been performed [9–17]. The optical [17] and EPR [15, 16] studies of Cr$^{3+}$ (3d$^3$)-doped α-RbAl(SO$_4$)$_2$ · 12H$_2$O alum determined eleven optical bands and three spin-Hamiltonian (SH) parameters ($g$ factors $g_{||}$, $g_{\perp}$ and zero-field splitting (ZFS) parameter $D$) and indicated that Cr$^{3+}$ ion replaces Al$^{3+}$ ion. Since in α-RbAl(SO$_4$)$_2$ · 12H$_2$O alum the site symmetry 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 α-RbAl(SO$_4$)$_2$ · 12H$_2$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 α-RbAl(SO$_4$)$_2$ · 12H$_2$O were also not given. In order to explain the optical and EPR data of Cr$^{3+}$-doped α-RbAl(SO$_4$)$_2$ · 12H$_2$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$^0$ ion 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 α-RbAl(SO$_4$)$_2$ · 12H$_2$O crystal.

2. Calculation

In the two-SOC-parameter model, the one-electron basis functions of a d$^0$ octahedral cluster change from the d orbitals $|d_z^2\rangle$ of central d$^0$ ion to the molecular orbitals

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(MO) including the \(|d_n\rangle\) and the \(p\) orbitals \(|p_n\rangle\) of ligand ion, namely \([18–20]\):

\[
|\psi_n\rangle = N_n^{1/2}(|d_n\rangle - \lambda_n|p_n\rangle),
\]

where the subscript \(n\) or \(t\) or \(e\) indicates the irreducible representation of \(O_h\) group, \(N_n\) and \(\lambda_n\) are the MO coefficients. The basis functions can give rise to two spin–orbit parameters \(\zeta, \zeta^t\) and two orbit reduction factors \(k, k^t\) \([18–20]\):

\[
\begin{align*}
\zeta &= N_t \left( \zeta_d^0 + \frac{1}{2} \lambda_d^2 \zeta_p^0 \right), \\
\zeta^t &= N_t \left( \zeta_d^0 - \frac{1}{2} \lambda_d \lambda_e \zeta_p^0 \right), \\
k &= N_t \left[ 1 - 2\lambda_t S_{dp}(t) + \frac{1}{2} \lambda_d^2 \right], \\
k^t &= N_t \left[ 1 - 2\lambda_t S_{dp}(t) - \lambda_e S_{dp}(e) - \frac{1}{2} \lambda_d \lambda_e \right],
\end{align*}
\]

where \(\zeta_d^0\) and \(\zeta_p^0\) 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 \(\alpha\)-RbAl(SO4)\(_2\) \cdot 12H\(_2\)O:Cr\(^{3+}\), 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 \(d^n\) ion in trigonal symmetry contains the free ion term \(H_t\), the CF term \(H_{CF}\) and the two SOC parameter terms \(H_{SO}[19, 20]\):

\[
H = H_t(B, C) + H_{CF}(B_{20}, B_{40}, B_{43}) + H_{SO}(\zeta, \zeta^t),
\]

where \(B\) and \(C\) are the Racah parameters, \(B_{20}\) are the CF parameters in the Wybourne notation \([25, 26]\), \(B_{40}\) and \(B_{43}\) are the relationships between the Wybourne notation and Ballhausen’s conventional notation in Ref. \([17]\) for CF parameters (as given in Ref. \([22]\)). The 120 \(\times\) 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 \(E(4A_2, M_e)\) and the eigenvectors \(|^4A_2, M_e\rangle\) 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 \(B_{2kl}\). The MO coefficients used in the calculations of the parameters in Eq. (2) are estimated from the normalization relationships \([18–20]\):

\[
N_n \left[ 1 - 2\lambda_n S_{dp}(\gamma) + \lambda_d^2 \right] = 1
\]

and the approximate correlations \([18–20]\):

\[
N_n^2 \left[ 1 - 2\lambda_n S_{dp}(\gamma) + \lambda_d^2 \gamma^2 S_{dp}^2(\gamma) \right],
\]

where \(B_0\) \((\approx 1030 \text{ cm}^{-1}\) \([23]\)) and \(C_0\) \((\approx 3850 \text{ cm}^{-1}\) \([23]\)) are the Racah parameters of free \(\text{Cr}^{3+}\) 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

\[
R \approx R_h + \frac{1}{2}(r_i - r_h) \quad [30]
\]

is used to estimate the distance \(R\). From \(R_h \approx 0.1923 \text{ nm}\) of the host \(\text{RbAl(SO}_4)_2 \cdot 12\text{H}_2\text{O}\) 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 \(\text{Cr}^{3+}\) center in \(\text{RbAl(SO}_4)_2 \cdot 12\text{H}_2\text{O}:\text{Cr}^{3+}\) crystal, thus, we obtain \(S_{dp}(t) \approx 0.0334\) and \(S_{dp}(e) \approx 0.0932\).

The CF parameters \(B_{2kl}\) 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 \(D_3\)) octahedral cluster, the SPM expressions of \(B_{2kl}\) are \([19, 20]\):

\[
\begin{align*}
B_{20} &= 6A_2(R)(3\cos^2 \beta - 1), \\
B_{40} &= 6\bar{A}_4(R)(35 \cos^4 \beta - 30 \cos^2 \beta + 3), \\
B_{43} &= -12\sqrt{35}\bar{A}_4(R)\sin^3 \beta \cos \beta,
\end{align*}
\]

where \(\bar{A}_4(R)\) \((k = 2, 4)\) are the intrinsic parameters and \(\beta\) is the angle between the direction of metal–ligand distance \(R\) and \(C_3\) axis. Since the ratio \(A_2(R)/A_4(R) \approx 8–12\) was found for \(3d^n\) ions in many crystals by studying the optical and EPR spectra \([20, 23, 33–39]\), we take the value \(A_2(R)/A_4(R) \approx 10\) here. The parameter \(A_4(R)\) and angle \(\beta\) are also treated as adjustable parameters. The four adjustable parameters \(B, C, A_4(R)\) and \(\beta\) 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 \(\text{Cr}^{3+}\)-
doped \(\alpha\)-RbAl(SO4)\(_2\) \cdot 12H\(_2\)O crystal at low temperature. The best matched values for the four parameters are \(B \approx 728 \text{ cm}^{-1}, C \approx 3100 \text{ cm}^{-1}\).

\[
A_4(R) \approx 1330 \text{ cm}^{-1}, \beta \approx 54.65^\circ.
\]

The MO coefficients and hence the parameters in Eq. (2) obtained from the value of \(f_n\) are tabulated in Table I. The CF parameters obtained from the SPM with values of \(A_4(R)\) and \(\beta\) 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**

<table>
<thead>
<tr>
<th>(N_t)</th>
<th>(N_e)</th>
<th>(\lambda_t)</th>
<th>(\lambda_e)</th>
<th>(\zeta) (\text{cm}^{-1})</th>
<th>(\zeta^t) (\text{cm}^{-1})</th>
<th>(k)</th>
<th>(k^t)</th>
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<tr>
<td>0.8260</td>
<td>0.8565</td>
<td>0.5615</td>
<td>0.4444</td>
<td>245</td>
<td>214</td>
<td>0.8698</td>
<td>0.6797</td>
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**TABLE II**

<table>
<thead>
<tr>
<th>(B_{20})</th>
<th>(B_{40})</th>
<th>(B_{43})</th>
</tr>
</thead>
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<tr>
<td>This work</td>
<td>Ref. [17]</td>
<td>This work(^a)</td>
</tr>
<tr>
<td>337</td>
<td>–980</td>
<td>–24901</td>
</tr>
<tr>
<td>337</td>
<td>–28700</td>
<td>–29642</td>
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<tr>
<td>337</td>
<td>–30789</td>
<td>–30789</td>
</tr>
</tbody>
</table>

\(^a\)Calculated from the relationships between the conventional and Wybourne CF notations and with the values of CF parameters in the conventional notations \(D_{eq}, D_{eq}\) and \(D_{eq}\) \([17]\).
The trigonal distortion of an octahedron can be characterized by the value of $|\beta - \beta_0|$, where $\beta_0 \approx 54.7^\circ$, 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 $\alpha$-RbAl(SO$_4$)$_2 \cdot 12$H$_2$O-Cr$^{3+}$ crystal is very small. The angle $\beta$ and hence the trigonal distortion $|\beta - \beta_0|$ in the Cr$^{3+}$ center are in good agreement with those (where $\beta_0 \approx 54.53(35)^\circ$ and hence $|\beta_0 - \beta_0| \approx 0.21(35)^\circ$) of the Al$^{3+}$ center in the host $\alpha$-RbAl(SO$_4$)$_2 \cdot 12$H$_2$O crystal within the experimental error. This finding that the very small trigonal distortion of Cr$^{3+}$ (or Al$^{3+}$) site in $\alpha$-RbAl(SO$_4$)$_2 \cdot 12$H$_2$O-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 $^{27}$Al NMR spectrum of RbAl(SO$_4$)$_2 \cdot 12$H$_2$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.

### 3. Discussion

The experimentally determined optical and EPR data of Cr$^{3+}$-doped $\alpha$-RbAl(SO$_4$)$_2 \cdot 12$H$_2$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 $d^4$ 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 $\alpha$-RbAl(SO$_4$)$_2 \cdot 12$H$_2$O is induced mainly by the oxygen (or water) octahedron around the Cr$^{3+}$ ion rather than the distant neighbors.

### Acknowledgments

This project is supported by the Initial Foundation of Mianyang Normal University (Grant No. MQD2011A05), the Key Project of Sichuan Provincial Science and Technology Department (Grant No. 2011SZZ029, 2012SZZ025, 2012JY0045).

### References


![TABLE III](image)

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

<table>
<thead>
<tr>
<th>Irreducible representation</th>
<th>Calculation</th>
<th>Experiment [17]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^2A_{2g}$ (+)$F'$</td>
<td>$^2A_{2g}$</td>
<td>0.0702</td>
</tr>
<tr>
<td>$^2E_g$ (+)$G$</td>
<td>$^2E_g$</td>
<td>14362</td>
</tr>
<tr>
<td>$^2T_{1g}$ (+)$G$</td>
<td>$^2E_g$</td>
<td>15077</td>
</tr>
<tr>
<td>$^2A_{1g}$</td>
<td>$^2A_{1g}$</td>
<td>15157</td>
</tr>
<tr>
<td>$^4T_{2g}$ (+)$F'$</td>
<td>$^4E_g$</td>
<td>17631</td>
</tr>
<tr>
<td>$^4A_{2g}$</td>
<td>$^4A_{2g}$</td>
<td>17825</td>
</tr>
<tr>
<td>$^2T_{2g}$ (+)$G$</td>
<td>$^2A_{1g}$</td>
<td>21664</td>
</tr>
<tr>
<td>$^2E_g$</td>
<td>$^2E_g$</td>
<td>21713</td>
</tr>
<tr>
<td>$^4T_{1g}$ (+)$F'$</td>
<td>$^4E_g$</td>
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</tr>
</tbody>
</table>

![TABLE IV](image)

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

<table>
<thead>
<tr>
<th>$g_{11}$</th>
<th>$g_{33}$</th>
<th>$D$ [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9978</td>
<td>1.9975(25)</td>
<td>1.9797</td>
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