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Crystal-field theory and the S-state splitting of Fe^{3+} in yttrium gallium garnet

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Calculating the S-state splitting of a d^5 ion (Fe^{3+}, Mn^{2+}) in a crystal has been a long-standing difficult problem since 1934 when it was discussed by Van Vleck and Penney. Low and Rosengarten have concluded that crystal-field theory is not capable of providing a unified interpretation for the spectrum and for the S-state zero-field splitting of $d^5\,{}^6S$ ions. In the present paper, by utilizing a method of combined perturbation composed of the electrostatic, crystal-field, and spin-orbit-coupling energies, and by diagonalizing a set of complete energy matrices constructed for a d^5 configuration and having a total order of 252, a reasonable interpretation is obtained for the d-d spectrum and the EPR cubic zero-field splitting of Fe^{3+} ions located at octahedral and tetrahedral sites in yttrium gallium garnet. This shows that crystal-field theory is as well suited for application to d^5 ions and to other d^n ions and that the earlier Low-Rosengarten conclusion is wrong. It is also shown that contributions to the ground-state splitting arising from various excited states of the d^5 configuration or from various components of the crystal field do not obey a linear-superposition rule. In the Appendix, a detailed explicit description of the matrices is given.

I. INTRODUCTION

Crystal-field theory has achieved great successes in explaining the optical spectra and the electron paramagnetic resonance (EPR) of transition-metal complexes. However, the d^5 ions (Fe^{3+}, Mn^{2+}) have been an exception. The calculation of the EPR cubic zero-field splitting (ZFS) of the ground state ${}^6S$ of a d^5 ion in crystals has been a long-standing difficulty since 1934 when it was discussed by Van Vleck and Penney.[1] The calculations made by Powell, Gabriel, and Johnston[2] and by Gabriel, Johnston, and Powell[3] show that only by accepting unusually large values for either the crystal-field-strength parameter Δ ($10Dq$) or the spin-orbit coupling coefficient ζ, or both, can the observed ZFS be accounted for. Low indicated in a summary report[4] that the basic mechanisms responsible for the S-state ZFS were not completely understood. The calculation made by Low and Rosengarten[5] shows also that, in order to account for such a ZFS, the value of ζ had to be much larger than that for a free ion, if the values of the optical parameters B, C, and Dq are determined from the optical spectrum. This behavior is hard to understand, and so they reached a pessimistic conclusion, i.e., the crystal-field theory is not capable of providing a unified explanation for the cubic ZFS and spectrum of $d^5\,{}^6S$ ions [the Low-Rosengarten (LR) conclusion]. Newman and Urban indicated in their summary report[6] that, although a considerable body of data exists on the parametrization of the ground-state splitting of ${}^6S$-state ions in crystals, relatively little progress has been made in obtaining a quantitative understanding of the mechanisms which determine these parameters. Such an S-state ZFS difficulty had continued until the end of the 1980s.[7]

Recently, this difficulty has been analyzed in some detail by Zhou, Zhao, and Ning[8] and it is attributed mainly to a model confusion arising from an incorrect phase relationship between Dq and ζ. They have achieved a reasonable interpretation, with use of crystal-field theory, for the d-d spectrum and S-state EPR ZFS of Mn^{2+} in ZnS, by a combined perturbation composed of electrostatic, crystal-field, and spin-orbit-coupling energies, and by diagonalizing the corresponding complete strong-field matrices, which are constructed within the irreducible representation spaces of the spinor group $O_h^*(d^5)$, the bases of which spaces are obtained by a suitable combination of the standard $O_h(d^5)$ bases of Tanabe and Sugano.[9] Thus the LR conclusion is shaken strongly.

The present paper is to put forward an interpretation for the *d-d* spectra and the *S*-state ZFS of Fe^{3+} ions located at octahedral and tetrahedral sites in yttrium gallium garnet (YGG). The method is based on Ref. 8 but with the Griffith standard bases[10] substituting for the Tanabe-Sugano bases.[9] The good agreement between the theoretical predictions and the experiments will show that the earlier LR conclusion can be entirely negated. At the end, discussions will be given on the discrepancy between the values of *B*, *C*, and *Dq* determined by Scott *et al.*[11] and those determined by the present paper and on the discrepancy between the two ZFS values calculated by Yu[12] and by this paper. In the Appendix, a detailed explicit description of our matrices will be given.

II. THEORY AND CALCULATION

The spin Hamiltonian for a d^5 ion in a cubic field can be written as

$$\mathcal{H}_s = g\mu_B \mathbf{H}\cdot\mathbf{S} + a(S_x^4+S_y^4+S_z^4)/6\ , \tag{1}$$

where a is the *S*-state cubic ZFS parameter. The real Hamiltonian can be written as

$$\mathcal{H} = \mathcal{H}_0 + V_e(B,C) + V_c(Dq) + \mathcal{H}_{\text{s.o.}}(\zeta)\ , \tag{2}$$

where $\mathcal{H}_0$ represents the free-ion Hamiltonian under the so-called center-field approximation, V_e the electrostatic repulsion energy between the valence electrons (i.e., the so-called electrostatic energy), V_c the cubic component of

TABLE I. The *d-d* spectra of Fe^{3+} in YGG:Fe^{3+} (in cm^{-1}).[a]

Calculated (oct)[b]				Observed			Calculated (tet)[c]			
	$d^5(O)$	$d^5(O^*)$		Ref. 15[d]	Ref. 11[e]	Ref. 11[f]	$d^5(T_d^*)$		$d^5(T_d)$	
$^6A_1(^6S)$	O	−38.07511	E''				−35.30618	E''	O	$^6A_1(^6S)$
		−38.0179	U'				−35.28764	U'		
$^4T_1(^4G)$	10224	10214	U'	10485	10640	10300	10331	U'	10492	$^4T_1(^4G)$
		10296	E'				10345	E''		
		10379	U'				10394	E'		
		10412	E''				10459	U'		
				14276	14290	13800	14429	E'	14475	$^4T_2(^4G)$
							14435	U'		
							14479	E''		
							14480	U'		
$^4T_2(^4G)$	15717	15662	E''	15970	16340	18730				
		15693	U'							
		15708	E'							
		15714	U'							
				19276	19380	18730	18334	U'	18500	$^4E(^4G)$ $^4A_1(^4G)$
							18367	E'		
							18413	E''		
							18459	U'		
				19841	20160	20160	20826	E''	20990	$^4T_2(^4D)$
				20244	20330	20330	20876	U'		
				20567	20640	20600	21027	U'		
				21051		21051	21092	E'		
$^4E(^4G)$ $^4A_1(^4G)$	21850	21390	E''		21160					
		21568	U'	21615		21640				
		21898	E'							
		21899	U'	22180						
				22503	22730	22730	23024	E''	23050	$^4E(^4D)$
				23229			23032	U'		
					23390	23440	23036	E'		
$^4T_2(^4D)$	24991	24816	E'	23874	23870	23950				
		24851	U'	24196	24230	24380				
		25067	U'	25487		25460				
		25231	E''	25810		25650				
				26132		26320	26935	E'	27091	$^4T_1(^4P)$
$^4E(^4D)$	27800	27761	U'	26697		26970	27057	U'		
		27700	E'				27093	E''		
		27771	E''			29000	27438	U'		

[a] The doublet levels calculated have not been listed.

[b] $B=850$, $C=2670$, $Dq=1360$, $\zeta=365$.

[c] $B=650$, $C=2400$, $Dq=-980$, $\zeta=347$.

[d] $Y_3Fe_{0.31}Ga_{4.69}O_{12}$.

[e] $Y_3Fe_{0.29}Ga_{4.71}O_{12}$.

[f] $Y_3Fe_{0.09}Ga_{4.91}O_{12}$.

TABLE II. The ZFS parameter a of Fe^{3+} in YGG:Fe^{3+} (in 10^{-4} cm^{-1}).[a]

	Calculated			Experimental (Ref. 16)	
	With complete matrix	Without doublets	Without quartets	4.2 K	295 K
oct	190.7	−2.45	0	189±7	185±4
tet	61.8	−1.65	0	62±4	62±3

[a] The values used for *B*, *C*, *Dq*, and ζ are the same as in Table I.

the crystal field, and $\mathcal{H}_{\text{s.o.}}$ the spin-orbit coupling energy. We take $\mathcal{H}_0$ as the unperturbed term and treat the remainder, $\mathcal{H}'=V_e+V_c+\mathcal{H}_{\text{s.o.}}$, as a combined perturbation on the 252-fold-degenerate level of $\mathcal{H}_0$, strictly according to the standard perturbation theory for degenerate cases in quantum mechanics. In the representation space of the spinor group O_h^*, the 252×252 matrix reduces into two two-fold-degenerate matrices $\underline{E}'$ (20×20) and $\underline{E}''$ (22×22) and one fourfold-degenerate matrix $\underline{U}'$ (42×42), as described in the Appendix. The crystal-field levels, hence the *d-d* spectrum bands, are given by the eigenvalues. The ZFS parameter a is determined by the two most lowest-lying eigenvalues according to the following relation:

$$3a=E_{\min}(\underline{U}')-E_{\min}(\underline{E}'') \ . \tag{3}$$

Because of the lack of uniqueness in pure spectral fitting, a method of simultaneously fitting to both the optical spectrum and the EPR data is used to determine the spectral parameters *B*, *C*, *Dq*, and ζ. In order to reduce the number of free fitting parameters and to reflect covalency, an average orbital reduction factor *N* (Ref. 13) is introduced; then we have

$$B=N^4B_0,\quad C=N^4C_0,\quad \zeta=N^2\zeta_0 \ , \tag{4}$$

where $B_0=1050$ cm^{-1}, $C_0=3806$ cm^{-1}, $\zeta_0=440$ cm^{-1} are the free Fe^{3+} parameters.[14] In our initial fitting, only *N* and *Dq* are taken as freely adjustable and we have $N_{\text{oct}}=0.92$, $(Dq)_{\text{oct}}=1360\ cm^{-1}$, $N_{\text{tet}}=0.89$, and $(Dq)_{\text{tet}}=-980\ cm^{-1}$. In the final fitting, all the parameters can be adjusted slightly. The final results are listed in Tables I and II.

III. DISCUSSION

It can be seen from Tables I and II that our theoretical predictions are in good agreement with the experimental results. This shows that crystal-field theory is as well suitable for application to d^5 ions as for other d^n ions, not only at an octahedral site but also at a tetrahedral site; hence the earlier Low-Rosengarten conclusion can be entirely negated.

It is shown from the calculated results listed in Table II that the cubic ZFS of the ground state ^6S arises mainly from the interaction of the ^6S state with both the quartets and the doublets via the spin-orbit coupling. However, the selection rule of spin-orbit coupling shows that a doublet does not affect the ^6S state directly but indirectly via the quartets. This is clearly shown in Table II, i.e., the value of a will be zero if it is calculated without the quartets. Obviously, the total contribution of the quartets and doublets to the ^6S-state ZFS does not equal the sum of the two independent contributions of the quartets and doublets. This is to say that simple arithmetic addition—the linear-superposition rule—is not valid here. Generally speaking, an eigenvalue of a matrix does not depend linearly on the matrix elements, and thus it cannot be a superposition of the independent contributions of the states which are taken as the bases of the matrix.

Different from ours, the parameter values determined by Scott *et al.*[11] by pure spectral fitting are

$$B=530\ cm^{-1},\ C=3100\ cm^{-1},\ \text{and}\ Dq=1310\ cm^{-1}\ ,$$

for octahedral sites;

$$B=744\ cm^{-1},\ C=2560\ cm^{-1},\ \text{and}\ Dq=654\ cm^{-1}\ ,$$

for tetrahedral sites.

If we substitute these values into our matrices and let ζ have the same values as in table I, the results calculated for a are

$$a_{\text{oct}}=141.6\times 10^{-4}\ cm^{-1}$$

and

$$a_{\text{tet}}=8.8\times 10^{-4}\ cm^{-1}\ .$$

Although the a_{oct} value does not deviate very far from the experimental value (185×10^{-4} cm^{-1}), the a_{tet} value is only one-seventh of the experimental value (62×10^{-4} cm^{-1}). In order to fit the experimental a_{tet} value, ζ has to be 768 cm^{-1}, being much larger than that (440 cm^{-1}) of a free Fe^{3+} ion. Therefore, the above parameter values of Scott *et al.*,[11] especially for the tetrahedral case, are not reasonable. As for why they took so small a value for $(Dq)_{\text{tet}}$, it is because they thought that the crystal-field strength *Dq* is generally at least twice as small for tetrahedrally coordinated ions as it is for octahedrally coordinated ions. However, this is incorrect, because the well-known relationship $\Delta_{\text{oct}}/\Delta_{\text{tet}}=-\frac{9}{4}$ is derived in cases in which the two coordination polyhedra have equal bond length and equal effective charge of the ligand, while the ligand bond length of Fe^{3+} in YGG is[17] $d_{\text{oct}}=1.995$ Å and $d_{\text{tet}}=1.849$ Å. Thus we have

$$|\Delta_{\text{oct}}/\Delta_{\text{tet}}|=\tfrac{9}{4}(q_{\text{oct}}/q_{\text{tet}})(d_{\text{tet}}/d_{\text{oct}})^5=1.54q_{\text{oct}}/q_{\text{tet}}\ .$$

Since $d_{\text{tet}}<d_{\text{oct}}$, we have $q_{\text{oct}}/q_{\text{tet}}<1$, leading to

$$|\Delta_{\text{oct}}/\Delta_{\text{tet}}|<1.54\ .$$

This requirement is well satisfied by our Dq ratio (1.388) but not by that (2.0) of Scott *et al.*[11]

Recently, the parameter values of Scott *et al.*[11] for the tetrahedral case had been adopted by Yu[12] to calculate the cubic a_{tet} with a fifth-order perturbation procedure. The result is 20×10^{-4} cm^{-1}, deviating very far from the experimental value (62×10^{-4} cm^{-1}), showing again the incorrectness of those values. This example shows that one should exercise great caution in attempting to predict accurate EPR experimental results with parameters determined roughly by pure spectral fitting. By the way, Yu[12] suggested that the tetragonal field component contributes a significant portion to the ^6S-state ZFS and nonetheless applied a linear-superposition rule to the calculation of the total contribution of the cubic and tetragonal field components. However, the ZFS does not depend linearly on the crystal field; thus if the contribution arising from the tetragonal component is nonzero, the superposition rule is not applicable here.

IV. CONCLUSIONS

(i) The optical absorption spectrum and the EPR cubic ZFS of the ground state ^6S of a Fe^{3+} ion located at either an octahedral or a tetrahedral site can well be accounted for by crystal-field theory within the d^5 configuration with a combined perturbation composed of electronstatic, cubic-crystal-field-component, and spin-orbit-coupling energies. So the earlier LR conclusion[5] is negated.

(ii) Generally speaking, contributions to ground-state splitting, arising whether from various excited states of the d^5 configuration or from various components of the crystal field, do not obey the simple linear-superposition rule.

(iii) In determining the spectral parameters B, C, Dq, and ζ, the method of a simultaneous fitting to both the optical spectrum and the EPR data is better than that of a pure spectral fitting.

(iv) The theoretical relationship $\Delta_{\text{oct}}/\Delta_{\text{tet}}=-\frac{9}{4}$ cannot be indiscriminantly applied in practical problems.

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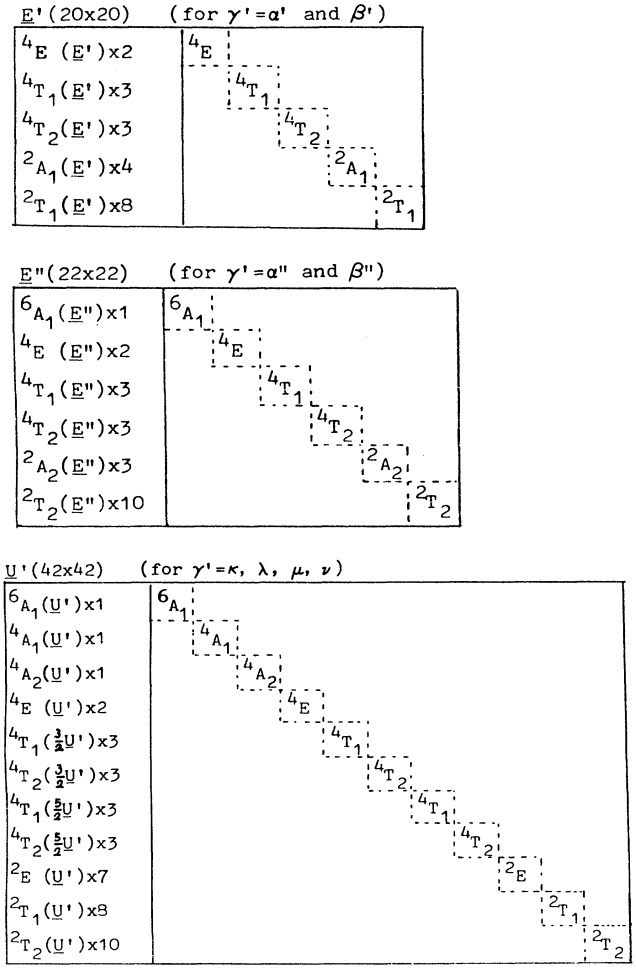
APPENDIX: STRONG-FIELD ENERGY MATRICES FOR $d^5(O_h^*)$

At first, we construct base functions $|i,S\Gamma\beta\Gamma'\gamma'\rangle$ for each irreducible representation Γ' (i.e., E',E'',U') of the spinor group $O_h^*(d^5)$ with the Griffith[10] standard bases $|i,S\Gamma M\gamma\rangle$ of the point group $O_h(d^5)$ according to the expression

$$|i,S\Gamma\beta\Gamma'\gamma'\rangle=\sum_{M,\gamma}\langle S\Gamma M\gamma|\beta\Gamma'\gamma'\rangle\,|i,S\Gamma M\gamma\rangle\ ,\tag{A1}$$

where γ' denotes different components of Γ', i stands for the ith strong-field configuration $t_2^n(S_1\Gamma_1)e^m(S_2\Gamma_2)$ in the electrostatic matrix table of Griffith[10] for d^5, and β distinguishes the repeated U' coming from $^4T_1$ or $^4T_2$ of $d^5(O_h)$.

TABLE III. The electrostatic matrices for $d^5(O_h^*)$.



The complete strong-field matrix of the combined perturbation energy $\mathcal{H}'=V_e+V_c+\mathcal{H}_{\text{s.o.}}$ with respect to the 252 bases (A1) will be diagonal in Γ' and γ' and degenerate in γ', and will thus be split into two twofold-degenerate matrices $\underline{E}'$ (20×20) and $\underline{E}''$ (22×22) and one four fold degenerate matrix $\underline{U}'$ (42×42). Each can be looked upon as the sum of the matrices for V_e, V_c, and $\mathcal{H}_{\text{s.o.}}$.

The V_e component of such a Γ' matrix is diagonal in S and Γ and thus forms a block-diagonal matrix as shown in Table III. Each block has the same S and Γ and is called an $S\Gamma$ block. Of a given $S\Gamma$ block, the order f and the $f\times f$ elements, i.e.,

$$\langle i,S\Gamma\beta\Gamma'\gamma'|V_e|j,S\Gamma\beta\Gamma'\gamma'\rangle=\langle iS\Gamma|V_e|jS\Gamma\rangle\ ,$$
$$i,j=1,2,\ldots,f\ ,\tag{A2}$$

are just the same as the $S\Gamma$ electrostatic matrix in Table A.30 of Griffith,[10] and the ith basis $|i,S\Gamma\beta\Gamma'\gamma'\rangle$ is a combination, according to (A1), of the ith set of degenerate bases $|i,S\Gamma M\gamma\rangle$ of the latter. All bases of the $S\Gamma$ block are denoted by a notation $S\Gamma(\Gamma')\times f$ in Table III.

The spin-orbit matrix belonging to each $\Gamma'(O_h^*)$ has been given by Schroeder.[18] But they can match only the electrostatic matrices of Tanabe and Sugano.[9] However, it can be seen from a comparison of these matrices with those of Griffith[10] that the two sets of standard bases used differ only in phase. Therefore, the spin-orbit matrices of Schroeder[18] can well match the electrostatic matrices of Griffith[10] if only the phase factor of their elements is revised accordingly, and can even be added directly to our V_e matrices respectively if again the sequence of the lines and rows is rearranged so as to be consistent with the sequence of the bases of our V_e matrices.

The matrices of the cubic crystal field will be fully diagonal in the $iS\Gamma\beta\Gamma'\gamma'$ representation, and the diagonal elements can be obtained as follows:

$$\langle t_2^n e^m, S\Gamma\beta\Gamma'\gamma' | V_c | t_2^n e^m, S\Gamma\beta\Gamma'\gamma' \rangle = (6m - 4n)Dq \ . \tag{A3}$$

This set of matrices so constructed is not identical with, but equivalent to, that in Ref. 8.

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