

Spin-singlet contributions to zero-field splitting of a  $3d^4$  ion at a distorted octahedral site and applications to  $\text{Cr}^{2+}$  ions in  $\text{Rb}_2\text{CrCl}_4$  and  $\text{CrF}_2$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2006 J. Phys.: Condens. Matter 18 1705

(<http://iopscience.iop.org/0953-8984/18/5/023>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 28/05/2010 at 08:54

Please note that [terms and conditions apply](#).

# Spin-singlet contributions to zero-field splitting of a $3d^4$ ion at a distorted octahedral site and applications to $\text{Cr}^{2+}$ ions in $\text{Rb}_2\text{CrCl}_4$ and $\text{CrF}_2$

Xiao-Ming Tan<sup>1</sup>, Xiao-Yu Kuang<sup>1,2,5</sup>, Kang-Wei Zhou<sup>2,3,4</sup>, Cheng Lu<sup>1</sup> and Qin-Sheng Zhu<sup>1</sup>

<sup>1</sup> Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, People's Republic of China

<sup>2</sup> International Centre for Materials Physics, Academia Sinica, Shenyang 110016, People's Republic of China

<sup>3</sup> Department of Physics, Sichuan University, Chengdu 610065, People's Republic of China

<sup>4</sup> CCAST(World Lab.), PO Box 8730, Beijing 100080, People's Republic of China

E-mail: [scu\\_txm@163.com](mailto:scu_txm@163.com) and [scu\\_kxy@163.com](mailto:scu_kxy@163.com)

Received 18 November 2005

Published 20 January 2006

Online at [stacks.iop.org/JPhysCM/18/1705](http://stacks.iop.org/JPhysCM/18/1705)

## Abstract

The complete energy matrix including all the spin states is constructed for  $d^4$  ions in tetragonal symmetry within a strong-field representation. The excitation levels, fine-structure splitting, and EPR parameters in  $\text{Rb}_2\text{CrCl}_4$  and  $\text{CrF}_2$  are studied with the energy matrix. The contributions of the spin singlets to zero-field splitting (ZFS) are investigated for the first time. The results show that the spin-singlet contribution to  $D$  is negligible, but the contributions to  $a$  and  $F$  cannot be neglected.

## 1. Introduction

Zero-field splitting (ZFS) and absorption spectra for  $d^4$  ions at tetragonal symmetry sites have been studied by many authors [1–12]. However, in the theoretical works [2–4, 8–10], the calculations are not complete because the contributions of the spin singlets are not considered. The reason is probably that it is very difficult to construct the complete energy matrix, that includes the spin singlets, because the Hamiltonian matrix of  $d^4$  ions has a dimension of  $210 \times 210$  if including all the spin states, but only  $160 \times 160$  if not including the spin singlets. To obtain more accurate ZFS, all  $2^{S+1}L$  multiplets with  $S = 2, 1$  and  $0$  should be considered, i.e., a complete calculation. In this paper, we shall construct the complete energy matrix ( $210 \times 210$ ) of  $d^4$  ions in tetragonal symmetry adapted to the double-group chain within a strong-field representation, and deal with the spin-singlet contributions to ZFS parameters. As an example,

<sup>5</sup> Author to whom any correspondence should be addressed.

the spin-singlet contributions to ZFS parameters of  $\text{Rb}_2\text{CrCl}_4$  and  $\text{CrF}_2$  are calculated. The results show that the spin singlets are important to  $a$  and  $F$ . This effect must influence the other related data, e.g., Mössbauer quadrupole splitting, magnetization, magnetic susceptibility, etc.

## 2. Theoretical model

### 2.1. $d^4(\text{O}_h^*)$ basis functions and energy matrix

First, we construct basis functions  $|q_i, S\Gamma\Gamma'\gamma'\rangle$  for each irreducible representation  $\Gamma'$  (i.e.  $A_1, A_2, E, T_1, T_2$ ) of the double group  $\text{O}_h^*(d^4)$  with the Griffith [13] strong-field functions  $|q_i, S\Gamma M\gamma\rangle$  of the point group  $\text{O}_h(d^4)$  according to the expression

$$|q_i, S\Gamma\Gamma'\gamma'\rangle = \sum_{M\gamma} \langle S\Gamma M\gamma | \Gamma'\gamma'\rangle |q_i, S\Gamma M\gamma\rangle \quad (1)$$

where  $\gamma'$  denotes different components of  $\Gamma'$  and  $q_i$  stands for the  $i$  th strong-field configuration  $t_2^n(S_1\Gamma_1)e^m(S_2\Gamma_2)$  in the electrostatic matrix table of Griffith [13] for the  $d^4$  configuration.

The Hamiltonian in a cubic field can be written as

$$H' = V_e(B, C) + V_c^{A_1}(Dq) + H_{S.O.}(\zeta) \quad (2)$$

where  $V_e$  is the electrostatic energy,  $B$  and  $C$  the Racah parameters;  $V_c^{A_1}$  is the cubic component of the crystal field,  $Dq$  the cubic crystal field parameter,  $H_{S.O.}$  is the spin-orbit coupling energy, and  $\zeta$  the spin-orbit coupling parameter. The complete strong-field matrix with respect to the 210 basis functions (equation (1)) will become a block diagonal form of ten  $\Gamma'\gamma'$  blocks. That is, the matrix splits into two onefold degenerate matrices  $A_1(14 \times 14)$  and  $A_2(8 \times 8)$ , one twofold degenerate matrix  $E(19 \times 19)$ , and two threefold degenerate matrices  $T_1(23 \times 23)$  and  $T_2(27 \times 27)$  (see table 1). Each can be looked upon as the sum of the matrices for  $V_e$ ,  $V_c^{A_1}$ , and  $H_{S.O.}$ .

The  $V_e$  component of each  $\Gamma'\gamma'$  matrix is diagonal about  $S$  and  $\Gamma$ , and thus forms a block-diagonal matrix (table 1). Of a given  $S\Gamma$  block, the matrix elements are just the same as the  $S\Gamma$  electrostatic matrix in Table A.30 of Griffith [13].

The matrices of the cubic crystal field  $V_c^{A_1}$  in each  $\Gamma'\gamma'$  block will be fully diagonal in the  $|q_i, S\Gamma\Gamma'\gamma'\rangle$  representation, and the diagonal elements can be obtained as follows:

$$\langle t_2^n e^m, S\Gamma\Gamma'\gamma' | V_c^{A_1} | t_2^n e^m, S\Gamma\Gamma'\gamma'\rangle = (6m - 4n)Dq. \quad (3)$$

The  $H_{S.O.}$  component of a  $\Gamma'\gamma'$  matrix is not diagonal and the elements can be obtained according to the following formula:

$$\begin{aligned} H_{S.O.}^{ij}(\Gamma'r', S_1\Gamma_1, S_2\Gamma_2) &= \langle q_i, S_1\Gamma_1\Gamma'\gamma' | H_{S.O.} | q_j, S_2\Gamma_2\Gamma'\gamma'\rangle \\ &= K' \langle q_i, S_1\Gamma_1 || V^{1T_1} || q_j, S_2\Gamma_2 \rangle \end{aligned} \quad (4)$$

where  $K'$  are the transferred coefficients,  $\langle q_i, S_1\Gamma_1 || V^{1T_1} || q_j, S_2\Gamma_2 \rangle$  are the reduced matrix elements. From equation (4), we can obtain all matrix elements of the spin-orbit interaction.

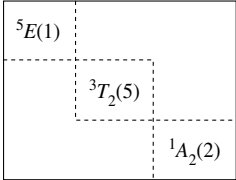
### 2.2. $d^4(D_{4h}^*)$ basis functions and energy matrix

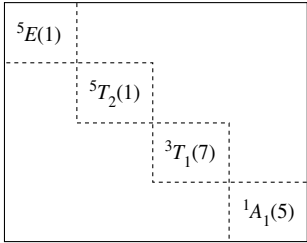
If the octahedral crystal field has a tetragonal distortion, say,  $D_{4h}$ , the Hamiltonian can be written as

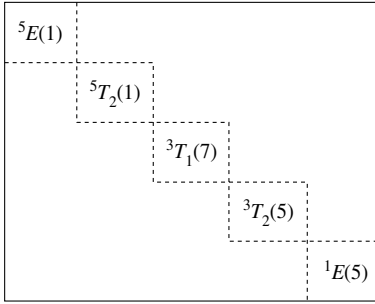
$$H' = V_e(B, C) + V_c^{A_1}(Dq) + H_{S.O.}(\zeta) + V^{E\theta}(\mu, \delta) \quad (5)$$

where  $V^{E\theta}$  is the tetragonal component of the crystal field and  $\mu, \delta$  are the tetragonal distortion parameters. We can construct the  $d^4(D_{4h}^*)$  basis functions for each irreducible representation  $\Gamma''$

**Table 1.** The energy matrices of  $d^4(O_h^*)$ .

$\Gamma' = A_2(8 \times 8)$


$\Gamma' = A_1(14 \times 14)$


$\Gamma' = E(19 \times 19), \gamma' = \theta, \varepsilon$


(i.e.  $A_1, A_2, E, B_1, B_2$ ) of the double group  $D_{4h}^*(d^4)$  with  $d^4(O_h^*)$  basis functions  $|q_i, S\Gamma\Gamma'\gamma'\rangle$  by the formula

$$|q_i, S\Gamma\Gamma' \rightarrow \Gamma''\gamma''\rangle = \sum_{\gamma'} \langle \Gamma'\gamma' | \Gamma''\gamma'' \rangle |q_i, S\Gamma\Gamma'\gamma'\rangle \quad (6)$$

where  $\langle \Gamma'\gamma' | \Gamma''\gamma'' \rangle$  are the coupling coefficients. The matrix of Hamiltonian (5) with respect to the 210  $d^4(D_{4h}^*)$  basis functions (equation (6)) will be a block diagonal form of six  $\Gamma''\gamma''$  blocks (see table 2). In each  $\Gamma''\gamma''$  block, the component of  $V_e + V_c^{A_1} + H_{S.O.}$  is again a block diagonal form of  $\Gamma'\gamma'$  blocks of the  $d^4(O_h^*)$  matrix (see table 2), thus only the  $V^{E\theta}$  component needs to be calculated. In each  $\Gamma''\gamma''$  block, the matrix elements of  $V^{E\theta}$  can be at any position. Finally, each matrix element of the complete energy matrix can be expressed to be a linear combination of  $B, C, \zeta, Dq, \mu,$  and  $\delta$ .

### 2.3. ZFS parameters of a $3d^4(D_{4h}^*)$ ion

For a high spin  $d^4$  ion at a tetragonally distorted octahedral site, the ZFS Hamiltonian [14] is

$$H_{ZFS} = D(S_Z^2 - 2) + \frac{a}{120}(35S_Z^4 - 155S_Z^2 + 72) + \frac{a}{48}(S_+^4 + S_-^4) + \frac{F}{180}(35S_Z^4 - 155S_Z^2 + 72) \quad (7)$$

**Table 1.** (Continued.)

$\Gamma' = T_1(23 \times 23), \gamma' = x, y, z$

${}^5E(1)$								
	${}^5T_2(1)$							
		${}^5T_2(1)$						
			${}^3A_1(1)$					
				${}^3E(3)$				
					${}^3T_1(7)$			
						${}^3T_2(5)$		
							${}^1T_1(4)$	

$\Gamma' = T_2(27 \times 27), \gamma' = \xi, \eta, \zeta$

${}^5E(1)$								
	${}^5T_2(1)$							
		${}^5T_2(1)$						
			${}^3A_2(2)$					
				${}^3E(3)$				
					${}^3T_1(7)$			
						${}^3T_2(5)$		
							${}^1T_2(7)$	

where  $a$ ,  $D$ , and  $F$  are just the so-called zero-field splitting parameters. The corresponding matrix is presented in table 3. Its eigenvalues  $E_i$  can be expressed as follows:

$$\begin{aligned}
 E_1 &= 2D + \frac{3}{5}a + \frac{F}{15} \\
 E_2 &= 2D - \frac{2}{5}a + \frac{F}{15} \\
 E_3 &= -D - \frac{2}{5}a - \frac{4}{15}F \\
 E_4 &= -2D + \frac{3}{5}a + \frac{2}{5}F.
 \end{aligned} \tag{8}$$

Thus we have

$$\begin{aligned}
 a &= E_1 - E_2 \\
 D &= -\frac{1}{7}(E_3 - E_1 - E_2 + E_4) \\
 F &= \frac{3}{7}(3E_4 - 3E_1 - 4E_3 + 4E_2).
 \end{aligned} \tag{9}$$

The values of  $E_i$  can be obtained by a comparison with the eigenvalues of the  $d^4(D_{4h}^*)$  matrix that correspond to the orbitally non-degenerate ground state.

**Table 2.** The energy matrices of  $d^4$  ( $D_{4h}^*$ ).

$\Gamma''\gamma''$	$\Gamma'\gamma'$
$A_2(23\times 23)$	$T_1z(23\times 23)$

$\Gamma''\gamma''$	$\Gamma'\gamma'$
$B_2(27\times 27)$	$T_2\zeta(27\times 27)$

$\Gamma''\gamma''$	$\Gamma'\gamma'$
$B_1(27\times 27)$	$A_2(8\times 8)$
	$E\varepsilon(19\times 19)$

$\Gamma''\gamma''$	$\Gamma'\gamma'$
$A_1(33\times 33)$	$A_1(14\times 14)$
	$E\theta(19\times 19)$

$\Gamma''\gamma''$	$\Gamma'\gamma'$
$E_x(50\times 50)$	$T_1x(23\times 23)$
	$T_2\xi(27\times 27)$

$\Gamma''\gamma''$	$\Gamma'\gamma'$
$E_y(50\times 50)$	$T_1y(23\times 23)$
	$T_2\eta(27\times 27)$

### 3. General study for spin-singlet contributions to ZFS of $3d^4$ ions

For studying of the spin-singlet contribution to the ZFS of a  $3d^4$  ion at a tetragonally distorted octahedral site, the ratios

$$r_a = \left| \frac{a - a'}{a} \right|, \quad r_D = \left| \frac{D - D'}{D} \right|, \quad r_F = \left| \frac{F - F'}{F} \right| \quad (10)$$

versus  $Dq$ ,  $\mu$ , and  $\delta$  are calculated (tables 4–6), where  $a$ ,  $D$ , and  $F$  are the ZFS parameters considering all the spin states, and  $a'$ ,  $D'$ , and  $F'$  those neglecting the spin singlets. In the calculations we adopt  $B = 810 \text{ cm}^{-1}$ ,  $C = 3347.3 \text{ cm}^{-1}$ , and  $\zeta = 227.2 \text{ cm}^{-1}$ . It is obvious that the larger the ratio  $r$ , the larger are the spin-singlet contributions. From tables 4–6, it can be seen that  $r_D$  is absolutely minute. This shows that the spin-singlet contribution to  $D$

**Table 3.** The spin-Hamiltonian matrix.

$S, M_S$	2, 2	2, -2	2, 0	2, 1	2, -1
2, 2	$2D + \frac{a}{10} + \frac{F}{15}$	$\frac{a}{2}$	0	0	0
2, -2	$\frac{a}{2}$	$2D + \frac{a}{10} + \frac{F}{15}$	0	0	0
2, 0	0	0	$-2D + \frac{3}{5}a + \frac{2}{5}F$	0	0
2, 1	0	0	0	$-D - \frac{2}{5}a - \frac{4}{15}F$	0
2, -1	0	0	0	0	$-D - \frac{2}{5}a - \frac{4}{15}F$

**Table 4.** Variation of ratio  $r$  with  $Dq$  (in  $\text{cm}^{-1}$ );  $\mu = 7800 \text{ cm}^{-1}$ ,  $\delta = 2000 \text{ cm}^{-1}$ ,  $B = 810 \text{ cm}^{-1}$ ,  $C = 3347.3 \text{ cm}^{-1}$ , and  $\zeta = 227.2 \text{ cm}^{-1}$  are used.

$Dq$	293	593	843	1243	1643	2043
$r_D$	$1.06 \times 10^{-4}$	$4.59 \times 10^{-4}$	0	$4.97 \times 10^{-4}$	$7.92 \times 10^{-4}$	$1.84 \times 10^{-3}$
$r_a$	0.37	0.36	0.36	0.40	0.43	0.43
$r_F$	0.21	0.28	0.37	0.33	0.37	0.40

**Table 5.** Variation of ratio  $r$  with  $\mu$  (in  $\text{cm}^{-1}$ );  $Dq = 743.3 \text{ cm}^{-1}$ ,  $\delta = 2000 \text{ cm}^{-1}$ ,  $B = 810 \text{ cm}^{-1}$ ,  $C = 3347.3 \text{ cm}^{-1}$ , and  $\zeta = 227.2 \text{ cm}^{-1}$  are used.

$\mu$	2200	4600	7000	8600	11000	13400
$r_D$	$3.86 \times 10^{-4}$	$1.73 \times 10^{-4}$	0	$1.01 \times 10^{-4}$	$5.41 \times 10^{-4}$	$5.74 \times 10^{-4}$
$r_a$	0.23	0.33	0.42	0.40	0.45	0.38
$r_F$	0.19	0.32	0.36	0.33	0.36	0.29

**Table 6.** Variation of ratio  $r$  with  $\delta$  (in  $\text{cm}^{-1}$ );  $Dq = 743.3 \text{ cm}^{-1}$ ,  $\mu = 7800 \text{ cm}^{-1}$ ,  $B = 810 \text{ cm}^{-1}$ ,  $C = 3347.3 \text{ cm}^{-1}$ , and  $\zeta = 227.2 \text{ cm}^{-1}$  are used.

$\delta$	200	1000	2200	3800	4600	5800
$r_D$	0	$5.12 \times 10^{-4}$	$2.92 \times 10^{-4}$	$2.69 \times 10^{-4}$	$3.0 \times 10^{-4}$	$3.98 \times 10^{-4}$
$r_a$	0.36	0.36	0.37	0.36	0.37	0.42
$r_F$	0.24	0.30	0.30	0.28	0.35	0.39

is negligible. From these tables, it can also be seen that  $r_a$  and  $r_F$  are comparatively big. For instance, when  $Dq = 1643 \text{ cm}^{-1}$ ,  $r_a = 0.43$ ,  $r_F = 0.37$  (table 4);  $\mu = 7000 \text{ cm}^{-1}$ ,  $r_a = 0.42$ ,  $r_F = 0.36$  (table 5); and  $\delta = 5800 \text{ cm}^{-1}$ ,  $r_a = 0.42$ ,  $r_F = 0.39$  (table 6). These results show, in fact, that the contributions of the spin singlets to  $a$  and  $F$  are important. We think that the contributions arise from the interaction of the spin quintuplets with both the spin triplets and the spin singlets via the spin-orbit coupling. However, the selection rule of spin-orbit coupling shows that the spin singlets do not affect the quintuplets directly but indirectly via the spin triplets.

#### 4. ZFS calculations for $\text{Cr}^{2+}$ in $\text{Rb}_2\text{CrCl}_4$ and $\text{CrF}_2$

After the above general discussion of the spin-singlet contribution to ZFS parameters, we deal with some specific crystals. In these compounds, the ZFS parameters have been calculated

**Table 7.** The absorption spectra for  $\text{Cr}^{2+}$  in  $\text{Rb}_2\text{CrCl}_4$  and  $\text{CrF}_2$  (in  $\text{cm}^{-1}$ ).

	$\text{Rb}_2\text{CrCl}_4$		$\text{CrF}_2$		
	Our results	Experiment [12]	Our results	Experiment [17]	
$^5\text{B}_1$	0	0	$^5\text{B}_1$	0	0
$^5\text{A}_1$	7 800	7 800	$^5\text{A}_1$	10 394	10 394
$^5\text{B}_2$	9 999.7	10 000	$^5\text{B}_2$	10 495	10 495
$^5\text{E}$	11 999.7	12 000	$^5\text{E}$	14 669	14 699
$^3\text{E}$	15 086.0		$^3\text{A}_2$	17 181	17 030
$^3\text{A}_2$	16 196.9		$^3\text{B}_1$	17 836	18 122
$^3\text{B}_1$	17 945.5		$^3\text{A}_1$	20 197	20 270
$^3\text{A}_2$	19 885.4		$^3\text{A}_2$	20 407	20 310
$^3\text{A}_1$	20 235.7		$^3\text{E}$	21 262	21 690
$^3\text{E}$	20 373.9		$^3\text{B}_1$	22 422	23 300
$^3\text{B}_1$	22 398.6		$^3\text{E}$	24 052	24 310
$^3\text{B}_2$	23 737.9		$^3\text{B}_2$	24 694	24 830
$^3\text{E}$	23 796.3		$^3\text{E}$	26 472	25 480

without considering the spin singlets. In this work, we shall calculate the ZFS parameters for  $\text{Rb}_2\text{CrCl}_4$  and  $\text{CrF}_2$  with all the spin states and discuss the different results.

#### 4.1. $\text{Rb}_2\text{CrCl}_4$

The symmetry of  $\text{Rb}_2\text{CrCl}_4$  approximates to  $\text{D}_{4h}$  and coordination about the  $\text{Cr}^{2+}$  is a tetragonally elongated octahedron [12]. Janke *et al* [12] have investigated its optical absorption spectra and obtained the energy levels. From their data, we obtained  $Dq = 743.3 \text{ cm}^{-1}$ ,  $\mu = 7800 \text{ cm}^{-1}$ , and  $\delta = 2000 \text{ cm}^{-1}$ . As for  $B$ ,  $C$ , and  $\zeta$ , we adopt the average covalency approximation model [15],

$$B = N^4 B_0, \quad C = N^4 C_0, \quad \zeta = N^2 \zeta_0 \quad (11)$$

where  $N$  ( $\leq 1$ ) is the average covalency reduction factor, where  $B_0$  ( $830 \text{ cm}^{-1}$ ),  $C_0$  ( $3430 \text{ cm}^{-1}$ ), and  $\zeta_0$  ( $230 \text{ cm}^{-1}$ ) are the Racah and spin-orbit coupling parameters for a free  $\text{Cr}^{2+}$  ion [13]. To fit the experimental data we take  $B = 810 \text{ cm}^{-1}$  [16], thus we obtained  $C = 3347.3 \text{ cm}^{-1}$  and  $\zeta = 227.2 \text{ cm}^{-1}$  by equation (11). From this, the calculated spectra and the ZFS parameters are both in good agreement with the observed results, as can be seen in table 7 and table 9.

#### 4.2. $\text{CrF}_2$

According to previous work [17],  $\text{Cr}^{2+}$  ions of  $\text{CrF}_2$  sit at an approximate tetragonally distorted octahedral site and its symmetry is  $\text{D}_{4h}$ . In this calculation, the value [18] of  $B = 800 \text{ cm}^{-1}$  is adopted to the  $\text{Cr}^{2+}$  ions. From equation (11), we get  $C = 3306 \text{ cm}^{-1}$ ,  $\zeta = 225.8 \text{ cm}^{-1}$ . Then, using the values  $Dq = 808.1 \text{ cm}^{-1}$ ,  $\mu = 10 394 \text{ cm}^{-1}$ , and  $\delta = 4174 \text{ cm}^{-1}$ , the theoretical energy levels and ZFS parameters of  $\text{CrF}_2$  are obtained, as can be seen in tables 7 and table 10. It should be pointed out that the experimental data of the ZFS parameters for  $\text{CrF}_2$  have not appeared in the literature, so we hope that the experiments for this can be done in the future.

In table 8, we present the fine structure of the ground and the first excited states for  $\text{Cr}^{2+}$  in  $\text{Rb}_2\text{CrCl}_4$  and  $\text{CrF}_2$ . It shows that the contributions from the spin singlets to the fine structure are non-negligible. From tables 9 and 10, it can be seen that the ratio  $r$  is more than 0.30 for  $a$  and 0.20 for  $F$  of  $\text{Cr}^{2+}$  in  $\text{Rb}_2\text{CrCl}_4$  and  $\text{CrF}_2$ , which shows again the important contributions of the spin singlets to  $a$  and  $F$ .



**Table 8.** The fine structure (in  $\text{cm}^{-1}$ ) of the ground and the first excited states of  $\text{Rb}_2\text{CrCl}_4$  and  $\text{CrF}_2$ .

$\text{Rb}_2\text{CrCl}_4$				$\text{CrF}_2$			
Considering singlets		Neglecting singlets		Considering singlets		Neglecting singlets	
0	0	0	$A_1$	0	0	$A_1$	
	0.011	0.007	$A_2$	0.010	0.006	$A_2$	
	6.116	6.112	E	6.001	5.997	E	
	8.154	8.150	$B_1$	8.001	7.997	$B_1$	
7800	7788.065	7788.072	$A_1$	10 379.913	10 379.928	$A_1$	
	7791.839	7791.837	E	10 383.638	10 383.637	E	
				0			
	7803.090	7803.088	$B_2$	10 394.278	10 394.282	$B_2$	
	7803.116	7803.113	$B_1$	10 394.710	10 394.709	$B_1$	
				10 394			

**Table 9.** The ZFS parameters (in  $10^{-3} \text{ cm}^{-1}$ , except ratio, dimensionless) for  $\text{Cr}^{2+}$  in  $\text{Rb}_2\text{CrCl}_4$ .

	Considering singlets	Neglecting singlets	$r$	Experiments	
				Ref. [10]	Ref. [11]
$D$	-2037.0	-2036.4	$2.95 \times 10^{-4}$	-2054	-2040
$a$	-11.0	-7.0	0.364		
$F$	18.0	12.86	0.286		

**Table 10.** The ZFS parameters (in  $10^{-3} \text{ cm}^{-1}$ , except ratio, dimensionless) for  $\text{Cr}^{2+}$  in  $\text{CrF}_2$ .

	Considering singlets	Neglecting singlets	$r$
$D$	-1998	-1998	0
$a$	-9.9	-6.0	0.394
$F$	16.7	11.6	0.305

## 5. Conclusion

The Hamiltonian matrix including all  $2S+1L$  states has been introduced for  $d^4$  ions in tetragonal symmetry. The matrix diagonalization method is used to study the spin-singlet contributions to zero-field splitting parameters of  $\text{Rb}_2\text{CrCl}_4$  and  $\text{CrF}_2$  for the first time. Our calculations show that the contributions of spin singlets to the ZFS parameters  $a$  and  $F$  are so large that neglecting this contribution one cannot obtain more accurate values of  $a$  and  $F$ . Thus many previous works neglecting the spin singlets should be reconsidered to obtain more accurate  $a$  and  $F$  parameters.

## Acknowledgments

This work was supported by National Natural Science Foundation of China (10374068) and the Doctoral Education Fund of the Education Ministry of China (20050610011).

## References

- [1] Bevilacqua G, Martinelli L, Vogel E E and Mualin O 2004 *Phys. Rev. B* **70** 075206
- [2] Jiang C Y, Du M L and Zhou Y Y 1994 *Phys. Rev. B* **50** 949
- [3] Zhou Y Y and Rudowicz C 1996 *J. Phys. Chem. Solids* **57** 1191
- [4] Zhou Y Y and Li F Z 1998 *J. Phys. Chem. Solids* **59** 1105
- [5] Mossin S, Weihe H and Barra A L 2002 *J. Am. Chem. Soc.* **124** 8764
- [6] Zhou M G and Xie L H 2000 *Mater. Sci. Eng. B* **75** 72
- [7] Garces N Y, Giles N C and Halliburton L E 2003 *J. Appl. Phys.* **94** 7567
- [8] Zhou Y Y and Li F Z 1995 *Phys. Rev. B* **51** 14176
- [9] Zhou Y Y and Li C L 1993 *Phys. Rev. B* **48** 16489
- [10] Rudowicz C, Du M L, Yeung Y Y and Zhou Y Y 1993 *Physica B* **191** 323
- [11] Hutchings M T, Als-Nielsen J, Lindgard P A and Walker P J 1981 *J. Phys. C: Solid State Phys.* **14** 5327
- [12] Janke E, Wood T E, Ironside C and Day P 1982 *J. Phys. C: Solid State Phys.* **15** 3809
- [13] Griffith J S 1961 *The Theory of Transition Metal Ions* (Cambridge: Cambridge University Press)
- [14] Kaufmann U 1976 *Phys. Rev. B* **14** 1848
- [15] Curie D, Barthou C and Canny B 1974 *J. Chem. Phys.* **61** 3048
- [16] Morrison C A 1989 Host materials for transition ions *Harry Diamond Lab. Report HDL-DS-89-1*
- [17] Lim P E and Stout J W 1975 *J. Chem. Phys.* **63** 4886
- [18] Konig E and Kremer S 1974 *Z. Naturf.* **29** 31