

# Pressure-induced shifts of energy levels of $\alpha$ -Al<sub>2</sub>O<sub>3</sub>:V<sup>3+</sup> and a complete ligand-field calculation

Ma Dong-ping

*Department of Physics, Chengdu University of Science and Technology, Chengdu 610065, People's Republic of China\**  
*and International Centre for Materials Physics, Academia Sinica, Shenyang 110015, People's Republic of China*

Ma Xiao-dong, Chen Ju-rong, and Liu Yan-yun

*Department of Physics, Chengdu University of Science and Technology, Chengdu 610065, People's Republic of China*  
 (Received 29 August 1996; revised manuscript received 4 April 1997)

An improvement of ligand-field theory has been developed. Based on our theory of pressure-induced shifts and the diagonalization of the complete energy matrix, the unified calculation of the whole energy spectrum and  $g$  factors of the ground state at normal pressure and their pressure-induced shifts has been carried out. All the calculated results for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>:V<sup>3+</sup> are in very good agreement with a great number of experimental data. It is found that the distinct differences in magnitude and/or sign for pressure-induced shifts of various levels are immediately determined by characteristic dependencies of levels on the parameters of interactions, and the pressure-induced shifts of levels can provide definite or crucial criteria for the correctness of assignments and calculations of them. [S0163-1829(97)00528-6]

## I. INTRODUCTION

As is well known, the ligand-field theory has been successful in explaining the optical and magnetic properties of transition-metal or rare-earth ions in crystals. However, the traditional theory only fit the experimental data of optical spectra, while it calculated the electron paramagnetic resonance (EPR) spectra by using the spin Hamiltonian (or effective Hamiltonian), isolating the information available from the optical measurement of excited states and introducing further parameters. Moreover, because the amount of experimental data of optical spectra is limited and their linewidths are usually large for transition-metal ions in crystals, the values of parameters and the results obtained by fitting these experimental data have rather large uncertainties. Hence, it is quite necessary to overcome the above-mentioned shortcomings.

In order to improve the traditional theory, firstly, we need introduce physical quantities that can provide distinct criteria for assignments and calculations of energy spectra or spectral lines, and we apply the theory of pressure-induced shifts (PS) developed by us.<sup>1-5</sup> It will be shown that PS of various levels or spectral lines are distinctly different usually in magnitude and sometimes even in sign. These differences are immediately determined by the characteristic dependencies of levels or spectral lines on parameters of interactions, and PS can provide definite (sometimes even crucial) criteria for the correctness of assignments and calculations of levels or spectral lines. Secondly, the unified calculation of the whole energy spectrum and  $g$  factors of the ground state and their PS will be carried out on the basis of the theory of PS and the diagonalization of the complete energy matrix (DCEM); especially, the wave functions obtained by DCEM will be employed to calculate  $g$  factors. This is because a correct microscopic-theoretical calculation should yield eigenfunctions that can be used to calculate other physical observables with a necessary precision; moreover, as we have shown,<sup>6</sup> it is very important to take into account the effects of excited

states in detail for the precise calculation of the optical spectra and properties of the ground state.

For  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>:V<sup>3+</sup>, especially the properties of its ground state [zero-field splitting (ZFS) and  $g$  factors], much research has been undertaken both theoretically and experimentally.<sup>7-20</sup> Among them, Ref. 9 was the most detailed theoretical work. However, in Ref. 9, the spin-orbit matrix elements were incomplete and there were some mistakes in them; moreover, the effective Hamiltonian appropriate to the  $T_1$  manifold was used to calculate the values of  $g_{\parallel}$  and  $g_{\perp}$ , which was not a good approximation; and some results for ZFS were incorrect.

In order to overcome the above-mentioned shortcomings of traditional theory, therefore, the unified calculation of the whole energy spectrum (including ZFS) and  $g$  factors of the ground state at normal pressure and their PS for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>:V<sup>3+</sup> will be carried out in the present work.

## II. CALCULATION OF THE ENERGY SPECTRUM AND $g$ FACTORS AND THEIR PS

### A. Calculation of the whole energy spectrum

As is well known, the V<sup>3+</sup> ions in vanadium corundum ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>:V<sup>3+</sup>) are surrounded by the trigonally distorted octahedra of six oxygen ions. The site symmetry of the V<sup>3+</sup> ions is  $C_3$ . However, the ligand-field calculation can be analyzed in terms of  $C_{3v}$ .<sup>7-9</sup> We have calculated all the matrix elements of trigonal-field and spin-orbit interactions. In Ref. 9, the spin-orbit matrix elements were incomplete, and we have found that the signs of all the spin-orbit matrix elements for the  $t_2e^3T_2$  strong-field term in Table A.2b of Ref. 9 are opposite to the correct ones. With these matrix elements and those of cubic-field and electrostatic interactions given by Ref. 21, we have constructed and checked the  $45 \times 45$  complete energy matrix of  $d^2$  electronic configuration in the strong-field scheme.

The whole energy spectrum is calculated by means of DCEM to fit the experimental data of the optical and micro-

wave spectra of  $\alpha\text{-Al}_2\text{O}_3:\text{V}^{3+}$  with six adjustable parameters, where  $B$  and  $C$  are Racah parameters,  $10Dq$  is the cubic-field parameter,  $\zeta$  is the spin-orbit coupling parameter,  $v$  and  $v'$  are the trigonal-field parameters. We employ the same observed data as those of Table 4 in Ref. 9, except four values (29 300, 30 150, and 34 500  $\text{cm}^{-1}$  and the ZFS  $D$ ). This is because Macfarlane<sup>7</sup> pointed out that the data about 30 000  $\text{cm}^{-1}$  are doubtful (they are not employed by us), and the new and more accurate experimental datum of  $D$  was given by Refs. 18 and 19 (it is adopted by us).

According to Refs. 7, 9, 18, and 19, among the experimental data, the sharp lines 8770, 9748, and 21025  $\text{cm}^{-1}$ , the ZFS 8.296  $\text{cm}^{-1}$ , and the separation between sharp lines 978  $\text{cm}^{-1}$  (see Table I) are more accurate. So, in the least-squares fit, larger weights should be given to them.

The iterative computations of DCEM are important and necessary. According to the eigenfunctions obtained by DCEM, the assignment of all the levels is carried out.

### B. Calculation of $g$ factors

For  $\alpha\text{-Al}_2\text{O}_3:\text{V}^{3+}$ , the ground strong-field term is  $t_2^2\ ^3T_1$  (see Fig. 1). Taking into account  $V_c$  (cubic field),  $H_e$  (electrostatic interaction), and  $V_{\text{trig}}$  (trigonal field), the  $t_2^2\ ^3T_1$  term is split into  $t_2^2\ ^3T_1\ ^3\hat{E}$  and  $t_2^2\ ^3T_1\ ^3\hat{A}_2$ . Throughout the present paper, the irreducible representations of  $C_{3v}$  are distinguished by the use of carets. It should be emphasized that both the combined action of  $V_{\text{trig}}$  and  $H_{\text{so}}$  (spin-orbit interaction) and the interaction between  $t_2^2\ ^3T_1\ ^3\hat{A}_2$  and excited states are absolutely necessary to give rise to ZFS of  $t_2^2\ ^3T_1\ ^3\hat{A}_2$ . The detailed calculations have shown that due to the interaction with excited states both  $t_2^2\ ^3T_1\ ^3\hat{A}_2\hat{A}_1$  and  $t_2^2\ ^3T_1\ ^3\hat{A}_2\hat{E}$  shift down, and the downshift of  $t_2^2\ ^3T_1\ ^3\hat{A}_2\hat{A}_1$  is larger than that of  $t_2^2\ ^3T_1\ ^3\hat{A}_2\hat{E}$ , which causes ZFS of  $t_2^2\ ^3T_1\ ^3\hat{A}_2$  (see Fig. 1). However, in all the figures given by Refs. 7–9,  $t_2^2\ ^3T_1\ ^3\hat{A}_2\hat{E}$  was higher than  $t_2^2\ ^3T_1\ ^3\hat{A}_2$ , which is wrong.

For clarity, we introduce the detailed notations labeling states  $\alpha^{2S+1}\Gamma^{2S+1}\Gamma'\Gamma_T$ , where  $\alpha$  labels the strong-field configuration,  $(2S+1)$  is the spin degeneracy,  $\Gamma$  is the irreducible representation of the  $O$  group,  $\Gamma'$  and  $\Gamma_T$  are the irreducible representations of  $C_{3v}$ , and  $\Gamma_T$  is the one taking into account the spin-orbit coupling. For example, the ground state is labeled by  $t_2^2\ ^3T_1\ ^3\hat{A}_2\hat{A}_1$  (see Fig. 1 and Table I).

By means of DCEM, we get the eigenfunction of  $t_2^2\ ^3T_1\ ^3\hat{A}_2\hat{A}_1$ ,

$$|t_2^2\ ^3T_1\ 0a_0\rangle' = \sum_{\alpha S \Gamma M_s M} \langle \alpha S \Gamma M_s M | t_2^2\ ^3T_1\ 0a_0 \rangle' \times |\alpha S \Gamma M_s M\rangle, \quad (1)$$

and the eigenfunctions of  $t_2^2\ ^3T_1\ ^3\hat{A}_2\hat{E}$ ,

$$|t_2^2\ ^3T_1\ 1a_0\rangle' = \sum_{\alpha S \Gamma M_s M} \langle \alpha S \Gamma M_s M | t_2^2\ ^3T_1\ 1a_0 \rangle' |\alpha S \Gamma M_s M\rangle \quad (2)$$

and

TABLE I. Energy spectrum of  $\alpha\text{-Al}_2\text{O}_3:\text{V}^{3+}$  at normal pressure.

$\alpha^{2S+1}\Gamma^{2S+1}\Gamma'\Gamma_T$	Energy ( $\text{cm}^{-1}$ )		Splitting ( $\text{cm}^{-1}$ )	
	Calculated <sup>a</sup>	Observed	Calculated <sup>a</sup>	Observed
$t_2^2\ ^3T_1\ ^3\hat{A}_2\hat{A}_1$	0	0		
$\ ^3\hat{A}_2\hat{E}$	8.296	8.296 <sup>b</sup>	8.296	8.296
$\ ^3\hat{E}\hat{E}(a)$	906.26	850 <sup>c</sup>		
$\ ^3\hat{E}\hat{E}(b)$	1020.35	960 <sup>d</sup>	114.09	110
$\ ^3\hat{E}\hat{A}_2$	1112.05			
$\ ^3\hat{E}\hat{A}_1$	1131.10			
$t_2^2\ ^1T_2\ ^1\hat{E}\hat{E}$	9128.79	8770 <sup>e</sup>		
$t_2^2\ ^1E\ ^1\hat{E}\hat{E}$	10 106.8	9748 <sup>f,g</sup>	978.0	978
$t_2^2\ ^1T_2\ ^1\hat{A}_1\hat{A}_1$	10 255.6			
$t_2e\ ^3T_2\ ^3\hat{A}_1\hat{A}_2$	16 956.8			
$\ ^3\hat{A}_1\hat{E}$	16 964.0			
$\ ^3\hat{E}\hat{A}_1$	17 347.4	17420 <sup>d</sup>		
$\ ^3\hat{E}\hat{A}_2$	17 352.4			
$\ ^3\hat{E}\hat{E}(a)$	17 391.9		81.2	90
$\ ^3\hat{E}\hat{E}(b)$	17 428.6	17510 <sup>d</sup>		
$t_2^2\ ^1A_1\ ^1\hat{A}_1\hat{A}_1$	20 649.7	21025 <sup>e</sup>		
$t_2e\ ^3T_1\ ^3\hat{A}_2\hat{A}_1$	25 000.5	24930 <sup>d</sup>		
$\ ^3\hat{A}_2\hat{E}$	25 014.4		322.4	380
$\ ^3\hat{E}\hat{A}_2$	25 322.9	25310 <sup>d</sup>		
$\ ^3\hat{E}\hat{A}_1$	25 347.9			
$\ ^3\hat{E}\hat{E}(a)$	25 393.7			
$\ ^3\hat{E}\hat{E}(b)$	25 439.6			
$t_2e\ ^1T_2\ ^1\hat{A}_1\hat{A}_1$	27 161.9			
$\ ^1\hat{E}\hat{E}$	27 557.7			
$t_2e\ ^1T_1\ ^1\hat{A}_2\hat{A}_2$	29 389.4			
$\ ^1\hat{E}\hat{E}$	29 904.9			
$e^2\ ^3A_2\ ^3\hat{A}_2\hat{A}_1$	35 125.77			
$\ ^3\hat{A}_2\hat{E}$	35 125.86			
$e^2\ ^1E\ ^1\hat{E}\hat{E}$	45 199.9			
$e^2\ ^1A_1\ ^1\hat{A}_1\hat{A}_1$	57 456.7			

<sup>a</sup>Obtained by using the parameter set of Eq. (16).

<sup>b</sup>Reference 18.

<sup>c</sup>Reference 11.

<sup>d</sup>Reference 12.

<sup>e</sup>Reference 8.

<sup>f</sup>Reference 9.

<sup>g</sup>Reference 13.

$$|t_2^2\ ^3T_1 - 1a_0\rangle' = \sum_{\alpha S \Gamma M_s M} \langle \alpha S \Gamma M_s M | t_2^2\ ^3T_1 - 1a_0 \rangle' \times |\alpha S \Gamma M_s M\rangle, \quad (3)$$

where the prime indicates that the mixture of all wave functions has been taken into account; the trigonal bases in Ref. 21 are employed.

Using these eigenfunctions,  $g_{\parallel}$  and  $g_{\perp}$  are calculated by

$$g_{\parallel} = \langle t_2^2\ ^3T_1\ 1a_0 |' (\hat{L}_z + g_s \hat{S}_z) | t_2^2\ ^3T_1\ 1a_0 \rangle' \quad (4)$$

and

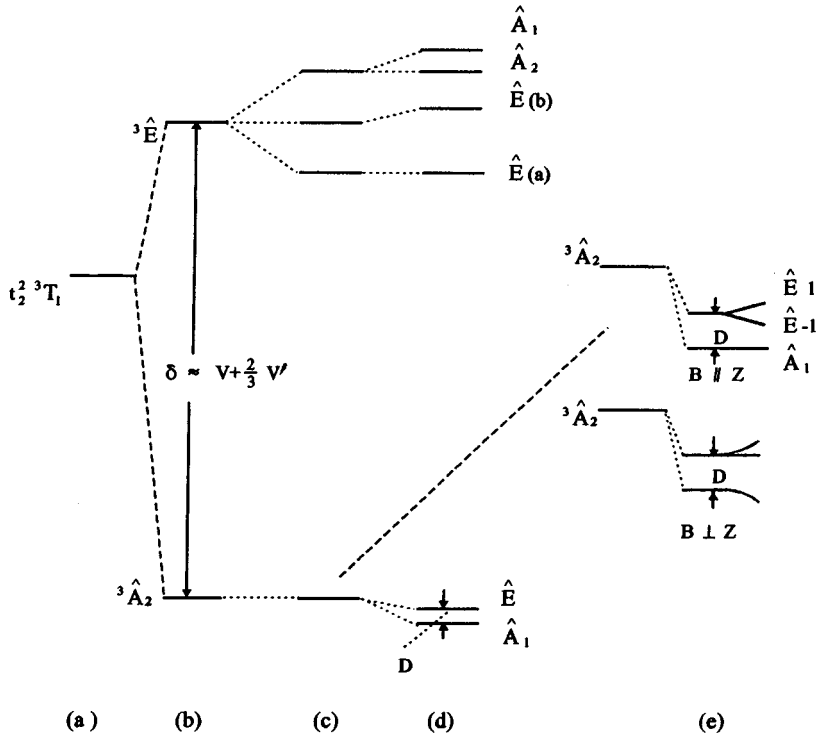


FIG. 1. The splittings and shifts of the  $t_2^2 {}^3T_1$  ground term in (a)  $V_c$  (cubic field) +  $H_e$  (electrostatic interaction), (b)  $V_c + H_e + V_{\text{trig}}$  (trigonal field), (c)  $V_c + H_e + V_{\text{trig}}$  + the first-order effect of spin-orbit interaction  $H_{\text{so}}$ , (d)  $V_c + H_e + V_{\text{trig}} + H_{\text{so}}$  (see text), (e) magnetic-field effect on  ${}^3\hat{A}_2$ .

$$g_{\perp} = \sqrt{2} \langle t_2^2 {}^3T_1 0a_0 |' (\hat{L}_x + g_s \hat{S}_x) | t_2^2 {}^3T_1 1a_0 \rangle' \\ = \langle t_2^2 {}^3T_1 0a_0 |' (\hat{L}_{-1}^{(1)} + g_s \hat{S}_{-1}^{(1)}) | t_2^2 {}^3T_1 1a_0 \rangle', \quad (5)$$

where  $g_s = 2.0023$ .

All the matrix elements relevant to Eqs. (4) and (5) have been calculated, where the orbital-angular-momentum reduction factors  $k$  and  $k'$  are used. With these results and the eigenfunctions obtained by DCEM,  $g_{\parallel}$  and  $g_{\perp}$  can readily be calculated by using a computer.

### C. Calculation of PS for the energy spectrum and $g$ factors

The physical essentials of PS of the ligand-field energy spectrum can be microscopically attributed to the expansion of the radial electron wave functions when the interionic distance is reduced under compression. The computational method of PS has been described previously,<sup>1-5</sup> and a great number of spectral PS have been successfully calculated and explained.

The expansion function  $\Phi(\chi)$  has been introduced to represent the expansion behavior of the electron wave functions, where  $\chi = (V/V_0)^{1/3} = R/R_0$ ,  $V_0$  and  $R_0$  are the crystal volume and the interionic distance at normal pressure, and  $V$  and  $R$  are the corresponding quantities under compression. We have derived that<sup>5</sup>

$$\Phi(\chi) = \chi^s \exp[-\frac{1}{2}D_1(1-\chi)^2 - \frac{1}{3}D_2(1-\chi)^3 - \dots]. \quad (6)$$

On the basis of the expansion of the electron wave functions, we have microscopically derived the expressions for the parameters  $B$ ,  $C$ ,  $Dq$ ,  $v$ ,  $v'$ , and  $\zeta$  as functions of  $\chi$  as<sup>1-5</sup>

$$B/B_0 = C/C_0 = \Phi(\chi), \quad (7)$$

$$Dq/Dq_0 = \chi^{-5} \Phi^{-4}(\chi) q_{\text{eff}} / (q_{\text{eff}})_0, \quad (8)$$

$$v = [\frac{3}{7} \langle A(r) \rangle_0 \chi^{-3} \Phi^{-2}(\chi) \\ + \frac{20}{63} \langle B(r) \rangle_0 \chi^{-5} \Phi^{-4}(\chi)] \frac{q_{\text{eff}}}{(q_{\text{eff}})_0}, \quad (9)$$

$$v' = \sqrt{2} [-\frac{1}{7} \langle A(r) \rangle_0 \chi^{-3} \Phi^{-2}(\chi) \\ + \frac{5}{63} \langle B(r) \rangle_0 \chi^{-5} \Phi^{-4}(\chi)] \frac{q_{\text{eff}}}{(q_{\text{eff}})_0}, \quad (10)$$

$$\langle A(r) \rangle_0 = -2\sqrt{2}v'_0 + v_0, \quad (11)$$

$$\langle B(r) \rangle_0 = \frac{27}{10}\sqrt{2}v'_0 + \frac{9}{5}v_0, \quad (12)$$

$$\zeta/\zeta_0 = \Phi^4(\chi), \quad (13)$$

$$q_{\text{eff}} / (q_{\text{eff}})_0 = \exp\{-t[\Phi^{-1}(\chi) - 1] - u[\Phi^{-1}(\chi) - 1]^2 \\ - \dots\}, \quad (14)$$

where  $q_{\text{eff}}$  is the effective charge of a ligand ion under compression; we use a subscript 0 to indicate the quantities at normal pressure, and the quantities without the subscript 0 are those under compression;  $S$ ,  $D_1$ ,  $D_2$ ,  $t$ , and  $u$  are the parameters for PS, and they depend on the crystal properties.

The  $P$ - $\chi$  dependence of  $\alpha\text{-Al}_2\text{O}_3:\text{V}^{3+}$  is calculated from the three-parameter Birch equation

$$P = \frac{3K_0}{2} \chi^{-5} \sum_{i=1}^3 b_i (\chi^{-2} - 1)^i, \quad (15)$$

where  $K_0 = 2504.1$  kbar,  $b_1 = 1.0000$ ,  $b_2 = 0$ , and  $b_3 = -0.4020$ .<sup>1,5</sup> The  $P$ - $\chi$  dependence is shown in Table IV.

TABLE II. The contributions to levels or separations between levels from various parameters (in unit  $\text{cm}^{-1}$ ).

	$\Delta E/\Delta (10Dq)$ [ $\times(10Dq)$ ]	$\Delta E/\Delta B$ ( $\times B$ )	$\Delta E/\Delta C$ ( $\times C$ )	$\Delta E/\Delta \zeta$ ( $\times \zeta$ )	$\Delta E/\Delta v$ ( $\times v$ )	$\Delta E/\Delta v'$ ( $\times v'$ )	The sum
$D$	0.018759	0.52269	-0.24004	14.13819	-5.47140	-0.66972	8.298
$[t_2^2 {}^3T_1 {}^3\hat{A}_2 - t_2^2 {}^3T_1 {}^3\hat{E}(a)]$	-21.68	24.76	-1.33	209.02	-0.99	-3.98	205.80
$[t_2^2 {}^3T_1 {}^3\hat{E}(b) - t_2^2 {}^3T_1 {}^3\hat{A}_2\hat{E}]$	-70.83	70.92	-0.14	45.84	847.67	118.61	1012.07
$(t_2^2 {}^1E^1\hat{E}\hat{E} - t_2^2 {}^1T_2^1\hat{E}\hat{E})$	-95.00	151.83	1.20	2.86	861.78	55.33	978.00
$t_2^2 {}^3T_1 {}^3\hat{E}\hat{E}(a)$	-57.86	57.35	0.50	-67.08	852.34	122.02	906.27
$t_2^2 {}^1E^1\hat{E}\hat{E}$	-304.95	4424.15	5000.00	40.37	850.92	96.35	10 106.8
$t_2 e^3 T_2 {}^3\hat{A}_1\hat{E}$	17 376.76	-813.80	1.43	42.68	273.95	82.96	16 964.0
$t_2^2 {}^1A_1 {}^1\hat{A}_1\hat{A}_1$	1933.41	8677.67	9255.15	33.96	678.04	71.33	20 649.6
$t_2 e^3 T_1 {}^3\hat{E}\hat{A}_2$	17 008.61	7524.73	-0.34	-14.41	761.63	42.64	25 322.9
$t_2 e^1 T_2 {}^1\hat{A}_1\hat{A}_1$	17 123.06	4659.56	4985.74	53.58	290.50	49.50	27 161.9
$e^2 {}^3A_2 {}^3\hat{A}_2\hat{A}_1$	35 215.23	-809.22	1.21	57.62	563.26	96.94	35 125.0

With the values of the parameters  $B_0$ ,  $C_0$ ,  $Dq_0$ ,  $v_0$ ,  $v'_0$ , and  $\zeta_0$  at normal pressure, the  $P$ - $\chi$  dependence and the theoretical formulas for  $\Phi(\chi)$ ,  $B$ ,  $C$ ,  $Dq$ ,  $v$ ,  $v'$ , and  $\zeta$ , by means of a least-squares fit to the experimental data of spectral PS for  $\alpha\text{-Al}_2\text{O}_3:\text{V}^{3+}$  (Ref. 22) using DCEM, the values of the parameters for PS can be determined. We found that it is sufficient to keep the first term of the series in Eq. (6) and the first term of the series in Eq. (14); i.e., we need only three parameters,  $S$ ,  $D_1$ , and  $t$ . Using these results, the values of  $B$ ,  $C$ ,  $Dq$ ,  $v$ ,  $v'$ , and  $\zeta$  at various pressures can be calculated. Then, at each pressure, the PS of the whole energy spectrum (including ZFS  $D$ ) for  $\alpha\text{-Al}_2\text{O}_3:\text{V}^{3+}$  can be theoretically evaluated uniformly and simultaneously by DCEM. Furthermore, by using the eigenfunctions obtained by DCEM at various pressures, the values of  $g_{\parallel}$  and  $g_{\perp}$  at each pressure can readily be evaluated.

### III. UNIFIED CALCULATIONS AND RESULTS

The main feature of the present work is the unified calculation of the whole energy spectrum (including ZFS  $D$ ) and  $g$  factors of the ground state at normal pressure and their PS on the basis of above-mentioned theory of PS and DCEM. For this purpose, on the basis of the calculation of the whole energy spectrum of  $\alpha\text{-Al}_2\text{O}_3:\text{V}^{3+}$  at normal pressure, we calculate the PS of the whole energy spectrum and compare the results of PS for optical spectra with corresponding experimental data to judge the correctness of the assignment of optical spectra and the accuracy of the calculation. Furthermore, we carry out the unified least-squares fit to both the experimental data of the optical and microwave spectra at normal pressure<sup>8,9,11-13,18</sup> and those of PS for the optical spectra,<sup>22</sup> i.e., the overall standard deviation (in which we give them different weights according to different accuracies of various experimental data) is minimized. In this way, we have finally determined the values of the parameters at normal pressure and the parameters for PS as follows:

$$10Dq_0 = 17854.0 \text{ cm}^{-1}, \quad B_0 = 618.2 \text{ cm}^{-1},$$

$$C_0 = 2502.0 \text{ cm}^{-1},$$

$$v_0 = 879.8 \text{ cm}^{-1}, \quad v'_0 = 188.5 \text{ cm}^{-1}, \quad \zeta_0 = 164.0 \text{ cm}^{-1},$$

$$S = 0.500, \quad D_1 = -20.0 \quad t = 5.80. \quad (16)$$

Using these values, all the levels of  $\alpha\text{-Al}_2\text{O}_3:\text{V}^{3+}$  at normal pressure and their PS have been evaluated and shown in Tables I, III, and IV, respectively.

Furthermore, by using the eigenfunctions of  $t_2^2 {}^3T_1 {}^3\hat{A}_2\hat{A}_1$  and  $t_2^2 {}^3T_1 {}^3\hat{A}_2\hat{E}$  obtained by DCEM at normal pressure, the values of  $g_{\parallel}$  and  $g_{\perp}$  have been evaluated and shown in Table V, where  $k = k' = 0.96$  have been taken in order to simplify and reduce the number of parameters.

From Tables I, III, IV, and V it can be seen that the calculated results are in very good agreement with all the observed data and much better than the previous work:<sup>6-9</sup> the calculated results of optical spectra are obviously better than those of the previous work<sup>6-9</sup> (for example, if the values 29 300, 30 150, and 34 500  $\text{cm}^{-1}$  cited by Ref. 9 are included,  $\sigma' = \sqrt{\sum_{i=1}^{13} (E_i^{\text{calc}} - E_i^{\text{obs}})^2 / 13} = 260 \text{ cm}^{-1}$  for the present work and  $\sigma' = 357 \text{ cm}^{-1}$  for Ref. 9); especially, the calculated results of  $g_{\parallel}$ ,  $g_{\perp}$ ,  $D$ , and the separation of sharp lines (i.e.,  $t_2^2 {}^1E^1\hat{E}\hat{E} - t_2^2 {}^1T_2^1\hat{E}\hat{E} = 978 \text{ cm}^{-1}$ ) are in excellent agreement with the observed data; furthermore, the present work has simultaneously calculated the PS of the whole energy spectrum, which are in excellent agreement with the extensive experimental data of PS for optical spectra. All of this indicates that the theory and method of the present work are very successful.

By DCEM, with small changes in parameters at normal pressure about the parameter set of Eq. (16), the rates of change of levels with respect to various parameters have been calculated. From these the contributions to typical levels or separations between levels from various parameters and their sum have been approximately evaluated by

$$E(x_1, x_2, \dots, x_6) \cong \sum_{i=1}^6 \frac{\Delta E}{\Delta x_i} x_i, \quad (17)$$

where  $x_1, x_2, \dots, x_6$  represent  $10Dq_0$ ,  $B_0$ ,  $C_0$ ,  $\zeta_0$ ,  $v_0$ , and  $v'_0$ , respectively. The results are shown in Table II. The comparison between the energies in Table I and the sums of the contributions in Table II indicates that the approximation is very good.

TABLE III. Pressure-induced shifts of the whole energy spectrum of  $\alpha\text{-Al}_2\text{O}_3\text{:V}^{3+}$ .

Level	Shift ( $\text{cm}^{-1}$ )					Average rate of shift ( $\text{cm}^{-1}/\text{kbar}$ )
	10.00 kbar	20.00 kbar	30.00 kbar	40.00 kbar	50.00 kbar	
$t_2^2\ ^3T_1\ ^3\hat{A}_2\hat{A}_1$	0.000	0.000	0.000	0.000	0.000	0.000
$\ ^3\hat{A}_2\hat{E}$	-0.067	-0.131	-0.192	-0.250	-0.307	-0.006
$\ ^3\hat{E}\hat{E}(a)$	4.784	9.562	14.342	19.114	23.888	0.478
$\ ^3\hat{E}\hat{E}(b)$	4.303	8.625	12.974	17.340	21.728	0.432
$\ ^3\hat{E}\hat{A}_2$	4.066	8.168	12.311	16.483	20.692	0.410
$\ ^3\hat{E}\hat{A}_1$	3.856	7.757	11.707	15.694	19.726	0.390
$t_2^2\ ^1T_2\ ^1\hat{E}\hat{E}$	-6.792	-13.168	-19.156	-24.764	-30.017	-0.639
$t_2^2\ ^1E\ ^1\hat{E}\hat{E}$	-3.136	-5.825	-8.092	-9.952	-11.427	-0.270
$t_2^2\ ^1T_2\ ^1\hat{A}_1\hat{A}_1$	-1.476	-2.527	-3.174	-3.433	-3.324	-0.106
$t_2e^3T_2\ ^3\hat{A}_1\hat{A}_2$	97.503	194.999	292.660	390.277	488.030	9.755
$\ ^3\hat{A}_1\hat{E}$	97.396	194.792	292.356	389.880	487.545	9.744
$\ ^3\hat{E}\hat{A}_1$	99.105	198.217	297.507	396.764	496.170	9.916
$\ ^3\hat{E}\hat{A}_2$	99.108	198.222	297.514	396.772	496.179	9.916
$\ ^3\hat{E}\hat{E}(a)$	99.026	198.065	297.289	396.487	495.839	9.909
$\ ^3\hat{E}\hat{E}(b)$	99.003	198.024	297.234	396.422	495.769	9.907
$t_2^2\ ^1A_1\ ^1\hat{A}_1\hat{A}_1$	2.548	5.776	9.658	14.154	19.243	0.321
$t_2e^3T_1\ ^3\hat{A}_2\hat{A}_1$	90.500	181.375	272.764	364.459	456.612	9.091
$\ ^3\hat{A}_2\hat{E}$	90.409	181.195	272.498	364.107	456.177	9.082
$\ ^3\hat{E}\hat{A}_2$	91.813	184.032	276.798	369.898	463.486	9.225
$\ ^3\hat{E}\hat{A}_1$	91.489	183.395	275.861	368.670	461.978	9.194
$\ ^3\hat{E}\hat{E}(a)$	91.433	183.288	275.706	368.473	461.743	9.189
$\ ^3\hat{E}\hat{E}(b)$	91.291	183.012	275.304	367.952	461.108	9.176
$t_2e^1T_2\ ^1\hat{A}_1\hat{A}_1$	88.971	178.434	268.525	359.030	450.094	8.949
$\ ^1\hat{E}\hat{E}$	90.683	181.853	273.647	365.847	458.604	9.120
$t_2e^1T_1\ ^1\hat{A}_2\hat{A}_2$	89.431	179.415	270.083	361.218	452.964	9.001
$\ ^1\hat{E}\hat{E}$	91.941	184.454	277.676	371.382	465.722	9.254
$e^2\ ^3A_2\ ^3\hat{A}_2\hat{A}_1$	196.154	392.328	588.863	785.339	982.117	19.627
$\ ^3\hat{A}_2\hat{E}$	196.150	392.321	588.853	785.327	982.101	19.627
$e^2\ ^1E\ ^1\hat{E}\hat{E}$	188.932	378.348	568.554	759.125	950.391	18.950
$e^2\ ^1A_1\ ^1\hat{A}_1\hat{A}_1$	167.492	336.259	506.538	677.913	850.648	16.882

The results of Table II have clearly and quantitatively shown the physical origins (i.e., the dependencies on the parameters of interactions) of various levels or separations between levels on the basis of DCEM. For example, the contribution to ZFS  $D$  from  $\zeta$  is the largest one, the contribution

from  $\nu$  is second, the contributions from  $\nu'$  and  $B$  are third and fourth, and those from  $\nu$ ,  $\nu'$ , and  $C$  are negative. The contribution to  $t_2e^3T_1\ ^3\hat{E}\hat{A}_2$  from  $10Dq$  is the largest one, the contribution from  $B$  is second, and the contribution from  $\nu$  is third.

TABLE IV.  $P$ - $\chi$  dependence and pressure-induced shifts of  $t_2e^3T_2\ ^3\hat{A}_1\hat{E}$  and  $t_2e^3T_1\ ^3\hat{E}\hat{A}_2$  of  $\alpha\text{-Al}_2\text{O}_3\text{:V}^{3+}$ .

$P$ (kbar)	$\chi$	Shift ( $10^2\ \text{cm}^{-1}$ )			
		$t_2e^3T_2\ ^3\hat{A}_1\hat{E}$		$t_2e^3T_1\ ^3\hat{E}\hat{A}_2$	
		Calc.	Obs. <sup>a</sup>	Calc.	Obs. <sup>a</sup>
10.00	0.998680	0.97	0.96	0.92	0.92
20.00	0.997383	1.95	1.96	1.84	1.87
30.00	0.996106	2.92	2.88	2.77	2.83
40.00	0.994851	3.90	3.87	3.70	3.77
50.00	0.993615	4.88	4.81	4.63	4.68

<sup>a</sup>Reference 22.

TABLE V. Magnetic resonance and infrared spectroscopy results of  $\alpha\text{-Al}_2\text{O}_3:\text{V}^{3+}$ .

	$g_{\parallel}$	$g_{\perp}$	$D$ ( $\text{cm}^{-1}$ )
Observed	$1.915 \pm 0.002^{\text{a}}$		
	$1.92 \pm 0.03^{\text{b}}$	$1.74 \pm 0.01^{\text{b,c,d}}$	$8.296 \pm 0.016^{\text{e}}$
Calculated	$1.922^{\text{f}}$	$1.735^{\text{f}}$	$8.296^{\text{f}}$
	$1.926^{\text{g}}$	$1.749^{\text{g}}$	$8.295^{\text{g}}$
	$1.944^{\text{h}}$	$1.626^{\text{h}}$	$8.16^{\text{h}}$

<sup>a</sup>Reference 17.

<sup>b</sup>Reference 14.

<sup>c</sup>Reference 15.

<sup>d</sup>Reference 16.

<sup>e</sup>Reference 18.

<sup>f</sup>The present work.

<sup>g</sup>Reference 6.

<sup>h</sup>Reference 9.

Furthermore, a very important fact is that the characteristic dependencies of levels on the parameters immediately determine the PS of levels. From Eqs. (7)–(14) it can be seen that  $B$ ,  $C$ , and  $\zeta$  give rise to red PS [i.e., the energies of levels decrease, noticing  $\Phi(\chi) < 1$ ], while  $Dq$  gives rise to blue PS [because the effect of  $\chi^{-5}\Phi^{-4}(\chi)$  is dominant] and  $v$  and  $v'$  are similar to  $Dq$ . According to Tables II and III, PS of some typical examples can be analyzed as follows. For separations between levels,  $D$  and  $[t_2^2 {}^3T_1 {}^3\hat{E}\hat{A}_2 - t_2^2 {}^3T_1 {}^3\hat{E}\hat{E}(a)]$  depend mainly on  $\zeta$ , so their PS are redshifts. Because  $[t_2^2 {}^3T_1 {}^3\hat{E}\hat{E}(b) - t_2^2 {}^3T_1 {}^3\hat{A}_2\hat{E}]$  and  $(t_2^2 {}^1E^1\hat{E}\hat{E} - t_2^2 {}^1T_2 {}^1\hat{E}\hat{E})$  depend mainly on  $v$  and  $v'$ , their PS are blueshifts. For levels,  $t_2^2 {}^3T_1 {}^3\hat{E}\hat{E}(a)$  depends mainly on  $v$  and  $v'$ , so its PS is a blueshift. The PS of  $t_2^2 {}^1E^1\hat{E}\hat{E}$  is a redshift because it depends primarily on  $B$  and  $C$ . The  $t_2e^3T_2 {}^3\hat{A}_1\hat{E}$  depends mainly on  $10Dq$ , hence its PS is a large blueshift. Although  $t_2^2 {}^1A_1 {}^1\hat{A}_1\hat{A}_1$  depends mainly on  $B$  and  $C$ , it also depends considerably on  $10Dq$  and  $v$ , and the effects of  $10Dq$  and  $v$  on its PS are larger than those of  $B$  and  $C$  [compare Eq. (7) with Eqs. (8) and (9)], so its PS is a small blueshift. Both  $t_2e^3T_1 {}^3\hat{E}\hat{A}_2$  and  $t_2e^1T_2 {}^1\hat{A}_1\hat{A}_1$  depend mainly on  $10Dq$ ; the former also depends considerably on  $B$ , while the latter also depends considerably on  $B$  and  $C$ . Consequently, they have large blue PS. The contribution to  $e^2 {}^3A_2 {}^3\hat{A}_2\hat{A}_1$  from  $10Dq$  is extraordinarily large, therefore, its blue PS is very large.

From the above-mentioned arguments we have obtained the very important conclusion that the distinct differences in magnitude and/or sign for PS of various levels (or spectral lines) are immediately determined by their characteristic dependencies on the parameters of interactions, and PS of levels (or spectral lines) can provide definite criteria for the correctness of assignments and calculations of them. Sometimes, PS of levels (for example,  $t_2^2 {}^1T_2 {}^1\hat{E}\hat{E}$ ,  $t_2^2 {}^1T_2 {}^1\hat{A}_1\hat{A}_1$ , and  $t_2^2 {}^1A_1 {}^1\hat{A}_1\hat{A}_1$ ) can provide crucial criteria.

#### IV. DISCUSSION AND CONCLUSIONS

The unified calculation of the whole energy spectrum (including ZFS  $D$ ) and  $g$  factors of the ground state at normal pressure and their PS has been carried out on the basis of our theory of PS and DCEM. Firstly, because PS of levels provide distinct or crucial criteria for the correctness of assignments and calculations of levels, it is highly important to include PS in the unified calculation. Secondly, for the precise calculation of the optical spectra and properties of the ground state, it is quite necessary to take into account all the effects of excited states by means of DCEM. Hence, the use of DCEM is very important. Thirdly, a correct microscopic-theoretical calculation should yield eigenfunctions that can be used to calculate other physical observables with a necessary precision.<sup>23</sup> Thus, it is also very important to apply the wave functions obtained by DCEM to calculate  $g$  factors.

The overall calculated results are in very good agreement with a great amount of experimental data. Especially, the calculated results of  $g_{\parallel}$ ,  $g_{\perp}$ ,  $D$ ,  $(t_2^2 {}^1E^1\hat{E}\hat{E} - t_2^2 {}^1T_2 {}^1\hat{E}\hat{E})$ , and PS are in excellent agreement with all the experimental data. All these have clearly demonstrated that the theory, method, and results of the present work are very successful and in very good agreement with the physical reality, and this is an important development.

By using the same approach, we have also carried out similar calculations for several crystals, and obtained very good results. The detailed reports for these calculations will be given later.

The work was supported by the National Natural Science Foundation of China, Grant. No. 19744001.

\*Corresponding address.

<sup>1</sup>Ma Dong-ping, Liu Yan-yun, Wang De-chao, and Chen Ju-rong, *J. Phys., Condens. Matter.* **7**, 4883 (1995).

<sup>2</sup>Ma Dong-ping, Wang Zhao-qing, Chen Ju-rong, and Zhang Zheng-gang, *J. Phys. C* **21**, 3585 (1988).

<sup>3</sup>Ma Dong-ping, Zheng Xi-te, Xu Yi-sun, and Zhang Zheng-gang, *Commun. Theor. Phys.* **9**, 291 (1988).

<sup>4</sup>Ma Dong-ping, Zheng Xi-te, Zhang Zheng-gang, and Xu Yi-sun, *Phys. Lett. A* **121**, 97 (1987).

<sup>5</sup>Ma Dong-ping, Zheng Xi-te, Xu Yi-sun, and Zhang Zheng-gang, *Phys. Lett. A* **115**, 245 (1986).

<sup>6</sup>Ma Dong-ping, Xu Yi-sun, and Hu Zhi-xiong, *Acta Phys. Sin.* **31**, 904 (1982).

<sup>7</sup>R. M. Macfarlane, *J. Chem. Phys.* **40**, 373 (1964).

<sup>8</sup>M. H. L. Pryce and W. A. Runciman, *Discuss. Faraday Soc.* **26**, 34 (1958).

<sup>9</sup>H. U. Rahman and W. A. Runciman, *J. Phys. C* **4**, 1576 (1971).

<sup>10</sup>A. Abragam, and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Oxford University Press, London, 1970).

<sup>11</sup>S. Foner and W. Low, *Phys. Rev.* **120**, 1585 (1960).

<sup>12</sup>D. S. McClure, *J. Chem. Phys.* **36**, 2757 (1962); W. C. Scott and M. D. Sturge, *Phys. Rev.* **146**, 262 (1966).

- <sup>13</sup>G. D. Jones and W. A. Runciman, *Proc. Phys. Soc. London* **76**, 996 (1960).
- <sup>14</sup>R. R. Joyce and P. L. Richards, *Phys. Rev.* **179**, 375 (1969).
- <sup>15</sup>A. R. Smith and R. W. Mires, *Phys. Rev.* **172**, 265 (1968).
- <sup>16</sup>L. J. Chailis and D. L. Williams, *J. Phys. C* **10**, L621 (1977).
- <sup>17</sup>G. M. Zverev and A. M. Prokhorov, *Zh. Eksp. Teor. Fiz.* **38**, 449 (1960) [*Sov. Phys. JETP* **11**, 330 (1960)].
- <sup>18</sup>J. Pontnau and R. Adde, *J. Phys. Chem. Solids* **36**, 1023 (1975).
- <sup>19</sup>M. Abou-Ghantous, C. A. Bates, and L. C. Goodfellow, *J. Phys. Chem. Solids* **37**, 1059 (1976).
- <sup>20</sup>F. I. Hasan, P. J. King, D. T. Murphy, and V. W. Rampton, *J. Phys. C* **12**, L513 (1979).
- <sup>21</sup>S. Sugano, Y. Tanabe, and H. Kamimura, *Multiplets of Transition-Metal Ions in Crystals* (Academic, New York, 1970).
- <sup>22</sup>S. Minomura and H. G. Drickamer, *J. Chem. Phys.* **35**, 903 (1961).
- <sup>23</sup>B. G. Wybourne, *Spectroscopic Properties of Rare Earths* (John Wiley & Sons, New York, 1965), p. 40.