Spin-Hamiltonian parameters of ^6S-state ions

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There are three alternative perturbation procedures which are equivalent when considering the contribution of the spin-orbit (SO) mechanism to the spin-Hamiltonian parameters of ^6S-state ions. We show that the study of the uniaxial stress on the zero-field splitting is an effective way of identifying the most important contributor among the various mechanisms leading to the ^6S-state splitting. Calculations are carried out for Mn^{2+} and Fe^{3+}-doped MgO and CaO crystals, indicating the SO mechanism to be predominant in the systems. The importance of utilizing the appropriate crystal-field model is stressed, and the observed axial term D of Fe^{3+} and Mn^{2+} ions at the tetrahedral and octahedral sites in several garnets are well explained by the SO mechanism, with the aid of the superposition model of the crystal field. The superposition model of the spin Hamiltonian proposed by Newman and Urban is shown to be capable of reaching results identical with those of the SO and other microscopic mechanisms. Illustrations are given indicating that the investigation of the intrinsic parameter and the power-law exponent of the superposition model is helpful in the identification of the dominant one among the mechanisms.

I. INTRODUCTION

During the past few decades, theoretical studies on the spin-Hamiltonian parameters of d^5 ions have become the subject of a considerable amount of work. The lack of orbital angular momentum in the ^6S ground state leads to considerable difficulty in explaining the observed effects of the crystal fields. Various mechanisms have been suggested to contribute to the ground-state splitting of the magnetic ions interacting with the lattices.

The Hamiltonian of a d^5 ion can be written as

$$H = H_0 + V + H_{s.o.} + H_{s.s.} , \tag{1}$$

where

$$V = \sum B_{kq} C_q^{(k)} \tag{2}$$

is the crystal field, H_0 the free-ion Hamiltonian; $H_{s.o.}$ and $H_{s.s.}$ are the spin-orbit and the spin-spin couplings, respectively. As usual, the crystal field V can be written as the sum of a cubic part V_c and a low-symmetry one V_l

$$V = V_c + V_l . \tag{3}$$

Because of the weakness of $H_{s.s.}$, important effects are expected due to the spin-orbit interaction. This effect may be thus called a spin-orbit (SO) mechanism. A study on it was published by Blume and Orbach (BO),[1] who treated the calculation within the ground d^5 configuration and took the spin-orbit coupling $H_{s.o.}$ and the low-symmetry component V_l of the crystal field as perturbation terms. The BO perturbation technique has been extended to tetragonal, rhombic, and trigonal symmetries[2,3] and

found to be able to account for the observed spin-Hamiltonian parameters of some systems. This procedure, however, is not the only way of calculating the spin-orbit coupling effect in a d^5 configuration. One may treat the total crystal field V as one of the perturbation terms together with the spin-orbit interaction $H_{s.o.}$,[4] or make the calculation in the strong-field scheme as done by Macfarlane for F-state ions.[5] The spin-orbit coupling effect on the ground-state splitting can also arise from the mixing of the excited electronic configurations into the ground $3d$.[5] The contribution due to this mixing has been considered by Orbach, Das, and Sharmal (ODS) (Ref. 6) and is known to be negligible for most of the cases involving Mn^{2+} and Fe^{3+} ions.[2,7,8] Perturbation involving the spin-spin interaction is called the spin-spin (SS) mechanism,[9] which contribute values to the spin-Hamiltonian parameters much smaller in magnitude than those due to the SO mechanism.[2,7,8]

Both the SO and the SS mechanisms are manifestations of the crystal-field effect. If we take into account the relativistic correlation crystal field in the Hamiltonian we have the so-called relativistic mechanism (RE).[10,11] This mechanism has been shown to matter in $4f^7$ ions[10] and was claimed to be of importance in $3d^5$ ions.[11] When considering the effect of the overlap and covalency between the orbitals of the magnetic ions and those of ligands we get the covalency and overlap mechanism (CO).[12] The importance of this mechanism was stressed in some literatures.

All the mechanisms have been suggested, and one thus wishes satisfactory interpretations for the observed spin-Hamiltonian parameters would be obtained by taking them into account. However it is not the case. Almost

all of the works reaching results in satisfactory agreement with the experimental data omitted one or more mechanisms which may be important in other systems. It thus becomes necessary to reexamine the calculation models suggested for the mechanisms and before having done this, identifying the most important one among the various mechanisms is helpful.

The main aims of the present work are (i) to reexamine the calculation models suggested for the SO mechanism, (ii) to establish a theory of the spin-lattice coupling for $3d^5$ ions in O_h coordinations, on which the most important mechanism is expected to be identified, and (iii) to investigate the superposition model of the spin Hamiltonian of S-state ions suggested by Newman and Urban[13] on the basis of microscopic theory.

We will distinguish three alternative perturbation procedures for the SO mechanism and show them to be equivalently correct. As a calculation of the crystal field plays a crucial role in evaluations for this mechanism, we expect the superposition model of the crystal field[14] which has been shown to be successful in interpreting the crystal-field splittings of $4f^n$ and some $3d^n$ ions to be applicable instead of the lattice-summation technique based on the point multipole model used in literatures. With the aid of this model the relationships will be established between the spin-Hamiltonian parameters and the crystalline ones. This will be given in Sec. II together with clarification of some confusions in literatures.

Section III shows a study on the spin-lattice coupling coefficients G_{11} and G_{44} of Fe^{3+} and Mn^{2+} ions substituted in MgO and CaO crystals, using the various mechanisms. The signs and the relative magnitude of G_{11} and G_{44} are found to serve as an indication that the SO mechanism is predominant. It seems that the study on the uniaxial stress effect is an effective way of identifying the most important mechanism.

In Sec. IV we will perform a SO mechanism calculation for Fe^{3+} and Mn^{2+} ions in several garnets with the use of the superposition model of crystal field. The results are satisfactory. The importance of taking parameters which fit the optical data is stressed.

Based on the microscopic theories, a discussion is made in Sec. V on the superposition model of the spin Hamiltonian of S-state ions which has been suggested by Newman and Urban[13] and employed extensively in recent years. We will show that the hypothesis on which this model is established seems to be unreliable but, to one's surprise, the results are always correct in the cases where the distortions are slight from cubic. Comparing the results given by this model and those by the SO mechanism leads to relationships between the parameters ($\bar{b}_2$ and $\bar{A}_4$, T_2 and t_4) of the two superposition models for the spin Hamiltonian and for the crystal field. The power-law exponent T_2 of the superposition model of the spin Hamiltonian changes its value according to the relative importance of the various mechanisms. It is allowed greater than 10 in theory and is found, for example, to be 19 for Mn^{2+} at the dodecahedral site (D_2) of lutetium gallium garnet (LuGaG). The study of the magnitude of T_2 and the sign of $\bar{b}_2$ is helpful for identifying the most important mechanism operating in a given system.

II. SO MECHANISM

As mentioned in Sec. I, the dominant contribution of the spin-orbit (SO) mechanism to the spin-Hamiltonian parameters of ^6S-state ions defined by

$$H_s = \sum_{i,j} S_i D_{ij} S_j + \text{rank-4 terms} \quad (i,j = x,y,z) \qquad (4)$$

arises from the combined effect of the crystal-field and the spin-orbit interaction within the ground $3d^5$ configuration. For axial symmetries only a splitting parameter D (or b_2^0) survives which is defined by

$$D = b_2^0 = D_{zz} - \tfrac{1}{2}(D_{xx} + D_{yy}) . \qquad (5)$$

When the symmetry is rhombic, an additional term E (or b_2^2) arises,

$$E = \tfrac{1}{3} b_2^2 = \tfrac{1}{2}(D_{xx} - D_{yy}) . \qquad (6)$$

There may be three alternative perturbation procedures approaching the contribution of the SO mechanism. Before investigating them, let us examine the formalism of crystal fields having low symmetries.

A. Formalism of crystal fields

Correctly identifying the cubic component from the total crystal field V of low symmetry is of importance in the calculation for SO mechanism. We consider three cases, rhombic, tetragonal, and trigonal symmetries.

The crystal fields of rhombic point-group symmetries (D_2, D_{2h}, and C_{2v}) can be considered as distorted from cubic fields (O_h and T_d) along the cubic axes [100] and [010], or along [110] and [$\bar{1}$10]. The crystal field can be written as

$$V = V_c + V_{\text{rhom}} ,$$

$$V_c = B_{44}[\pm \sqrt{14/5} C_0^{(4)} + (C_4^{(4)} + C_{-4}^{(4)})] , \qquad (7)$$

$$\begin{aligned} V_{\text{rhom}} = {} & B_{20} C_0^{(2)} + B_{22}(C_2^{(2)} + C_{-2}^{(2)}) + B_{40}' C_0^{(4)} \\ & + B_{42}(C_2^{(4)} + C_{-2}^{(4)}) , \end{aligned}$$

where

$$B_{40}' = B_{40} \mp \sqrt{14/5} B_{44} . \qquad (8)$$

The upper signs apply to the coordination system (denoted by I hereafter) in which the principle axes X, Y, and Z are parallel to [100], [010], and [001], respectively, while the lower ones to that (denoted by II hereafter) in which the X, Y, and Z are along [110], [$\bar{1}$10], and [001], respectively. By letting $B_{22} = B_{42} = 0$ the expressions hold for tetragonal point-group symmetries (D_{2d}, C_{4v}, D_4, and D_{4h}). The cubic-field parameter Dq in all the symmetries relates to the components B_{40} and B_{44} by

$$Dq = \tfrac{1}{42}(B_{40} \pm \sqrt{14/5} B_{44}) . \qquad (9)$$

Similarly, the trigonal point-group symmetries (D_{3d} and C_{3v}) can be considered as distorted from cubic along [111]. Choosing $Z \| [111]$ one has

$$V = V_c + V_{tri} \ ,$$

$$V_c = B_{43}[\pm\sqrt{7/10}C_0^{(4)} + (C_3^{(4)} - C_{-3}^{(4)})] \ , \tag{10}$$

$$V_{tri} = B_{20}C_0^{(2)} + B_{40}'C_0^{(4)} \ ,$$

where

$$B_{40}' = B_{40} \pm \sqrt{7/10}B_{43} \ . \tag{11}$$

The upper signs correlate to the lower ones by a 60° rotation of X and Y axes around the C_3 axis. In this case,

$$Dq = -\tfrac{1}{28}(B_{40} \pm \sqrt{7/10}B_{43}) \ . \tag{12}$$

B. Three alternative perturbation procedures

We have mentioned that the effect of the SO mechanism can be considered by three perturbation procedures. One method has been suggested by Blume and Orbach.[1] It treats the spin-orbit coupling $H_{s.o.}$ and the low-symmetry components of crystal field V_l as perturbation terms. This widely-used procedure is called the BO mechanism in literatures and is expected to be able to approximate the contribution fairly well as a result of usual weakness of V_l. For convenience we denote it by SO-I.

Another procedure is on the basis of treating the total crystal field V and the spin-orbit interaction $H_{s.o.}$ as perturbations.[4] At first glance one may possibly think the convergence of the perturbation series questionable, as the perturbation term V includes a strong part V_c, the cubic component of crystal field. However, it does converge rapidly in a wide range of Dq, as will be shown below. This procedure will be called SO-II in this paper.

Besides these two methods, which are considered in the weak-field scheme, one may make the perturbation calculation in the strong-field scheme by taking the cubic field V_c and the diagonal part of free-ion Hamiltonian H_0 as an unperturbed Hamiltonian and leaving the perturbations as the spin-orbit coupling $H_{s.o.}$, the low-symmetry field V_l, and the off-diagonal part of H_0. This technique was proposed by Mcfarlane in calculating the spin-Hamiltonian parameters of F-state ions and is expected to obtain good results for the cases with $|Dq| \gtrsim B$.[5] We expect it applies well to ^6S-state ions, where the strong-field scheme is known to work quite well in the interpretation of the crystal-field splittings of the excited states.

In what follows we will recall briefly the main aspects of the published works on SO-I and SO-II, then establish the theory on SO-III, and finally make a comparison among them. Several interesting things will be found and some confusions suffered in literatures will be pointed out.

C. SO-I procedure

This procedure has been applied to rhombic and tetragonal symmetries in the lowest- (third-) order treatment.[2,3] In rhombic symmetry it has been found by Sharma, Orbach, and Das[2] (for correction see Ref. 7) that

$$D(\text{SO-I}) = -(\sqrt{5}/12)\xi^2(2P_{\alpha\alpha} - P_{\alpha\beta})P_{\alpha\gamma}B_{40}' \ , \tag{13}$$

$$E/D(\text{SO-I}) = -2\sqrt{2/5}B_{42}/B_{40}' \ , \tag{14}$$

where ξ is the spin-orbit coupling constant and $P_{\alpha\alpha}$, $P_{\alpha\beta}$, and $P_{\alpha\gamma}$ are defined in the original paper. The authors have used a D parameter which is defined by $H_s = D[3S_z^2 - S(S+1)]$ and is therefore just $\tfrac{1}{3}$ of that we use; B_{kq} in the present paper relate B_k^q by

$$B_{40}' = -B_{40}'\langle r^4 \rangle, \quad B_{20} = -B_2^0\langle r^2 \rangle \ ,$$

and

$$B_{k2} = -B_k^2\langle r^k \rangle, \quad k = 2, 4 \ .$$

In trigonal symmetry the formula becomes[3]

$$D(\text{SO-I}) = (\sqrt{5}/63)\xi^2(7P_{\alpha\alpha} + 4P_{\alpha\beta})P_{\alpha\gamma}B_{40}'$$
$$- (3\sqrt{5}/14)\xi^2 P_{\alpha\beta}P_{\alpha\gamma}B_{20} \ . \tag{15}$$

It must be pointed out that the expression (14), which was derived in the basis functions of coordination system I,[2] is valid only in the coordinate system I. In the coordinate system II, in which the component B_{44} has an opposite sign to that in I due to a 45° rotation of X and Y axes around the Z axis, the basis functions of irreducible representations are different from those of I. This can be readily seen from the relative directions of the C_3, or [111], axis with respect to the principle axes X and Y in the different coordinate systems. The basis functions can be constructed from available tables of Griffith[15] and the consequent result of D is found to be the same in form as (13). The formula of E, however, becomes

$$E/D(\text{SO-I}) \doteq -\sqrt{2/5}B_{42}/B_{40}' \tag{14'}$$

instead of (14).

It is not surprising that both coordinate systems I and II have the same expression of axial term D. In fact, they have identical Z axes. When I turns to II by 45° rotation, B_{40} remains unchanged whereas B_{44} changes its sign; the unbalanced term B_{40}' stays unaltered from the definition (8) and similar expressions of D in the different systems are therefore expected.

Attention must be paid to the appropriate choice of coordinate system and to the correct application of the formulas (14) and (14') in the calculation of the E term for rhombic symmetry. In addition, crystal-field parameters should be evaluated in the same system. For instance, the crystals MnF_2 and ZnF_2 are distorted from O_h symmetry along [110] and [$\bar{1}$10], and therefore system II and correspondingly formula (14') are appropriate. In view of these we feel the results of E calculated by Sharma, Orbach, and Das[2,7] for Mn^{2+} ions in MnF_2 and ZnF_2 doubtful, because they are obtained by using the formula (14). We think correct results should be half of those the authors listed, although this will lead to a greater discrepancy in comparison with the experiments.

D. SO-II procedure

This procedure is able to avoid the complication of choosing a coordinate system. The rank-2 spin-Hamiltonian parameters have been written in a general

form for arbitrary symmetry in lowest- (fourth-) order consideration.[16] A next (sixth-) order calculation has been carried out for trigonal symmetry.[17] In a rhombic symmetry, one has,[16,18]

$$D^{(4)}(\text{SO-II}) = \frac{3\xi^2}{70P^2D}(-B_{20}^2 - 21\xi B_{20} + 2B_{22}^2)$$

$$+ \frac{\xi^2}{63P^2G}(-5B_{40}^2 - 4B_{42}^2 + 14B_{44}^2) , \quad (16)$$

$$E^{(4)}(\text{SO-II}) = \frac{\sqrt{6}\xi^2}{70P^2D}(2B_{20} - 21\xi)B_{22}$$

$$+ \frac{\xi^2}{63P^2G}(3\sqrt{10}B_{40} + 2\sqrt{7}B_{44})B_{42} , \quad (17)$$

where

$$P = 7B + 7C, \quad G = 10B + 5C, \quad D = 17B + 5C , \quad (18)$$

B and C being the Racah parameters. Similarly in trigonal symmetry,[17,19]

$$D^{(4)}(\text{SO-II}) = \frac{3\xi^2}{70P^2D}(-B_{20} - 21\xi B_{20})$$

$$+ \frac{\xi^2}{126P^2G}(-10B_{40}^2 + 7B_{43}^2) . \quad (19)$$

Unlike the procedure in SO-I, SO-II predicts rank-two crystal field B_{2q} to contribute to the spin-Hamiltonian parameters in the lowest-order treatment for rhombic symmetry. However these contributions as well as those of B_{42}^2 to D are usually negligible for small distortions. Omitting these, the formula (16) reduces to

$$D^{(4)}(\text{SO-II}) = -\frac{10\xi^2}{3P^2G}B_{40}'Dq \quad (20)$$

for both the coordinate systems I and II, whereas (17) reduces to

$$E^{(4)}/D^{(4)}(\text{SO-II}) = -2\sqrt{2/5}B_{42}/B_{40}' , \quad (21)$$

$$E^{(4)}/D^{(4)}(\text{SO-II}) = -\sqrt{2/5}B_{42}/B_{40}' \quad (21')$$

for the coordinate systems I and II, respectively. The relationships (21) and (21') are identical with (14) and (14'), predicted by SO-I, respectively. This is not surprising. Due to the perturbation treatment, the procedure SO-II should be appropriate in weak-field cases. It is still correct even when the low-symmetry components are comparable with the cubic part. On the other hand, SO-I operates only in small-distortion cases; it is still valid even when the cubic field is very strong. In small-distortion cases, SO-I should include results of SO-II and the agreements between (14) and (21) and between (14') and (21') are, therefore, expected.

We have seen that in the weak-distortion cases, SO-II give the same relationship between E and D of rhombic symmetry as SO-I predicts. The relationships break down when the low-symmetry components of the crystal field are comparable in magnitude with the cubic part.

For strong fields the contribution arising from the next order must be taken into account. In trigonal symmetry the next- (sixth-) order expression has been published[17]

and can be shortened as

$$D^{(6)}(\text{SO-II}) = \frac{400}{63}\frac{\xi^2}{P^2G^2F}(56F - P)Dq^3B_{40}' \quad (22)$$

by omitting terms in $B_{20}^nB_{40}'^m$ $(n + m \geq 2)$, where $F = 22B + 7C$. Similarly for tetragonal symmetry, we have

$$D^{(6)}(\text{SO-II}) = -\frac{400}{3}\frac{\xi^2}{P^2G^2}(4/P + 1/F)Dq^3B_{40}' . \quad (23)$$

E. SO-III procedure

Let us now apply the SO-III perturbation procedure to establish relationships between D, E, and crystal-field parameters in rhombic symmetry. According to Macfarlane[5] and by using the coupling coefficients tabulated by Sugano, Tanabe, and Kamimura,[20] we find, in the lowest (third) order

$$D(\text{SO-III}) = -(\tfrac{1}{12})\xi^2B_{40}'(1/E_1^2 - 1/E_2^2) , \quad (24)$$

$$E/D(\text{SO-III}) = -2\sqrt{2/5}B_{42}/B_{40}' , \quad (25)$$

where

$$E_1 = 10B + 6C - 10Dq , \quad (26)$$

$$E_2 = 10B + 6C + 10Dq . \quad (27)$$

The obtained formulas hold only for the coordinate system I and for strong crystal field with slight distortions. It is seen that the relation between E and D, (25), is in agreement with (14) and (21), obtained by SO-I and SO-II, respectively. The formulas appropriate for the coordinate system II may be derived in a similar way. We expect an identical result to (14') or (21') in this system.

F. Comparison

The three perturbation procedures correlate the spin-Hamiltonian parameters with the crystal-field ones in different ways. They are all approximate calculations and their results apply to different situations. Numerical results of dependence of D on the cubic field strength Dq are listed in Table I for tetragonal symmetry and in Table II for trigonal one. The tables show that the procedures are equivalently correct in accounting for the dominant contribution of the SO mechanism.

We now need an accurate calculation for comparison. Such a calculation is diagonalizing the full-energy matrices including the spin-orbit interaction. It is considerably tedious and difficult. One will meet rather large energy matrices. Another problem arises more from the independent spin-Hamiltonian parameters than from the two independent energy-level separations of the ground ^6S due to the Kramers degeneracy. Even for axial symmetry there exist two rank-4 splitting parameters a and F and one rank-2 term D; these three parameters cannot be identified from the two energy separations. Therefore an approximation has to be made.

It follows from the above discussions on the three pro-

TABLE I. Dq dependence of the axial-field splitting parameter D of Mn^{2+} ion in tetragonal symmetry, calculated by assuming $B'_{40}=1000$, $B_{20}=0$, $B=911$, $C=3273$, $\alpha=65$, $\beta=-131$, and $\xi=337$ cm^{-1} (Dq is in cm^{-1} and D in 10^{-4} cm^{-1}).

Dq	500	600	700	800	900	1000	1100	1200	1300
					SO-I				
D	-88	-109	-131	-156	-183	-214	-250	-291	-339
					SO-II				
$D^{(4)}$	-82	-98	-114	-131	-147	-163	-180	-196	-212
$D^{(6)}$	-5	-8	-13	-19	-28	-39	-51	-70	-89
D (total)	-87	-106	-127	-150	-175	-202	-231	-266	-301
					SO-III				
D	-78	-96	-116	-137	-161	-188	-218	-253	-294
					Accurate				
D	-88	-108	-130	-153	-180	-210	-245	-285	-332

cedures that the rank-2 spin-Hamiltonian parameters D_{ij} result from the interaction between the ground ^6S state and the excited quartets in their lowest-order treatments. This implies that the contribution of doublets is of little importance. On the other hand, the cubic field-splitting parameter a has been shown to arise predominantly from the excited states with doublets.[21] A similar situation may presumably take place for other rank-4 spin-Hamiltonian parameters. Therefore, for the purpose of deducing the rank-two parameters D_{ij}, one may neglect the doublets in diagonalizing the full-energy matrices and at the same time, neglect the effect of the rank-4 terms in the spin Hamiltonian (4).

Based on this idea we derive the full-energy matrices including $H_{s.o.}$ in tetrahedral symmetry. The consequent results are given in the last line of Table I for comparison with the perturbation calculations.

Tables I and II are calculated by assuming very small low-symmetry components of crystal fields for which both SO-I and SO-III are available. It is seen from Table I that each of the procedures gives results consistent with those calculated by diagonalization. Although the cubic fields are treated as perturbations, the SO-II has a good convergence for both the symmetries. Especially in the cases $|Dq| \lesssim 1000$ cm^{-1}, the sixth order contributes a value less than $\frac{1}{4}$ of the lowest order's. This thus clears up the suspicion on the correctness of this procedure

made by Baur and Sharma[22] and by Zhou and Zhao,[23] who argued that the use of the cubic field as one of the perturbation terms would lead to a divergent series. The correctness of SO-II can be observed from the fact that only even orders affect D_{ij} in this procedure, unlike in others. As a consequence of this fact, it can be estimated

$$D^{(6)}/D^{(4)}(\text{SO-II})\sim(\langle V\rangle/E)^2\sim(10Dq/P)^2 . \quad (28)$$

From this a convergence can be seen when $|10Dq| < \frac{1}{2}P$. For a given crystal, the relative importance of $D^{(6)}$ and $D^{(4)}$ can be observed from (19), (20), (22) and (23). We have

$$D^{(6)}/D^{(4)}(\text{SO-II})=\begin{cases} 40Dq^2(4F+P)/PGF \\ \quad (\text{tetragonal}) \\ 40Dq^2(56F-P)/63PGF \\ \quad (\text{trigonal}) \end{cases} \quad (29)$$

consistent with (28). This expression determines the suitability of SO-II for practical problems and reflects the fact that SO-II is applicable only for weak-field causes.

G. Crystal-field parameters

Reasonable calculation of crystal-field parameters is of importance in the evaluation of the SO mechanism. In

TABLE II. The Dq dependence of the axial-field splitting parameter D of Mn^{2+} ion in trigonal symmetry, calculated by assuming $B'_{40}=1000$, $B_{20}=-1000$, $B=911$, $C=3273$, $\alpha=65$, $\beta=-131$, and $\xi=337$ cm^{-1} (Dq is in cm^{-1} and D in 10^{-4} cm^{-1}).

Dq	500	600	700	800	900	1000	1100	1200	1300
					SO$-$I				
D	60	75	91	108	130	152	180	214	252
					SO$-$II				
$D^{(4)}$	66	77	88	99	111	122	133	144	155
$D^{(6)}$	2	4	5	8	12	16	21	27	34
D (total)	68	81	93	107	123	138	154	171	189

principle, the crystal-field parameters B_{kq} can be determined from available spectroscopic data. However a difficulty arises due to the weak and broad optical bands observed in a d^5 system. For most of the crystals the splittings induced by the low-symmetry components of the crystal field are difficult to observe even in low temperatures, although the cubic parameter Dq can be determined quite easily. The problem becomes considerably complicated in the cases where the distortion is so slight that the low-symmetry components are comparable with the spin-orbit interaction. An available crystal-field model is thus helpful in the calculation.

Such a model must be justified by comparing the obtained crystal-field parameters of which the cubic one Dq is most important with the optical data. In the works of Sharma and Sharma et al.,[2,3,7,8] an ionic crystalline potential was assumed, and the lattice-summation technique was employed. This model has been used by a large number of consequent works, in which both good and bad results have been published. For instance, it was reported that this model leads SO-I to give values of D an order of magnitude smaller than and of the opposite sign to the experimental results of Mn^{2+} ion on the three independent sites in yttrium aluminum garnet (YAlG).[24,25] This casts doubt on the procedure SO-I. But the theory of Sharma et al. on SO-I is correct doubtlessly, as shown above. The lattice-summation model is unreasonable.

This assertion is made because this model gives the wrong crystal-field parameters. For instance, it gives $Dq \approx 300$ cm^{-1} for MnF_2 and $ZnF_2:Mn^{2+}$ from the calculation of Sharma, Orbach, and Das[2] and $Dq \approx 100$ cm^{-1} for Mn^{2+} in the three sites in YAlG according to Hodges, Dormann, and Makram.[24] The deduced Dq values are rather far from the observed results [e.g., $Dq = 830$ cm^{-1} for MnF_2 and 920 cm^{-1} for $Mn^{2+}:ZnF_2$ (Ref. 26)].

As the D term depends on B'_{40} a measuring of the relative value of B_{40} and B_{44} (or B_{43}), rather than B_{40} and B_{44} (or B_{43}), fortuitously good results could be reached in some situations—it is possible to get available B'_{40} although the obtained B_{40} and B_{44} (or B_{43}) are separately wrong.

So far the microscopic origin of crystal field is not well understood yet. However, it is known that the main contribution comes from the ligands around the magnetic ions.

We expect the superposition model of crystal field suggested by Newman[14] is available for $3d^5$ systems. This model has been shown to be quite successful in explaining the crystal-field splittings of $4f^n$ ions by considerable works. More recently, this model has been employed to deal with some $3d^n$ ions [e.g., $Cr^{3+}:Al_2O_3$ (Ref. 27) and Fe^{2+} in garnets (Ref. 28)], and the results are satisfactory.

As an empirical theory, the superposition model expresses crystal-field parameters as[14]

$$B_{kq} = \sum_j \overline{A}_k(R_j)K_{kq}(\theta_j,\phi_j) , \tag{30}$$

the summation being taken over all ligands. The expressions of K_{kq} are given in Table III, and $\overline{A}_k(R)$ may be

TABLE III. Expressions of $K_{kq}(\theta,\phi)$ $[K_{k-q}=(-1)^q K_{kq}^*]$.

k	q	K_{kq}
2	0	$3\cos^2\theta - 1$
2	1	$-\frac{1}{2}\sqrt{6}\sin2\theta\exp(-i\phi)$
2	2	$\frac{1}{2}\sqrt{6}\sin^2\theta\exp(-i2\phi)$
4	0	$35\cos^4\theta - 30\cos^2\theta + 3$
4	1	$-2\sqrt{5}\sin\theta(7\cos^3\theta - \cos\theta)\exp(-i\phi)$
4	2	$\sqrt{10}\sin^2\theta(7\cos^2\theta - 1)\exp(-i2\phi)$
4	3	$-2\sqrt{35}\sin^3\theta\cos\theta\exp(-i3\phi)$
4	4	$\frac{1}{2}\sqrt{70}\sin^4\theta\exp(-i4\phi)$

given by the power law[14]

$$\overline{A}_k(R) = \overline{A}_k(R_0)(R_0/R)^{t_4} . \tag{31}$$

For regular octahedral and tetragonal coordinations, $\overline{A}_4$ correlates Dq, respectively, by

$$\overline{A}_4 = \begin{cases} 3Dq/4 & \text{for } O_h \\ -27Dq/16 & \text{for } T_d . \end{cases} \tag{32}$$

Similarly we have, from (9) and (12), that

$$Dq = \begin{cases} \frac{1}{42}\overline{A}_4[4(35\cos^4\theta - 30\cos^2\theta + 3) \\ \qquad -28(1-\cos^2\theta)^2] & \text{for } D_{2d} \\ -\frac{3}{14}\overline{A}_4[(35\cos^4\theta - 30\cos^2\theta + 3) \\ \qquad -7\sqrt{2}\cos\theta\sin^3\theta] & \text{for } D_{3d} \end{cases} \tag{32'}$$

for tetrahedral D_{2d} and octahedral D_{3d}, respectively.

Through the superposition model it is easy to express the spin-Hamiltonian parameters in terms of crystalline ones. Such expressions can be simplified by neglecting the quadratic terms in low-symmetry field components. For instance, we have for tetrahedral D_{2d} coordination

$$D(\text{SO-I}) = (\sqrt{5}/63)\overline{A}_4\xi^2(2P_{\alpha\alpha} - P_{\alpha\beta})P_{\alpha\gamma}K(\theta;D_{2d}) , \tag{33}$$

$$D(\text{SO-II}) = -\frac{640}{1701P^2G}\left[1 + \frac{10240(4F+P)}{729PGF}\overline{A}_4^2\right]$$
$$\times \xi^2\overline{A}_4^2K(\theta;D_{2d}) , \tag{34}$$

$$D(\text{SO-III}) = -(\tfrac{1}{63})\overline{A}_4\xi^2(1/E_1^2 - 1/E_2^2)K(\theta;D_{2d}) , \tag{35}$$

where

$$K(\theta;D_{2d}) = 49\eta^4 - 42\eta^3 - 114\eta^2 + 112\eta \tag{36}$$

with

$$\eta = 3\cos^2\theta - 1 .$$

Similarly for octahedral D_{3d} one has

$$D(\text{SO-II}) = -\frac{20\xi^2}{21P^2G}\,\overline{A}\,_4^2\left[1+\frac{640(56F-P)}{567PGF}\,\overline{A}\,_4^2\right]$$

$$\times K(\theta;D_{3d})\ , \tag{37}$$

where

$$K(\theta;D_{3d})=49\eta^4-70\eta^3-36\eta^2+56\eta\ . \tag{38}$$

The fourth and the sixth orders are included in the expressions (34) and (37) of SO-II.

The obtained expressions enable one to calculate the spin-Hamiltonian parameters from crystalline data. However, we would like to point out that the parameters such as B, C, Dq, and ξ should be those which fit the optical data so as to make the SO mechanism calculation reasonable.

H. Conclusions

We make conclusions on the SO mechanism as follows.

(i) The three perturbation procedures are equivalently correct as approximate calculation methods. Of them the procedure SO-I is the best one in view to give a good approach in the lowest-order treatment for an accurate calculation, although all of them arrive at identical results when the perturbation orders are taken high enough.

(ii) In rhombic fields with small distortions, the three procedures predict an identical relationship between D and E, i.e., E/D being proportional to B_{42}/B'_{40}. Attention must be paid to the coordinate system in this symmetry.

(iii) Correct evaluation of crystal-field parameters is of importance. The ionic model for the crystalline potential based on the lattice summation seems doubtful. On the other hand, the superposition model of crystal field suggested by Newman is expected to result in reasonable relationships between the spin-Hamiltonian parameters and crystalline-structure ones.

III. Mn^{2+} AND Fe^{3+} IONS IN STRESS-DISTORTED O_h COORDINATIONS

We now focus our attention on the uniaxial-stress effect on the spin-Hamiltonian parameters of Mn^{2+} and Fe^{3+} ions substituted into the MgO and CaO crystals. The effect is described by the spin-lattice coupling coefficients G_{11} and G_{44}. We try to employ various mechanisms to explain the observed results, and the main aim is to determine which of the mechanisms is most important. The basic idea is that if one mechanism is the most important at a stress state, it is still important at all stress states so that it predominates the spin-lattice coupling coefficients.

It has been shown that the so-called Watanabe and the ODS processes contribute nothing to the spin-lattice coupling coefficients of a ^6S-state ion in O_h symmetry.[29] It remains thus four mechanisms to be considered: SS, CO, RE, and SO discussed in Sec. II. The mechanisms predict different crystal-structure dependencies of the spin-

Hamiltonian parameters and consequently different values of G_{11} and G_{44}. The study of the uniaxial-stress effect is therefore helpful in identification of the most important mechanism.

A. Contribution of the SO mechanism

Let us first investigate the SO mechanism. In Sec. II the superposition model of the crystal field has been employed to establish the relationships between the spin-Hamiltonian parameters and the crystalline-structure ones through SO-I, SO-II, or SO-III perturbation procedure. With the application of external stress, the crystals are distorted from cubic and the spin-lattice coupling coefficients G_{11} and G_{44} are readily calculated following Blume and Orbach[1] (for a correction on the expressions of G_{11} and G_{44}, see Ref. 29). We obtain, in the lowest orders,

$$G_{11}(\text{SO-I})=-(2\sqrt{5}/3)t_4\xi^2Dq(2P_{\alpha\alpha}-P_{\alpha\beta})P_{\alpha\gamma}\ ,$$

$$G_{44}(\text{SO-I})=(\sqrt{5}/7)\xi^2[14DqP_{\alpha\alpha}$$

$$\qquad\qquad +(8Dq+18\overline{A}_2)P_{\alpha\beta}]P_{\alpha\gamma}\ , \tag{39}$$

$$G_{11}(\text{SO-II})=80t_4\xi^2Dq^2/3P^2G\ ,$$

$$G_{44}(\text{SO-II})=-40\xi^2Dq^2/P^2G\ , \tag{40}$$

$$G_{11}(\text{SO-III})=(\tfrac{2}{3})t_4\xi^2Dq(1/E_1^2-1/E_2^2)\ ,$$

$$G_{44}(\text{SO-III})=-(\tfrac{2}{7})Dq\xi^2[2(1/E_1^2-1/E_2^2)$$

$$\qquad\qquad +3(1/E_1E_3-1/E_2E_3)]\ , \tag{41}$$

where

$$E_3=19B+7C\ .$$

In the derivation of the second expression of (41), terms in $\overline{A}_2$ have been omitted. It follows from (39)–(41) that G_{44} is independent of the power-law exponent and that G_{11} is proportional to t_4. In the point-charge limitation, $t_4=5$ and the results (39) and (40) are deduced to those given by Yu and Zhao recently.[29]

It has been noted that the parameters, such as B, C, Dq, $\overline{A}_2$, and t_4, needed in the calculation should be taken fitting another experimental data. B, C, and Dq can be readily determined from optical data. However the spin-orbit coupling constant ξ is difficult to be obtained in this way because of the broad optical bands and the Jahn-Teller effect on the excited orbital degeneracy states. For $3d^n(n\neq5)$ ions a possible way of getting ξ exists in the analysis of the EPR g factors. But this method is apparently useless for $3d^5$ ions as the observed g factors have minute differences from the free-ion value 2.0023. An effective way is to deduce from the observed cubic zero-field splitting parameter a, which is very sensitive to $\xi(a\sim\xi^4)$.[30] After obtaining the values of B, C, and Dq from optical spectrum, one may get the ξ value by fitting the observed a by using the energy matrices including the spin-orbit interaction.[31] In this way, we find $B=800$, $C=3000$, $Dq=1200$, and $\xi=280$ cm^{-1} for Mn^{2+}:MgO, and $B=480$, $C=3380$, $Dq=1340$, and $\xi=430$ cm^{-1} for

Fe^{3+}:MgO from the published experimental data.[32,33] For CaO crystal, we assume it has identical values of B, C, and ξ to MgO due to their similar crystalline structures. Fitting the observed a (Ref. 34) requires $Dq=850$ cm^{-1} and 1050 cm^{-1} for Mn^{2+}:CaO and Fe^{3+}:CaO, respectively.[30]

The remaining parameters t_4 and $\bar{A}_2$ cannot be obtained in the same way; they are observable only in the experiments at external stress. The observed variation of a with hydrostatic pressure has shown an ionic crystalline potential at Mn^{2+} and Fe^{3+} sites in MgO lattice.[32] This implies $t_4=5$. As no optical experiment at uniaxial stress has been published, we take $\bar{A}_2=5000$ and 4000 cm^{-1} for MgO and CaO, respectively, for both Mn^{2+} and Fe^{3+} ions. These values are comparable with 6300 ± 800 cm^{-1} of Fe^{2+} in pyrope-almandine garnets (i.e., magnesium and/or iron aluminum garnets) and 5500 cm^{-1} of Co^{2+} in $CdCl_2$.[28] Since $\bar{A}_2$ affects only G_{44} and since $|P_{\alpha\alpha}|\gg|P_{\alpha\beta}|$, changes in the value of $\bar{A}_2$ in the range 5000 ± 5000 cm^{-1} does not significantly influence the final results.

The calculated results are displayed in Table IV. The agreement between the theoretical and experimental values[35,36] is excellently good, especially those in SO-I, not only for the numbers of G_{11} and G_{44} but for their proportion ratio G_{11}/G_{44}.

It is mentioned that SO-II predicts a constant of G_{11}/G_{44}, $-2t_4/3$, in the lowest-order treatment. This value corresponds to weak-field situations. The correction of the variation of G_{11}/G_{44} on the crystal field strength Dq arises from higher orders. On the other hand, SO-I reaches more satisfactory values of G_{11} and G_{44} and their ratio G_{11}/G_{44} for all the cases studied even in the lowest-order consideration. From Table IV one can see a tendency that the stronger the crystal field is, the larger the ratio G_{11}/G_{44} becomes.

The values[7,8] obtained by the lattice-summation model for Fe^{3+} and Mn^{2+} ions in MgO lattice are also listed in Table IV for comparison. It is seen that they are not so good as the results obtained by the superposition model in this work, especially for Fe^{3+}:MgO the lattice-

summation model gives a G_{11} value 1 order of magnitude less than those observed experimentally. The calculations by Sharma, Orbach, and Das[7] and Sharma[8] for these systems have indicated that the SS and the CO mechanisms are of little importance. This, together with the negligibility of the RE mechanism, will be confirmed by the following analysis of the ratio G_{11}/G_{44}.

B. Contributions from other mechanisms

Let us now turn to investigate the contributions due to other mechanisms. We focus our attention on the ratio G_{11}/G_{44}.

The CO mechanism has been discussed considerably since 1962. A brief review on the works in this problem has been made by Novák and Veltruský.[37] In their paper they developed the work of Sharma, Orbach, and Das[38] and pointed out some unreasonable assumptions made by some workers.[38-40] A general formula of the spin-Hamiltonian parameters in arbitrary symmetry has been suggested as[37]

$$D = \sum_j d(R_j)(3\theta_{zj}^2 - 1) ,$$

$$E = (\tfrac{3}{2}) \sum_j d(R_j)(\theta_{xj}^2 - \theta_{yj}^2) , \qquad (42)$$

$$D_{\alpha\beta} = 3 \sum_j d(R_j)\theta_{\alpha j}\theta_{\beta j} \quad (\alpha,\beta=x,y,z;\alpha\neq\beta) ,$$

where θ_{xj}, θ_{yj}, and θ_{zj} are directional cosines of the jth ligand. By using self-consistent-field radical wave functions of free ions the R dependence of $d(R)$ has been calculated for Mn^{2+} and Fe^{3+} surrounded by O^{2-} and F^{1-} ions. For Mn^{2+}-O^{2-} and Fe^{3+}-O^{2-} pairs, the results may be expressed approximately as[41]

$$d(R)=0.378/R^5, \quad d(R)=2.289/R^5 \qquad (43)$$

(in units of Å^{-5}cm^{-1}) respectively.

This theory enables us to yield

$$G_{11}(CO)=-(\tfrac{5}{3})G_{44}(CO)=-(\tfrac{40}{3})d(R) . \qquad (44)$$

TABLE IV. The spin-lattice coupling constants G_{11} and G_{44} (in units of cm^{-1} per unit strain) of Mn^{2+} and Fe^{3+} ions in MgO and CaO crystals.

| | G_{11} | | G_{44} | | G_{11}/G_{44} | | |
	MgO	CaO	MgO	CaO	MgO	CaO	Reference
			Mn^{2+}				
SO-I	0.44		−0.22		−2.0		7
	1.52	0.59	−0.27	−0.13	−5.6	−4.5	This work
SO-II	0.92	0.46	−0.28	−0.14	−3.3	−3.3	This work
SO-III	1.38	0.54	−0.34	−0.14	−4.1	−3.9	This work
Expt.	1.50(5)	0.48(6)	−0.31(1)	−0.10(2)	−4.8	−4.8	35,36
			Fe^{3+}				
SO-I	0.45		−0.46		−1.0		8
	5.58	2.40	−0.75	−0.49	−7.4	−4.9	This work
SO-II	2.79	1.63	−0.84	−0.49	−3.3	−3.3	This work
SO-III	5.50	2.53	−1.33	−0.64	−4.1	−4.0	This work
Expt.	5.5(2)	1.5(2)	−0.83(3)	−0.45(4)	−6.6	−3.3	35,36

The result shows (i) negative G_{11} and positive G_{44} of opposite sign to the experimental findings, and (ii) $G_{11}/G_{44} = -(\frac{5}{3}) = -1.7$ being a constant for all the crystals, a number which is far from the observed values (see Table IV). In addition the contributions are one order of magnitude less than the observed results (e.g., $G_{11} = -0.12$ for $MgO:Mn^{2+}$). This provides an indication that the contribution due to the CO mechanism is negligible in the systems under study. The conclusion is in support of Sharma, Orbach, and Das[7] and Sharma.[8]

We have seen that according to the work of Novák and Veltruský, opposite contribution to G_{11} and G_{44} is obtained. A similar case is thus expected to occur in static situations. In fact it has been revealed that the CO mechanism leads to an opposite contribution to the axial term in Mn^{2+} ions doped into K_2ZnF_4 (Ref. 37), K_2MgF_4 (Ref. 37), and $CaCO_3$ (Ref. 41) crystals, which have axial symmetries. This perhaps can be considered as an indication that this mechanism is not the most important for most of the cases, although it is not negligible in some systems especially in those with F^{1-} ions as ligands.[37]

As far as the RE mechanism is concerned, the spin-Hamiltonian parameters b_q^n are proportional to B_{2q}.[10,11,42-44] Assuming the crystalline potential at the magnetic ions is primarily ionic, one has

$$G_{11}/G_{44}(RE) = -1 . \tag{45}$$

A similar situation occurs in the SS mechanism. The ratio $G_{11}/G_{44} = -1$ is far from the observed values, and one therefore may conclude these mechanisms to be negligible in the cases studied.

A large number of works have been published which show the SS mechanism contributes rather small values to the spin-Hamiltonian parameters in comparison with the SO mechanism.[2-4,7,8,17-19] On the other hand, however, the importance of the RE mechanism was stressed in some literatures.[10,42-44] Most of the works were based on the lattice-summation model calculating the relativistic correlation crystal fields. As pointed out in Sec. II this model seems to be questionable in evaluation of crystal fields since it leads to results that dramatically disagree with the observed values. It thus also should be questioned using this model in the calculation of relativistic correlation crystal fields. Furthermore, the evaluation of the most important parameter $\langle b_2(11) \rangle$ of the RE mechanism by the free-ion wave functions[11,42-44] seems to be doubtful. In general, the wave functions of a magnetic ion in a solid state differ from those in a free-ion state. There has been a good evidence that the $3d$ orbitals expand dramatically in a solid state,[45,46] but detailed behavior of the Dirac wave functions is not well known when the magnetic ion is located in a lattice. The RE mechanism was first suggested to explain the ^8S-state splittings of $4f^7$ ions[10] and applied to a $3d^5$ system by other workers.[11,42-44] However, it should be pointed out that the rare-earth ions have an essentially different feature from the iron-group ions. For a rare-earth ion, the open $4f$ shell is inner orbitals shielded by $5s$ orbitals, whereas for an iron-group ion the open $3d$ shell is the outermost one and is subject to much stronger interaction with the surrounding ions than the rare-earth ions when they are in a lattice. Because of this, the $4f$ orbitals of a rare-earth ion in a solid state are expected to be well localized but the $3d$ orbitals of an iron-group ion does expand dramatically due to the interaction with the lattice. One should consider this effect in the evaluation of the RE mechanism for $3d^5$ ions.

C. Conclusions

The behaviors of G_{11} and G_{44} of ^6S-state ions predicted by the SO, CO, and RE mechanisms are summarized in Table V. We conclude as follows.

(i) The SO mechanism is the most important for Mn^{2+} and Fe^{3+} ions substituted into MgO and CaO crystals, because it gives correct amplitudes of G_{11} and G_{44} and explains the ratio G_{11}/G_{44} very well.

(ii) The CO and the RE mechanisms fail in explaining the observed G_{11}/G_{44}; in particular the CO mechanism leads to wrong signs of G_{11} and G_{44}. Both mechanisms are negligible in the cases under investigation.

The situation is quite similar to $Mn^{2+}:CaCO_3$. Yu and Zhao[41] have found one of the spin-lattice coupling constants G_A^1 proportional to the axial term D for a ^6S-state ion in D_{3d} symmetry. With the aid of the superposition model of a crystal field they found $G_A^1/D = -(2t_4/3)$ in the lowest-order treatment of SO-II. By taking $t_4 = 7$, $G_A^1 = 3.55 \times 10^{-2} \text{ cm}^{-1}$ and $G_A^1/D = -4.7$ were obtained which are in good agreement with $G_A^1 = 3.41 \times 10^{-2}$ cm^{-1} and $G_A^1/D = -4.51$ observed experimentally in $Mn^{2+}:CaCO_3$.[47] The CO and RE mechanisms were found to reach values -1.67 and -1 of G_A^1/D, respectively, and therefore are negligible in this system.

IV. Mn^{2+} AND Fe^{3+} IONS AT THE TETRAHEDRAL AND OCTAHEDRAL SITES IN GARNETS

In this section we carry out a calculation of SO mechanism for Mn^{2+} and Fe^{3+} ions as impurities at the tetrahedral (D_{2d}) and the octahedral (D_{3d}) sites in garnets YAlG, LuAlG, LuGaG, yttrium gallium garnet (YGaG), and yttrium iron garnet (YFeG or YIG). A superposition model analysis in Sec. V will show this mechanism is most important.

The calculation may be performed by applying Eqs. (33)–(38), and the results are nearly identical for the three alternative perturbation procedures. For simplicity we utilize the SO-II, for which the simple expressions (34) and (37) are very conveniently applied.

TABLE V. The signs and the relative magnitudes of G_{11} and G_{44} of a ^6S-state ion in O_h symmetry.

Mechanism	G_{11}	G_{44}	G_{11}/G_{44}
SO	+	−	≥ 3.33
CO	−	+	1.67
RE	+	−	1
Expt.[a]	+	−	≥ 3.3

[a]References 35 and 36.

The garnets have isomorphous crystalline structures[48] and thus have presumably identical values of B, C, and ξ when Mn^{2+} and Fe^{3+} ions are substituted. Knowing the parameters B, C, and Dq, the intrinsic parameter $\overline{A}_4$ may be deduced from (32'), and the spin-orbit coupling coefficient ξ can be obtained by analyzing the cubic zero-field splitting parameter a as did in Sec. III. However this method of justifying ξ is available only for the octahedral sites. Crystals without inversion symmetry possess odd-parity crystal fields, and the induced effect on the cubic zero-field splitting is not well known up to now. In fact the simple crystal-field theory omitting the odd-parity crystal-field effect fails in explaining the observed a of crystals without the inversion symmetry.[30] For the tetrahedral sites of garnets we take ξ as an adjustable parameter.

A. Octahedral sites

Only the optical spectra of Fe^{3+} doped into YGaG and YFeG have been published to our knowledge. It has been reported that[49] $B=530$, $C=3100$, and $Dq=1310$ cm^{-1} for YGaG:Fe^{3+} and $B=530$, $C=3220$, and $Dq=1300$ cm^{-1} for YFeG. Analysis of the observed $a=0.0189$ cm^{-1} (Ref. 50) of YGaG:Fe^{3+} by one of our recent works[30] yields $\xi=395$ cm^{-1} (calculated $a=0.190$ cm^{-1}). The spin-Hamiltonian parameters may be calculated by assuming all other garnets have identical values of B, C, and ξ to YGaG or to YFeG. Although the values of C are different from each other for YGaG and YFeG, the deduced spin-Hamiltonian parameters are almost identical, as displayed in Table VI. The sixth-order contributions, measured by the second term in the square bracket of (37), are around 15% of the lowest order for all the cases. In the calculation, the ionic limitation

$t_4 = 5$ has been taken.

For Mn^{2+} in the octahedral sites no optical experiments have been reported to our knowledge. For our purpose, we rewrite (37) as

$$D = \overline{B}_2 K(\theta; D_{3d}) \,,$$

$$\overline{B}_2 = -(20\xi^2/21P^2G)\overline{A}_4^2 \left[1 + \frac{640(56F - P)}{567PGF}\overline{A}_4^2\right] ,$$

(46)

where $K(\theta; D_{3d})$ is given in (38) and we regard $\overline{B}_2$ as a whole as an adjustable parameter. Owing to the expectedly small contribution of the sixth order we have approximately $\overline{B}_2 \propto \overline{A}_4^2$. Taking $\overline{B}_2(1.995\ \text{Å}) = -55 \times 10^{-4}$ cm^{-1}, we calculate the spin-Hamiltonian parameters listed in Table VI. As one can see, the results obtained by this simple model are excellently good in comparison with the experimental values.[25]

B. Tetahedral sites

Similarly to (46), we have from (34)

$$D = \overline{B}_2 K(\theta; D_{2d}) \,,$$

$$\overline{B}_2 = -(640\xi^2/1701P^2G)\overline{A}_4^2 \left[1 + \frac{10240(4F + P)}{729PGF}\overline{A}_4^2\right]$$

(47)

for the tetrahedral sites. The calculated results are listed in Table VII for comparison with the experimental values.[25,50] One also sees a good agreement. In the calculation $B=744$, $C=2560$, and $Dq=-654$ cm^{-1} of YGaG:Fe^{3+},[49] and $\xi=250$ cm^{-1} have been used for the Fe^{3+} ions. For the Mn^{2+} ions $\overline{B}_2$ (1.995 Å)$=-20 \times 10^{-4}$ cm^{-1} has been taken as an adjustable parameter.

TABLE VI. The axial spin-Hamiltonian parameter D of Mn^{2+} and Fe^{3+} ions in the octahedral (D_{3d}) sites in garnets. All are in units of 10^{-4} cm^{-1}.

	YAlG	LuAlG	LuGaG	YGaG	YFeG (YIG)
R (Å)[a]	1.937	1.939	1.987	1.995	2.019
θ (deg)[a]	52.4	51.6	49.8	50.6	50.3
model I[b]	−956	−1218	−1311	−1107	−1024
D model II[c]	−975	−1244	−1334	−1140	−1041
expt.[d]	−1053	−935	−1290	−1320	−1356
$[\overline{B}_2(1.995\ \text{Å}) = -55 \times 10^{-4}\ \text{cm}^{-1}]$					
D (calc.)	−440	−562	−621	−526	−492
D (expt.)[e]	−418	−565	−648	−511	

[a]Reference 48.
[b]Calculated by assuming that all the garnets have the same values 530 cm^{-1} of B, 3100 cm^{-1} of C, and 395 cm^{-1} of ξ as YGaG and by deducing $\overline{A}_4$ from $Dq=1310$ cm^{-1} of YGaG according to (31) and (32') with $t_4 = 5$.
[c]Calculated by assuming that all the garnets have the same values 530 cm^{-1} of B, 3220 cm^{-1} of C, and 395 cm^{-1} of ξ as YFeG and by deducing $\overline{A}_4$ from $Dq=1300$ cm^{-1} of YFeG according to (31) and (32') with $t_4 = 5$.
[d]Reference 50.
[e]Reference 25.

TABLE VII. The axial spin-Hamiltonian parameter D (in units of 10^{-4} cm^{-1}) of Fe^{3+} and Mn^{2+} ions at the tetrahedral (D_{2d}) sites in garnets.

	YAlG	LuAlG	LuGaG	YGaG
R (Å)[a]	1.761	1.760	1.852	1.849
θ(deg)[a]	49.95	49.69	48.90	49.45
		Fe^{3+}		
D (calc.)	-1331	-1384	-815	-738
D (expt.)[b]	-1028	-1249	-1131	-880
	Mn^{2+}	$[\bar{B}_2(1.995$ Å$)=-20\times10^{-4}$ cm$^{-1}]$		
D (calc.)	-651	-677	-442	-400
D (expt.)[c]	-512	-920	-626	-320

[a]Reference 48.
[b]Reference 50.
[c]Reference 25.

C. Discussion

In the calculations, the assumption has been made that the crystalline structure in the vicinity of magnetic ions is unchanged from those of the host lattices. However this is not the case, as is well known. To know the crystalline structure changes owing to the presence of magnetic impurities is of importance and has become a common problem in the study of the zero-field splitting of ^6S-state ions. Actually almost all the published theories concerning various mechanisms relate the spin-Hamiltonian parameters with the crystalline ones, and according to the theories the changes in crystalline structure parameters will result in significant changes in the spin-Hamiltonian parameters.

It has been shown that the structure parameters of a host crystal substituted with a magnetic ion are between those of the host crystal and those of the corresponding complex crystal.[51,52] If this holds as a general consequence, one could expect, for instance, a larger R value of LuAlG:Fe^{3+} than 1.939 Å of the host crystal LuAlG, comparing it with 2.033 Å of lutetium iron garnet (LaFeG or LuIG), at the D_{3d} site. This implies a smaller value of $\bar{A}_4$ than the deduced 1118 cm^{-1} as $\bar{A}_4 \propto R^{-5}$. The calculation of a confirms this argument. By the deduced $\bar{A}_4 = 1118$ cm^{-1} (or $Dq = 1490$ cm^{-1}) we reach $a = 0.0451$ cm^{-1}, which is much greater than the experimental value 0.0292 cm^{-1}.[50] A best fit requires $\bar{A}_4 = 1050$ cm^{-1} (or $Dq = 1400$ cm^{-1}) which corresponds to $D = -1083\times10^{-4}$ cm^{-1}, a better result than -1218×10^{-4} cm^{-1} given in Table VI in comparison with the experimental value of -935×10^{-4} cm^{-1}.[50]

It is noted that the CO, RE, and SS mechanisms contribute to D in proportional to $\eta = 3\cos^2\theta - 1$ for D_{2d} and D_{3d} symmetries. In the case where the distortions are slight from cubic, $\eta \ll 1$ and the terms in η^n ($n \geq 2$) have little importance in the SS mechanism [see (33)–(38)]. In these cases D (SO) is approximately proportional to η. Thus calculated results based on the SO mechanism by treating ξ or Dq as an adjustable parameter actually include part of the contribution of other mechanisms. This

may be one of the reasons why the simple SO model of taking $\bar{B}_2$ in (46) and (47) as an adjustable parameter achieves satisfactory agreement between theoretical and experimental values for Mn^{2+} in both sites. This also indicates the importance of taking such parameters as ξ and Dq which fit other spectroscopic data in the calculation of SO mechanism.

V. ON THE SUPERPOSITION MODEL

In 1975, Newman and Urban suggested a superposition model of the spin Hamiltonian for $^8S(f^7)$-state ions.[12] This model was proposed to be applicable to $^6S(d^5)$-state ions[53] and has been widely adopted in analyzing the spin-Hamiltonian parameters of Mn^{2+} and Fe^{3+} ions as an empirical model since then.[53-57] In the present section we try to justify this model on the basis of microscopic theory.

The basic hypothesis of the superposition model is that the spin-Hamiltonian parameters are the superposition of contributions of ligands for crystals with axial symmetry.[12] Accordingly the axial term D can be expressed as

$$D = \sum_i \bar{b}_2(R_j)\tfrac{1}{2}(3\cos^2\theta_j - 1), \tag{48}$$

where the intrinsic parameter $\bar{b}_2(R)$ may be written in the power law

$$\bar{b}_2(R_j) = \bar{b}_2(R_0)(R_0/R_j)^{T_2}. \tag{49}$$

We have denoted the power-law exponent by T_2 for distinguishment from t_n of the superposition model of a crystal field.

Apparently, the hypothesis and the resultant expressions for b_k^q of the superposition model can be thought to be correct if the spin-Hamiltonian parameters b_k^q predicted by all the microscopic mechanisms can be expressed as linear to the crystal-field components B_{kq}. As a fact, the CO, RE, and SS mechanisms do contribute to b_2^q in the way $b_2^q \propto B_{2q}$. The corresponding contributions to the superposition model parameters $\bar{b}_2$ and T_2 are displayed in Table VIII. However, the SO mechanism results in b_2^q mainly by the quadratic processes of B_{4q}, as shown in Sec. II. This implies that the contributions of ligands to the spin-Hamiltonian parameters are not superpositionable in the framework of SO mechanism. As described in

TABLE VIII. Contributions of various mechanisms to the intrinsic parameter $\bar{b}_2$ and the power-law exponent T_2 of superposition model of the spin Hamiltonian.

	Octahedral coordinations	
SO	$\bar{b}_2 = -(160\xi^2/9P^2G)\bar{A}_4^2$	$T_2 \geq 2t_4$
CO	$\bar{b}_2 = 2d$	$T_2 = 5$
RE	$\bar{b}_2 = (-eq)(6\xi\langle b_2(11)\rangle/125R^3P)$	$T_2 = 3$
	Tetrahedral coordinations	
SO	$\bar{b}_2 = -5(4/3)^5\xi^2\bar{A}_4^2/P^2G$	$T_2 \geq 2t_4$
RE	$\bar{b}_2 = (-eq)(6\xi\langle b_2(11)\rangle/125R^3P)$	$T_2 = 3$

Sec. II, the D term can only be expressed as $D = -f(Dq)\xi^2 B'_{40}$, where $f(Dq)$ is a complex function of crystal field strength Dq and B'_{40} is a linear combination of B_{40} and B_{44} (or B_{43}). The hypothesis of the superposition model of the spin Hamiltonian is correct only in the cases where the SO mechanism is negligible compared with others.

However, as shown by considerable workers (e.g., Refs. 53–57), the superposition model is able to describe successfully the observed spin-Hamiltonian parameters of ^6S-state ions in a large number of crystals. Even in the stressed MgO and CaO lattices doped with Fe^{3+} and Mn^{2+} ions, where we have shown in Sec. III the SO mechanism to be dominant, the superposition model has been shown to be able to explain the observed effects quite well.[53] It thus seems to be quite surprising why such a simple theory is so useful.

Let us pay attention to the results the superposition model gives rather than the hypothesis on which it was set up. We consider two simple situations: tetrahedral D_{2d} and octahedral D_{3d} coordinations. The superposition model gives

$$D = \begin{cases} 2\bar{b}_2(R)\eta & (\text{for } D_{2d}) \\ 3\bar{b}_2(R)\eta & (\text{for } D_{3d}) \end{cases} \tag{50}$$

with $\eta = 3\cos^2\theta - 1$. Comparing the expressions with (33)–(38), we find that the results (50) of the superposition model are identical with those of SO mechanism on the condition that the terms in η^n ($n \geq 2$) are negligible compared with the linear terms. This condition is satisfied in the case of small distortion, where $\eta \ll 1$. The intrinsic parameter $\bar{b}_2(R)$ arising from the SO mechanism can be deduced by comparing (50) with (33)–(38) and by omitting the terms in η^n with $n \geq 2$, but a power law (49) cannot be found for general cases. However, in

the cases where the crystal field is so weak that the lowest-order treatment of SO-II works well one obtains a power law with $T_2 = 2t_4$ and correspondingly $\bar{b}_2 \propto \bar{A}^2_4$. In strong-field cases one may take T_2 larger than $2t_4$ so as to include part of contributions of higher orders.

The effect of the SO mechanism on the superposition model parameters $\bar{b}_2$ and T_2 can also be considered by studying the uniaxial-stress effect on the zero-field splitting of cubic coordination systems. For instance, in O_h symmetry, one has

$$G_{11} = -(\tfrac{4}{3})T_2\bar{b}_2(R) ,$$
$$G_{44} = 4\bar{b}_2(R) \tag{51}$$

in the superposition model. It is seen that both the spin-lattice coupling constants are proportional to $\bar{b}_2$ and that G_{44} does not relate with T_2. Comparing (51) with (39) and (41) that work even in strong fields, one fails in getting $\bar{b}_2$ and T_2 definitely except that one considers T_2 depending on Dq or $\bar{A}_4$. However, in the weak-fields cases where $|P_{\alpha\alpha}| \gg |P_{\alpha\beta}|$, T_2 relates to t_4 and $\bar{b}_2$ to Dq. One has

$$\bar{b}_2 = (\sqrt{5}/2)\xi^2 Dq P_{\alpha\alpha}P_{\alpha\gamma}$$
$$= (\sqrt{5}/3)2\xi^2\bar{A}_4 P_{\alpha\alpha}P_{\alpha_\gamma} ,$$
$$T_2 = 2t_4 \tag{52}$$

in SO-I. This result is consistent with that obtained from (40) of SO-II, i.e.,

$$\bar{b}_2 = -(10\xi^2/P^2 G)Dq^2$$
$$= -(160\xi^2/9P^2 G)\bar{A}^2_4 ,$$
$$T_2 = 2t_4 \tag{53}$$

TABLE IX. Superposition model analysis of the axial spin-Hamiltonian parameter D (in units of 10^{-4} cm^{-1}) of Fe^{3+} and Mn^{2+} ions in garnets.

	YAlG	LuAlG	LuGaG	YGaG	YFeG (YIG)
Octahedral sites (D_{3d})					
Fe^{3+}, $\bar{b}_2(1.965$ Å$) = -0.2223$ cm^{-1} and $T_2 = 6$					
D (calc.)	-849	-1137	-1559	-1270	-1305
D (expt.)[a]	-1053	-935	-1290	-1320	-1356
Mn^{2+}, $\bar{b}_2(1.965$ Å$) = -0.0996$ cm^{-1} and $T_2 = 14$					
D (calc.)	-427	-567	-639	-504	
D (expt.)[b]	-418	-563	-648	-511	
Tetrahedral sites (D_{2d})					
Fe^{3+}, $\bar{b}_2(1.8$ Å$) = -0.2058$ cm^{-1} and $T_2 = 6$					
D (calc.)	-1136	-1203	-1028	-938	
D (expt.)[a]	-1028	-1249	-1131	-880	
Mn^{2+}, $\bar{b}_2(1.8$ Å$) = -0.1244$ cm^{-1} and $T_2 = 7$					
D (calc.)	-702	-743	-604	-552	
D (expt.)[b]	-512	-920	-626	-318	

[a]Reference 50.
[b]Reference 25.

TABLE X. Superposition model analysis of the spin-Hamiltonian parameters of Mn^{2+} ions in D_2 sites of garnets, D and E are in 10^{-4} cm^{-1}.

		LuAlG	YAlG	LuGaG
Experimental[a]	D	-382.2	-307.5	-335.4
	E	-127.4	-167.8	-101.3
$\bar{b}_2(2.35$ Å$)$, in units of 10^{-4} cm^{-1}		-170	-220	-166
T_2		14	5	19
Theoretical[b]	D	-382.4	-302	-336.8
	E	-127.4	-171	-100.5
Theoretical[c]	D	-369	-345	-296
	E	-158	-131	-142

[a]Reference 25.
[b]Calculated by $\bar{b}_2$ and T_2 listed.
[c]Calculated by $\bar{b}_2(2.35$ Å$)=-200\times10^{-4}$ cm^{-1} and $T_2=10$ for all the crystals.

$(P_{\alpha\alpha}P_{\alpha\gamma}$ is proportional to Dq in the range $Dq \lesssim 800$ cm$^{-1})$. The formulas (53) are self-consistent. In fact, because $\bar{b}_2$ depends quadratically on $\bar{A}_4$ which relate R in the way $\bar{A}_4 \propto R - t_4$, $T_2 = 2t_4$ is apparent from (49). Evidently, in strong-field cases T_2 as an adjustable parameter is allowed larger than $2t_4$ when assuming $\bar{b}_2 \propto \bar{A}_4^2$.

It has been shown in Sec. III that the spin-lattice coupling effect in MgO and CaO lattices doped with Mn^{2+} and Fe^{3+} ions can be well understood by the SO mechanism with $t_4 = 5$. From the above discussions we expect $T_2 \geq 10$. This is comparable with $T_2 = 14\pm2$, 14 ± 4, 20 ± 2, and 10 ± 2 of Mn^{2+}:MgO, Mn^{2+}:CaO, Fe^{3+}:MgO, and Fe^{3+}:CaO, respectively, which are deduced from the experimental data (Table IV) by employing (51). It is noted that Fe^{3+}:MgO has a stronger field $(Dq=1340$ cm$^{-1})$ and consequently a greater value of T_2.

From the above discussion we have seen that the superposition model is able to give reasonable results in the cases where the crystals are disturbed slightly from cubic, although the hypothesis on which this model is established is unreliable due to the importance of the SO mechanism. This conclusion is made from the analysis of several special situations but actually holds as a general consequence for coordinations of interest. For most of the cases the superposition model is applicable. However, when $\bar{b}_2$ and T_2 are treated as adjustable parameters, the deduced results have involved dominant contributions of all the microscopic mechanisms.

It is interesting to notice the signs and the numbers of T_2 coming from the various mechanisms (Table VIII). Analyzing the observed data by the superposition model is helpful in identifying the most important mechanism. The Mn^{2+} and Fe^{3+} ions at the tetrahedral and the octahedral sites in garnets provides a circumstance. The results listed in Table IX are obtained by the best fitting of the experimental data. The obtained negative $\bar{b}_2$ is con-

sistent in sign with those predicted from the SO and RE mechanisms. Thus either SO or RE may be the most important one. On the other hand, T_2 is found to be 6 for Fe^{3+} at D_{2d} and D_{3d}, 7 for Mn^{2+} at D_{2d}, and 14 for Mn^{2+} at D_{3d}. Comparing these values with $T_2 \geq 10$, $T_2 = 5$, and $T_2 = 3$ of SO, CO, and RE, respectively, leads to conclusion that the SO mechanism is the most important one. Following calculation of the intrinsic parameter $\bar{b}_2$ may serve as a support for this conclusion. As an example, for Fe^{3+} at the octahedral sites we have $\bar{b}_2 = -0.2835$ cm^{-1} theoretically, which is comparable with the fitted value of -0.2223 cm^{-1}. In fact, the good agreement between the calculated and the observed values obtained in Sec. IV is in strong support of the conclusion made here.

In lattices having axial symmetries, where only one (D) of the spin-Hamiltonian parameters exists, the $\bar{b}_2$ and T_2 cannot be determined uniquely. Some works deduced $\bar{b}_2$ by keeping $T_2 = 7$ unchanged (e.g., Refs. 54 and 57). The values of $\bar{b}_2$ obtained in this way are not more physically interesting, except for in their sign. As has been indicated, T_2 could change its number dramatically, according to the relative importance of the mechanisms; different values of T_2 lead to different values of $\bar{b}_2$, leaving the sign of $\bar{b}_2$ unchanged, however. The $\bar{b}_2$ and T_2 can be obtained uniquely only in the cases where more than one spin-Hamiltonian parameter survives. For example, the dodecahedral sites in garnets have D_2 symmetry and D and E have been observed for Mn^{2+} in LuAlG, YAlG, and LuGaG.[24,25] From the observed values we deduce $\bar{b}_2$ and T_2 for each of the crystals, as listed in Table X. It is seen that the intrinsic parameters are negative and are close in magnitude for all the cases and that the values of T_2 are 14, 5, and 19 for LuAlG, YAlG, and LuGaG, respectively. This perhaps may be regarded as an indication that stronger distortion occurs in YAlG than in others when the Mn^{2+} ions are substituted. Calculated values by $\bar{b}_2 = 0.02$ cm^{-1} and $T_2 = 10$ for all the crystals are listed in Table X for comparison. A good agreement is seen, and the SO mechanism being the most important can be concluded.

In conclusion, using the superposition model of the spin Hamiltonian suggested by Newman and Urban we are able to reach identical results with those predicted by the SO model and other mechanisms in the cases where the crystals are slightly distorted from cubic, although the hypothesis on which this model rests is unreliable in general. The investigation of $\bar{b}_2$ and T_2 is helpful in identifying the most important among the various mechanisms.

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