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Zero-field splitting of $^4T_2$ term for $3d^3$ ions in tetragonal symmetry

QUN WEI[1,2,*] and QI-MING XU[1]
[1]College of Material Science and Engineering, Xi'an University of Architecture and Technology, Xi'an 710055, China
[2]Department of Physics, Baoji University of Arts and Science, Baoji 721007, Shaanxi, China
[*]Corresponding author. E-mail: weiaqun@163.com

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Abstract. By taking into account slight interactions, i.e. spin-spin, spin-other-orbit and orbit-orbit interactions, in addition to spin-orbit interaction, the zero-field splitting of $^4T_2$ state for $3d^3$ ions at tetragonal symmetry has been studied. The convergence of the approximation perturbation formula of $^4T_2$ state for $3d^3$ ions at tetragonal symmetry has been investigated, and the contributions to zero-field splitting arising from magnetic interaction and tetragonal crystal field are discussed. It is found that there exists combined mechanism between magnetic interactions and tetragonal crystal field.

Keywords. Zero-field splitting; $^4T_2$ term; tetragonal crystal field; $3d^3$ ions.

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1. Introduction

It is known that the microscopic spin Hamiltonian (MSH) theory enables correlations of the optical spectroscopy and structural data with the spin Hamiltonian (SH) parameters extracted from the electron paramagnetic resonance (EPR) spectra. There are two major approaches to the microscopic derivation of the SH parameters, i.e. the complete diagonalization method (CDM) and the perturbation method (PTM). Both CDM and PTM have been extensively used to investigate the SH parameters of transition metal (TM) and rare earth (RE) ions. In the past decades, using these two approaches, the properties of zero-field splitting (ZFS) of ground state and first excited state of TM ions and RE ions at various symmetry crystal fields (CF) have been studied by many researchers [1–8]. Recently, by taking into account slight magnetic interactions, i.e. spin-spin (SS) interaction, spin-other-orbit (SOO) interaction, orbit-orbit (OO) interaction [9–12], in addition to spin-orbit (SO) interaction, Yang *et al* [13–17] studied the contribution to the ZFS of ground state and first excited state from slight magnetic interactions, and the contributions to zero-field splitting of low-lying states arising from slight magnetic interaction and trigonal crystal field are investigated in ref. [18]. To the best of our knowledge, the contributions to the ZFS of $^4T_2$ state for 3d^3 ions at tetragonal symmetry have not been studied. For the first time, the contributions to the ZFS of $^4T_2$ state are studied in this paper, and the convergence of the approximation perturbation formula of $^4T_2$ state for 3d^3 ions at tetragonal symmetry has been discussed.

2. Theory

Recently, an extended CDM/MSH program has been developed [13] for numerical calculations of the energy levels and eigenvectors as well as the SH parameters D, $g_\parallel$, $g_\perp$ and Δg of the ground state for 3d^3 configurations at trigonal type I (C_{3v}, D_3, D_{3d}) on the basis of the original CDM/MSH program [8,19,20]. Now, we developed the program further, and the program has been extended to include tetragonal type I (C_{4v}, D_{2d}, D_4, D_{4h}) for 3d^3 ions. The original Hamiltonian includes the Coulomb interaction H_{ee}, the SO coupling interaction H_{SO}, and the crystal field Hamiltonian H_{CF}. In the extended CDM/MSH program three additional terms, i.e. the H_{SOO}, H_{SS}, and H_{OO} terms have been included in the Hamiltonian. Thus, the Hamiltonian for a 3d^3 configuration, in the intermediate CF coupling scheme can be taken as [13]

$$H = H_{\text{ee}}(B, C) + H_{\text{CF}}(B_{kq}) + H_{\text{M}}(\zeta_d, M_0, M_2), \tag{1}$$

where H_{ee} represents electrostatic interactions, H_{M} represents magnetic interactions, and can be written as [13]

$$\begin{aligned} H_{\text{M}}(\zeta_d, M_0, M_2) = {} & H_{\text{SO}}(\zeta_d) + H_{\text{SS}}(M_0, M_2) \\ & + H_{\text{SOO}}(M_0, M_2) + H_{\text{OO}}(M_0, M_2), \end{aligned} \tag{2}$$

where ζ_d is the SO interaction parameter, and M_0 and M_2 are the Marvin's radial integrals [10,21] used for representing the SS, SOO, and OO interactions. H_{CF} represents the CF interactions, and may be given for tetragonal symmetry I (C_{4v}, D_{2d}, D_4, D_{4h}) in the Wybourne notation as [22]

$$H_{\text{CF}} = B_{20}C_0^{(2)} + B_{40}C_0^{(4)} + B_{44}C_4^{(4)} + B_{4-4}C_{-4}^{(4)}, \tag{3}$$

where the CF parameters B_{kq} measure the strength of interaction between the open-shell electrons of paramagnetic ions and their surrounding crystalline environment [22,23] and hence play an important role in the CF studies, and can be expressed as [24]

$$B_{20} = \delta - \mu, \tag{4}$$

$$B_{40} = 21Dq - \frac{3}{5}(3\mu + 4\delta), \tag{5}$$

$$B_{44} = 21\sqrt{\frac{5}{14}}Dq, \tag{6}$$

where Dq is the cubic CF parameter and the parameters μ and δ measure the net tetragonal CF components which vanish identically in cubic symmetry. It should be pointed out that, for tetragonal symmetry, the CF parameter $B_{44} = B_{4-4}$. The method of calculations of the matrix elements of H_{ee}, H_{SO}, and H_{CF} has been described in ref. [19], and those for H_{SS}, H_{SOO}, and H_{OO} in refs [13] and [25].

The free-ion ^4F ground term of 3d^3 ions splits in octahedral symmetry into $^4A_2$, $^4T_2$, and $^4T_1$ terms, where $^4A_2$ is the ground state, and do not split in tetragonal CF, but its irreducible representation changed into $^4B_1$. The SS and SOO effects of zero-field splitting of ground state $^4B_1$ have been studied systematically in ref. [17]. The 12-fold-degenerated $^4T_2$ term is split by tetragonal CF and magnetic interactions into six two-fold-degenerated terms, two of them are $^4B_2$ terms, four of them are ^4E terms. We define the splitting $\Delta(^4T_2)$ as the difference between the average of $^4B_2$ terms and the average of ^4E terms, i.e.

$$\Delta(^4T_2) = \varepsilon[^4B_2(T_2)] - \varepsilon[^4E(T_2)]. \tag{7}$$

In ref. [26], Fairbank and Klauminzer obtained the perturbation loops of $^4T_2$ state of Cr^{3+} ions in MgO crystal, which are in tetragonal symmetry. One can obtain the perturbation expression from the perturbation loops as

$$\begin{aligned}\Delta(^4T_2) = {} & \delta + \frac{3}{4}\mu + \frac{3}{16}\frac{\mu^2}{(D_4 - D_1)} - \frac{3}{32}\frac{\mu^3}{(D_4 - D_1)^2} \\ & - \frac{3\mu^4 + 16\mu^2\delta^2 - 8\mu^3\delta}{512(D_4 - D_1)^3} - \frac{9}{4}\frac{\mu^2\delta B^2}{(D_4 - D_1)^2(D_5 - D_1)^2}\end{aligned} \tag{8}$$

with $D_1 = W(^4T_2) - W(^4A_2) = 10Dq$, $D_4 = W(a^4T_1) - W(^4A_2) = 10Dq + 12B$, and $D_5 = W(b^4T_1) - W(^4A_2) = 20Dq + 3B$ [27,28].

3. Numerical results

To study the properties of ZFS of the $^4T_2$ state, as an example, we calculate the ZFS of MgO:Cr^{3+} crystal taking into account slight magnetic interactions. Spectral parameters used in the calculations are [15,26]: $B = 530$ cm^{-1}, $C = 3410$ cm^{-1}, $Dq = 1645$ cm^{-1}, $\zeta_d = 240$ cm^{-1}, $k = 0.7$, $\mu = -3200$ cm^{-1}, $\delta = 1350$ cm^{-1}, $M_0 = 0.0990$ cm^{-1}, $M_2 = 0.0078$ cm^{-1}. The calculated values, using CDM and PTM respectively, and observed value are listed in table 1. In table 1, CDM$^{(1)}$ represents the calculation result with SO interaction only and CDM$^{(2)}$ the calculation results with SO, SOO, and OO interactions.

To study the validity of PTM, we take the same parameters as above, the variations of $\Delta(^4T_2)$ with the CFPs Dq, μ, and δ, are calculated by CDM and PTM, respectively. In the CDM, we considered SO interaction only. In order to cover wide range of CFP values, the CFPs μ and δ are chosen from -3000 to 3000 cm^{-1}, and that of Dq from 400 to 2000 cm^{-1}, and the calculations were performed in steps of 200 cm^{-1}. The results obtained from CDM and PTM are presented in

Table 1. Zero-field splitting of $^4T_2$ state for Cr^{3+} ions at tetragonal symmetry (in cm^{-1}).

	PTM	CDM$^{(1)}$	CDM$^{(2)}$	Exp. [26]
$\Delta(^4T_2)$	−616.20	−665.23	−663.72	±600

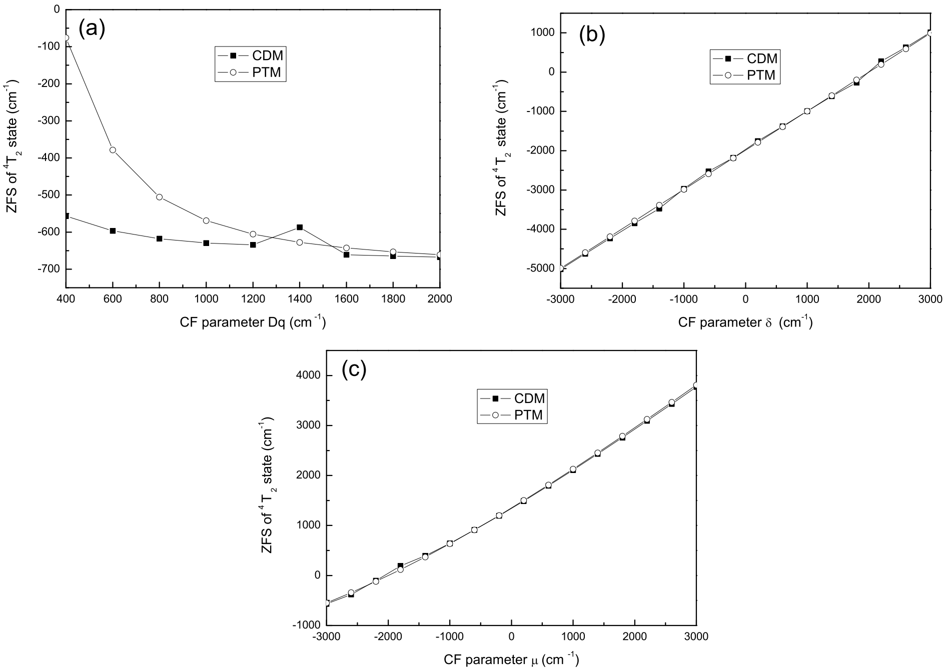

Figure 1. The ZFS for $^4T_2$ state of Cr^{3+} ions ($B = 530$ cm^{-1}, $C = 3410$ cm^{-1}, $\zeta_d = 240$ cm^{-1}, $k = 0.7$, $M_0 = 0.0990$ cm^{-1}, $M_2 = 0.0078$ cm^{-1}) at tetragonal symmetry vs. (**a**) Dq ($\mu = -3200$ cm^{-1}, $\delta = 1350$ cm^{-1}), (**b**) δ ($Dq = 1645$ cm^{-1}, $\mu = -3200$ cm^{-1}), and (**c**) μ ($Dq = 1645$ cm^{-1}, $\delta = 1350$ cm^{-1}).

figure 1. We can see from figure 1 that the calculated results of CDM and PTM vs. μ and δ are in good agreement with each other.

In order to illustrate the relative validity of the PTM, it is convenient to define the percentage ratio:

$$\eta = 100\frac{|D_{\mathrm{SO(CDM)}} - D_{\mathrm{SO(PTM)}}|}{|D_{\mathrm{SO(CDM)}}|}\%. \tag{9}$$

The percentage ratio vs. Dq is presented in figure 2, and the major data points are listed in table 2. From table 2, one can see that the percentage ratio is in the range $2.08 < \eta < 89.29\%$, and η is less than 8.88% when Dq is more than 1200 cm^{-1}. This indicates that the approximation PTM formula (eq. (8)) for $\Delta(^4T_2)$ do not work well in the case of weak crystal field.

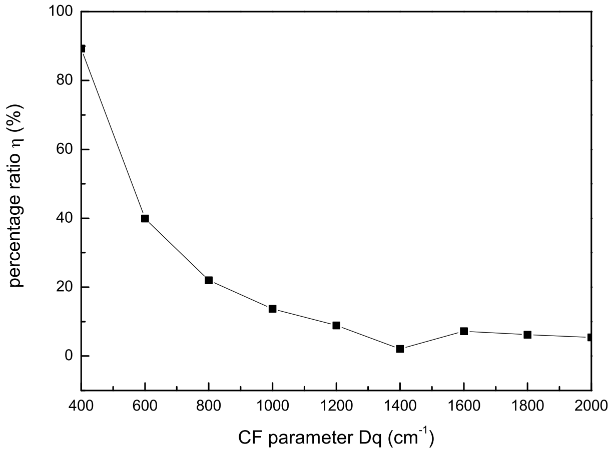

Figure 2. The percentage ratio vs. Dq ($\mu = -3200$ cm^{-1}, $\delta = 1350$ cm^{-1}).

To study the contributions to $\Delta(^4T_2)$ from slight magnetic interactions, including SS, SOO, and OO interactions, the calculated results with various magnetic interactions vs. Dq are listed in table 2. The subscripts represent the magnetic interactions considered in eq. (2) in the symbols Δ_{SO}, $\Delta_{\mathrm{SO+SS}}$, $\Delta_{\mathrm{SO+SOO}}$, $\Delta_{\mathrm{SO+SS+SOO}}$, Δ_{Total}. By comparing these terms, one can see that the contributions from SS, SOO or OO interaction are always slight, and follow the order: $\Delta_{\mathrm{SOO}} > \Delta_{\mathrm{OO}} > \Delta_{\mathrm{SS}}$.

In the approximation perturbation expression (eq. (8)), the energy dominators D_1, D_4, and D_5 are only associated with spin quartets. This means that the expression is obtained by considering spin quartets only. To study the contribution from spin doublets, we calculated the ZFS of $^4T_2$ state with all the magnetic interactions but the spin doublets were omitted, and the results are listed in table 2 as Δ_{quar}. By comparing Δ_{quar} and Δ_{Total}, one can discover that the contribution from quartets are dominant. The contribution from spin doublets are less than 1% except the data point $Dq = 1400$ cm^{-1} which is about 10%. We calculated the ZFS of $^4T_2$ state in two cases: considering magnetic interactions without tetragonal CF, and considering tetragonal CF without magnetic interactions. The results are listed in table 2 as Δ_{Hm} and Δ_{Tetra}, respectively. Comparing these two groups of data, one can deduce that, magnetic interactions and tetragonal CF can yield the splitting respectively, and the contribution to the ZFS is mainly from tetragonal CF. This result also can be derived by the numerical results of perturbation expression (see table V in ref. [26]), and we discover that the sum of Δ_{Tetra} and Δ_{Hm} is not equal to Δ_{Total}. It has been referred in ref. [18] that there exists combined mechanism between magnetic interactions and trigonal CF in the ZFS of low-lying states for 3d^3 ions in trigonal CF. Here we also can draw a conclusion that there exists combined mechanism between magnetic interactions and tetragonal CF in the ZFS of $^4T_2$ state for Cr^{3+} ions in tetragonal CF. But this combined mechanism is slight. This can also be seen from eq. (8), and there are no cross terms between tetragonal CF and magnetic interactions.

Table 2. Zero-field splitting of ${}^4T_2$ state vs. Dq for Cr^{3+} ions at tetragonal symmetry (in cm^{-1}).

Dq	PTM	CDM								η (%)
		Δ_{SO}	$\Delta_{\mathrm{SO+SS}}$	$\Delta_{\mathrm{SO+SOO}}$	$\Delta_{\mathrm{SO+SS+SOO}}$	Δ_{Total}	Δ_{quar}	Δ_{Hm}	Δ_{Tetra}	
400	−59.64	−559.07	−559.16	−556.24	−556.32	−556.95	−557.73	−5.83	−525.09	89.29
600	−358.23	−598.30	−598.36	−595.83	−595.89	−596.54	−597.91	−6.79	−570.24	39.95
800	−481.82	−619.06	−619.11	−616.82	−616.87	−617.53	−619.75	−6.78	−594.85	21.98
1000	−543.23	−630.92	−630.97	−628.85	−628.90	−629.56	−633.41	−5.81	−610.25	13.71
1200	−577.82	−635.34	−635.40	−633.45	−633.51	−634.13	−642.74	−2.20	−620.76	8.88
1400	−599.28	−589.09	−589.20	−587.86	−587.97	−587.06	−649.51	36.51	−628.39	2.08
1600	−613.62	−662.92	−662.91	−660.55	−660.54	−661.21	−654.64	−18.74	−634.17	7.20
1800	−623.78	−666.20	−666.22	−664.11	−664.12	−664.77	−658.67	−14.52	−638.71	6.17
2000	−631.31	−668.86	−668.89	−666.83	−666.86	−667.52	−661.91	−12.37	−642.36	5.42

4. Summary

The ZFS of $^4T_2$ state for 3d^3 ions in tetragonal CF has been investigated using the extended CDM/MSH program and PTM expression. Our investigations show that, the convergence of PTM expression in the case of strong field is preferable. The contributions to ZFS arising from the SS, SOO, and OO interactions have been taken into account in addition to the major ones due to the SO interaction. The ZFS of $^4T_2$ state are interpreted systematically. It is found that there exists combined mechanism between magnetic interactions and tetragonal CF in the ZFS of $^4T_2$ states of 3d^3 ions.

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