

Cubic zero-field splitting of a 6S -state ion

Yu Wan-Lun

Institute of Solid State Physics, Sichuan Normal University, Chengdu 610066, Sichuan, People's Republic of China

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The zero-field splitting of a 6S -state ion in a cubic field has been studied in detail within the d^5 configuration. It is found that the splitting arises mainly from the coupling among the excited states 4T_1 , 2T_2 , and 2E and the ground state 6A_1 via the spin-orbit interaction. The splitting parameter a can be expressed approximately as $F_0\xi^4 + F_1\xi^5$, where F_0 and F_1 are independent of the spin-orbit coupling constant ξ and have a property $|F_0| \gg |F_1|$. Analytical formulas of F_0 and F_1 are derived by a perturbation calculation with the help of the procedure suggested by Macfarlane. Based on this, a very simple expression of a is obtained semiempirically. Calculations are carried out for the splittings of Fe^{3+} and Mn^{2+} ions substituted as impurities in several octahedrally coordinated lattices and for the splitting parameter dependences on pressure for Fe^{3+} and Mn^{2+} in MgO crystals. The results are in good agreement with the values observed experimentally, indicating a successful interpretation of the crystal-field theory for the cubic zero-field splittings of 6S -state ions in octahedral coordinations. The power law $a \propto R^{-m}$ has been investigated on a theoretical basis. This is indicated to be able to reasonably account for the observed data for a system that has Dq or a values close to each other. In particular, a reasonable value $m = 12 \pm 2$ is expected for Mn^{2+} ions having $Dq \lesssim B$.

I. INTRODUCTION

One of the most important spin-Hamiltonian parameters of a 6S -state ion is the cubic zero-field splitting parameter a , which is defined by the spin Hamiltonian

$$H_s = (a/6)[S_x^4 + S_y^4 + S_z^4 - \frac{1}{5}S(S+1)(3S^2 + 3S - 1)]. \quad (1)$$

The study of a has become very interesting in crystal-field theory as an effective way of investigating the crystalline potentials at the magnetic ion sites. The parameter a measures the energy difference between the Γ_7 and Γ_8 representations of the ground state 6S :

$$3a = E(\Gamma_8) - E(\Gamma_7). \quad (2)$$

A large number of works have been published on the theoretical study of a .¹⁻⁶ Two kinds of calculations were presented; one applied the perturbation theory to give an approximation approach¹⁻³ and the other diagonalized the full energy matrices, including the spin-orbit interaction $H_{s.o.}$.⁴⁻⁶ The following has been found:

(i) a is positive in the range $|Dq| \geq 200 \text{ cm}^{-1}$, where Dq refers to the cubic field parameter.¹⁻⁶

(ii) The spin-spin interaction has a negligible contribution.

(iii) The odd processes of the spin-orbit interaction have an effect so that $a(+Dq) \neq a(-Dq)$ (Refs. 2 and 3).

(iv) Omitting the spin doublets reduces the calculated splitting by almost 2 orders of magnitude.^{2,3}

Efforts have also been devoted to accounting for the observed data.³⁻⁶ Low and Rosengarten⁵ concluded that one was unable to achieve this unless a spin-orbit coupling parameter ξ larger than that found in the free ion is used. Taking $\xi < 300 \text{ cm}^{-1}$, and using for B and C (The Racah parameters) the values for MnO , Gabriel,

Johnston, and Powell⁴ found that the observed cubic zero-field splitting of $\text{MgO}:\text{Mn}^{2+}$ can be accounted for if the cubic field parameter Dq is about 30% greater than that observed in MnO . This seems to be confirmed by later optical spectra measurements reported by Koid and Blazey⁷ and by the high-order perturbation calculation published by Du and Zhao.³

Due to the lack of the orbital angular momentum in the ground state 6S , the calculation of the zero-field splitting is rather complicated. A diagonalization calculation will result in two large matrices having dimensions 22×22 and 42×42 . Although seeming to be simpler, a perturbation calculation is still considerably tedious, because the spin-orbit interaction begins to affect the splitting at fourth order. Powell, Gabriel, and Johnston² have performed a numerical perturbation calculation up to sixth order by regarding the spin-orbit and the spin-spin interactions as the perturbation Hamiltonian. A sixth-order perturbation formula has been recently reported by Du and Zhao,³ who treated the cubic crystal field and the spin-orbit coupling as perturbations of the free-ion Hamiltonian, as did by Watanabe.¹ The formula is only expected to work well in the cases where the crystal fields are weak. It thus becomes worthwhile to develop a technique of simplifying the diagonalization calculation and to find a simple analytical expression of a for the purpose of application.

The main aims of the present work are (i) to investigate the splitting parameter a in more detail, in particular its dependence on the spin-orbit coupling constant ξ , (ii) to deduce effectively the dimensions of the energy matrices for simplifying the diagonalization calculations, (iii) to obtain an expression of a that is very simple and appropriate for a wide range of Dq , and (iv) to justify the achievement of the crystal-field theory in the explanation

of the cubic zero-field splitting.

Using the spin-orbit coupling matrices of d^5 configuration,⁸ we calculate the splitting parameter a as a function of Dq . The results are quite different from those of Powell, Gabriel, and Johnston.² An investigation of the ζ -dependence indicates $a \approx F_0\zeta^4 + F_1\zeta^5$, where F_0 and F_1 are functions of Dq , B , and C , and $|F_0| \gg |F_1|$. The diagonalization including only the 6A_1 , 4T_1 , 2T_2 , and 2E states is found to give results almost identical to those with the complete energy matrices, making it possible to deduce the dimensions 42×42 and 22×22 to 24×24 and 14×14 for the Γ_8 and Γ_7 representations, respectively. Calculations for Fe^{3+} and Mn^{2+} in several lattices indicate that crystal-field theory is successful in interpreting the observed cubic zero-field splittings of 6S -state ions. These will be presented in the following section. In Sec. III a perturbation formula is derived by employing the procedure developed by Macfarlane.⁹ The formula is much simpler than that published by Du and Zhao³ and is shown to be appropriate for a wide range of Dq . Based on this formula, we in Sec. IV deduce semiempirically an expression of a , that involves two terms only and is shown to be a very good approximation to the accurate diagonalization calculation. Section V displays a study of the high-pressure dependences of the splittings of Mn^{2+} and Fe^{3+} ions in MgO crystals. The results are satisfactory in comparison with the experimental findings. The power law $a \propto R^{-m}$ is discussed in Sec. VI together with the effect of the odd-parity crystal-field component. We shall show it is theoretically reasonable in accounting for the observed data.

II. DIAGONALIZATION CALCULATIONS

The spin-orbit coupling matrices of d^5 configuration were derived by Schroder⁸ in the strong-field scheme of Tanabe and Sugano.¹⁰ Combining these with the electrostatic and crystal-field matrices reported by Tanabe and Sugano¹⁰ enables one to calculate the ground-state splitting of a 6S -state ion in an accurate way. In this section, our attention is focused on the investigation of the splitting based on the diagonalization calculation.

A. Complete diagonalization

The energy matrices include Γ_6 , Γ_7 , and Γ_8 representations. The ground state 6S enters into the last two, of which the matrices have dimensions 22×22 and 42×42 , respectively. Taking $B=900$, $C=3000$, and $\zeta=400 \text{ cm}^{-1}$, and utilizing Eq. (2) the splitting parameter a is calculated as a function of Dq , as displayed in the second column of Table I. A sensitive dependence can be seen. It is noted that the results are quite different from those of Powell, Gabriel, and Johnston,² which are listed in the last column of the same table for comparison. The present calculation obtains $a(+|Dq|) > a(-|Dq|)$, consistent with other works (Refs. 3 and 6), whereas Powell, Gabriel, and Johnston gave $a(+|Dq|) < a(-|Dq|)$.

One should expect the Powell-Gabriel-Johnston perturbation scheme could result in a very good approximation to an accurate calculation. Their scheme regards the spin-orbit coupling as the perturbation term and their calculation was performed to sixth order (the lowest or-

TABLE I. The cubic zero-field splitting $3a$ of a 6S -state ion as a function of Dq , calculated by assuming $B=900$, $C=3300$, and $\zeta=400 \text{ cm}^{-1}$. Column a lists values evaluated by the complete diagonalization, b by the simplified diagonalization, c by the perturbation formula (13), and d by the semiempirical expression (18). The values are in units of 10^{-4} cm^{-1} .

Dq (cm^{-1})	This work				Powell
	a	b	c	d	<i>et al.</i> (Ref. 2)
1600	465	467	354	424	
1400	223	224	187	212	
1200	117	117	104	114	80.2
1000	63.6	63.5	58.6	63.3	42.1
800	34.4	34.2	32.4	35.5	21.1
600	17.7	17.4	16.5	19.5	9.45
400	7.86	7.68	7.07	9.75	3.06
200	2.4	2.3	1.9	3.75	0.178
100	0.86	0.81			
0	0	0	0	0	0
-100	-0.23	-0.16			
-200	0.18	0.32	1.0	-0.5	2.4
-400	3.07	3.40	5.1	3.68	7.86
-600	9.47	10.1	13.2	10.5	17.7
-800	21.2	22.3	27	21.8	34.4
-1000	42.1	44.0	50	41.0	63.6
-1200	80.3	83.6	89	74.8	117
-1400	155	161	160	138	
-1600	317	328	299	263	

der affecting the splitting is fourth in their scheme). Because of the weakness of the spin-orbit interaction, the Powell-Gabriel-Johnston calculation should be accurate enough, but the results are out of one's expectation.

In the perturbation scheme of Powell, Gabriel, and Johnston,² one may have a perturbation expansion

$$a = F_0 \zeta^4 + F_1 \zeta^5 + F_2 \zeta^6 + F_3 \zeta^7 + \dots = \zeta^4 \sum_{k=0}^{\infty} F_k \zeta^k, \quad (3)$$

where F_k are functions of Dq , B , and C , and have a property $|F_k| \gg |F_{k+1}|$. The first term comes from the fourth order, and the second from the fifth, etc. Because the d^5 configuration is complementary itself, inverting the signs of Dq and ζ obtains an identical result:

$$a(-Dq, -\zeta, B, C) = a(Dq, \zeta, B, C). \quad (4)$$

This requires the coefficients of the even powers of ζ to be even functions of Dq but those of the odd powers of ζ to be odd:

$$F_{2n}(-Dq, B, C) = F_{2n}(Dq, B, C) \quad (n=0, 1, 2, \dots), \quad (5)$$

$$F_{2n+1}(-Dq, B, C) = -F_{2n+1}(Dq, B, C) \quad (n=0, 1, 2, \dots). \quad (6)$$

Thus we may define $a(\text{even})$ and $a(\text{odd})$, even and odd functions of Dq , respectively, as follows:

$$a(\text{even}) = \zeta^4 \sum_{n=0}^{\infty} F_{2n} \zeta^{2n}, \quad (7)$$

$$a(\text{odd}) = \zeta^4 \sum_{n=0}^{\infty} F_{2n+1} \zeta^{2n+1},$$

such that

$$a = a(\text{even}) + a(\text{odd}). \quad (8)$$

From the facts that $a(+|Dq|) > a(-|Dq|)$ and that $a(+|Dq|) > 0$ it follows that

$$a(\text{even}) > 0, \quad F_0 > 0, \quad (9)$$

and that, for $Dq > 0$,

$$a(\text{odd}) > 0, \quad F_1 > 0. \quad (10)$$

Comparing $a(Dq)$ of the present calculation with $a(-Dq)$ of Powell, Gabriel, and Johnston,² one may find them almost identical. This perhaps suggests that Powell, Gabriel, and Johnston have actually used $-\zeta$ in place of ζ or $-Dq$ in place of Dq .

The even and the odd parts of a , $a(\text{even})$, and $a(\text{odd})$ can be identified from the total value with the help of the properties (5) and (6). The average of $a(|Dq|)$ and $a(-|Dq|)$ obviously gives $a(\text{even})$ while the half of the difference between them is just $a(\text{odd})$. Their values are listed in Table II as the functions of Dq . With decreasing Dq , they decrease, whereas their relative percentage $a(\text{odd})/a(\text{even})$, increases. In particular, when Dq drops from 200 to 100 cm^{-1} , $a(\text{odd})$ becomes greater than $a(\text{even})$ so that $a(-|Dq|)$ changes from positive to negative (see Table I also).

The perturbation theory of Du and Zhao³ makes this

TABLE II. The $3a(\text{even})$ and $3a(\text{odd})$ as functions of Dq .

Dq (cm^{-1})	$3a(\text{even})$ (10^{-4} cm^{-1})	$3a(\text{odd})$ (10^{-4} cm^{-1})	$3a(\text{odd})/3a(\text{even})$ (%)
1600	391	74	18.9
1400	189	34	18.0
1200	98.6	18.4	18.7
1000	52.9	10.8	20.4
800	27.8	6.6	23.7
600	13.6	4.1	30.3
400	5.4	2.4	43.6
200	1.3	1.1	86
100	0.315	0.545	173

understandable. This theory treats the cubic crystal field as one of the perturbation terms, together with the spin-orbit interaction, and is thus expected to operate well for weak fields. Taking $B=911$ and $C=3273 \text{ cm}^{-1}$ reduces the reported sixth- (the lowest) order formula to a simple expression

$$3a = 9.3 \times 10^{-20} \zeta^4 Dq^2 + 4.1 \times 10^{-20} \zeta^5 Dq, \quad (11)$$

where ζ and Dq are in units of cm^{-1} . The first term gives $a(\text{even})$ while the second $a(\text{odd})$. Since it is proportional to Dq^2 , $a(\text{even})$ decreases more rapidly than $a(\text{odd})$, that is linear in Dq , when Dq decreases. Furthermore, when Dq drops its value less than 0.44ζ , $a(\text{even})$ becomes smaller than $a(\text{odd})$ and as a consequence a becomes negative in the range $0 > Dq > -0.44\zeta$ ($=150 \text{ cm}^{-1}$ for a Mn^{2+} ion with $\zeta=340 \text{ cm}^{-1}$). Small and negative values of Dq arise from the lattices with tetrahedral coordinations, but no such system has been found where $|Dq| < 300 \text{ cm}^{-1}$. Therefore, observable negative value of a should not be expected for an actual crystal, according to the theory.

B. Reduction of the matrices

The 22×22 matrix of Γ_7 representation involves multiplets

$${}^6A_1(1), {}^4T_1(3), {}^2T_2(10), {}^4T_2(3), {}^4E(2), {}^2A_2(3),$$

whereas the 42×42 matrix of Γ_8 includes

$${}^6A_1(1), {}^4T_1(6), {}^2T_2(10), {}^2E(7), {}^4T_2(6), {}^2T_1(8),$$

$${}^4A_1(1), {}^4A_2(1), {}^4E(2),$$

the numbers in brackets referring to the dimensions of the corresponding ${}^{2s+1}\Gamma$ subspaces. In order to reduce these matrices for calculating the splitting, we first note that the 4T_1 is the only multiplet that couples with the ground state 6A_1 , via the spin-orbit interaction. It has been pointed out by Powell, Gabriel, and Johnston that omitting the spin-doublets reduces the calculated splitting by almost 2 orders of magnitude.² This forbids one to omit the spin doublets but allows one to throw out all the spin quartets except 4T_1 from the full energy matrices, so that the dimensions of the Γ_7 and Γ_8 matrices are reduced from 22×22 and 42×42 to 17×17 and 32×32 , respectively.

Multiplets that couple with 4T_1 are expected to have much stronger effects on the ground-state splitting. From the work of Schroder⁸ it follows that $\langle {}^4T_1\Gamma_7 | H_{s.o.} | {}^2A_2\Gamma_7 \rangle = 0$. This implies that 2A_2 can be omitted and one thus obtains a 14×14 Γ_7 matrix.

The matrix of the Γ_8 representation can be further reduced to 24×24 dimension by omitting 2T_1 . This is because 2T_1 does not appear in the lowest order treatment in the Macfarlane's perturbation scheme, as will be shown in Sec. III, and therefore contributes a small value to the splitting.

Thus we have reduced the Γ_7 matrix from 22×22 to 14×14 and the Γ_8 matrix from 42×42 to 24×24 . The reduced matrices involve the 6A_1 , 4T_1 , 2T_2 , and 2E states only. With them the splitting is calculated, as displayed in the column 3, Table I, for comparison with those with the complete matrices. The results calculated with the reduced and the complete energy matrices are almost identical, especially for $Dq > 0$. This indicates that the reduced matrices are effective and can be used as a solid basis of a simplified diagonalization calculation of the splitting. In the following sections, "the diagonalization calculation" refers to a calculation with the reduced matrices.

C. Dependence on ζ

Figure 1 shows the value of $3a/\zeta^4$ as a function of ζ . The dependence is almost linear such that the discrepancy is so slight in the given range $0 < \zeta < 450 \text{ cm}^{-1}$ that it is difficult to be drawn in the figure.

This dependence can be well explained by the Powell-Gabriel-Johnston perturbation series, Eq. (3). The first term, $F_0\zeta^4$ comes from the lowest (the fourth) order and therefore predominates the expansion, and the second, $F_1\zeta^5$, comes from the second lowest (the fifth) order and is thus of second importance, governing

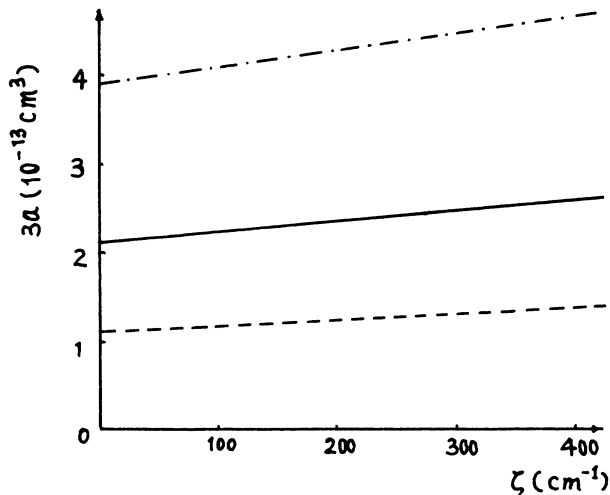


FIG. 1. The cubic zero-field splitting of a 6S -state ion as a function of the spin-orbit coupling constant ζ , calculated by taking $B=900 \text{ cm}^{-1}$, $C=3300 \text{ cm}^{-1}$, and $Dq=800 \text{ cm}^{-1}$ (---), 1000 cm^{-1} (—), and 1200 cm^{-1} (- · - · -).

$a(Dq) \neq a(-Dq)$. The remaining terms, those in ζ^k with $k \geq 6$, have little significance in comparison with the first two terms. Consequently, one has approximately

$$a \simeq F_0\zeta^4 + F_1\zeta^5. \quad (12)$$

D. Comparison with experiments

We now calculate the cubic zero-field splittings of Mn^{2+} and Fe^{3+} ions in several octahedrally coordinated lattices; the main aim is to justify the successfulness of the crystal-field theory. As the splitting parameter a depends on B , C , Dq , and ζ , we must take these parameters that fit the excited energy levels so as to make the calculated results reasonable.

The optical spectra of crystals $\text{KZnF}_3:\text{Mn}^{2+}$, $\text{RbCdF}_3:\text{Mn}^{2+}$, and RbMnF_3 have been reported.^{11,12} The excited states' splittings due to the spin-orbit coupling have been observed for RbMnF_3 .¹¹ As these crystals have a similar crystalline structure, it is to be expected that they have similar values for B , C , and ζ . In fact, the B and C have been reported to be 830 and 3122 for $\text{KZnF}_3:\text{Mn}^{2+}$, 822 and 3151 for RbMnF_3 , and 825 and 3136 for $\text{RbCdF}_3:\text{Mn}^{2+}$, in units of cm^{-1} .¹² It thus is reasonable to assume both $\text{KZnF}_3:\text{Mn}^{2+}$ and $\text{RbCdF}_3:\text{Mn}^{2+}$ have an identical value of ζ to RbMnF_3 , 320 cm^{-1} .¹¹ The cubic field parameter Dq has been reported to be 822 cm^{-1} for $\text{KZnF}_3:\text{Mn}^{2+}$ and 715 cm^{-1} for $\text{RbCdF}_3:\text{Mn}^{2+}$.¹² Substitution of these parameters into the full energy matrices yields

$$a = 6.93 \times 10^{-4} \text{ cm}^{-1}$$

[experimental $6.3(1) \times 10^{-4} \text{ cm}^{-1}$, Ref. 13] for $\text{KZnF}_3:\text{Mn}^{2+}$, and

$$a = 4.77 \times 10^{-4} \text{ cm}^{-1}$$

[experimental $4.7(3) \times 10^{-4} \text{ cm}^{-1}$, Ref. 14] for $\text{RbCdF}_3:\text{Mn}^{2+}$. The results are in good agreement with those observed experimentally. This enables us to conclude that the crystal field theory is successful in interpreting the cubic zero-field splittings of 6S -state ions in crystals with octahedral coordinations.

Useful information about the crystalline potentials and the spin-orbit interaction can be provided by the observed splitting parameter a . The successfulness of the crystal-field theory makes it possible to derive the parameters Dq and ζ from available ESR data. Knowledge about the spin-orbit interaction has a special importance in the study of the rank-two spin-Hamiltonian parameters, such as D and E , whose origins are not well understood although the spin-orbit effect was suggested to be one of the most important mechanisms. As an application, we deal with Mn^{2+} and Fe^{3+} ions doped in MgO and CaO lattices.

The optical spectra of Fe^{3+} in a MgO crystal was first observed by Low and Rosengarten⁵ with bands at 12 100, 15 200, 18 200, and 25 500 cm^{-1} . The authors remarked that some of the bands may actually belong to Mn^{2+} in the crystal, although the reported spectra has become a basis of the calculation of a by Kuang and Chen,⁶ who

used a Dq value of 1500 cm^{-1} , that is significantly greater than 1350 cm^{-1} reported by Low and Rosengarten, for accounting for the experimental value of a , $203.7 \times 10^{-4}\text{ cm}^{-1}$ (a value of $115 \times 10^{-4}\text{ cm}^{-1}$ for a will be obtained with the use of $Dq = 1350\text{ cm}^{-1}$). Available spectra was reported later by Blazey¹⁵ and by Cheng and Kemp.¹⁶ Six bands have been found at 10000, 13500, 21740, 25120, 27500, and 30970 cm^{-1} . From this it follows that $B = 480$, $C = 3380$, and $Dq = 1340\text{ cm}^{-1}$.¹⁵⁻¹⁷ Optical bands at 23500, 25700, 28100, and 33200 cm^{-1} have been found in $\text{Mn}^{2+}:\text{MgO}$;⁷ this enables us to obtain $B = 800$, $C = 3000$, and $Dq = 1200\text{ cm}^{-1}$. The optical spectra has not been reported for Fe^{3+} and Mn^{2+} in CaO, to our knowledge.

With the use of $B = 480$, $C = 3380$, and $Dq = 1340\text{ cm}^{-1}$ (Refs. 15-17) and adjusting ζ to fit the observed $a = 203.7 \times 10^{-4}\text{ cm}^{-1}$ (Ref. 18), we obtain $\zeta = 430\text{ cm}^{-1}$ for $\text{Fe}^{3+}:\text{MgO}$ (calculated $a = 197 \times 10^{-4}\text{ cm}^{-1}$). Similarly, we find $\zeta = 280\text{ cm}^{-1}$ for $\text{Mn}^{2+}:\text{MgO}$ in which a was reported to be $18.3 \times 10^{-4}\text{ cm}^{-1}$.¹⁹ Assuming MgO and CaO have similar values of B , C , and ζ makes it possible to deduce the cubic field parameter Dq from the observed ground-state splittings for $\text{Fe}^{3+}:\text{CaO}$ and $\text{Mn}^{2+}:\text{CaO}$; the results are 1050 and 850 cm^{-1} , respectively. All of the results are summarized in Table III. The deduced values for the parameters Dq and ζ have been shown to fit the spin-lattice coupling constants G_{11} and G_{44} of these crystals very well.²¹

The Fe^{3+} ions have cubic zero-field splitting parameters a 1 order of magnitude greater than Mn^{2+} ions in MgO and CaO crystals (Refs. 18-20, see Table III). Similar case exists in other circumstances. For example, a was found to be $52.7 \times 10^{-4}\text{ cm}^{-1}$ for Fe^{3+} in a KZnF_3 crystal but to be $6.3 \times 10^{-4}\text{ cm}^{-1}$ for Mn^{2+} in the same lattice.^{13,22} This fact can be understood partly as the result of stronger spin-orbit interaction in Fe^{3+} ions than in Mn^{2+} ones. Since a depends on ζ very sensitively, as is shown plausibly in (12), a small increase in ζ will increase

a dramatically. For instance, $\zeta(\text{Fe}^{3+})$ being larger than $\zeta(\text{Mn}^{2+})$ by a factor of 1.536 causes $a(\text{Fe}^{3+})$ being greater than $a(\text{Mn}^{2+})$ by a factor of 6, in the MgO and CaO crystals. Another thing leading to $a(\text{Fe}^{3+}) \gg a(\text{Mn}^{2+})$ is that $Dq(\text{Fe}^{3+}) > Dq(\text{Mn}^{2+})$.

III. PERTURBATION CALCULATION

The strong-field scheme of Tanabe and Sugano has advantage of the weak-field scheme in the description of the crystal-field splittings for a d^5 ion. The d^5 configuration is complementary itself. And owing to this, the diagonal elements of a cubic crystalline potential vanish identically in the weak field scheme but only survive in the strong field scheme. In the cases where $Dq > B$, by treating the diagonal elements in the strong-field scheme as the energies of corresponding optical terms we are able to understand well the crystal field splittings, which is referred to as the strong-field approximation in literature. Thus one expects the Macfarlane's perturbation procedure,⁹ which is based on the strong-field scheme, operates well for interpreting the ground-state splittings of d^5 ions.

In the Macfarlane's procedure,⁹ the matrices of Coulomb interaction H_0 are divided into two parts: diagonal and off diagonal. The off-diagonal part of H_0 is treated as a perturbation term together with the spin-orbit interaction $H_{s.o.}$, whereas the diagonal part and the cubic field serve as the unperturbed Hamiltonian.

In this model, the fourth order begins to affect the cubic zero-field splitting, contributing a value proportional to ζ^4 . The next order gives rise to two terms; one is proportional to ζ^4 and the other to ζ^5 . Similarly the sixth-order perturbation involves three terms in ζ^4 , ζ^5 , and ζ^6 . As it is the lowest, the fourth order predominates a and therefore F_0 , defined in Eq. (3). In a similar fashion, the fifth order is the main origin of F_1 and the sixth order governs F_2 . Because F_0 and F_1 have the most impor-

TABLE III. The cubic zero-field splittings of Fe^{3+} and Mn^{2+} ions in crystals.

Ions lattices	Mn^{2+} KZnF_3	Mn^{2+} RbCdF_3	Mn^{2+} MgO	Mn^{2+} CaO	Fe^{3+} MgO	Fe^{3+} CaO
B (cm^{-1})	830	825	800	800	480	480
C (cm^{-1})	3122	3136	3000	3000	3380	3380
Dq (cm^{-1})	822	715	1200	850	1340	1050
References	12	12	7		15-17	
ζ (cm^{-1})	320 ^a	320 ^a	280	280	430	430
	a (10^{-4} cm^{-1})					
Calc. ^b	6.93	4.77	18.5	5.53	197	66
c	6.6	4.6	16.2	5.3	188	69
d	6.99	4.96	17.3	5.5	194	67
Expt.	6.3(1)	4.7(2)	18.3(2)	5.6(2)	203.7	63.7
References of expt.	13	14	18-20	19,20	18	19,20

^aThat of RbMnF_3 , see Ref. 11.

^bCalculated by the diagonalization.

^cCalculated by the perturbation model.

^dCalculated by the semiempirical expression.

tance in the splitting, we calculate the fourth-order perturbation and the terms in ζ^5 of the fifth order.

In the calculation we neglect the coupling between 4T_1 and other spin quartets, for the reason remarked on in the preceding section. Only two processes are found to have an effect in the lowest order:

$${}^6A_1 \xrightarrow{H_{s.o.}} {}^4T_1 \xrightarrow{H_{s.o.}} {}^2T_2 \xrightarrow{H_{s.o.}} {}^4T_1 \xrightarrow{H_{s.o.}} {}^6A_1 ,$$

$${}^6A_1 \xrightarrow{H_{s.o.}} {}^4T_1 \xrightarrow{H_{s.o.}} {}^2E \xrightarrow{H_{s.o.}} {}^4T_1 \xrightarrow{H_{s.o.}} {}^6A_1 .$$

Other spin doublets, such as 2T_1 , 2A_1 , and 2A_2 , are

found to contribute nothing. This implies that the splitting comes mainly from the coupling of the ground state with the excited multiplets 4T_1 , 2T_2 , and 2E , consistent with the conclusion made in the preceding section.

The next order perturbation involves a large number of terms. To find the dominant ones among them we notice that ${}^2T_2(t_2^5)$ or ${}^2T_2(t_2e^4)$ has the lowest energy level ($15B + 10C - 20|Dq|$) in comparison with all other spin doublets. Processes involving the two terms should have an important effect and are only considered in our calculation.

With the use of the spin-orbit coupling matrices⁸ and the crystal-field matrices,¹⁰ it is obtained that

$$a = (\zeta^4/20) \left\{ \left[\frac{1}{E_1} + \frac{1}{E_2} \right]^2 \left[-\frac{8}{E_{11}} - \frac{2}{E_{12}} + \frac{1}{E_5} + \frac{1}{E_6} \right] + \left[\frac{1}{E_2} + \frac{1}{E_3} \right]^2 \left[-\frac{8}{E_{15}} - \frac{2}{E_{16}} + \frac{1}{E_8} + \frac{1}{E_9} \right] \right. \\ \left. + \left[\left[\frac{1}{E_1} + \frac{1}{E_3} \right]^2 - \frac{4}{(E_1^0)^2} \right] \left[-\frac{2}{E_{13}} + \frac{4}{E_{14}} + \frac{6}{E_7} \right] \right. \\ \left. + 24 \left[\frac{1}{E_1^2 E_4} + \frac{1}{E_3^2 E_{10}} - \frac{2}{(E_1^0)^2 E_4^0} \right] + \frac{8}{E_2 E_{13}} \left[\frac{2}{E_1^0} - \frac{1}{E_1} - \frac{1}{E_3} \right] \right. \\ \left. + \left[\frac{1}{E_1^0} + \frac{1}{E_2^0} \right]^2 \left[\frac{16}{E_{11}^0} + \frac{4}{E_{12}^0} - \frac{2}{E_5^0} - \frac{2}{E_6^0} \right] \right\} \\ + (\zeta^5/5) \left[12 \left[\frac{1}{E_1^2 E_4^2} - \frac{1}{E_3^2 E_{10}^2} \right] + \frac{2}{E_1 E_4} \left[\frac{1}{E_1} + \frac{3}{E_2} \right] \left[\frac{1}{E_5} + \frac{1}{E_6} \right] \right. \\ \left. - \frac{2}{E_3 E_{10}} \left[\frac{1}{E_3} + \frac{3}{E_2} \right] \left[\frac{1}{E_8} + \frac{1}{E_9} \right] \right] , \quad (13)$$

where E_i refer to the energy levels of the multiplets, measured from the ground 6A_1 state:

$$E_1 = E({}^4T_1, t_2^4({}^3T_1)e) = 10B + 6C + 12\alpha - 10Dq ,$$

$$E_2 = E({}^4T_1, t_2^3({}^2T_2)e^2({}^3A_2)) = 19B + 7C + 10\alpha ,$$

$$E_3 = E({}^4T_1, t_2^2({}^3T_1)e^3) = 10B + 6C + 12\alpha + 10Dq ,$$

$$E_4 = E({}^2T_2, t_2^5) = 15B + 10C + 22\alpha - 20Dq ,$$

$$E_5 = E({}^2T_2, t_2^4({}^3T_1)e) = 27B + 9C + 18\alpha - 10Dq ,$$

$$E_6 = E({}^2T_2, t_2^4({}^1T_2)e) = 17B + 9C + 22\alpha - 10Dq ,$$

$$E_7 = E({}^2T_2, t_2^3({}^2T_2)e^2({}^1A_1)) = 37B + 12C + 14\alpha ,$$

$$E_8 = E({}^2T_2, t_2^2({}^1T_2)e^3) = 17B + 9C + 22\alpha + 10Dq ,$$

$$E_9 = E({}^2T_2, t_2^2({}^3T_1)e^3) = 27B + 9C + 18\alpha + 10Dq ,$$

$$E_{10} = E({}^2T_2, t_2e^4) = 15B + 10C + 22\alpha + 20Dq ,$$

$$E_{11} = E({}^2E, t_2^4({}^1A_1)e) = 31B + 12C + 14\alpha - 10Dq ,$$

$$E_{12} = E({}^2E, t_2^4({}^1E)e) = 22B + 9C + 20\alpha - 10Dq ,$$

$$E_{13} = E({}^2E, t_2^3({}^2E)e^2({}^3A_2)) = E({}^2T_2, t_2^3({}^2T_1)e^2({}^3A_2)) = 19B + 8C + 26\alpha ,$$

$$E_{14} = E({}^2E, t_2^3({}^2E)e^2({}^1E)) = E({}^2T_2, t_2^3({}^2T_1)e^2({}^1E)) = 23B + 8C + 18\alpha ,$$

$$E_{15} = E({}^2E, t_2^2({}^1A_1)e^3) = 31B + 12C + 14\alpha + 10Dq ,$$

$$E_{16} = E({}^2E, t_2^2({}^1E)e^3) = 22B + 9C + 20\alpha + 10Dq ,$$

$$E_i^0 = E_i(Dq = 0) .$$

The inclusion of the Trees correction α in E_i is according to the work of Mehra.²³ It is easy to see that formula (13) satisfies the properties (5)–(10).

Table I shows the dependence of a on the cubic field strength, calculated by the perturbation formula. The results are excellent compared with the diagonalization calculations. The same case can be seen from the Table III, where an agreement between the calculated and the observed splittings of Mn^{2+} and Fe^{3+} doped crystals is displayed. This indicates that the obtained formula is reasonable in the interpretation of the cubic zero-field splitting of 6S -state ions.

IV. SEMIEMPIRICAL EXPRESSION

Although it is more convenient to be applied than the diagonalization, the obtained perturbation formula (13) is still tedious. The present section makes an attempt to simplify it semiempirically.

Comparison between Eq. (3) and formula (13) can obtain the expressions of F_0 and F_1 arising from the perturbation. It is easy to see that the leading term of F_0 is $6/5E_1^2E_4$ for $Dq > 0$ and $6/5E_3^2E_{10}$ for $Dq < 0$ while the main term of F_1 is $12/5E_1^2E_4^2$ for $Dq > 0$ and $-12/5E_3^2E_{10}^2$ for $Dq < 0$. This is not only because these terms include greater numerical coefficients than the others, but also, most importantly, because they involve much smaller denominators due to the lowest energy levels E_1 and E_4 of ${}^4T_1(t_2^4({}^3T_1)e)$ and ${}^2T_2(t_2^5)$ for $Dq > 0$, respectively, and E_3 and E_{10} of ${}^4T_1(t_2^2({}^3T_1)e^3)$ and ${}^2T_2(t_2e^4)$ for $Dq < 0$, respectively. Thus we may write

$$F_0 = \frac{1}{D_1^2 D_2} H_0, \quad F_1 = \frac{1}{D_1^2 D_2^2} H_1, \quad (14)$$

where D_1 is the energy of ${}^4T_1(t_2^4({}^3T_1)e)$ ($Dq > 0$) or ${}^4T_1(t_2^2({}^3T_1)e^3)$ ($Dq < 0$), and D_2 that of ${}^2T_2(t_2^5)$ ($Dq > 0$) or ${}^2T_2(t_2e^4)$ ($Dq < 0$), in the strong-field approximation:

$$D_1 = 10B + 6C + 12\alpha - \Delta, \quad D_2 = 15B + 10C + 22\alpha - 2\Delta, \quad (15)$$

with

$$\Delta = 10|Dq|, \quad (16)$$

and H_0 and H_1 are functions of B , C , and Dq .

The accurate expressions of H_0 and H_1 are considerably difficult to be found. On the contrary, their approximate expressions can be easily obtained empirically by comparing (14) with diagonalization calculations. As a result we have

$$H_0 \approx \frac{3\Delta - C}{10(B + C)}, \quad H_1 \approx \pm \frac{B}{100}, \quad (17)$$

and, correspondingly,

$$a \approx \frac{\zeta^4}{10D_1^2 D_2} \left[\left[\frac{3\Delta - C}{B + C} \right] \pm \left[\frac{\zeta B}{10D_2} \right] \right], \quad (18)$$

where the plus and the minus symbols apply to $Dq > 0$ and $Dq < 0$, respectively.

With the use of the semiempirical expression (18), we

have calculated the splitting dependence on Dq and the splitting parameters of Mn^{2+} and Fe^{3+} ions in several lattices, as shown in Tables I and III, respectively. It can be seen that the results are in better agreement with those evaluated by the diagonalizations than the results calculated by the perturbation formula in the Dq range of practical interest. This suggests that the observed semiempirical expression of a is applicable as a very good approximation of an accurate calculation in the investigation of the ground-state splitting of 6S -state ions in cubic fields.

V. PRESSURE DEPENDENCE FOR Mn^{2+} AND Fe^{3+} IONS IN MgO LATTICE

The cubic zero-field splitting of Mn^{2+} and Fe^{3+} ions substituted as impurities in MgO crystal has been observed by Walsh¹⁸ at different hydrostatic pressures. It has been found that a increases linearly with increasing pressure P , processing variation coefficient $\partial \ln a / \partial P = 4.03 \times 10^{-6} \text{ kbar}^{-1}$ for both crystals at room temperature, and in the range $P \leq 10 \text{ kbar}$. We now try to explain this.

The crystal will be concentrated under applied pressure, resulting in changes in crystal-field parameter Dq and in B , C , and ζ and, therefore, in the splitting parameter a . The induced changes in B , C , and ζ are usually negligible for those ionic crystals compared with the change in Dq that is known to depend on the interatomic distance R of the substituted crystals very sensitively.²⁴ In a small range of R , one may write

$$Dq = KR^{-n}, \quad (19)$$

where K and n , positive numbers, are independent of R . A recent study of Rodrguez and Moreno¹² on the MnF_6^{4-} system indicated n being 4.4, which is slightly less than $n=5$ of ionic crystalline field model. From (19) it follows that

$$(\partial \ln a / \partial P)_T = \frac{1}{3} n \beta \mu, \quad (20)$$

where

$$\beta = -\frac{3}{R} (\partial R / \partial P)_T, \quad \mu = (\partial \ln a / \partial \ln Dq). \quad (21)$$

β is the local compressibility of the crystal in the vicinity of the magnetic impurity.

The pressure variation coefficient $(\partial \ln a / \partial P)_T$ can now be calculated theoretically by adopting formulas (20) and (21) and by using the analytical expressions of a , (13) and (18), or the diagonalization method. Listed in the Table IV are the results of $\text{Mn}^{2+}:\text{MgO}$ and $\text{Fe}^{3+}:\text{MgO}$, calculated under the simple assumption of ionic crystalline potential ($n=5$) and that the local compressibility of the crystals in the vicinity of the magnetic impurities is unchanged from that of the host crystal. We see that the values obtained by the diagonalization and by the semiempirical expression are almost identical. The agreement between the calculated and the observed results is satisfactory. Table IV also lists the predicted pressure variation coefficients of a of Fe^{3+} and Mn^{2+} in CaO . In the calculation, the parameters B , C , Dq , and ζ have been

TABLE IV. The pressure variation coefficients of the cubic zero-field splittings of Mn^{2+} and Fe^{3+} ions in MgO and CaO crystals, calculated under the assumption that the local compressibility in the vicinity of a magnetic impurity is unchanged from that of the host lattice.

Crystals	β (10^{-4} kbar $^{-1}$)	μ		$\left[\frac{\partial \ln a}{\partial P} \right]_{T=300 \text{ K}}$		$(10^{-6}$ kbar $^{-1}$)
	observed (Ref. 25)	calc.	calc.	calc.	observed (Ref. 18)	
$\text{Mn}^{2+}:\text{MgO}$	5.9	4.28 ^a	4.17 ^b	3.71 ^a	3.61 ^b	4.03
$\text{Mn}^{2+}:\text{CaO}$	8.4	2.92	2.73	4.01	3.82	
$\text{Fe}^{3+}:\text{MgO}$	5.9	5.50	5.38	4.77	4.66	4.03
$\text{Fe}^{3+}:\text{CaO}$	8.4	3.63	3.60	5.08	5.04	

^aCalculated by the diagonalization with the reduced matrices.

^bCalculated by the semiempirical model.

taken from Table III that fit the optical spectra, and the a observed at normal pressure and the values of β are taken from Ref. 25.

The values of $(\partial \ln a / \partial P)_{T=300 \text{ K}}$ have been observed to be identical for both $\text{Fe}^{3+}:\text{MgO}$ and $\text{Mn}^{2+}:\text{MgO}$.¹⁸ This thus requires, as can be seen from (20), the values of μ for both to be identical if the local compressibility in the vicinity of the substitutional ions are unchanged from that of the host lattice and if both crystalline potentials follow the same power law. However, $\mu(\text{Fe}^{3+})$ is calculated to be greater than $\mu(\text{Mn}^{2+})$ by about 30%. This suggests three possibilities: (1) $n(\text{Fe}^{3+})=n(\text{Mn}^{2+})$ but $\beta(\text{Fe}^{3+}) \neq \beta(\text{Mn}^{2+})$, (2) $\beta(\text{Fe}^{3+})=\beta(\text{Mn}^{2+})$ but $n(\text{Fe}^{3+}) \neq n(\text{Mn}^{2+})$, and (3) $n(\text{Fe}^{3+}) \neq n(\text{Mn}^{2+})$ and $\beta(\text{Fe}^{3+}) \neq \beta(\text{Mn}^{2+})$. If the point-charge model operates very well for both crystals, $n(\text{Fe}^{3+})=n(\text{Mn}^{2+})=5$, the compressibility β of the substituted crystal $\text{Fe}^{3+}:\text{MgO}$ should be smaller than that of the host lattice by about 15% whereas that of $\text{Mn}^{2+}:\text{MgO}$ larger by an amount of 10%. On the other hand, if the compressibilities of the substituted crystals are unchanged from that of the host lattice MgO,

$$\beta(\text{Fe}^{3+})=\beta(\text{Mn}^{2+})=5.2 \times 10^{-4} \text{ kbar}^{-1}$$

(Ref. 25), $n=4.3$ and 5.4 could be obtained for $\text{Fe}^{3+}:\text{MgO}$ and for $\text{Mn}^{2+}:\text{MgO}$, respectively, the first being comparable with $n=4.4$ obtained in MnF_6^{4-} system by Rodrguez and Moreno.¹² Studies on the exponent n will be highly helpful for understanding the changes in the compressibility of the host crystal when it is doped with the impurities.

The uncertainties of the parameters Dq and ζ will change slightly the calculated μ and therefore $\partial \ln a / \partial P$, but do not influence the conclusion made above. It can be verified that a remarkable change in ζ will induce a change in μ very slight and that the μ value for a given value of ζ is little different from that at $\zeta=0$. For instance, when changing the value of ζ from 0 to 500 cm^{-1} , the value of μ goes from 4.14 to 4.19, for $B=800$, $C=3000$, and $Dq=1200 \text{ cm}^{-1}$. Thus one has, from (18),

$$\mu(\zeta) \approx \mu(\zeta=0) = \left[2 \left(\frac{1}{D_1} + \frac{1}{D_2} \right) + \frac{1}{\Delta - C/3} \right] \Delta, \quad (22)$$

where D_1 and D_2 are defined in (15). This indicates a sensitive dependence of μ on Dq . Plotted in Fig. 2 is the

dependence of a and μ on Dq , for $B=800$, $C=300$, and $\zeta=280 \text{ cm}^{-1}$ (suitable for Mn^{2+} ions in MgO, CaO, and SrO crystals). It can be seen that one must use Dq of about 1400 cm^{-1} for $\text{Mn}^{2+}:\text{MgO}$ in order to make its μ value equal to 5.5 of $\text{Fe}^{3+}:\text{MgO}$. This unreasonable value of Dq is too large to fit the optical spectra and the ground-state splitting at normal pressure. Therefore, it is impossible to obtain an identically theoretical value of $(\partial \ln a / \partial P)_T$ for Fe^{3+} and Mn^{2+} in MgO unless one assumes $n(\text{Fe}^{3+}) \neq n(\text{Mn}^{2+})$ or $\beta(\text{Fe}^{3+}) \neq \beta(\text{Mn}^{2+})$.

VI. DISCUSSIONS

A. The power law of a

It has been assumed empirically that^{26,27}

$$a = AR^{-m}, \quad (23)$$

where A and m are positive numbers and are independent of the distance R between the magnetic cation and the nearest-neighbor anions. Because of (19), it is

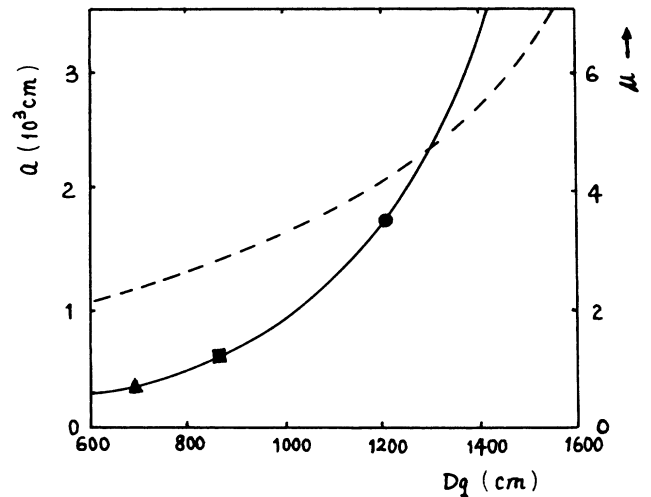


FIG. 2. The Dq dependences of a (—) and μ (---), calculated by assuming $B=800 \text{ cm}^{-1}$, $C=3000 \text{ cm}^{-1}$, and $\zeta=280 \text{ cm}^{-1}$. The experimental values for Mn^{2+} ions in MgO (●), CaO (■) and SrO (▲) are also shown.

equivalent to the assumption

$$a = A' \Delta^{-k} \quad (24)$$

in which positive numbers A' and k are unrelated with Δ . A comparison between these two power laws of a obtains

$$m = kn, \quad (25)$$

n being defined in (19).

The power-law exponent m was reported to be 12 ± 4 by Newman and Siegel²⁶ for $\text{Fe}^{3+}:\text{KNbO}_3$ and 7 by Müller²⁷ for Fe^{3+} ions in lattices having O^{2-} as ligands. Practically, the power law (23) cannot account for the experimental data unless the assumption is made that the interatomic distances are different from those of the host lattices.^{27,28} This assumption is understandable since the radii of the magnetic impurities differ from those of the substituted cations,²⁸ as has been verified by the x-ray absorption fine-structure experiments.²⁹ Rubio *et al.*²⁸ have assumed $m = 12 \pm 1$ to determine the values of R of fluoroperovskites doped with Mn^{2+} and Fe^{3+} ions from the observed cubic zero-field splittings, and the results for Mn^{2+} are consistent with those obtained by Barriuso and Moreno³⁰ from the isotropic superhyperfine constants.

If (23) and (24) can hold as general laws, one will have

$$k = \partial \ln a / \partial \ln Dq = \mu, \quad (26)$$

$$m = n\mu. \quad (27)$$

As shown in Eq. (22) and in Fig. 2, the μ is a sensitive function of Dq and therefore depends on R sensitively. So the power-law exponent m in (23) is actually related with R and k in (24) with Δ . This enables one to conclude that the power laws of a do not hold as general laws.

Thus we do not expect that reasonable results can be obtained by a fixed m for crystals in which the values of R or a are spread remarkably. However, in the case where crystals have Dq or a values close to each other, the power law (23) with an exponent m given by (27) is reasonable for accounting for the experimental data. In particular, for the lattices having Dq smaller than and around the Racah parameter B , the μ varies slowly with Dq and therefore the power law is expected to work quite well. As an example, we consider here the fluoroperovskites doped with Mn^{2+} ions, in which it has been found experimentally $B = 825 \pm 5$, $C = 3135 \pm 15$, and $Dq = 770 \pm 55$, in units of cm^{-1} .²² From Eq. (22) we have $\mu = 2.50 \pm 0.2$. This corresponds to $m = 11 \pm 1$ by $n = 4.4$ (Ref. 12) and to 12.5 ± 1 by $n = 5$ of the point-charge model. The latter is more consistent with $m = 12 \pm 1$ used empirically by Rubio *et al.*²⁸

Since both a and μ increase with increasing Dq (see Fig. 2), a crystal with a greater a processes a larger μ and therefore a larger m . It can be seen from Fig. 2 that, for $n = 5$, $m = 21$ for $\text{Mn}^{2+}:\text{MgO}$ ($a = 18.3 \times 10^{-4} \text{ cm}^{-1}$), 14 for $\text{Mn}^{2+}:\text{CaO}$ ($a = 5.6 \times 10^{-4} \text{ cm}^{-1}$) and 12 for $\text{Mn}^{2+}:\text{SrO}$ ($a = 3 \times 10^{-4} \text{ cm}^{-1}$). For Mn^{2+} -containing octahedral lattices having Dq smaller than or around B , taking M being 12 ± 2 is reasonably expected to be able to account for the observed splittings very well.

B. The odd-parity crystal-field effect

So far, our attention was focused on the splitting in octahedral coordinations. We have shown that it and its pressure dependence can be understood very well by the simple crystal-field theory. We now turn our attention on the crystals having tetrahedral coordinations.

In this case the parameter Dq is small in magnitude and negative in sign. From the theory presented in Sec. II, one expects small ground-state splittings. For instance, $\text{ZnS}:\text{Mn}^{2+}$ has a B of 405 cm^{-1} , C of 3437 cm^{-1} , and Dq of -575.2 cm^{-1} .³¹ Due to a stronger covalency effect this crystal is expected to have a spin-orbit interaction constant ζ less than 280 cm^{-1} of $\text{Mn}^{2+}:\text{MgO}$ or $\text{Mn}^{2+}:\text{CaO}$, the latter having a Dq value of 850 cm^{-1} (see Table III); we estimate $\zeta = 250 \text{ cm}^{-1}$. From these data one may expect a smaller splitting parameter a for $\text{Mn}^{2+}:\text{ZnS}$ than $a = 5.6 \times 10^{-4} \text{ cm}^{-1}$ observed in $\text{Mn}^{2+}:\text{CaO}$.²⁰ Calculation according to (18) yields $a = 1.5 \times 10^{-4} \text{ cm}^{-1}$. On the contrary, the experimental value is $7.9 \times 10^{-4} \text{ cm}^{-1}$,¹⁸ greater than that of $\text{Mn}^{2+}:\text{CaO}$. The calculated value is less than the experimental value by a factor of about 5. The experimental value cannot be accounted for by the theory presented in preceding sections unless one takes $\zeta = 380 \text{ cm}^{-1}$, a value greater than the free-ion one, 340 cm^{-1} .

A similar situation exists in other tetrahedral crystals. The crystal $\text{Mn}^{2+}:\text{ZnSe}$ is expected to have a smaller value of Dq and therefore a smaller value of a than those of $\text{Mn}^{2+}:\text{ZnS}$. On the contrary, it is found experimentally that a is $19.7 \times 10^{-4} \text{ cm}^{-1}$ in this crystal,³² two times larger than $7.9 \times 10^{-4} \text{ cm}^{-1}$ observed in $\text{Mn}^{2+}:\text{ZnS}$ (Ref. 18), and even greater than $18.3 \times 10^{-4} \text{ cm}^{-1}$ found in $\text{Mn}^{2+}:\text{MgO}$.¹⁹ Other examples are $a = 27 \times 10^{-4} \text{ cm}^{-1}$ of $\text{Mn}^{2+}:\text{CdTe}$,³³ $30 \times 10^{-4} \text{ cm}^{-1}$ of $\text{Mn}^{2+}:\text{ZnTe}$,³² $128 \times 10^{-4} \text{ cm}^{-1}$ of $\text{Fe}^{3+}:\text{ZnS}$,³⁴ and $96 \times 10^{-4} \text{ cm}^{-1}$ of $\text{Fe}^{3+}:\text{CdS}$.³⁵

This implies another mechanism that exists only in tetrahedral fields and that gives rise to a much greater positive contribution to a than that calculated from the simple crystal-field theory presented in preceding sections. A significant difference between tetrahedral and octahedral fields is that the former has an odd-parity field component, which will bring a mixing between the ground configuration $3d^5$ and the excited configurations of odd parity such as $3d^4 4p$, $3d^4 4f$, $3d^4 5p$, etc. However, the effect of the odd-parity field through the mixing can be regarded as an equivalent even-parity field acting on the ground configuration $3d^5$, so that this effect has actually been taken into account when the Dq is treated as a parameter adjusted from the optical spectra, as is shown below.

A tetrahedral field contains two parts: one is of even parity and another is of odd parity:

$$V = \sum_{k,q} A_q^k D_q^k = V(\text{even}) + V(\text{odd}). \quad (28)$$

The effect of $V(\text{odd})$ on the energies of multiplets of $3d^5$ configuration can be calculated successfully by means of the perturbation theory. To the lowest order, this effect may be expressed as

$$\sum_{\psi_{\text{odd}}} \frac{\langle 3d^5 LSM_L M_S | V(\text{odd}) | \psi_{\text{odd}} 3d^4 nl' \rangle \langle \psi_{\text{odd}} 3d^4 nl' | V(\text{odd}) | 3d^5 L' S' M'_L M'_S \rangle}{E_{3d} - E_{\text{odd}}}, \quad (29)$$

where $nl' = 4p, 4f, 5p, 5f$, etc. The energy separations $E_{\text{odd}} - E_{3d}$ are of order of 10^5 cm^{-1} and can be approximated averagely as one energy ΔE so that (29) can be written as³⁶

$$\langle 3d^5 LSM_L M_S | V_{\text{eq}} | 3d^5 L' S' M'_L M'_S \rangle \quad (30)$$

with

$$V_{\text{eq}} = -\frac{1}{\Delta E} \sum_{\psi_{\text{odd}}} V(\text{odd}) | \psi_{\text{odd}} 3d^4 nl' \rangle \langle \psi_{\text{odd}} 3d^4 nl' | V(\text{odd}). \quad (31)$$

The equivalent crystal-field V_{eq} is given by³⁶

$$V_{\text{eq}} = \sum_{K, Q} A_Q^K D_Q^K, \quad (32)$$

where

$$A_Q^K = \sum_{t, k, p, q} (-1)^{p+q+1} (2k+1)(2l'+1) \begin{Bmatrix} k & K & t \\ q & -Q & p \end{Bmatrix} \begin{Bmatrix} k & K & t \\ l & l' & l \end{Bmatrix} \\ \times \begin{Bmatrix} l & k & l' \\ 0 & 0 & 0 \end{Bmatrix} \begin{Bmatrix} l' & t & l \\ 0 & 0 & 0 \end{Bmatrix} \begin{Bmatrix} l & K & l \\ 0 & 0 & 0 \end{Bmatrix}^{-1} \frac{\langle r^k \rangle_{dl'} \langle r^t \rangle_{dl'}}{\langle r^K \rangle_{dd}} \frac{A_q^k A_p^t}{E_{\text{odd}} - E_{3d}}, \quad (33)$$

where k and t take odd numbers. Apparently, V_{eq} is of even parity and has the same angular dependence as the $V(\text{even})$ given in (28). Therefore, the crystal-field V given by (28) is equivalent to $V(\text{even}) + V_{\text{eq}}$, where V_{eq} is given by (32) and (33), and $V(\text{even}) + V_{\text{eq}}$ has identical matrix elements in form with $V(\text{even})$ in $3d^5$ configuration. Consequently, the crystal-field parameter $Dq = Dq(\text{even}) + Dq(\text{odd})$, where $Dq(\text{even})$ comes from $V(\text{even})$ and $Dq(\text{odd})$ from V_{eq} or, equivalently, from $V(\text{odd})$. A Dq parameter adjusted from the optical spectra is the sum of $Dq(\text{even})$ and $Dq(\text{odd})$ rather than one of them. Thus the contribution to a due to $V(\text{even})$ and that due to $V(\text{odd})$ can be all taken into account by treating Dq as a parameter adjusted from the optical spectra. One is unable to distinguish $Dq(\text{odd})$ from the total value of Dq and a coming from $V(\text{odd})$ from the total value of a by means of experiment. A similar discussion is suitable for the effect of the configuration interaction through the even-parity field $V(\text{even})$.

We have shown that the odd-parity field does not constitute a new mechanism. It contributes to Dq and therefore to a in the same way as the even-parity field does; its contribution to a has actually been taken into account when Dq is treated as an adjustable parameter although this contribution is indistinguishable from the total value by experiment.

The significant disagreement between the theory and the experiments remarked at the beginning of this subsection shows a failure of the current crystal-field theory in the interpretation of the cubic zero-field splitting of ${}^6S(d^5)$ ions in tetrahedral fields. The splitting in this case should be mainly due to other effect. It is noted that the mentioned tetrahedral crystals are II-VI compounds. In them strong covalence bonding exists between the central cation and the nearest anions. The covalency effect has

been known to be one of the origins of the splitting of the excited states ${}^4E(G)$ and ${}^4A_1(G)$ of a $3d^5$ ion, whose levels are degenerate according to the current crystal-field theory (see, e.g., Ref. 37). This effect is possibly one of the main origins of the cubic zero-field splittings of 6S -state ions in tetrahedral fields.

VII. CONCLUSIONS

We note the following.

(i) The simple crystal-field theory that regards the Coulomb interaction, the crystal field, and the spin-orbit coupling as the total Hamiltonian in d^5 configuration is successful in the interpretation of the cubic zero-field splitting and their pressure dependence of 6S -state ions in regular octahedral coordinates.

(ii) The splitting arises predominantly from the coupling among the multiplets 6A_1 , 4T_1 , 2T_2 , and 2E via the spin-orbit interaction, making it possible to reduce effectively the matrices of the Γ_7 and Γ_8 representations from 22×22 and 42×42 dimensions to 14×14 and 24×24 , respectively.

(iii) The splitting parameter a can be expressed as $F_0 \zeta^4 + F_1 \zeta^5$ to a very good approximation. Approximate analytical expressions of F_0 and F_1 have been given by a perturbation approach and by a semiempirical model.

(iv) The power law of a is reasonable to account for the experimental data for a system having Dq or a close to each other, although the power-law exponent m actually depends on the interatomic distance. In particular, $m = 12 \pm 2$ is theoretically reasonable for Mn^{2+} -containing crystals having $Dq \lesssim B$.

(v) The simple crystal-field theory is not capable of explaining the splittings in tetrahedral fields. The covalency effect seems to be most important in this case.

Our attention of the present work has been focused only on the regular cubic situations. For crystals of low symmetries, the cubic zero-field splitting parameter a should be perturbed by the low symmetric components of the crystal field, although this effect is expected to be small. Finally, the negative splitting parameters observed in less of crystals,^{38,39} have not been discussed here. This

cannot be explained by the present work. These problems await further studies.

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