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Stark level $^4T_1(G)$ in MgO:Mn^{2+}

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It is shown that Low's conjecture, that the Stark level $^4T_1(G)$ in MgO:Mn^{2+} would be higher than 14000 cm^{-1} from the ground state, is in accord with EPR experiments. Furthermore, possible reasons for the difference between our results and previous ones are given.

I. INTRODUCTION

Low's conjecture that the Stark level $^4T_1(G)$ in MgO:Mn^{2+} would be higher than 14000 cm^{-1} from the ground state is a very important criterion to know whether a crystal-field calculation may or may not be adequate to account for the ground-state splitting and the optical spectra.[1] At present the crystal-field spin-orbit coupling mechanism has been remarkably successful in explaining many of the features of spectra of transition-metal ions in crystals,[2–6] and many works have referred to the EPR and optical spectra of the d^5 configuration[7–16] However, none of the previous analyses can be used to confirm Low's speculation. In the following, we verify that Low's conjecture is in accord with EPR experiments by diagonalizing the complete matrix for the ligand-field spin-orbit coupling perturbation.

II. ZERO-FIELD SPLITTING

The spin Hamiltonian for the ^6S-state ions in cubic symmetry can be expressed relative to the threefold axes of the cube as[17]

$$\hat{H}(\mathbf{S}) = g\beta\mathbf{H}\cdot\mathbf{S} - (a/180)(O_4^0 + 20\sqrt{2}O_4^3) . \qquad (1)$$

Parameter a is associated with a fourth-order spin operator and represents a cubic component of the crystalline electric field, and the spin operators have the following form:

$$\begin{aligned} O_4^0 &= 35S_z^4 - [30S(S+1)-25]S_z^2 - 6S(S+1) \\ &\quad + 3S^2(S+1)^2 , \qquad (2) \\ O_4^3 &= \tfrac{1}{4}[S_z(S_+^3+S_-^3) + (S_+^3+S_-^3)S_z] , \end{aligned}$$

Employing matrix elements[18] and free-ion wave functions $|{}^6S,5/2,M_J\rangle$ the explicit expression for zero-field splitting can be written as

$$\begin{aligned} &\text{quartet state: } E(\Gamma_8) = a , \\ &\text{doublet state: } E(\Gamma_7) = -2a , \qquad (3) \\ &\text{zero-field splitting: } E(\Gamma_8) - E(\Gamma_7) = 3a . \end{aligned}$$

The effect of the cubic field is therefore to split the sixfold degenerate state into a quartet and a doublet state, which, respectively, have energies a and $-2a$ relative to the original level. The zero-field splitting can be used to determine the Stark level $^4T_1(G)$ in the d^5 configuration.

III. CHECKING THE ENERGY MATRIX

The perturbation-energy matrix for the d^n configuration has been constituted by many workers,[19–29] and a method for checking the matrix elements of the spin-orbit interaction has been proposed by Schroeder.[29] In the following, we give a general scheme for checking the complete matrix for the ligand-field spin-orbit coupling perturbation which includes the previous conditions.

Our complete matrix has been constituted for the perturbation Hamiltonian[16]

$$\hat{H} = \hat{H}_{e\text{-}e} + \hat{H}_{\text{so}} + \hat{V}(C_3) , \qquad (4)$$

where

$$\hat{H}_{e\text{-}e} = \tfrac{1}{2}\sum_{i,j} e^2/r_{ij} ,$$

$$\hat{H}_{\text{so}} = \zeta\sum_i \mathbf{l}_i\cdot\mathbf{S}_i ,$$

and

$$\hat{V}(C_3) = \sum_i V_i(C_3) .$$

This matrix can be checked by diagonalizing it and employing the following conditions.

(1) $\hat{V}(C_3) = 0$ and $\hat{H} = \hat{H}_{e\text{-}e} + \hat{H}_{\text{so}}$. In this case the eigenvalues would be in agreement with the J-J coupling calculation.[29]

(2) $\hat{H}_{\text{so}} = 0$ and $\hat{H} = \hat{H}_{e\text{-}e} + \hat{V}(D_{3d})$. In this case the eigenvalues would be in agreement with the requirements of group theory, and we have repeated Wan's calculation.[30]

(3) $\hat{H} = \hat{H}_{e\text{-}e} + \hat{H}_{\text{so}} + \hat{V}(O_h)$. In this case we have repeated Powell's result.[10,16]

(4) $\hat{H} = \hat{H}_{e\text{-}e} + \hat{H}_{\text{so}} + \hat{V}(D_3)$. In this case we have repeated Hempel's calculation.[24]

Therefore, we have confirmed the previous results and shown that a reliable calculation for ground-state splitting can be obtained by diagonalizing our complete matrix.[16]

IV. COMPARISON OF OUR RESULTS WITH THOSE OF DU AND ZHAO

The cubic zero-field splitting for the Mn^{2+} ion in crystals has been studied by Du and Zhao[14] (DZ). They dis-

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TABLE I. Comparison of our results for $3a$ with those of Du and Zhao (Ref. 14), all numbers in units of cm^{-1}. Initial parameters $B=911$, $C=3273$, $\zeta=336.6$.

D_q	$10^4(3a)$[a]	$10^4(3a^{(6)}+3a^{(8)})$[b]	$10^4(3a^{(6)})$[b]
1600	233.9	52.9	33.6
1200	58.4	25.7	19.4
800	17.0	10.4	9.0
400	3.8	2.69	2.58

[a] This paper.
[b] See Ref. 14.

TABLE II. The Stark level $^4T_1(G)$ of MgO:Mn^{2+} for various values of the ground-state splitting. All are in units of cm^{-1}.

Ground-state splitting $[10^4(3a)]$	52.5	56.2	60.1	55.8[a]
Crystal-field strength D_q	980	1000	1020	<1100[b]
Stark level				
$^4T_1(G)$	14999	14806	14614	>14000[b]
$^4A_1(G), {}^4E(G)$	23279	23279	23279	23474[c]

[a] See Ref. 33.
[b] See Ref. 1.
[c] See Ref. 34.

cussed this problem in the framework of a high-order perturbation calculation. By taking the same values of the electrostatic parameters, the spin-orbit-coupling coefficient, and the crystal-field strength D_q, as those of DZ,[14] we obtain the zero-field splitting. From Table I we find that our data for the ground-state splitting are about two times larger than those of DZ. This implies that the ground-state splitting of the Mn^{2+} ion in MgO can be fitted by using the crystal-field spin-orbit-coupling mechanism but not requiring the crystal-field strength D_q to be larger than $1200\ \mathrm{cm}^{-1}$.

V. STARK LEVEL $^4T_1(G)$ IN MgO:Mn^{2+}

The spectra of the Mn^{2+} and Fe^{3+} ions have been summarized by Jørgensen.[31] His tables show that for the same ligand ions the Stark level $^4T_1(G)$ of Mn^{2+} would be higher than that of Fe^{3+}. For example, the Stark level $^4T_1(G)$ of $\mathrm{Mn}(6\mathrm{H_2O})^{2+}$ (at $18900\ \mathrm{cm}^{-1}$) is higher than that of $\mathrm{Fe}(6\mathrm{H_2O})^{3+}$ (at $12600\ \mathrm{cm}^{-1}$). Therefore, one can expect that the Stark level $^4T_1(G)$ of MgO:Mn^{2+} would be higher than that of MgO:Fe^{3+} (at $12100\ \mathrm{cm}^{-1}$).[1]

The Stark level $^4T_1(G)$ in MgO:Mn^{2+} has not yet been observed, and there have been some speculations about it.[1,10] Low and Rosengarten[1] discussed a series of spectra of Mn^{2+} and conjectured that the Stark level $^4T_1(G)$ in MgO:Mn^{2+} would be more than $14000\ \mathrm{cm}^{-1}$ above the ground state. This conjecture is a very important criterion to determine whether a crystal-field calculation may or may not be adequate in accounting for the ground-state splitting and the optical spectra.[1]

By using the average covalency parameter[14] N, we have

$$B=N^4B_0,\ C=N^4C_0,\ \alpha=N^4\alpha_0,\ \beta=N^4\beta_0\ , \qquad (5)$$

where the Racah parameters $B_0=918\ \mathrm{cm}^{-1}$, $C_0=3273\ \mathrm{cm}^{-1}$, the Tress correction $\alpha_0=65\ \mathrm{cm}^{-1}$, and the Racah correction $\beta_0=-131\ \mathrm{cm}^{-1}$ are as determined by Curie, Barthou, and Canny.[32] Taking the same value of the average covalency factor[14] N ($N=0.965$) and employing the spin-orbit coupling coefficient of Low and Rosengarten ($\zeta=320\ \mathrm{cm}^{-1}$),[1] we obtain the crystal-field strength D_q by diagonalizing the complete matrix to fit the ground-state splitting.[33] The Stark level $^4T_1(G)$ of MgO:Mn^{2+} from 14600 to $15000\ \mathrm{cm}^{-1}$ is therefore obtained for various values of the ground-state splitting (see Table II). Our results show that Low's conjecture that the Stark level $^4T_1(G)$ of MgO:Mn^{2+} would be higher than $14000\ \mathrm{cm}^{-1}$ from the ground state is in agreement with the EPR experiments.

In conclusion, a general scheme for checking the complete matrix for the ligand-field spin-orbit coupling perturbation has been proposed, and by diagonalizing the complete matrix to fit the ground-state splitting we have confirmed Low's conjecture that the Stark level $^4T_1(G)$ of MgO:Mn^{2+} would be higher than $14000\ \mathrm{cm}^{-1}$ from the ground state. Our result is also in agreement with that of Jørgensen, and shows that a crystal-field calculation may be adequate in accounting for the ground-state splitting and the optical spectra.

APPENDIX: EXPRESSION FOR THE CRYSTAL-FIELD PARAMETERS

$$Y_1=(5/196\pi)^{1/2}v_{20}\langle r^2\rangle,\ Y_2=(1/196\pi)^{1/2}v_{40}\langle r^4\rangle\ ,$$

$$Y_3=(5/56\pi)^{1/2}v_{43}^{c}\langle r^4\rangle,\ Y_4=i(5/56\pi)^{1/2}v_{43}^{s}\langle r^4\rangle\ .$$

The expression for Y_3 and Y_4 in our previous work[16] contains a typographical error.

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