

# Effect of Configuration Mixing and Covalency on the Energy Spectrum of Ruby

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For the purpose of improving the analysis hitherto done of the optical and microwave spectrum of ruby, a calculation has been performed in the strong cubic field scheme, taking into account the effect of configuration mixing of the higher excited  $t_2^3e$  states into the  $t_2^3$  states. In the calculation, covalency of the  $t_2$  and  $e$  electrons is also introduced in a simplified fashion besides the spin-orbit interaction, trigonal field and Zeeman energy. The result shows that configuration mixing and covalency play a very important role in giving zero-field splittings and  $g$  values of the  $t_2^3$  states. It is also found that there is not much difference between the degrees of covalency for the  $t_2$  and  $e$  electrons, although they are fairly large for both electrons. The best zero-field splitting of the ground state thus obtained is  $0.24\text{ cm}^{-1}$  with the correct sign.

## INTRODUCTION

RECENTLY the optical and paramagnetic resonance spectrum of ruby has been intensively studied, and it has given detailed knowledge of both the excited states and the ground state of this system.

The analysis of the spectrum hitherto done<sup>1</sup> is based on the crystal field theory in the strong cubic field scheme, treating the spin-orbit interaction and the low symmetry crystal field as perturbations. In the analysis, the effect of configuration mixing<sup>2</sup> of the higher excited states (above  $\sim 25\,000\text{ cm}^{-1}$  in energy) into the optically important excited states (below  $\sim 25\,000\text{ cm}^{-1}$  in energy) is entirely neglected. This means that the problem is treated in the strong cubic field limit. Although such a treatment has explained many aspects of the observed spectrum fairly well, some optical absorption lines have not been identified and some quantitative discrepancies associated with the identified lines have not been removed.

Generally, we can expect that configuration interaction plays an important role in the states with a half-filled electron configuration such as those giving rise to the sharp optical absorption lines in ruby. This fact is explained as follows: In these states, the spin-orbit and low-symmetry crystal field perturbations give no first-order effect, so that the effect on energy is expected to be at most of the order of magnitude of  $H'^2/C$ , which is the second order:  $H'$  stands for the magnitude of either spin-orbit or low symmetry crystal field perturbations, and  $C$  for the strength of the Coulomb interaction which gives rise to the energy separation between states with the same electron configuration. On the other hand, if the configuration interaction is combined with the perturbations men-

tioned above, the effect is at most of the order of magnitude of  $H'C/\Delta$ , where  $\Delta$  represents the strength of the cubic field. By inserting the rough values  $H'\sim 300\text{ cm}^{-1}$ ,  $C\sim 5000\text{ cm}^{-1}$ ,  $\Delta\sim 20\,000\text{ cm}^{-1}$ , we can easily see the importance of the configuration interaction.

Recent success of the microwave resonance experiment in the lower Kramers doublet of the  $t_2^3\ ^2E$  excited state of ruby performed by Geschwind, Collins, and Schawlow<sup>3</sup> may be considered to indicate the importance of the configuration mixing, because otherwise forbidden magnetic dipole transitions between the Zeeman levels are made possible mainly by the effect of the configuration mixing as Clogston's calculation<sup>4</sup> has shown [the processes (4) and (5) in his paper are dominant].

In view of these circumstances, it is felt that a more detailed calculation involving the configuration interaction is necessary, if the observed energy spectrum of ruby is to be accounted for completely. In this paper, therefore, we shall mention results of a numerical calculation which involves Coulomb interactions between states with the  $t_2^3$  and  $t_2^3e$  electron configurations as well as the spin-orbit and trigonal field interactions. In the calculation the covalency of  $d$  electrons shall be introduced in a conventional manner, as will be explained in the next section. The results shall be compared with the quantities experimentally determined by the use of optical and microwave resonance techniques.

## METHOD OF CALCULATION

The energy levels of ruby may be classified as follows:

$$\begin{aligned} \text{ground level:} & \quad t_2^3\ ^4A_2; \\ \text{excited levels I:} & \quad t_2^3\ ^2E(\equiv\ ^a^2E), \\ & \quad t_2^3\ ^2T_1(\equiv\ ^a^2T_1), \\ & \quad t_2^3\ ^2T_2(\equiv\ ^a^2T_2), \end{aligned}$$

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<sup>1</sup> S. Sugano and Y. Tanabe, J. Phys. Soc. Japan **13**, 880 (1958).

<sup>2</sup> The mixing is due to the Coulomb interaction among states with the same symmetry  $ST$  but with different electron configurations  $t_2^3e^N-n$ . Particularly in our paper, the mixing between the states with the  $t_2^3$  and  $t_2^3e$  configuration will henceforth be referred to as configuration mixing, which is abbreviated as C.M.

<sup>3</sup> S. Geschwind, R. J. Collins, and A. L. Schawlow, Phys. Rev. Letters **3**, 545 (1959).

<sup>4</sup> A. M. Clogston, Phys. Rev. **118**, 1229 (1960).

$$t_2^2 e^4 T_2,$$

$$t_2^2 e^4 T_1;$$

excited levels II:  $t_2^2(^1A_1)e^2E(= {}^bE)$ ,  
 $t_2^2(^1E)e^2E(= {}^cE)$ ,  
 $t_2^2(^3T_1)e^2T_1(= {}^bT_1)$ ,  
 $t_2^2(^1T_2)e^2T_1(= {}^cT_1)$ ,  
 $t_2^2(^3T_1)e^2T_2(= {}^bT_2)$ ,  
 $t_2^2(^1T_2)e^2T_2(= {}^cT_2)$ ,  
 $t_2^2 e^2 A_2$ ,  
 $t_2^2 e^2 A_1$ ,  
 $t_2^2 e^2 T_1$ ;

where the energies of the excited levels I fall in the visible spectral region and the energies of the excited levels II are considered to fall in the ultraviolet region. The other excited levels with the  $t_2 e^2$  and  $e^2$  configurations are supposed to lie higher than the so-called charge-transfer levels.<sup>5</sup> Therefore, except for the  $t_2 e^2 {}^4T_1$  state in group II, the significant crystal field levels may be considered to be those with electron configurations  $t_2^3$  and  $t_2^2 e$ .

As already mentioned in the previous section, we here take all these significant crystal field levels into account (except for the  $t_2 e^2 {}^4T_1$  state), and solve a  $80 \times 80$  secular determinant numerically which involves the trigonal field and the spin-orbit interaction as well as the cubic field and the Coulomb interaction. In order to obtain the  $g$  values of these levels, matrix elements of the Zeeman energy with the magnetic field parallel or perpendicular to the trigonal axis are further introduced into this determinant. The reason why the  $t_2 e^2 {}^4T_1$  state is neglected is simply that, since there is no matrix element, for any interaction considered above, between the  $t_2 e^2 {}^4T_1$  state and the state with the  $t_2^3$  configuration responsible for the spectral lines, inclusion of this state does not affect significantly the results concerning the properties of the microwave spectrum and of the sharp optical lines, which we are going to discuss in this paper.

For constructing the secular determinant, Tanabe and Kamimura's table<sup>6</sup> was used. Double-barred matrices of spin-orbit interaction for  $t_2^n e^{N-n}$ -systems ( $n=1, \dots, 6; N-n=1, \dots, 4$ ) have been already calculated by Tanabe.<sup>7</sup> Newly calculated double-barred matrices of the trigonal field and the angular momentum operator are listed in the Appendix. Here it is assumed that the trigonal field has the symmetry  $T_2$ : the trigonal fields with the other symmetries  $A_2$  and  $T_1$

are considered weak because they commence, respectively, from the sixth- and fourth-order terms in the expansion in the electron coordinates.

The parameters introduced in the secular equations are: cubic field parameter  $Dq$ , Racah's parameters  $A$ ,  $B$ , and  $C$ , which denote the Coulomb interaction between the electrons,  $\zeta$  and  $\zeta'$  for the spin-orbit interaction defined as

$$\zeta = -2(t_2 \frac{1}{2} x_+ | v_{s.o.} | t_2 \frac{1}{2} x_+),$$

$$\zeta' = -\sqrt{2}(t_2 \frac{1}{2} x_+ | v_{s.o.} | e \frac{1}{2} u_+),$$

$K$  and  $K'$  for the trigonal field defined as

$$K = (t_2 x_+ | v_{\text{trig}} | t_2 x_+),$$

$$K' = -(1/\sqrt{2})(t_2 x_+ | v_{\text{trig}} | e u_+),$$

and orbital angular momentum reduction factors  $k$  and  $k'$  defined as

$$k = -(t_2 x_+ | l_z | t_2 x_+),$$

$$k' = -(1/\sqrt{2})(t_2 x_+ | l_z | e u_+),$$

where  $v_{s.o.}$ ,  $v_{\text{trig}}$ , and  $l_z$  are the single electron operators of the spin-orbit interaction, the trigonal field and the  $z$ -component (along the trigonal axis) of the orbital angular momentum, respectively,  $x_+$  and  $u_+$  are the trigonal bases given in reference 1. In case the  $t_2$  and  $e$  orbitals are constructed from  $3d$ -orbitals, we have

$$\zeta = \zeta', \quad K = K', \quad k = k' = 1.$$

Further we introduce the covalency parameter  $\epsilon$  after Koide and Pryce,<sup>8</sup> which was used successfully by Stout<sup>9</sup> for the analysis of the manganous fluoride spectrum. This parameter was originally introduced in the sense that in the evaluation of the Coulomb and

TABLE I. The location of the  $t_2^3$  states in absence of a magnetic field.

Energy levels		Calc. I with C.M. <sup>a</sup> (cm <sup>-1</sup> )	Calc. I without C.M. <sup>a</sup> (cm <sup>-1</sup> )	Obs (cm <sup>-1</sup> )
${}^4A_2$	$\pm \frac{3}{2}$	0.00	0.00	0.00
	$\pm \frac{1}{2}$	0.16	0.06	0.38 <sup>b</sup>
${}^aE$	$\pm \frac{1}{2} u_{\mp} (R_1)$	13550	14588	14418 <sup>c</sup>
	$\pm \frac{1}{2} u_{\pm} (R_2)$	13576	14626	14447 <sup>c</sup>
${}^aT_1$	$\pm \frac{1}{2} a_0 (R_3')$	14219	14711	...
	$\pm \frac{1}{2} a_{\pm} (R_2')$	14340	14709	...
	$\pm \frac{1}{2} a_{\mp} (R_1')$	14356	14713	...
${}^aT_2$	$\pm \frac{1}{2} x_{\pm} (B_1)$	21643	24540	20993 <sup>c</sup>
	$\pm \frac{1}{2} x_{\mp} (B_2)$	21749	24526	21068 <sup>c</sup>
	$\pm \frac{1}{2} x_0 (B_3)$	22055	24452	21357 <sup>d</sup>

<sup>a</sup> The used values of the parameters are  $Dq=1667$ ,  $B=700$ ,  $\zeta=170$ ,  $K=-330$  (cm<sup>-1</sup>),  $\epsilon=0.19$ , and  $k=0.62$ .

<sup>b</sup> A. A. Manenkov and A. M. Prokhorov, J. Exptl. Theoret. Phys. (U.S.S.R.), 762 (1955); Soviet Phys.-JETP 1, 611 (1955).

<sup>c</sup> S. Sugano and I. Tsujikawa, J. Phys. Soc. Japan 13, 899 (1958).

<sup>d</sup> Reference 12.

<sup>8</sup> S. Koide and M. H. L. Pryce, Phil. Mag. 3, 607 (1958).

<sup>9</sup> J. W. Stout, J. Chem. Phys. 31, 709 (1959).

<sup>5</sup> D. S. McClure, *Solid State Physics* edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1960), Vol. 9, p. 399.

<sup>6</sup> Y. Tanabe and H. Kamimura, J. Phys. Soc. Japan 13, 394 (1958).

<sup>7</sup> Y. Tanabe, Supplement Prog. Theoret. Phys. (Kyoto) No. 14, 17 (1960).

TABLE II. The zero-field splittings of the  $t_2^3$  states for various calculations.

Energy levels	Calc. I with C.M. (cm <sup>-1</sup> )	Calc. II with C.M. <sup>a</sup> (cm <sup>-1</sup> )	Calc. I without C.M. (cm <sup>-1</sup> )	Calc. A <sup>b</sup> (cm <sup>-1</sup> )	Calc. A with C.M. (cm <sup>-1</sup> )	Obs <sup>c</sup> (cm <sup>-1</sup> )
$^4A_2: W(1/2) - W(3/2)$	0.16	0.24	0.06	0.01	0.12	0.38
$^2E: W(R_2) - W(R_1)$	26	32	37	30	22	29
$^2T_1: W(R_3') - W(R_2')$	-121	-123	2	53	-142	...
$^2T_1: W(R_2') - W(R_1')$	-16	-22	-4	15	-15	...
$^2T_2: W(B_3) - W(B_2)$	306	304	-74	-200	313	290
$^2T_2: W(B_2) - W(B_1)$	106	127	-14	45	101	75

<sup>a</sup> The used values of the parameters are  $Dq=1667$ ,  $B=700$ ,  $\zeta=207$ ,  $K=-330$  (cm<sup>-1</sup>),  $\epsilon=0.19$  and  $k=0.76$ .

<sup>b</sup> The perturbation calculation without C.M.;  $Dq=1800$ , ( $B=740$ ),  $\zeta=140$ ,  $K=-350$  (cm<sup>-1</sup>) and  $\epsilon=0$ . It should be noticed that the factor  $(2/3)^{1/2}$  in the third term of the formula for the zero-field splitting of the ground state given in reference 1 should be omitted.

<sup>c</sup> These values are derived from Table I.

exchange integrals the amplitude of each  $e$  orbital is diminished by the factor  $(1-\epsilon)^{1/2}$  compared to the amplitude of each  $t_2$  orbital. Note that this does not mean that the  $t_2$  orbital is not deformed: We may introduce the covalency of the  $t_2$  orbital through the reduction of the  $B$ ,  $\zeta$ , and  $k$  values compared to those of the free ion. In our calculation, simply to decrease the number of the appearing parameters, we extend this idea to the evaluation of  $\zeta$ ,  $K$ , and  $k$  putting  $\zeta' = (1-\epsilon)^{1/2}\zeta$ ,  $K' = (1-\epsilon)^{1/2}K$ , and  $k' = (1-\epsilon)^{1/2}k$ . The theoretical justification of these relations is not clear, but, considering the fact that the quantities we shall be mainly concerned with are rather insensitive to the values of the primed parameters, we will use these tentative relations.

The number of the parameters can be further reduced by the relation  $C=4B$  which is usually used and seems reasonable. The parameters  $A$  and  $Dq$  appear always in the combination  $10Dq-2\epsilon A$  in the diagonal elements of the states with the  $t_2^3e$  configuration. The effect of  $A$  can, therefore, be included in the cubic field strength by modifying the definition of  $Dq$ . It should, however, be noticed that, since  $A$  comes from the Coulomb interaction between the electrons, the modified  $Dq$  can no longer be defined as the energy separation between the  $e$  and  $t_2$  molecular orbitals in a single electron system.

The remaining adjustable parameters are now  $Dq$ ,  $B$ ,  $\zeta$ ,  $K$ ,  $\epsilon$ , and  $k$ .

### NUMERICAL CALCULATION AND RESULTS

In the numerical calculation, we can further reduce the number of the effective parameters in the following way: The excitation energies to the  $^2E$  and  $^2T_2$  states are almost determined by the value of parameter  $B$  alone, so that the  $B$  value can be estimated by using the experimental positions of the  $R$  and  $B$  lines. Then,  $\epsilon$  is determined so as to give the observed separation between the  $U$  and  $Y$  bands<sup>1</sup> because this separation is to be approximately equal to  $12(1-\epsilon)B$ . By the use of these values of  $B$  and  $\epsilon$ , we can estimate the value of  $Dq$  from the position of the  $U$  band: The excitation energy to the  $^4T_2$  state is  $\sim(10Dq+10\epsilon B)$ .<sup>10</sup> The  $K$

<sup>10</sup> This  $Dq$  is the newly defined  $Dq$  including the effect of  $A$ .

value should fall in the neighborhood of  $-350$  cm<sup>-1</sup> because this value reproduces the trigonal splitting of each band which has been observed.<sup>11</sup> Then, by using the fact that the initial splitting of the  $^2E$  state is not very sensitive to the effect of the configuration mixing and is given as a function of  $K\zeta$ , we can estimate the  $\zeta$  value from the observed splitting.

Thus, we can estimate fairly good values of  $Dq$ ,  $B$ ,  $\epsilon$ ,  $K$ , and  $\zeta$  from the beginning: actually these values were settled in the first few trials of the calculation. The only remaining parameter,  $k$ , is sensitively related to the  $g$  values of the excited states, especially of the  $^2T_2$  state, in combination with the effect of the configuration mixing. Therefore, in the last few trials, we adjusted only the  $k$  value so as to give reasonable  $g$  values.

The programming of the diagonalization problem for the IBM 7090 computer was carried out by Miss B. B. Cetlin. Details on the computational procedures used are to be published elsewhere.

The eigenvalues of the  $t_2^3$  states obtained in the calculation (denoted as "Calc. I with C.M."), which seems best among many trials in giving reasonable agreement with every aspect of the experimental data, are listed in Table I. In Table II, the zero-field splittings obtained in several trials of the calculation are summarized. "Calc. II with C.M." also gives reasonable agreement in the zero-field splittings but it is worse than "Calc. I with C.M." in giving the  $g$  values (Table III). "Calc. A with C.M." is the direct improvement of "Calc. A" by inclusion of the configuration interaction. The calculated  $g$  values with magnetic fields parallel and perpendicular to the trigonal axis are given in Tables III and IV, respectively. The listed  $g_{11}$  and  $g_4$  values of the ground state are those used in the usual spin Hamiltonian. The definition of the  $g_{11}$  values of the excited states is explained in reference 1, and  $g_4$  values are given in their absolute values. It should be noticed that the applied magnetic field strength in our calculation is  $1/\beta$  cm<sup>-1</sup> so that the Zeeman energy is always very small compared with the zero-field splittings of the excited states.

In order to see clearly the effect of the configuration

<sup>11</sup> G. Kuwabara *et al.* (to be published).

TABLE III. The  $g_{II}$  values of the  $t_2^3$  states for various calculations.

Energy levels	Calc. I with C.M.	Calc. II with C.M.	Calc. I without C.M.	Calc. A <sup>a</sup> with C.M.	Obs
$g_{II} (^4A_2)$	1.9869	1.9806	1.9870	1.9789	$1.9840 \pm 0.0006^b$
$g_{II} (R_1)$	-2.59	-2.72	-3.20	-2.88	$-2.44 \pm 0.08^c$
$g_{II} (R_2)$	1.23	1.03	0.43	0.93	$1.48 \pm 0.08^d$
$g_{II} (R_1')$	-0.92	-1.21	0.96	0.49	...
$g_{II} (R_2')$	3.93	4.34	4.35	5.07	...
$g_{II} (R_3')$	3.11	3.93	1.48	2.79	...
$g_{II} (B_1)$	0.96	0.72	0.62	0.12	$0.8 \pm 0.2^d$
$g_{II} (B_2)$	-2.97	-3.17	-3.28	-3.76	$-3.4 \pm 0.4^d$
$g_{II} (B_3)$	1.65	1.48	1.52	1.69	

<sup>a</sup> This is calculated with  $k=1$ .<sup>b</sup> Reference *b* in Table I.<sup>c</sup> Reference 3.<sup>d</sup> Reference *c* in Table I.

interaction, a  $44 \times 44$  secular determinant, in which the excited levels II were neglected, was also solved by using the same values of the parameters as those used for "Calc. I with C.M." The results are given in Tables I, II, and III for the sake of comparison. The experimental values are also listed for comparison, when available.

## DISCUSSION

### A. Location of the Energy Levels

We shall discuss the positions of the  $^2E$ ,  $^2T_1$ , and  $^2T_2$  cubic states (all with the  $t_2^3$  configuration): The positions of the  $^4T_1$  and  $^4T_2$  states are calculated to give the observed positions by adjusting  $Dq$  and  $\epsilon$ , so that they need no further discussion.

In the strong cubic field limit, it is expected that the  $^2E$  and  $^2T_1$  states are nearly degenerate and the energy ratio of the  $^2T_2$  to the  $^2E$  state is  $5/3$ . The degeneracy is removed and the ratio is reduced by the effect of configuration mixing in the real system. However, since the  $B$  value, which determines the magnitude of the configuration mixing, is confined to a limited range in order to give the proper energy of the  $^2E$  state ( $\sim 21B$  if  $C/B=4$  is assumed), the obtainable reduction of the ratio and the separation of the  $^2T_1$  state from the  $^2E$  state are rather limited as long as the ratio  $C/B$  remains fixed. As the column of "Calc. I with C.M." in Table I shows, the ratio

can be reduced to 1.60 against the observed 1.45 but it is found impossible to reduce the ratio further without sacrificing the agreement with respect to the position of the  $^2E$  state.

The only possible way to get better agreement in calculating both the positions of the  $^2E$  state and of the  $^2T_2$  state is to assume a smaller value for  $C/B$ . For example, assuming  $C/B=2.9$ , it has been found that we can obtain  $14\,500\text{ cm}^{-1}$  for  $^2E$  and  $22\,500\text{ cm}^{-1}$  for  $^2T_2$ , which gives the ratio 1.55. However, we did not go farther along this line because of two reasons; (1) It does not seem plausible to use the small value of 2.9 for  $C/B$  although we have no definite reason to reject this possibility. (2) It is found that the use of  $C/B=2.9$  makes the zero-field splittings of the  $^2T_2$  state quantitatively worse.

Therefore, it should be noted that all the results quoted in this paper are derived assuming  $C/B=4$ .

### B. Zero-Field Splittings

The zero-field splitting of the ground state happens to be almost zero if we neglect the excited states II. Inclusion of these excited states improves the splitting tremendously as Table II shows. This fact should not be interpreted as being entirely due to the effect of configuration mixing. Instead, it is partly due to the inclusion of the  $^2T_2$  state which connects with the ground state through spin-orbit interaction. However, the improved splitting is still smaller than the observed one, and it is likely that the remaining discrepancy could only be removed by taking into account such other effects as the spin-spin interaction and the anisotropy of the spin-orbit interaction.<sup>1</sup>

The zero-field splitting of the  $^2E$  state is slightly decreased by inclusion of the higher excited states. Therefore, the previously determined value of  $\zeta$ ,  $140\text{ cm}^{-1}$ , is found to be too small.

The configuration mixing most strongly affects the zero-field splitting of the  $^2T_2$  state. Especially, the relative position of the  $B_3$  component to those of the  $B_1$  and  $B_2$  components is inverted by inclusion of the

TABLE IV. The  $|g_1|$  values of the  $t_2^3$  states.

Energy levels	Calc. I with C.M.	Obs
$g_1 (^4A_2)$	1.9890	$1.9867 \pm 0.0006^a$
$g_1 (R_1)$	0.004	$< 0.06^b$
$g_1 (R_2)$	0.04	
$g_1 (R_1')$	1.35	...
$g_1 (R_2')$	0.89	...
$g_1 (R_3')$	2.36	...
$g_1 (B_1)$	0.01	...
$g_1 (B_2)$	0.13	...
$g_1 (B_3)$	2.10	...

<sup>a</sup> Reference *b* in Table I.<sup>b</sup> Reference 3.

configuration mixing. The energy separation between the  $B_3$  and  $B_2$  components is found to be  $\sim 300 \text{ cm}^{-1}$ , which indicates that a little broad line found by Deutschbein<sup>12</sup> at  $21357 \text{ cm}^{-1}$  may be ascribed to the transition to the  $B_3$  component. Thus, the puzzle, that one component of the  $a^2T_2$  state cannot be identified in the previous calculation, seems to be removed.<sup>13</sup> The  $B_3$  component shifts further toward the shorter wavelength side if we assume a smaller value of  $C/B$  such as 2.9. The calculated splitting of the  $B_1$  and  $B_2$  components, which was too small in the previous calculation, is now too large compared with the experimental value. This discrepancy cannot be removed by any reasonable choice of parameter values and seems to indicate some failure of our approximation.

The calculated zero-field splittings of the  $U$  and  $Y$  bands are shown in Fig. 1. Although the observed widths of these bands are broad, compared with the spin-orbit splittings of each trigonal component, the  $U$  band shows a fairly sharp vibrational structure called a precursor.<sup>14</sup> One vibrational structure, which is located at the long wavelength end of the precursor, has a spectral width of  $\sim 40 \text{ cm}^{-1}$ , and the next structure separated from the first one by  $\sim 200 \text{ cm}^{-1}$  has the width  $\sim 60 \text{ cm}^{-1}$ .<sup>11</sup> The spectral width of the first one is much smaller than the expected over-all spin-orbit splittings,  $\sim 80 \text{ cm}^{-1}$ , of the  ${}^4\mathcal{E}({}^4T_2)$  trigonal component: all split components are expected to have equal intensities. This fact provides us an interesting problem, namely, why are spin-orbit splittings not observable when associated with vibrational structures. Roughly speaking, this could be due to strong vibronic coupling in degenerate states compared with the spin-orbit

coupling, but a rigorous answer should be submitted after more detailed consideration.

### C. $g$ Values

The  $g$  values of the ground state turn out to be in fair agreement with the experimental values as Tables III and IV show.

The deviation of the absolute  $g$  values of the  $a^2E$  components from the free spin value is sensitive to both the relative position of the  $a^2T_1$  and  $a^2E$  states and to the orbital angular momentum reduction factor  $k$ . The former is essentially determined by the effect of configuration mixing. We have found that the "Calc. I with C.M.," in which a small  $k$  value such as 0.62 is used, furnishes the best  $g$  values among those given by many trials.

The  $g$  values of the  $a^2T_2$  components depend upon the amount of configuration mixing and the  $k$  value, but are more sensitive to the latter. Considering large experimental errors due to the width of the spectral lines, we may think that the "Calc. I with C.M." gives rough agreement with the observed values.

### D. Concluding Survey

Assuming suitable values of the parameters in our calculation scheme, we have calculated out the whole energy spectrum of ruby in the visible region both for the field free case and for external magnetic fields parallel and perpendicular to the trigonal axis. The calculated spectrum for example, that of "Calc. I with C.M.," may be considered to be in fair agreement with observation.

It has been shown that a mixture of the higher excited states II into the excited states I lying in the visible spectral region is essential in giving the correct relative position of the  $B_3$  component of the  $a^2T_2$  state to the  $B_1$  and  $B_2$  components.<sup>13</sup> Furthermore, it has also been found that both the configuration mixing and covalency of the  $t_2$  electron introduced through  $k$  play very important roles in giving  $g$  values of the excited states. Inclusion of excited states II improves the zero-field splitting of the ground state, which has been found to be almost zero in the approximation neglecting excited states II.

The fact that the value of  $k$  ( $k=0.62$ ) is close to the value previously found in "Calc. A" (Table II), seems accidental, because the  $g$  values of the  $a^2T_2$  states are expected to depend upon the effect of the configuration mixing. The large deviation of  $k$  and  $k'$  from unity is an indication that both the  $t_2$  and  $e$  orbitals show remarkable covalency. On the other hand, the small value of  $\epsilon$  ( $\epsilon=0.19$ ), according to the original idea of Koide and Pryce,<sup>8</sup> means that the amplitude of the  $e$  orbital is diminished by a factor of only 0.9 compared to the amplitude of  $t_2$ .

These facts seem to tell us that there is not so much difference as usually expected between the degrees of

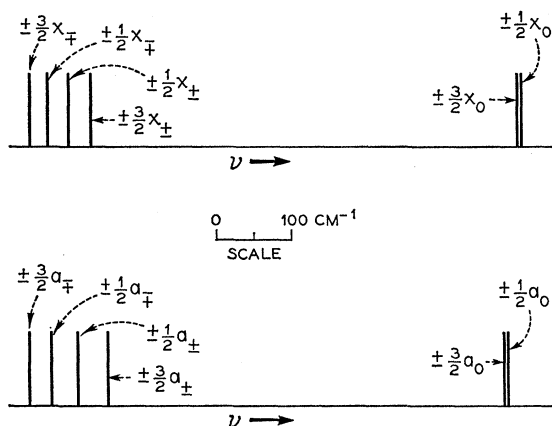


FIG. 1. The schematic diagram of the splittings of the  ${}^4T_1$  and  ${}^4T_2$  states in "Calc. I with C.M."

<sup>12</sup> E. O. Deutschbein, Ann. Physik 14, 729 (1932).

<sup>13</sup> Recently, W. Low [J. Chem. Phys. 33, 1162 (1960)] has also arrived at the same conclusion, but his discussion is based on the calculation involving no trigonal field.

<sup>14</sup> B. N. Grechushnikov and P. P. Feofilov, J. Exptl. Theoret. Phys. (USSR) 29, 384 (1955) [translation: Soviet Phys.-JETP 2, 330 (1956)].

covalency for the  $t_2$  and  $e$  electrons though they are fairly large for both electrons.

It should, however, be borne in mind that the energy ratio of the  ${}^2T_2$  to the  ${}^2E$  state and the zero-field splitting between the  $B_1$  and  $B_2$  components of the  ${}^2T_2$  state are not in satisfactory agreement with the experimental data: For example, if we assume  $C/B = 2.9$  in order to improve the energy ratio as mentioned previously, the above-mentioned conclusion concerning the covalency should be changed. Therefore, it is desirable to look for origins of these discrepancies, which would probably be beyond the scope of our approximation.

The finding of no spin-orbit splitting associated with vibrational structures of the absorption band necessitates detailed studies of the dynamical Jahn-Teller effect involving spin-orbit interaction.

#### ACKNOWLEDGMENTS

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#### APPENDIX I

Double-barred matrices of the trigonal field ( $\alpha ST \| V(T_2) \| \alpha' ST'$ ) within the  $t_2^3$  and  $t_2^2e$  configurations. Unlisted matrices are vanishing, throughout Appendixes I and II.

$\alpha ST$	$\alpha' ST'$	The values
$t_2^3 {}^4A_2$	$t_2^3 ({}^3T_1)e {}^4T_1$	$-2\sqrt{3}K'$
$t_2^3 {}^2E$	$t_2^3 {}^2T_2$	$-6K$
$t_2^3 {}^2E$	$t_2^3 ({}^3T_1)e {}^2T_1$	$-2\sqrt{3}K'$
$t_2^3 {}^2E$	$t_2^3 ({}^1T_2)e {}^2T_2$	$-2\sqrt{3}K'$
$t_2^3 {}^2T_1$	$t_2^3 {}^2T_2$	$3\sqrt{2}K$
$t_2^3 {}^2T_1$	$t_2^3 ({}^1E)e {}^2E$	$-\sqrt{6}K'$
$t_2^3 {}^2T_1$	$t_2^3 ({}^3T_1)e {}^2T_1$	$(3/\sqrt{2})K'$
$t_2^3 {}^2T_1$	$t_2^3 ({}^1T_2)e {}^2T_1$	$-(3/\sqrt{2})K'$
$t_2^3 {}^2T_1$	$t_2^3 ({}^3T_1)e {}^2T_2$	$(3\sqrt{3}/\sqrt{2})K'$
$t_2^3 {}^2T_1$	$t_2^3 ({}^1T_2)e {}^2T_2$	$(\sqrt{3}/\sqrt{2})K'$
$t_2^3 {}^2T_1$	$t_2^3 ({}^1E)e {}^2A_2$	$-\sqrt{6}K'$
$t_2^3 {}^2T_2$	$t_2^3 ({}^1A_1)e {}^2E$	$-2\sqrt{2}K'$
$t_2^3 {}^2T_2$	$t_2^3 ({}^1E)e {}^2E$	$-\sqrt{2}K'$
$t_2^3 {}^2T_2$	$t_2^3 ({}^3T_1)e {}^2T_1$	$(3/\sqrt{2})K'$
$t_2^3 {}^2T_2$	$t_2^3 ({}^1T_2)e {}^2T_1$	$-(3/\sqrt{2})K'$
$t_2^3 {}^2T_2$	$t_2^3 ({}^3T_1)e {}^2T_2$	$-(3\sqrt{3}/\sqrt{2})K'$
$t_2^3 {}^2T_2$	$t_2^3 ({}^1T_2)e {}^2T_2$	$-(\sqrt{3}/\sqrt{2})K'$
$t_2^3 {}^2T_2$	$t_2^3 ({}^1E)e {}^2A_1$	$\sqrt{2}K'$
$t_2^3 ({}^3T_1)e {}^4T_2$	$t_2^3 ({}^3T_1)e {}^4T_2$	$-(3/\sqrt{2})K$

$\alpha ST$	$\alpha' ST'$	The values
$t_2^3 ({}^3T_1)e {}^4T_2$	$t_2^3 ({}^3T_1)e {}^4T_1$	$(3\sqrt{3}/\sqrt{2})K$
$t_2^3 ({}^3T_1)e {}^4T_1$	$t_2^3 ({}^3T_1)e {}^4T_1$	$-(3/\sqrt{2})K$
$t_2^3 ({}^1A_1)e {}^2E$	$t_2^3 ({}^1T_2)e {}^2T_1$	$-2\sqrt{6}K$
$t_2^3 ({}^1A_1)e {}^2E$	$t_2^3 ({}^1T_2)e {}^2T_2$	$-2\sqrt{6}K$
$t_2^3 ({}^1E)e {}^2E$	$t_2^3 ({}^1T_2)e {}^2T_1$	$\sqrt{6}K$
$t_2^3 ({}^1E)e {}^2E$	$t_2^3 ({}^1T_2)e {}^2T_2$	$-\sqrt{6}K$
$t_2^3 ({}^3T_1)e {}^2T_1$	$t_2^3 ({}^3T_1)e {}^2T_1$	$-(3/\sqrt{2})K$
$t_2^3 ({}^3T_1)e {}^2T_1$	$t_2^3 ({}^3T_1)e {}^2T_2$	$(3\sqrt{3}/\sqrt{2})K$
$t_2^3 ({}^1T_2)e {}^2T_1$	$t_2^3 ({}^1T_2)e {}^2T_1$	$(3/\sqrt{2})K$
$t_2^3 ({}^1T_2)e {}^2T_1$	$t_2^3 ({}^1T_2)e {}^2T_2$	$-(3\sqrt{3}/\sqrt{2})K$
$t_2^3 ({}^1T_2)e {}^2T_1$	$t_2^3 ({}^1E)e {}^2A_2$	$-\sqrt{6}K$
$t_2^3 ({}^3T_1)e {}^2T_2$	$t_2^3 ({}^3T_1)e {}^2T_2$	$(3/\sqrt{2})K$
$t_2^3 ({}^3T_1)e {}^2T_2$	$t_2^3 ({}^1E)e {}^2A_1$	$\sqrt{6}K$

#### APPENDIX II

Double-barred matrices of the orbital angular momentum ( $gST \| L \| \alpha' ST'$ ) within the  $t_2^3$  and  $t_2^2e$  configurations.

$\alpha ST$	$\alpha' ST'$	The values
$t_2^3 {}^4A_2$	$t_2^3 ({}^3T_1)e {}^4T_2$	$-2\sqrt{3}ik'$
$t_2^3 {}^2E$	$t_2^3 {}^2T_1$	$2\sqrt{3}ik$
$t_2^3 {}^2E$	$t_2^3 ({}^1T_2)e {}^2T_1$	$-2\sqrt{3}ik'$
$t_2^3 {}^2E$	$t_2^3 ({}^3T_1)e {}^2T_2$	$-2\sqrt{3}ik'$
$t_2^3 {}^2T_1$	$t_2^3 {}^2T_1$	$\sqrt{6}ik$
$t_2^3 {}^2T_1$	$t_2^3 ({}^1E)e {}^2E$	$\sqrt{6}ik'$
$t_2^3 {}^2T_1$	$t_2^3 ({}^3T_1)e {}^2T_1$	$(3\sqrt{3}/\sqrt{2})ik'$
$t_2^3 {}^2T_1$	$t_2^3 ({}^1T_2)e {}^2T_1$	$(\sqrt{3}/\sqrt{2})ik'$
$t_2^3 {}^2T_1$	$t_2^3 ({}^3T_1)e {}^2T_2$	$(3/\sqrt{2})ik'$
$t_2^3 {}^2T_1$	$t_2^3 ({}^1T_2)e {}^2T_2$	$-(3/\sqrt{2})ik'$
$t_2^3 {}^2T_1$	$t_2^3 ({}^1E)e {}^2A_1$	$\sqrt{6}ik'$
$t_2^3 {}^2T_2$	$t_2^3 {}^2T_2$	$\sqrt{6}ik$
$t_2^3 {}^2T_2$	$t_2^3 ({}^1A_1)e {}^2E$	$-2\sqrt{2}ik'$
$t_2^3 {}^2T_2$	$t_2^3 ({}^1E)e {}^2E$	$\sqrt{2}ik'$
$t_2^3 {}^2T_2$	$t_2^3 ({}^3T_1)e {}^2T_1$	$-(3\sqrt{3}/\sqrt{2})ik'$
$t_2^3 {}^2T_2$	$t_2^3 ({}^1T_2)e {}^2T_1$	$-(\sqrt{3}/\sqrt{2})ik'$
$t_2^3 {}^2T_2$	$t_2^3 ({}^3T_1)e {}^2T_2$	$-(3/\sqrt{2})ik'$
$t_2^3 {}^2T_2$	$t_2^3 ({}^1T_2)e {}^2T_2$	$(3/\sqrt{2})ik'$
$t_2^3 {}^2T_2$	$t_2^3 ({}^1E)e {}^2A_2$	$-\sqrt{2}ik'$
$t_2^3 ({}^3T_1)e {}^4T_2$	$t_2^3 ({}^3T_1)e {}^4T_2$	$-(\sqrt{3}/\sqrt{2})ik$
$t_2^3 ({}^3T_1)e {}^4T_2$	$t_2^3 ({}^3T_1)e {}^4T_1$	$(3/\sqrt{2})ik$
$t_2^3 ({}^3T_1)e {}^4T_1$	$t_2^3 ({}^3T_1)e {}^4T_1$	$(\sqrt{3}/\sqrt{2})ik$
$t_2^3 ({}^1E)e {}^2E$	$t_2^3 ({}^1T_2)e {}^2T_1$	$-\sqrt{6}ik$
$t_2^3 ({}^1E)e {}^2E$	$t_2^3 ({}^1T_2)e {}^2T_2$	$\sqrt{6}ik$
$t_2^3 ({}^3T_1)e {}^2T_1$	$t_2^3 ({}^3T_1)e {}^2T_1$	$(\sqrt{3}/\sqrt{2})ik$
$t_2^3 ({}^3T_1)e {}^2T_1$	$t_2^3 ({}^3T_1)e {}^2T_2$	$(3/\sqrt{2})ik$
$t_2^3 ({}^1T_2)e {}^2T_1$	$t_2^3 ({}^1T_2)e {}^2T_1$	$-(\sqrt{3}/\sqrt{2})ik$
$t_2^3 ({}^1T_2)e {}^2T_1$	$t_2^3 ({}^1T_2)e {}^2T_2$	$-(3/\sqrt{2})ik$
$t_2^3 ({}^1T_2)e {}^2T_1$	$t_2^3 ({}^1E)e {}^2A_1$	$-\sqrt{6}ik$
$t_2^3 ({}^3T_1)e {}^2T_2$	$t_2^3 ({}^3T_1)e {}^2T_2$	$-(\sqrt{3}/\sqrt{2})ik$
$t_2^3 ({}^1T_2)e {}^2T_2$	$t_2^3 ({}^1T_2)e {}^2T_2$	$(\sqrt{3}/\sqrt{2})ik$
$t_2^3 ({}^1T_2)e {}^2T_2$	$t_2^3 ({}^1E)e {}^2A_2$	$\sqrt{6}ik$