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Spin-triplet contribution to zero-field splittings for Fe^{2+} in $GeFe_2O_4$

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The zero-field splitting (ZFS) parameters D and $F-a$ of Fe^{2+} ions in $GeFe_2O_4$ are considered by diagonalizing the crystal-field and spin-orbit interaction Hamiltonian matrix. Results show that the spin-triplet contributions to ZFS are important, and the stronger the trigonal crystal field and the covalency effect assumed, the larger are these contributions.

I. INTRODUCTION

This paper is one in a series of systematic studies of the $3d^4$ and $3d^6$ ions in crystals (see, Refs. 1–14 and references therein). In the past decades, most studies of the zero-field splitting (ZFS) for $3d^4$ and $3d^6$ ions in crystals were based on the ^5D approximation, i.e., only the contributions of high-spin state ^5D of these ions to ZFS are considered and those of low-spin states ^3L $(L=P,D,F,G,H)$ are neglected (see, e.g., Refs. 2–4, 6–8, and 15–26). Recently, a series of ZFS studies[9–11,13,14,27] for Fe^{2+}, Fe^{4+}, and Cr^{2+} ions in several crystals showed the important spin-triplet contribution to ZFS. Particularly, Refs. 13 and 14 investigated systematically and comprehensively these contributions by the matrix diagonalization (MD) and the perturbation formula methods, respectively. However, all these treatments[9–11,13,14,27] are only in tetragonal symmetry. The present paper deals with the situation for $3d^4$ and $3d^6$ ions at trigonal sites.

II. THEORY

In the intermediate crystal-field (CF) coupling scheme,[28,29] the Hamiltonian for $3d^4$ and $3d^6$ ions is taken as

$$H=H_0+H' , \tag{1}$$

where H_0 is the free-ion Hamiltonian, which matrices are the function of Racah parameters B and C as well as Trees' correction factor α, shown clearly in Refs. 30–32. And the perturbation term H' in Eq. (1) represents the CF interaction, e.g., the trigonal (point groups: C_{3v}, D_3, and D_{3d}) CF Hamiltonian, in terms of the Wybourne notation[33]

$$H_{CF}=B_{20}C_0^{(2)}+B_{40}C_0^{(4)}+B_{43}(C_3^{(4)}+C_{-3}^{(4)}) , \tag{2}$$

where $C_q^{(k)}$ are the normalized spherical harmonics, and the spin-orbit (SO) coupling term is

$$H_{\rm S.O.}=\sum_i \xi(r_i)\mathbf{l}_i\cdot\mathbf{s}_i . \tag{3}$$

Following Refs. 34–36, the perturbation Hamiltonian matrices, as function of the SO parameter ξ and the CF parameters B_{20}, B_{40}, and B_{43}, are obtained [having dimensions of 29×29, 25×25, and 53×53 for the irreducible representations[37] $\Gamma_1(A_1)$, $\Gamma_2(A_2)$, and $\Gamma_3(E)$ of C_{3v}, D_3, and D_{3d} point groups, respectively].

For the orbital-singlet ground-state case, provided the first excited state lies high enough, the ZFS of the ground $S=2$ spin state is given in terms of the extended Stevens operator $O_k^q(s_x,s_y,s_z)$ (Refs. 38 and 39) as

$$H_{\rm ZFS}=\tfrac{1}{3}b_2^0O_2^0+\tfrac{1}{60}(b_4^0O_4^0+b_4^3O_4^3) . \tag{4}$$

The conversion between the ZFS parameters b_k^q in Eq. (4) and several other notations can be found in Rudowicz' review,[39] e.g.,

$$b_2^0=D,\quad b_4^0=\tfrac{1}{3}(F-a),\quad b_4^3=\tfrac{20}{3}\sqrt{2}a \tag{5}$$

for the conventional case. A method for determination of the ZFS parameters of $3d^5$ ion in crystals by direct diagonalization of the Hamiltonian matrix has been used recently[40] due to the development of the computer techniques. The matrix diagonalization approach for $3d^4$ and $3d^6$ ions at tetragonal sites has been worked out recently.[8,13] This approach for trigonal symmetry is shown below.

Diagonalization of the matrix of Eq. (1) yields, among others, the fine-structure energy levels e_i $(i=1,2,3)$ of the ground orbital singlet $(S=2)$, i.e., the actual ZFS. On the other hand, the eigenvalues of the ZFS Hamiltonian (4) matrix within the spin states $|S=2,M_s\rangle$ suitable for trigonal symmetry can be solved as

$$\begin{aligned}
E_1&=-2b_2^0+\tfrac{6}{5}b_4^0 ,\\
E_2&=\tfrac{1}{2}b_2^0-\tfrac{3}{10}b_4^0-\tfrac{3}{2}[(b_2^0+\tfrac{2}{3}b_4^0)^2+(\tfrac{1}{30}b_4^3)^2]^{1/2} ,\\
E_3&=\tfrac{1}{2}b_2^0-\tfrac{3}{10}b_4^0+\tfrac{3}{2}[(b_2^0+\tfrac{2}{3}b_4^0)^2+(\tfrac{1}{30}b_4^3)^2]^{1/2} ,
\end{aligned} \tag{6}$$

where E_1 is the singlet corresponding to the spin state $|0\rangle$, and E_2 and E_3 the doublets to $(\cos\theta|2\rangle+\sin\theta|-1\rangle$, $\cos\theta|-2\rangle-\sin\theta|1\rangle)$ and $(\sin\theta|2\rangle-\cos\theta|-1\rangle$, $\sin\theta|-2\rangle+\cos\theta|1\rangle)$, respectively. The correspondence between e_i arising from Eq. (1) and E_j in Eq. (6) can be easily found by identifying the spin states $(\sum a_i|S=2,M_s\rangle)$ for each e_i and comparing them with those in Eq. (6). The ZFS parameters b_2^0 and b_4^0 are obtained by neglecting b_4^3 for $b_2^0 \gg b_4^3$ (Refs. 16, 38, and 39) as follows:

$$\begin{aligned}
b_2^0&=D=\tfrac{1}{7}(2E_3-E_2-E_1) ,\\
b_4^0&=\tfrac{1}{3}(F-a)=\tfrac{1}{7}(E_3-4E_2+3E_1) .
\end{aligned} \tag{7}$$

This is the result of the MD method for $3d^4$ and $3d^6$ ions in trigonal symmetry. From Eq. (7), the ZFS parameters can be obtained by diagonalizing the complete Hamiltonian matrix or only the quintet one for considering or neglecting the spin-triplet contribution.

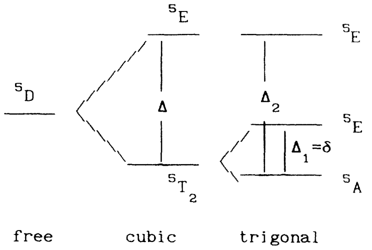

FIG. 1. Energy levels of ^5D in cubic and trigonal crystal field.

III. RESULTS AND DISCUSSION

The trigonal CF splittings and the ZFS parameters in $GeFe_2O_4$ had been studied in ^5D approximation by many authors (see, e.g., Refs. 16, 41, 42, and references therein). However, one can find that in these works the different trigonal CF splitting δ (from 640 to 1300 cm^{-1}) and SO coupling parameter ξ (from -320 to -400) were assumed. Along with this, the following two considerations have arisen in the study of spin-triplet contribution in $GeFe_2O_4$: (a) Numerical calculations by the MD method require the values of the Racah and Trees parameters B, C, and α as well as the SO coupling parameter ξ. For $3d$ ions in crystals, these parameters can be expressed as follows:[43]

$$B=K^2B_0,\quad C=K^2C_0,\quad \alpha=K^2\alpha_0,\quad \xi=K\xi_0\,, \tag{8}$$

where K is the average covalency reduction factor, $B_0=917$, $C_0=4040$, $\xi_0=-404$ (Ref. 38), and $\alpha_0=86$ (Ref. 44) (in cm^{-1}) are of free Fe^{2+} ions. The different values of ξ used previously are caused by the different values taken of K (i.e., the different assumed strengths of the covalency effect), and then, the different values of B, C, and α should be considered in the present paper. The results versus the values of K are shown in Table I. (b) Numerical calculations by the MD method require also the values of the CF parameters B_{20}, B_{40}, and B_{43}. It is well known that the cubic CF splits the free-ion ^5D ground state into an orbital doublet ^5E and a triplet $^5T_2$, and the triagonal distortion perturbation further separates $^5T_2$ into an orbital singlet ^5A and a doublet ^5E (see Fig. 1). The values of B_{20}, B_{40}, and B_{43} can be obtained from[38]

$$\Delta=10Dq=-\frac{5}{14}\left[B_{40}+\frac{\sqrt{70}}{10}B_{43}\right],$$

$$\Delta_1=\delta=-\frac{5}{14}(B_{20}+B_{40})-\frac{3}{14}\left[\left[-B_{20}+\frac{5}{9}B_{40}\right]^2+\left[\frac{2\sqrt{35}}{9}B_{43}\right]^2\right]^{1/2},$$

$$\Delta_2=-\frac{5}{14}(B_{20}+B_{40})+\frac{3}{14}\left[\left[-B_{20}+\frac{5}{9}B_{40}\right]^2+\left[\frac{2\sqrt{35}}{9}B_{43}\right]^2\right]^{1/2} \tag{9}$$

using known values of Δ and Δ_i. In the case where only Δ_1 $(=\delta)$ and Δ are available, one can use tentatively $\Delta_2=\Delta+\Delta_1$.[16] Clearly, the different values of δ $(=\Delta_1)$, i.e., the different trigonal CF assumed in the previous works may yield different values of B_{20}, B_{40}, and B_{43}. And the various ZFS parameters D and $F-a$ arising from variation of δ $(=\Delta_1)$ are listed in Tables II and III for $K=1$ and 0.85, respectively. In Tables I–III the value of $\Delta=10\,000$ cm^{-1} for $GeFe_2O_4$ (Refs. 16, 41, and 42) is used.

From Tables I–III, one can see clearly that there is a large difference of the numerical results D and $F-a$ obtained by diagonalizing the complete Hamiltonian matrix and only the quintet one. This shows, in fact, the impor-

TABLE I. Variation of ZFS parameters with K, the values of Δ_1 $(=\delta)=1000$ and $\Delta=10\,000$ cm^{-1} are used (in cm^{-1}, except ratio r—dimensionless).

		^5D approximation	^5D and ^3L combination	Ratio r
$K=1$	$b_2^0(D)$	12.2717	16.1433	0.32
	$3b_4^0(F-a)$	0.6575	0.4911	0.25
$K=0.95$	$b_2^0(D)$	11.2008	15.3325	0.37
	$3b_4^0(F-a)$	0.5600	0.3768	0.33
$K=0.9$	$b_2^0(D)$	10.1661	14.6740	0.44
	$3b_4^0(F-a)$	0.4715	0.2599	0.45
$K=0.85$	$b_2^0(D)$	9.1208	14.1725	0.55
	$3b_4^0(F-a)$	0.3880	0.1308	0.66
$K=0.8$	$b_2^0(D)$	8.1665[a]	14.1819	0.74
	$3b_4^0(F-a)$	0.3175	-0.0334	1.11
$K=0.75$	$b_2^0(D)$	7.2544	15.1815	1.09
	$3b_4^0(F-a)$	0.2556	-0.3134	2.23

[a] This value is close to that of $D=8.45$ cm^{-1} with $K=0.8$ and Δ_1 $(=\delta)=10\,000$ cm^{-1} obtained in Ref. 42.

TABLE II. Variation of ZFS parameters with Δ_1 ($=\delta$), the values of $K=1$ and $\Delta=10\,000$ cm^{-1} are used (in cm^{-1}, except ratio r—dimensionless).

		^5D approximation	^5D and ^3L combination	Ratio r
Δ_1 ($=\delta$)=700	$b_2^0(D)$	14.2180	18.2098	0.28
	$3b_4^0(F-a)$	1.847	0.9105	0.23
Δ_1 ($=\delta$)=850	$b_2^0(D)$	13.1957	17.1252	0.30
	$3b_4^0(F-a)$	0.8760	0.6721	0.23
δ_1 ($=\delta$)=1000	$b_2^0(D)$	12.2717[a]	16.1433	0.32
	$3b_4^0(F-a)$	0.6575	0.4911	0.25
Δ_1 ($=\delta$)=1150	$b_2^0(D)$	11.4613	15.2809	0.33
	$3b_4^0(F-a)$	0.5038	0.3598	0.29
Δ_1 ($=\delta$)=1300	$b_2^0(D)$	10.7555[a]	14.5287	0.35
	$3b_4^0(F-a)$	0.3943	0.2650	0.33

[a] These values are close to those (Ref. 16) of $D=13.05$ with $K=1$ and Δ_1 ($=\delta$)=1000, and $D=10.65$ with $K=1$ and Δ_1 ($=\delta$)=1300 (in cm^{-1}, except K), respectively.

tant spin-triplet contributions to ZFS of Fe^{2+} in $GeFe_2O_4$. It should be noted that the values of $D=12.2717$ with Δ_1 ($=\delta$)=1000, and $D=10.7555$ with Δ_1 ($=\delta$)=1300 (cm^{-1}) in Table II ($K=1$) as well as $D=8.1665$ with Δ_1 ($=\delta$)=1000 cm^{-1} and $K=0.8$ in Table I, obtained by diagonalizing only quintet matrices, are very similar to those (except the spin-spin interaction contribution to D) with the same values of Δ_1 ($=\delta$) and K obtained previously by the perturbation formulas in the ^5D approximation.[16,42] The very large different values of D with just these values of Δ_1 ($=\delta$) and K, calculated by diagonalizing complete matrix and only quintet one, show that the contribution of excited triplet states to ZFS is not negligible in this crystal.

For further studying of the spin-triplet contribution to the ZFS, the ratios

$$r(b_k^q)=\left|\frac{b_k^q(\text{diagonalizing complete matrix})-b_k^{q\prime}(\text{diagonalizing quintet matrix})}{b_k^{q\prime}}\right|$$

(i.e., ratio between the spin-triplet contribution and the spin-quintet one) are also listed in Tables I–III. It is obvious that the larger the ratio r, the larger are the spin-triplet contributions. From these tables, it can be seen that (i) the ratio r between the spin-triplet contribution and the spin-quintet one is more than 0.27 for D and 0.23 for $F-a$ in $GeFe_2O_4$, which shows the important contributions of the spin triplets and (ii) in most circumstances the larger the trigonal CF splitting Δ_1 ($=\delta$) and the smaller the covalency reduction factor K, the larger are the values of r. This means that the stronger the trigonal crystal field and the covalency effect assumed, the larger are the spin-triplet contributions to ZFS in this crystal. It has been shown that by increasing of the crystal-structure distortion from perfectly cubic symmetry, the energies of some spin triplets become lower,[13,30,32,38] and the spin-triplet contributions to ZFS should increase at the same time. However, a systematical study of the mechanism of the covalency effect on the CF levels and the ZFS parameters has not appeared in literature, to our knowledge.

TABLE III. Variation of ZFS parameters with Δ_1 ($=\delta$), the values of $K=0.85$ and $\Delta=10\,000$ cm^{-1} are used (in cm^{-1}, except ratio r—dimensionless).

		^5D approximation	^5D and ^3L combination	Ratio r
Δ_1 ($=\delta$)=700	$b_2^0(D)$	10.8107	16.0480	0.48
	$3b_4^0(F-a)$	0.7572	0.3766	0.50
Δ_1 ($=\delta$)=850	$b_2^0(D)$	9.8989	15.0381	0.52
	$3b_4^0(F-a)$	0.5341	0.2318	0.57
Δ_1 ($=\delta$)=1000	$b_2^0(D)$	9.1208	14.1725	0.55
	$3b_4^0(F-a)$	0.3880	0.1308	0.66
Δ_1 ($=\delta$)=1150	$b_2^0(D)$	8.4623	13.4372	0.59
	$3b_4^0(F-a)$	0.2903	0.0626	0.78
Δ_1 ($=\delta$)=1300	$b_2^0(D)$	7.9023	12.8100	0.62
	$3b_4^0(F-a)$	0.2232	0.0166	0.93

It should be noted that in Table I the values of r for the rank-4 ZFS parameter $b_4^0(F-a)$ are larger than those of $r(b_2^0)$ when $K\leq 0.9$, whereas there is the case of

$r(b_4^0)<r(b_2^0)$ for $K\geq 0.95$. Moreover one can find that the relation $r(b_4^0)<r(b_2^0)$ for $K=1$ in Table II or $r(b_4^0)>r(b_2^0)$ for $K=0.85$ in Table III is independent of the change of the trigonal CF splitting Δ_1 $(=\delta)$. It has been shown recently[13] that the spin-triplet contributions to the rank-4 parameters b_4^q $(q=0,4)$ are larger than those to the rank-2 one b_2^0 in tetragonal symmetry. However, in trigonal symmetry there exists the opposite case, i.e., $r(b_4^0)<r(b_2^0)$ when $K\geq 0.95$. This problem needs further study and a systematical investigation on the spin-triplet contribution to ZFS of $3d^4$ and $3d^6$ ions at trigonal sites will be provided in a forthcoming paper.[45]

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