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Zero-field splitting of a ^{6}S-state ion in tetragonal symmetry

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Abstract. The perturbation procedures suggested in the spin–orbit (SO) coupling mechanism contributing to the ^{6}S-state splitting are examined in detail and found to be all correct for tetragonal symmetry, on the basis of a diagonalization calculation. The Blume–Orbach procedure is most appropriate. The sixth-order perturbation must be taken into account in strong fields for the procedure proposed by Watanabe and developed by Yu and Zhao, and the expression is given here.

Among the various mechanisms which contribute to the zero-field splitting of ^{6}S-state ions, the spin–orbit (SO) coupling mechanism has been found to be most important for many substances and thus has become the subject of many recent papers [1–5]. There are at least three alternative approaches to the perturbation procedure [1]. Among them the well known and extensively used Blume–Orbach procedures [6, 7] (called SO-I hereafter) was recently indicated as not appropriate for rhombic symmetry [3]. The procedure proposed by Watanabe [8] and developed by Yu and Zhao [2] (denoted SO-II hereafter) was also criticized as incorrect [4]. This paper will examine the procedures in detail on the basis of a diagonalization calculation and will show them to be all correct for tetragonal symmetry.

For our purpose, we omit the spin doublets, the contribution of which to the splitting parameter D is of the order two orders of magnitude higher than the lowest value [1, 2, 6–8] and thus must be three or more orders of magnitude less than the total value. We need to consider the Γ_7 representation of D_4', whose matrix is 26×26 dimensional. The $\Gamma_7(D_4')$ symmetry-adapted 'weak-field' basis $|l^N\alpha SLJM_J\rangle$ is found to be

$$|JM_J\rangle \qquad M_J = -\tfrac{3}{2} \pm 4n \tag{1}$$

with $n = 0, 1, 2, \ldots$ and $|M_J| \leqslant J$. The elementary elements for the crystal field V and the spin–orbit interaction H_{so} are given as

$$\langle l^N\alpha SLJM_J|V|l^N\alpha' S'L'J'M_J'\rangle = \sum_{kq} (-1)^{2J-M_J+S+L'} \begin{pmatrix} J & k & J' \\ -M_J & q & M_J' \end{pmatrix} \begin{Bmatrix} J' & k & J \\ L & S & L' \end{Bmatrix}$$
$$\times ((2J+1)(2J'+1))^{1/2} \langle l\|C^{(k)}\|l\rangle \langle l^N\alpha SL\|U^{(k)}\|l^N\alpha' S'L'\rangle B_{kq}\delta_{SS'} \tag{2}$$

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$$\langle l^N \alpha SLJM_J | H_{so} | l^N \alpha' S'L'J'M_J' \rangle = (-1)^{L+S'+J} (l(l+1)(2l+1))^{1/2} \begin{Bmatrix} L & S & J \\ S' & L' & 1 \end{Bmatrix}$$

$$\times \langle l^N \alpha SL \| V^{(11)} \| l^N \alpha' S'L' \rangle \xi \delta_{JJ'} \delta_{M_J M_J'}. \tag{3}$$

Here, the summation in (2) is taken over $k = 2, 4$ and $q = 0, \pm 4$. The values of the reduced matrix elements can be found from [9]. $D(= b_2^0)$ is given as

$$D = \tfrac{1}{4}[W(\tfrac{5}{2}, \tfrac{5}{2}) - W(-\tfrac{3}{2}, -\tfrac{3}{2})]. \tag{4}$$

Table 1 shows D versus D_q, the cubic component of a field. The calculation was made by assuming $B = 911$ and $C = 3273$ for the Racah parameters, $\alpha = 65$ and $\beta = -131$ for the Trees–Racah corrections and $\xi = 337\ \text{cm}^{-1}$ for the SO coupling constant of Mn^{2+} ions. Another reasonable choice for the parameters will not change the conclusion drawn here. All the procedures, including SO-III (developed according to Macfarlane [10]; see [1]) reach values, in the lowest-order perturbation, close to and less than those by diagonalization except for SO-II, which is bad when $D_q > 700\ \text{cm}^{-1}$. The next (sixth) order of this procedure must be taken into account for strong fields, and the expression is calculated following Yu and Zhao [2] to be

$$\begin{aligned} D^{(6)} = {} & (2\xi^2/108045P^2DFG)(15B_{20}B_{40}[(24B_{20} - 25B_{40})(B_{20} + B_{40}) + 350B_{44}^2) \\ & + 14B_{20}B_{44}^2(50B_{40} - 69B_{20})] + (2\xi^2/63^2P^3G^2) \\ & \times (252B_{44}^4 - 25B_{40}^4 - 20B_{40}^2B_{44}^2) - (2B_{20}^2\xi^2/735P^3DG)(2B_{44}^2 + 5B_{40}^2) \\ & + (\xi^2/194481P^2G^2F)[5684B_{44}^4 - 140B_{40}^2B_{44}^2 - 675B_{40}^4 \\ & - 27B_{20}^2(25B_{40}^2 + 42B_{44}^2) + 90B_{20}B_{40}(-15B_{40}^2 + 42B_{44}^2)] \\ & - 9B_{20}^4\xi^2/2450P^3D^2 - (B_{20}^2\xi^2/200075P^2D^2F) \\ & \times [1050B_{44}^2 + (24B_{20} - 25B_{40})^2]. \end{aligned} \tag{5}$$

After it is taken into account, SO-II gives a value less than the accurate value by at most 17% in the range $|D_q| \leqslant 1500\ \text{cm}^{-1}$.

In figure 1 we display the B_{20}-dependence of D. We see that SO-II gives a correct B_{20}-dependence. Neither SO-I nor SO-III gives the correct relation for B_{20} in their lowest order and thus suggests a constant independence. The effect of B_{20} is not negligible if it is large; it contributes to D a value [1, 2, 8]

$$D(B_{20}) = -(3\xi^2/70P^2D)(B_{20}^2 + 21\xi B_{20}). \tag{6}$$

In figure 2, one can see that $D > 0$ for compressed tetrahedral D_{2d} symmetry and that $D < 0$ for elongated symmetry. When $\theta < 53°$, SO-I and SO-III are not so good as SO-II compared with the diagonalization calculation. In particular, when $\theta = 49°$, D(SO-I) or D(SO-III) is only half the total value. This is understandable according to (6). For positive B_{20}, $D(B_{20})$ is large. B_{20} is negative in compression, leading to negligible $D(B_{20})$, and we see that SO-I and SO-III operate well.

A perturbation procedure can work well when the perturbation term is much smaller than the unperturbed Hamiltonian. The SO-I procedure treats the low-symmetric part of a field as a perturbation term and is thus expected to be appropriate for weak distortion. Indeed, it does not work well when the component B_{20} is large, in the lowest-order perturbation, as can be seen in figure 1 and table 2. There could be doubt that the SO-II procedure might be divergent [4] as it treats the cubic field as a perturbation term. Baur

Table 1. D_q-dependence of the axial-field splitting parameter D for Mn^{2+} ions in tetragonal symmetry, calculated by assuming that $B = 911$, $C = 3273$, $\xi = 337$, $\alpha = 65$, $\beta = -131$, $B_{20} = -1000$ and $B'_{40} = 1000$.

D_q (10^{-4} cm^{-1})	D(SO-I) (10^{-4} cm^{-1})	D(SO-II) (10^{-4} cm^{-1})			D(SO-III) (10^{-4} cm^{-1})	D (diagonalization) (10^{-4} cm^{-1})
		$D^{(4)}$	$D^{(6)}$	Total		
400	−69	−55	−3	−58	−66	−83
500	−88	−73	−6	−79	−78	−103
600	−109	−89	−11	−100	−105	−124
700	−131	−106	−17	−123	−126	−147
800	−156	−122	−26	−148	−150	−172
900	−184	−139	−36	−175	−176	−200
1000	−215	−156	−50	−206	−206	−232
1100	−250	−172	−67	−239	−240	−268
1200	−291	−189	−87	−276	−280	−309
1300	−340	−206	−110	−316	−327	−359
1400	−397	−222	−138	−360	−383	−418
1500	−467	−239	−169	−408	−451	−489

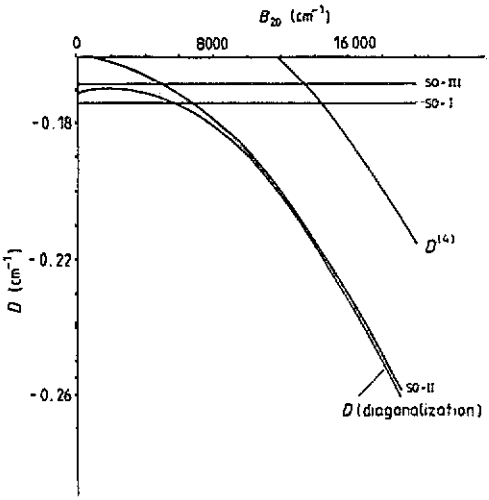

Figure 1. D versus B_{20}, for $B = 911$, $C = 3273$, $\xi = 337$, $\alpha = 65$, $\beta = -131$, $D_q = 1200\ \text{cm}^{-1}$ and $B'_{40} = 6000\ \text{cm}^{-1}$.

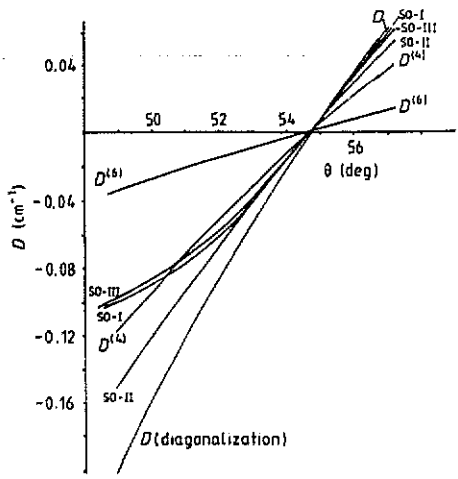

Figure 2. θ-dependence of D in D_{2d} symmetry, evaluated by using $B = 911$, $C = 3273$, $\alpha = 65$, $\beta = -131$, $D_q = 850\ \text{cm}^{-1}$, $\xi = 337$, $\bar{A}_4 = -(27/16)D_q$ and $\bar{A}_2 = 10\bar{A}_4$.

Table 2. Zero-field splitting parameter D for Fe^{3+} ions in garnets.

	$D\ (10^{-4}\ \text{cm}^{-1})$			
Procedure	$Y_3Al_5O_{12}$[a]	$Lu_3Al_5O_{12}$[a]	$Y_3Ga_5O_{12}$[b]	$Lu_3Ga_5O_{12}$[b]
SO-I	−1232	−1302	−735	−812
SO-II[c]	−1643	−1765	−1032	−1175
SO-III	−1289	−1363	−709	−783
Diagonalization	−1493	−1617	−846	−969
Experiments [1]	−1028	−1249	−880	−1131

[a] Calculated by taking $B = 554$, $C = 3412$ and $D_q = -1036\ \text{cm}^{-1}$ [12].
[b] Calculated by taking $B = 744$, $C = 2560$ and $D_q = -655\ \text{cm}^{-1}$ [13].
[c] The sixth order was taken into account.

and Sharma [4] expressed this doubt without numerical support. In fact, SO-II does converge when $|D_q| \leqslant 1500\ \text{cm}^{-1}$, as shown in table 1, although it does not work as well as SO-I in the lowest-order treatment. This indicates that SO-II is applicable to most crystals when the sixth order is taken into account. To understand the convergence of SO-II, we note that only perturbation orders of even index contribute to the splitting, unlike the situation for SO-I. This leads to the estimation

$$D^{(4)}/D^{(6)}(\text{SO-II}) \sim (\langle V_c \rangle / E_0)^2 \sim (10D_q/G)^2,$$

with E_0 denoting free-ion energies among which $G = 10B + 5C$ is the smallest (for Mn^{2+} and Fe^{3+} ions in crystals, $G \simeq 23000$–$26000\ \text{cm}^{-1}$).

To support the conclusion of the correctness of the perturbation procedures we calculate D for Fe^{3+} in garnets. The results are displayed in table 2. In the calculation,

we have taken values of B, C and D_q determined from the optical spectra [13] and $\xi = 225\ cm^{-1}$. The superposition model [14] was adopted in deducing B_{20} and B'_{40}, with crystalline structure data taken from [15]. $\bar{A}_4$ was deduced from the reported D_q, according to [1]; t_2 and t_4 were taken to be 3 and 5, respectively. $\bar{A}_2$ is much greater than $\bar{A}_4$ [14] and was taken to be $8\bar{A}_4$ in our calculation; it does not influence the calculation values significantly. The results indicate that the perturbation procedures reach values close to those evaluated by diagonalization. We considered only the SO mechanism and found that $\xi = 225\ cm^{-1}$ can fit the experimental data reasonably. However, a better understanding of the splitting of the crystals needs to take into account all other mechanisms.

We have shown that all the three perturbation procedures are correct in tetragonal symmetry. However, SO-I and SO-III work well only when the low-symmetric field components are small, because they treat the components as a perturbation term. SO-II works satisfactorily when the sixth order is taken into account. The conclusions also hold for trigonal symmetry, as shown recently by Wang *et al* [16].

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