

***d*-orbital theory and high-pressure effects upon the EPR spectrum of ruby**

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At the present time there is no satisfactory theory of *d-d* transition in ruby which relates its spectrum to its crystalline parameters; consequently a theoretical problem of predicting high-pressure EPR effects seems far from solution. In the present paper a quantitative relationship between crystalline parameters and spectra is established. The calculation results agree well with experimental findings.

I. INTRODUCTION

The spectra of Cr^{3+} in Al_2O_3 had been analyzed by Sugano *et al.*^{1,2} and others³⁻⁹ on the basis of crystal-field parameters determined from experiments. However, at the present time there is no satisfactory theory of *d-d* transition in ruby that relates its spectrum to its crystalline parameters. Consequently, a theoretical prediction of high-pressure zero-field splitting of ruby is not available. In this work we will investigate the theoretical difficulty on the basis of an analytical approximation of Watson's *d* orbit. The calculated results agree well with experimental findings.

II. *d*-ORBIT MODEL FOR d^n CONFIGURATION

For the d^n configuration, the *d* electrons can receive the Coulomb action of the nucleus and also the electrostatic actions of electrons of various inner shells. In the central-field approximation, this effective potential consists of the spherical shell potential, the Coulomb potential, and the potential arising from the uniform electric charge distribution, and can be expressed by

$$V(r) = \frac{3}{r} \frac{a_1 N_1 \zeta_1 \exp(-\zeta_1 r) + a_2 N_2 \zeta_2 \exp(-\zeta_2 r)}{a_1 N_1 \exp(-\zeta_1 r) + a_2 N_2 \exp(-\zeta_2 r)} - \frac{1}{2} \frac{a_1 N_1 \zeta_1^2 \exp(-\zeta_1 r) + a_2 N_2 \zeta_2^2 \exp(-\zeta_2 r)}{a_1 N_1 \exp(-\zeta_1 r) + a_2 N_2 \exp(-\zeta_2 r)} - E. \quad (4)$$

$$V_i(r_i) = C_0 + C_1 r_i^{-1} + C_2 r_i + C_3 r_i^2 + \dots, \quad (1)$$

where the first two terms on the right-hand side are the Condon-Shortley equivalent potential.¹⁰ The exponential function of the double-zeta type satisfies the physical requirement expressed by Eq. (1). This will be proved as follows.

In a central field, the wave equation of a single *d* electron is approximately given by

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + 3r^{-2} - V(r) - E \right] r R_d(r) = 0 \quad (2)$$

in atomic units. Here the configuration admixture is neglected.

The double-zeta exponential function is

$$R_d(r) = a_1 N_1 r^2 \exp(-\zeta_1 r) + a_2 N_2 r^2 \exp(-\zeta_2 r),$$

$$N_j = \left[\frac{(2\zeta_j)^7}{6!} \right]^{1/2}, \quad j = 1, 2 \quad (3)$$

$$a_1^2 + a_2^2 + 2a_1 a_2 \left[\frac{2\sqrt{\zeta_1 \zeta_2}}{\zeta_1 + \zeta_2} \right]^7 = 1.$$

Substituting Eq. (3) into Eq. (2) and solving the effective central potential, we have

Expanding Eq. (4) into a series, we have

$$\begin{aligned}
 V(r) = & -\frac{3a_1N_1a_2N_2(\xi_1-\xi_2)^2}{(a_1N_1+a_2N_2)^2} - \frac{1}{2} \frac{a_1N_1\xi_1^2+a_2N_2\xi_2^2}{a_1N_1+a_2N_2} - E + \frac{3}{r} \frac{a_1N_1\xi_1+a_2N_2\xi_2}{a_1N_1+a_2N_2} \\
 & - \frac{a_1N_1a_2N_2(\xi_1-\xi_2)^2}{(a_1N_1-a_2N_2)^3} [a_1N_1(\xi_1-2\xi_2)+a_2N_2(\xi_2-2\xi_1)]r \\
 & + \left[\frac{1}{4} \frac{a_1N_1a_2N_2(\xi_1-\xi_2)^3}{(a_1N_1+a_2N_2)^3} (a_1N_1-a_2N_2)(\xi_1+\xi_2) \right. \\
 & \left. - \frac{1}{2} \frac{a_1N_1a_2N_2(\xi_1-\xi_2)^4}{(a_1N_1+a_2N_2)^4} (a_1^2N_1^2+a_2^2N_2^2+4a_1N_1a_2N_2) \right] r^2 + \dots, \quad \xi_1 > \xi_2. \quad (5)
 \end{aligned}$$

This expression is consistent with Eq. (1). From this it can be seen that the adoption of the exponential function of double-zeta type as the radial d -orbital function is reasonable. Now, with Eq. (3) as d -orbital function, several problems are to be noted.

A. Spin-orbital coupling coefficient

The Hamiltonian operator of spin-orbital (so) interaction of an N -electron system is given by

$$\mathcal{H}_{so} = \sum_{i=1}^N \mathcal{H}(i) \quad (6)$$

with

$$\mathcal{H}(i) = \zeta(r_i) \vec{l} \cdot \vec{s}, \quad (7)$$

$$\zeta(r_i) = -\frac{e}{2m^2c^2r} \frac{d}{dr} V(r_i). \quad (8)$$

For a d orbit, the so coefficient is

$$\begin{aligned}
 \zeta_d^0 &= \hbar^2 \langle R_d | \zeta(r) | R_d \rangle \\
 &= \frac{-e\hbar^2}{2m^2c^2} \left\langle \frac{1}{r} V(r) \right\rangle. \quad (9)
 \end{aligned}$$

In units of cm^{-1} , the so coefficient becomes

$$\begin{aligned}
 \zeta_d^0 &= 5.844167 \left[\frac{9}{8} \left[\frac{a_1^2N_1^2}{\xi_1^3} + \frac{a_2^2N_2^2}{\xi_2^3} + \frac{16a_1N_1a_2N_2}{(\xi_1+\xi_2)^3} \right] \right. \\
 &\quad \left. + 12a_1N_1a_2N_2 \frac{(\xi_1-\xi_2)^2}{(\xi_1+\xi_2)^5} \right]. \quad (10a)
 \end{aligned}$$

Considering the correction of Blume and Watson,⁷ we have

$$\zeta_d = \zeta_d^0 - 3M^0(dd) + \frac{6}{7}M^2(dd). \quad (10b)$$

B. Racah electrostatic parameters

The Hamiltonian operator of the electron-electron repulsion interaction can be written as

$$\mathcal{H}_e = \frac{1}{2} \sum_{i \neq j}^n \frac{e^2}{r_{ij}}, \quad i, j = 1, 2, 3, \dots, n. \quad (11)$$

The contributions of the electron-electron interaction to levels of the d^n system can be described in terms of Racah parameters,¹¹⁻¹³

$$\begin{aligned}
 A_0 &= F^0 - \frac{49}{441}F^4, \\
 B_0 &= \frac{1}{49}F^2 - \frac{5}{441}F^4, \\
 C_0 &= \frac{35}{441}F^4,
 \end{aligned} \quad (12)$$

where

$$\begin{aligned}
 F^k &= e^2 \int_0^\infty \int_0^\infty R_d(r_1)^2 \frac{r_1^k}{r_{>}^{k+1}} R_d(r_2)^2 \\
 &\quad \times r_1^2 r_2^2 dr_1 dr_2. \quad (13)
 \end{aligned}$$

By using the formula

$$\begin{aligned}
 J^k(\alpha, \beta) &= \int_0^\infty \int_0^\infty r_1^6 r_2^6 \frac{r_1^k}{r_{>}^{k+1}} e^{-\alpha r_1} e^{-\beta r_2} dr_1 dr_2 \\
 &= \frac{(6+k)!}{\beta^{7+k}} \left[\frac{(5-k)!}{\alpha^{6-k}} - \sum_{m=0}^{6+k} \frac{\beta^m}{m!} \frac{(5-k+m)!}{(\beta+\alpha)^{6-k+m}} \right] + \frac{(6+k)!}{\alpha^{7+k}} \left[\frac{(5-k)!}{\beta^{6-k}} - \sum_{m=0}^{6+k} \frac{\alpha^m}{m!} \frac{(5-k+m)!}{(\alpha+\beta)^{6-k+m}} \right], \quad (14)
 \end{aligned}$$

the parameters F^k in Eq. (13) can be calculated.

III. ANALYTICAL APPROXIMATION OF WATSON'S d ORBIT

By following previous works^{8,14} and introducing three mathematical conditions governing overlap, $R_d(r) \approx R_d^W(r)$ (W denotes Watson) ($r \leq 0.3$ a.u.),

$$[\langle R_d(r) | R_d^W(r) \rangle]^{1/2} \approx 1 \text{ and } (\langle R_d | r^{-1} | R_d \rangle)^{1/2} \approx [\langle R_d^W | r^{-1} | R_d^W \rangle]^{1/2},$$

then the analytic approximation of Watson's⁶ self-consistent field d orbit is given by

$$R_d(r) = 0.591474 \left[\frac{9.32327}{6!} \right]^{1/2} r^2 \exp(-4.6616r) + 0.6014980 \left[\frac{3.30527}{6!} \right]^{1/2} r^2 \exp(-1.6526r), \quad (15)$$

which is a parametrized wave function. Using an IBM-130 computer, we find

$$\begin{aligned} A_0 &= 150\,848, \quad \langle r^2 \rangle = 2.4843, \\ B_0 &= 920.48, \quad \langle r^4 \rangle = 16.4276, \\ C_0 &= 3330.71, \quad \langle r^{-3} \rangle = 3.0841, \\ \xi_d &= 240, \quad \mathcal{P} = g_e g_N \beta_e \beta_N \langle r^{-3} \rangle = -0.0033, \end{aligned} \quad (16)$$

where A_0 , B_0 , C_0 , ξ_d , and \mathcal{P} are in cm^{-1} units, and $\langle r \rangle$ values are in a.u. Here \mathcal{P} is the hyperfine con-

stant of the nucleus of Cr. Comparison of theory with experiment is given in Table I.

IV. $d-d$ TRANSITION IN RUBY

Ruby ($\text{Al}_2\text{O}_3:\text{Cr}^{3+}$) is an important material for lasers. There are many precise experimental data accumulated on its level study that lend ruby very favorably to theoretical study. In ruby, Cr^{3+} is surrounded by six O^{2-} ions, its stereostructure belongs

TABLE I. Spectrum of free Cr^{3+} ion.

Term	J	Energy levels (cm^{-1})	
		Theoretical values	Experimental values ^{a,b}
4F	3/2	0	0 ^a
	5/2	200	235.8 ^a
	7/2	480	555.6 ^a
	9/2	840	945.6 ^a
4P	1/2	13 749	14 059, ^a 13 640 ^b (17)
	3/2	13 871	14 177.1 ^a
	5/2	14 343	14 471.3 ^a
2G	7/2	14 998	15 051.8, ^a 14 660 ^b
	9/2	15 363	15 401.6 ^a
2P	3/2	18 548	19 438.6, ^a 18 400 ^b
	1/2	18 620	19 519.2 ^a (15,16)
2D_2	3/2	20 455	20 649.9, ^a 19 930 ^b
	5/2	20 469	20 664.3 ^a
2H	9/2	20 523	21 065.9, ^a 20 590 ^b
	11/2	20 790	21 320.7 ^a
2P	7/2	33 448	34 262.8 ^a
	5/2	33 590	34 555.7 ^a
2D_1	5/2	51 846	52 975.3 ^a
	3/2	51 995	53 142.0 ^a

Trees correction^c: 75 cm^{-1}
Racah correction^c: -131 cm^{-1}

^aReferences 16 and 17.

^bReference 18.

^cReferences 11, 12, and 15.

to the C_3 point group³; $\alpha_1=63.1^\circ\pm 1^\circ$, $R_1=1.857\pm 0.015 \text{ \AA}$, $\alpha_2=47.7^\circ\pm 1^\circ$, $R_2=1.966\pm 0.015 \text{ \AA}$. Under the O_h approximation, we have⁹

$$\begin{aligned}
 E(^4A_2) &= -1.2\Delta, \\
 E(^2E_a) &= -1.2\Delta 9B + 3C, \\
 E(^2E_b) &= E(^2E_a) + \Delta + 5B, \\
 E(^2E_c) &= E(^2E_a) + 14B + 3C + \Delta, \\
 E(^2T_{1a}) &= E(^2E_a), \\
 E(^2T_{1b}) &= E(^2E_a) + \Delta, \\
 E(^2T_{1c}) &= E(^2E_a) + \Delta + 6B, \\
 E(^2T_{2a}) &= 158 + 4C - 1.2\Delta, \\
 E(^2T_{2b}) &= E(^2E_a) + \Delta, \\
 E(^2T_{2c}) &= E(^2E_a) + \Delta + 10B, \\
 E(^4T_2) &= -0.2\Delta, \\
 E(^4T_{1a}) &= -0.2\Delta + 12B - Y, \\
 E(^4T_{1b}) &= 0.8\Delta + 3B + Y, \\
 E(^2A_1) &= -0.2\Delta + 4B + 3C, \\
 E(^2A_2) &= -0.2\Delta + 24B + 3C,
 \end{aligned} \tag{17}$$

with

$$\begin{aligned}
 \Delta &\approx \frac{5}{3}N^2 \left[\frac{e^2\langle r^4 \rangle}{R_1^5} + \frac{e^2\langle r^4 \rangle}{R_2^5} \right], \\
 Y &\approx 36B^2/(\Delta - 9B + Y), \\
 B &\approx N^4B_0, \\
 C &\approx N^4C_0, \\
 N^2 &= (N_\pi^2 + N_\sigma^2)/2, \\
 N_\pi^{-2} &= 1 + 4\beta_\pi S_\pi + \beta_\pi^2, \\
 N_\sigma^{-2} &= 1 + 4\alpha_\sigma S_\sigma + \alpha_\sigma^2,
 \end{aligned} \tag{18}$$

where α_σ and β_π denote covalent bonding coefficients (two empirical constants), $\alpha_\sigma = -0.7104$, $\beta_\pi = 0.1770$, S_σ and S_π denote the overlap integral between the $3d$ orbit (Cr^{3+}) and $2p$ orbit (O^{2-}), and

$$R_{2p}(\text{O}^{2-}) = \text{STO}(1.725), \tag{19}$$

where STO denotes Slater orbital. Comparison of theory with experiment is given in Table II.

V. ZERO-FIELD SPLITTING AND TRIGONAL FIELD SPLITTING

With consideration of the combined effects of trigonal-field and spin-orbit coupling and the utilization of the third-order perturbation theory,⁹ the zero-field splitting of ruby in the ground state is given by

TABLE II. $d-d$ transition in ruby.

Transition	Theoretical frequency ^b (cm^{-1})	Experimental frequency ^a (cm^{-1})
$^4A_{2g} \rightarrow ^2E_a$	14 440	14 433, 14 447, 14 418
$^2T_{1a}$	14 440	15 105, 14 957, 15 169, 15 190
		15 038
4T_2	17 505	18 000
$^2T_{2a}$	21 434	21 139, 20 993, 21 068, 21 357
		21 139
$^4T_{1a}$	24 707	24 800
2A_1	28 174	29 700
$^2T_{2b}$	31 946	31 000
$^2T_{1b}$	31 946	32 300
2E_b	35 582	34 300
$^2T_{1c}$	36 309	36 800
$^4T_{1b}$	38 717	39 000
$^2T_{2c}$	39 218	40 500
2A_2	42 700	42 300

^aReferences 2-4.

^b O_h approximation.

TABLE III. Trigonal- and zero-field splitting.

Transition	Theoretical values ^b (cm ⁻¹)	Experimental values ^a (cm ⁻¹)
⁴ A ₁ → ⁴ E(⁴ T ₂)	17 399	18 000
⁴ A ₁ (⁴ T ₂)	17 806	18 400
² E(² T _{2a})	21 286	20 993—21 357
² A ₁ (² T _{2a})	21 737	
⁴ E(⁴ T _{1a})	24 361	24 400
⁴ A ₂ (⁴ T _{1a})	25 399	25 200
⁴ A ₂ (⁴ T _{1b})	38 612	39 000
⁴ E(⁴ T _{1b})	38 928	39 400
$B(\pm\frac{1}{2})-E(\pm\frac{3}{2})$	0.37	0.383

^aReferences 2—4 and 19.^bC_{3v} approximation.

$$\begin{aligned}
E(\pm\frac{1}{2})-E(\pm\frac{3}{2}) \approx & N^6 \zeta_d^2 V \left[\frac{4}{9[E(^4T_2)-E(^4A_2)]^2} - \frac{4}{9[E(^2T_{2b})-E(^4A_2)]^2} \right] \\
& + N^6 \zeta_d^2 V' \left[\frac{4\sqrt{2}}{3[E(^4T_2)-E(^4A_2)][E(^4T_{1a})-E(^4A_2)]} \right. \\
& + \frac{2\sqrt{2}}{[E(^2T_{2a})-E(^4A_2)][E(^4T_{1a})-E(^4A_2)]} \\
& + \frac{2\sqrt{2}}{3[E(^2T_{2b})-E(^4A_2)][E(^4T_{1a})-E(^4A_2)]} \\
& \left. + \frac{2\sqrt{2}}{[E(^2T_{1a})-E(^4A_2)][E(^4T_{1a})-E(^4A_2)]} \right]. \quad (20)
\end{aligned}$$

In the range of experimental error, we have chosen the best values (α measured in deg and R in Å) as

$$\begin{aligned}
\alpha_1 &= 62.7, \quad R_1 = 1.857, \\
\alpha_2 &= 46.7, \quad R_2 = 1.966, \quad (21)
\end{aligned}$$

and using the d orbit in Eq. (15), we find (in units of cm⁻¹)

$$\begin{aligned}
N^2 V &\approx N^2 (3D\sigma - \frac{20}{3}D\tau) = 903, \\
N^2 V' &\approx N^2 \left[\sqrt{2}D\sigma - \frac{5\sqrt{2}}{3}D\tau \right] = 587, \quad (22)
\end{aligned}$$

$$E(\pm\frac{1}{2})-E(\pm\frac{3}{2}) = 0.37.$$

($P=0$ kbar). Comparison of theory with experiment is given in Table III. It follows from Table III that the calculation results agree well with experimental findings. This removes "a long-standing theoretical difficulty."^{19,20}

VI. HIGH-PRESSURE EFFECTS UPON $d-d$ AND EPR SPECTRA OF RUBY

According to the work by Drickamer *et al.*,²⁰ we have

$$\frac{d}{dP}(V/V_0) \approx -3.175 \times 10^{-4}, \quad (23)$$

$$\frac{d\alpha}{dP} \approx 1.587 \times 10^{-3},$$

measured in kbar⁻¹ and degkbar⁻¹, respectively. By using the Eqs. (17), (18), and (20)–(23), the high-pressure $d-d$ and EPR spectra may be computed. Comparison of theory with experiment is given in Table IV.

In the calculation, the trigonal-field parameters are given by

TABLE IV. High-pressure *d-d* and EPR spectrum.

Transition	Theoretical frequency (cm ⁻¹)	Experimental frequency ^a (cm ⁻¹)
$\nu_1(^4A_1 \rightarrow ^4E(^4T_2))$	1 kbar	
	$\nu_1=17399, \Delta\nu_1=0$	$\Delta\nu_1=0$
	63 kbar	
	$\nu_1=17963, \Delta\nu_1=564$	$\Delta\nu_1=600$
$\nu_{ }(^4A_1 \rightarrow ^4A_1(^4T_2))$	1 kbar	
	$\nu_{ }=17806, \Delta\nu_{ }=0$	$\Delta\nu_{ }=0$
	63 kbar	
	$\nu_{ }=18385, \Delta\nu_{ }=579$	$\Delta\nu_{ }=600-900$
$E(\pm\frac{1}{2})-E(\pm\frac{3}{2})$	128 kbar	
	$\nu_1=18601, \Delta\nu_1=1202$	$\Delta\nu_1=1100$
	1 kbar	
	0.37	0.38
	63 kbar	
	0.42	0.43
	128 kbar	
	0.454	

^aReferences 19 and 21.

$$D\sigma = -\frac{3}{7} \left[(3 \cos^2 \alpha_1 - 1) \frac{e^2 \langle r^2 \rangle}{R_1^3} + (3 \cos^2 \alpha_2 - 1) \frac{e^2 \langle r^2 \rangle}{R_2^3} \right], \quad (24)$$

$$D\tau = - \left[\frac{1}{28} (35 \cos^4 \alpha_1 - 30 \cos^2 \alpha_1 + 3) + \frac{\sqrt{2}}{4} \sin^3 \alpha_1 \cos \alpha_1 \right] \frac{e^2 \langle r^4 \rangle}{R_1^5}$$

$$- \left[\frac{1}{28} (35 \cos^4 \alpha_2 - 30 \cos^2 \alpha_2 + 3) + \frac{\sqrt{2}}{4} \sin^3 \alpha_2 \cos \alpha_2 \right] \frac{e^2 \langle r^4 \rangle}{R_2^5}.$$

It follows from Table IV that the theoretical difficulty for high-pressure zero-field splitting²⁰ can be removed by using the analytical approximation of Watson's *d*-orbit and empirical molecular orbital theory.

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