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Optical spectrum and local lattice structure for ruby

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Abstract. By diagonalizing the 120 × 120 complete energy matrices for d^3 ion in trigonal crystal field, which contains the electrostatic interaction, the trigonal field as well as the spin-orbit interaction, the unified calculation of the whole optical and EPR spectra for ruby are made. And matrix elements of the Zeeman energy with the magnetic field parallel or perpendicular to the trigonal axis are introduced into the complete energy matrices for obtaining the g factors of the energy levels. It is concluded that zero-field splitting and optical spectra as well as g factors are in good agreement with the experimental data and the distorted local lattice structure is determined firstly results from a stretching of the O^{2-} ions along the C_3 axis. The pressure-induced shifts of energy levels, g factors and local lattice structure are also discussed. In particular, all the calculations are carried out successfully within the framework of the crystal-field model which is consistent with the opinion of Macfarlane and Sturge that if all terms within the d^3 configuration are included, one need not go outside conventional crystal-field theory.

PACS. 71.70.Gm Exchange interactions – 75.30.Et Exchange and superexchange interactions – 71.70.Ch Crystal and ligand fields

1 Introduction

The application of ruby (α-Al_2O_3) in optical masers has made an extensive study of its optical and EPR spectra both experimentally and theoretically [1–12]. In ruby, Cr^{3+} is surrounded by six O^{2-} ions, its stereostructure belongs to the C_3 point group. In previous theoretical study, there are two basic approaches to energy level calculation of ruby: one begins with high-order perturbation or diagonalization the complete energy matrices. Macfarlane [5] pointed out that the calculated results by diagonalizing the complete energy matrices, the energy spectrum of ruby at normal pressure are in better agreement with experiment than those by using the approximation involving the lower strong-field configurations and only second-degree terms in the noncubic part of the field. Furthermore, because the crystal field is actually of only intermediate strength, considerable mixing of strong-field states occurs. First- and second-order perturbation theory is not always useful [11]. Therefore in our calculation, the complete energy matrices for d^3 configuration in trigonal field are diagonalized based on the weak-field basis function. By using this method the EPR and optical spectra for ruby are reproduced satisfactorily. Especially, the distorted local lattice structure is determined firstly which is very sensitive to the EPR and optical spectra. It is shown that the local structure of ruby closes to that of Cr_2O_3 and the crystal lattice has an elongation effect. In present work, the matrix elements of the Zeeman energy with the magnetic field parallel or perpendicular to the C_3 are introduced into the complete energy matrices in order to obtain the g factors. It is appears that the g factors are very sensitive to the orbital angular momentum reduction factor, which should be included in the Zeeman energy besides included in the spin-orbit interaction. Finally, the effect of pressure on the energy levels, g factors and local lattice structure are discussed.

2 Theory

The Cr^{3+} ion in ruby is in a site of trigonal symmetry C_3 [11]. The EPR spectra of Cr^{3+} in a trigonal ligand-field may be analyzed by employing the spin-Hamiltonian [13]:

$$\hat{H}_s = \mu_B \vec{H} \cdot \vec{g} \cdot \vec{S} + D\left[S_z^2 - 1/3S\left(S+1\right)\right] \qquad (1)$$

in which $\mu_B (\mu_B = e\hbar/2mc)$ is the Bohr magneton. From equation (1) the explicit expression of the energy in $^4A_2$ state for a zero magnetic field can be written as:

$$E(\pm 1/2) = -D$$
$$E\left(\pm 3/2\right) = D. \qquad (2)$$

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The zero-field-splitting ΔE in the ground-state ${}^4\mathrm{A}_2$ may be expressed as a function of the EPR parameter D:

$$\Delta E = E\,(\pm 3/2) - E\,(\pm 1/2) = 2D. \tag{3}$$

The perturbation Hamiltonian for a d^3 configuration ion in a zero magnetic field may be represented as:

$$\hat{H} = \hat{H}_{ee} + \hat{H}_{so} + \hat{H}_{CF} = \sum_{i<j} e^2/r_{i,j} + \zeta \sum_i l_i s_i + \sum_i V_i, \tag{4}$$

where ζ is the spin-orbit coupling coefficient and V_i is the ligand-field potential

$$V_i = \gamma_{00} Z_{00} + \gamma_{20} r_i^2 Z_{20}(\theta_i, \phi_i) + \gamma_{40} r_i^4 Z_{40}(\theta_i, \phi_i) + \gamma_{43}^c r_i^4 Z_{43}^c(\theta_i, \phi_i) + \gamma_{43}^s r_i^4 Z_{43}^s(\theta_i, \phi_i). \tag{5}$$

The 120 × 120 complete energy matrices for a d^3 configuration ion corresponding to the perturbation Hamiltonian (4) have been constructed. The matrix elements are the functions of the Racah parameters B and C, Trees correction α, seniority correction β, the spin-orbit coupling coefficient ζ, and the ligand field parameters that are of the forms for Cr^{3+} ion in $\mathrm{Al_2O_3}$ system:

$$\begin{aligned} B_{20} &= (3/2)[G_2(p_1)(3\cos^2\theta_1 - 1) + G_2(p_2)(3\cos^2\theta_2 - 1)], \\ B_{40} &= (3/8)[G_4(p_1)(35\cos^4\theta_1 - 30\cos^2\theta_1 + 3) \\ &\quad + G_4(p_2)(35\cos^4\theta_2 - 30\cos^2\theta_2 + 3)], \\ B_{43}^c &= (3\sqrt{35}/4)[G_4(p_1)\cos\theta_1\sin^3\theta_1 \\ &\quad + G_4(p_2)\cos\theta_2\sin^3\theta_2], \end{aligned} \tag{6}$$

where $G_2(p_i)$ and $G_4(p_i)$ are expressed as:

$$\begin{aligned} G_2(p_i) &= -qeG^2(p_i), \\ G_4(p_i) &= -qeG^4(p_i), \end{aligned} \tag{7}$$

$$G^k(p_i) = \int_0^{R_{p_i}} R_{3d}^2(r) r^2 \frac{r^k}{R_{p_i}^{k+1}} dr + \int_{R_{p_i}}^{\infty} R_{3d}^2(r) r^2 \frac{R_{p_i}^k}{r^{k+1}} dr, \tag{8}$$

p_1, p_2 represent the ligand ions in the octahedral coordination respectively and θ_1, θ_2 the corresponding angles between metal-ligand bonds and C_3 axis. Since the bond lengths in the two octahedra in ruby are not the same, we may predict that:

$$\begin{aligned} G_2(p_1) &\neq G_2(p_2), \\ G_4(p_1) &\neq G_4(p_2). \end{aligned} \tag{9}$$

According to the Van Vleck approximation for $G^k(p_i)$ integral [14], we can obtain the relations:

$$G_2(P_i) = \frac{A_2}{{R_{P_i}}^3},\ G_4(P_i) = \frac{A_4}{{R_{P_i}}^5}, \tag{10}$$

where

$$A_2 = -eq_\tau\langle r^2\rangle, \quad A_4 = -eq_\tau\langle r^4\rangle, A_2/A_4 = \langle r^2\rangle/\langle r^4\rangle.$$

The ratio of $\langle r^2\rangle/\langle r^4\rangle = 0.151227$ is obtained from the radial wave function of Cr^{3+} ion in complexes [12]. A_4 as a constant for octahedral $(\mathrm{CrO_6})^{9-}$ cluster, its value can be determined from the optical spectra and the Cr–O bond length of the $\mathrm{Cr_2O_3}$ crystal [15,16]. By this way, we derive $A_4 = 35.5978$ au and $A_2 = 5.3834$ au for octahedral $(\mathrm{CrO_6})^{9-}$ cluster and we will take them in the following calculation. The advantage of confirming the value of A_4 is to reduce the number of adjustable parameter and make the choosing of parameters more reasonable, once the value of A_4 is determined there are only electrostatic parameters B, C and spin-orbit coupling coefficient ζ are adjustable parameters.

Considering the magnetic field effect, equation (4) can be expressed as:

$$\begin{aligned} \hat{H} &= \hat{H}_{ee} + \hat{H}_{so} + \hat{H}_{CF} + \hat{H}_{zeeman} \\ &= \sum_{i<j} e^2/r_{i,j} + \zeta \sum_i l_i s_i + \sum_i V_i + \beta(k\vec{\mathrm{L}} + g_e\vec{\mathrm{S}}) \cdot \vec{\mathrm{H}}, \end{aligned} \tag{11}$$

the fourth term represents the Zeeman energy, and k is the orbital angular momentum reduction factor. In explicitly, the Zeeman energy can be expressed by parallel or perpendicular component to the C_3 axis as follows:

$$\hat{H}_\parallel = \beta(k\hat{L}_z + g_e\hat{S}_z) \cdot H_z \tag{12}$$

$$\hat{H}_\perp = \beta(k\hat{L}_x + g_e\hat{S}_x) \cdot H_x. \tag{13}$$

By using equations (12) and (13), the 120 × 120 complete energy matrices containing the Zeeman energy are obtained. Subsequently, the basic feature of ZFS and optical spectra, local lattice structure and g factors ($g_\parallel$, $g_\perp$) in normal and high pressure can be determined for ruby by diagonalizing the complete energy matrices.

3 Calculations

3.1 The local lattice structure and energy levels

Although the energy levels of ruby has been extensively studied [3–10], the corresponding local lattice structure of it has not been detailed reported. In the following, we will focus on the local lattice structure of ruby by analyzing the EPR and optical spectra. Because the structure similarity between the ruby and $\mathrm{Cr_2O_3}$ and the crystal field acting on Cr^{3+} in $\mathrm{Al_2O_3{:}Cr^{3+}}$ is similar to that in $\mathrm{Cr_2O_3}$ [15], we predict that the structure parameters R, θ of ruby may tend to that of $\mathrm{Cr_2O_3}$. The major difference between the two structures is the magnitude of crystal-field strength, which will induce the variation of R directly. In general, the crystal-field strength Dq is in inverse to R^5 (R be the bond length). In this case, the Dq of ruby is about 200 cm^{-1} larger than that of $\mathrm{Cr_2O_3}$, therefore, the mean bond length of ruby should slightly shorter than that of $\mathrm{Cr_2O_3}$ (the mean bond length of $\mathrm{Cr_2O_3}$ is 1.9925 Å) [15]. For quantitative calculation, we introduce two parameters $\Delta\theta_1$, $\Delta\theta_2$ to describe the trigonal distortion in ruby.

Table 1. Cr^{3+} quartet levels in ruby, all units in cm^{-1}.

		Theoretical[a]	Expt.[b]
$^4T_2$	^4E	17 684	18 000
	$^4A_1$	17 965	18 450
$^4T_1$	^4E	24 016	24 400
	$^4A_2$	25 275	25 200
$^4T_1$	^4E	38 368	39 000
	$^4A_2$	38 892	39 400

[a] $B = 650\ cm^{-1}$, $C = 3120\ cm^{-1}$, $\zeta = 0, R_1 = 1.895$ Å, $R_2 = 2.004$ Å, $\theta_1 = 62.6°$, $\theta_2 = 47.52°$. [b] Reference [8].

The approximate relationship is used to evaluate the Cr–O bond lengths in Al_2O_3:Cr^{3+} system:

$$\begin{aligned} R_1 &= R_{10} + \Delta R, \\ R_2 &= R_{20} + \Delta R, \end{aligned} \tag{14}$$

where $R_{10} = 1.857$ Å and $R_{20} = 1.966$ Å, which are the Al–O bond lengths of Al_2O_3. The value of $\Delta R = 0.038$ Å is determined approximately by the optical spectra of ruby [6–8], which will be fixed in the following calculation. The angles between Cr–O bond and C_3 axis in Al_2O_3:Cr^{3+} system may be expressed as:

$$\begin{aligned} \theta_1 &= \theta_{10} + \Delta\theta_1, \\ \theta_2 &= \theta_{20} + \Delta\theta_2, \end{aligned} \tag{15}$$

where $\theta_{10} = 63.1°$, $\theta_{20} = 47.7°$, which are the angles between Al–O bond and C_3 axis, $\Delta\theta_1$, $\Delta\theta_2$ represent the trigonal distortion. Thus, the trigonal ligand-field parameters (B_{20}, B_{40}, B_{43}^c) are only the functions of $\Delta\theta_1$ and $\Delta\theta_2$. As for the parameters B, C, ζ, we take the classical values that approved by many researchers as follows [5,6,9]:

$$B = 650\ cm^{-1}, C = 3120\ cm^{-1}, \quad \zeta = k\zeta_0 = 170\ cm^{-1} (k = 0.62).$$

Then by diagonalizing the complete energy matrices the optical and EPR spectra of the Al_2O_3:Cr^{3+} system in normal pressure, which can be calculated from the EPR parameters and equation (3), are simulated with use of two distortion parameters $\Delta\theta_1$, $\Delta\theta_2$. The final theoretical results of local structure parameters $R_1 = 1.895$ Å, $R_2 = 2.004$ Å, $\theta_1 = 62.6°$, $\theta_2 = 47.52°$ for the octahedral Cr^{3+} center in Al_2O_3:Cr^{3+} crystal in normal pressure are determined. It appears that the mean Cr–O bond length of ruby is 1.9495 Å, which is slightly less than that of Cr_2O_3 (1.9925 Å). All results are listed in Tables 1 and 2. We can see from Tables 1 and 2 that both the EPR and the energy levels are in the experimental range, especially the ZFS parameter D is more precise than that of in the previous works [10,12]. And the splitting of quartet energy levels with spin-orbit coupling interaction is neglectable compared to that of without the spin-orbit coupling interaction. The ration of $^2T_2$:^2E is calculated as 1.517 (observed 1.47), and the energy levels ^2E, $^2T_1$, $^2T_2$ are sensitive to the ratio of C/B, whereas, the energy levels $^4T_1$, $^4T_2$ are relatively insensitive to it . In general, the range of ratio C/B is about $4 \sim 5$ [17], the ratio of $^2T_2$:^2E is roughly calculated as $1.543 \sim 1.511$ by diagonalizing the complete energy matrices in present work, i.e. the ratio of $^2T_2$:^2E is in inverse proportion to the C/B. Therefore, in this case we adopt the ratio of C/B as 4.8 is relatively reasonable.

Table 2. Optical spectra and zero-field splitting of Cr^{3+} in ruby, all units in cm^{-1}.

	Theoretical[a]	Expt.[b]
^2E	14 076	14 418
	14 096	14 447
$^2T_1$	14 557	14 957
	14 838	15 168
	14 850	15 190
$^4T_2$	17 651	
	17 673	
		18 000
	17 694	
	17 723	
	17 977	
		18 450
	17 894	
	21 353	20 993
$^2T_2$	21 448	21 068
	21 932	21 357
	24 019	
$^4T_1$	24 024	
		24 400
	24 030	
	24 037	
	25 283	25 200
	25 284	
	38 375	
$^4T_1$	38 388	39 000
	38 880	
	38 903	39 400
	38 918	
	38 932	
$E(\pm1/2) - E(\pm3/2)$	0.383	0.383

[a] $B = 650\ cm^{-1}$, $C = 3120\ cm^{-1}$, $\zeta = 170$, $R_1 = 1.895$ Å, $R_2 = 2.004$ Å, $\theta_1 = 62.6°$, $\theta_2 = 47.52°$. [b] References [6–8,18,19].

3.2 g factors

In previous works [4,9,10], the authors only considered the effect of orbital angular momentum reduction factor k on the spin-orbit interaction. In our calculation, the orbital angular momentum reduction factor k is included in the Zeeman energy besides included in the spin-orbit interaction as suggested by Kahn [21]. The theoretical g factors are in fair agreement with the experimental values as shown in Table 3 by diagonalizing the complete energy matrices, in which a small $k = 0.62$ is used [5,10]. In general, the magnitude of $g_{\parallel}$, $g_{\perp}$ is related to the signs of ZFS parameter D, i.e. the value of Δg ($\Delta g = g_{\parallel} - g_{\perp}$) is

Table 3. Comparison of energy levels, g factors and local lattice structure between normal and high pressure.

d–d transition and EPR spectrum			g factors	Local Lattice structure
Transition	Theoretical[a]	Expt.[b]	Theoretical[a,c]	
$\nu_\perp(^4A_1 \rightarrow {}^4E(^4T_2))$	1 kbar $\nu_\perp = 17\,684, \Delta\nu_\perp = 0$	$\Delta\nu_\perp = 0$	1 kbar $g_\parallel = 1.9859$	1 kbar $R_1 = 1.895$ Å $R_2 = 2.004$ Å
	63 kbar $\nu_\perp = 18\,233, \Delta\nu_\perp = 549$	$\Delta\nu_\perp = 600$	63 kbar $g_\parallel = 1.9855$	63 kbar $R_1 = 1.883$ Å $R_2 = 1.992$ Å
$\nu_\parallel(^4A_1 \rightarrow {}^4A_1(^4T_2))$	1 kbar $\nu_\parallel = 17\,965,\ \Delta\nu_\parallel = 0$	$\Delta\nu_\perp = 0$	1 kbar $g_\perp = 1.9866$	1 kbar $\theta_1 = 62.6$ $\theta_1 = 47.5$
	63 kbar $\nu_\parallel = 18\,468,\ \Delta\nu_\parallel = 503$	$\Delta\nu_\parallel = 600 \sim 900$	63 kbar $g_\perp = 1.9872$	63 kbar $\theta_1 = 62.8$ $\theta_2 = 47.6$
$E(\pm 1/2) - E(\pm 3/2)$	1 kbar 0.383	0.383		
	63 kbar 0.43	0.43		

[a] See footnote to Table 2. [b] References [18,20]. [c] The experimental values of g factors in normal pressure is $g_\parallel = 1.9840 \pm 0.006$, $g_\perp = 1.9867 \pm 0.006$ [10,18,19].

positive when the ZFS parameter D with the plus sign, whereas, when the ZFS parameter D with negative sign the value of Δg is negative. In Al_2O_3:Cr^{3+} system, the value of $g_\perp$ is larger than that of $g_\parallel$, which corresponds to the negative ZFS parameter D.

3.3 High-pressure effects upon energy levels, g factors and local lattice structure

In general, EPR is regarded as an ideal technique for probing the internal changes in a solid subjected to high pressure [18], however, there is no satisfactorily and detailed theoretical research in an EPR spectrum under pressure in present. In the present paper, the high-pressure effect on energy levels, g factors and local lattice structure are quantitatively calculated by diagonalizing the complete energy matrices as Table 3 shown. Under various pressures, the values of B, C, ζ are different, but the difference between 1 kbar and 63 kbar is small [4]. Therefore, in our calculation of EPR spectrum under 63 kbar, the values of $B = 650$ cm^{-1}, $C = 3120$ cm^{-1}, $\zeta = 170$ cm^{-1} is also adopted. Moreover, the ligand-field strength Dq will become larger with the increase of pressure [4], which is in inverse to R^5, so the Cr–O bond length of ruby in 63 kbar should become shorter than that of in 1 kbar. In Table 3, the comparison of energy levels, g factors as well as local lattice structure between 1 kbar and 63 kbar are given. It is shown that the g factors ($g_\parallel$, $g_\perp$) are in direct proportion to the pressure and the bond lengths tend to become shorter with the increasing of pressure. The unified calculation of pressure shifts of energy levels, g factors as well as local lattice structure can provide important criteria for the correctness of our methods. Our theoretical results of local lattice structure, especially the Cr-O bond length, are compared to the experiment data given by Gaudry [22]. The longer Cr-O bond length (2.004A) is in good agreement with the experiment datum (2.01A), however, the shorter Cr-O bond length (1.895A) is some smaller than the experimental Cr-O bond length (1.92A). The discrepancy may be ascribed to the error of spectra. Certainly, our theoretical results, especially the local lattice structure, need to be verified by further experiment.

4 Conclusions

The main feature of ruby, such as zero-field splitting and optical spectrum, g factors as well as local lattice structure, are satisfactorily explained within the crystal-field framework by diagonalizing the complete energy matrices. Our calculations further verify the opinion of Macfarlane about crystal-field theory used to study the energy levels of ruby. The other main point in present paper is that the

120×120 complete energy matrices are constructed, in which the orbital angular momentum reduction factor k is introduced. Finally, the high pressure effect upon the zero-field splitting and optical spectrum, g factors as well as local lattice structure is quantitatively calculated and discussed, which will provide some information to the further study of EPR spectrum under pressure.

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