

Cubic zero-field splitting and site symmetry of Mn^{2+} in ZnS

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(Received 7 June 1990; revised manuscript received 10 September 1990)

Serious difficulties exist in explaining the cubic zero-field splitting (ZFS) of $d^{5-6}S$ ions, such as Mn^{2+} and Fe^{3+} , with the crystal-field theory. The calculated cubic ZFS values are always much smaller than the experimental results. Low and Rosengarton have concluded that the crystal-field theory is not capable of providing a unified explanation for the cubic ZFS and spectrum of $d^{5-6}S$ ions, unless a spin-orbit-coupling parameter ζ , larger than that found in free ions, is used. In the present paper, a unified theoretical explanation is presented for the spectrum and cubic ZFS of ZnS:Mn^{2+} , by diagonalizing a group of complete, strong-field-energy matrices of the d^5 configuration. The theoretical predictions are in very good agreement with observations, so that the above-mentioned conclusion made by Low and Rosengarton can be refuted. Moreover, it is proved that the difficulties met by Gabriel, Johnston, and Powell in explaining the cubic ZFS of $d^{5-6}S$ ions are entirely due to an incorrect relative phase relationship between the cubic field parameter Dq and the spin-orbit coupling parameter ζ in their method. The results of the present paper show that the Mn^{2+} ions seem to be coordinated by a double shell of $4\text{Zn} + 6\text{S}$ ions instead of a single shell of 4S .

In the last three decades much work¹⁻⁸ has been devoted to the research of the spectrum and paramagnetic properties of ZnS:Mn^{2+} . However, serious difficulties have existed in explaining the cubic zero-field splitting (ZFS) of $d^{5-6}S$ ions, such as Mn^{2+} and Fe^{3+} , with crystal-field theory. For example, the cubic ZFS values calculated by Gabriel, Johnston, and Powell⁹ (GJP) and Low and Rosengarton⁸ (LR) were always much smaller than the observed values, so that they concluded that crystal-field theory is not capable of providing a unified explanation for the cubic ZFS and spectrum of $d^{5-6}S$ ions. Recently, a similar conclusion was reached by Yu,¹⁰ i.e., the crystal-field theory is not capable of explaining the cubic ZFS of $d^{5-6}S$ impurity ions in crystals having tetrahedral structure, such as the Mn^{2+} in ZnS .

The aim of the present work is to give a unified analysis of the cubic ZFS and spectrum of ZnS:Mn^{2+} by a strict complete calculation within a strong-field representation, so as to examine whether the crystal-field theory has really become invalid for such problems. The calculations are based on diagonalizing a group of complete strong-field-energy matrices of the d^5 configuration. The steps and results are as follows.

The first step is to derive the energy matrices, which should involve the cubic-crystal field and the spin-orbit coupling, based on the d^5 -electrostatic matrices given by Tanabe and Sugano¹¹ and the spin-orbit-coupling matrices given by Schroeder.¹² The result is just the

irreducible-representation matrices of the double group O^*/T_d^* , i.e., $E'(20 \times 20)$, $E''(22 \times 22)$, $U'(42 \times 42)$. Each matrix element is a polynomial of the spectral parameters, i.e., the cubic-crystal-field parameter Dq , the Racah parameters B and C and the spin-orbit-coupling parameter ζ . The spectrum and the ground state ZFS of the d^5 ions are determined by the eigenvalues of the matrices, while the cubic ZFS parameter a is determined by

$$3a = E_{\min}(U') - E_{\min}(E'') . \quad (1)$$

The second step is to check the matrices according to Schroeder's method.¹² The results are the 84 eigenvalues reduce to 5 degenerate levels if $B = C = Dq = 0$ but $\zeta \neq 0$; they reduce to 16 if $Dq = \zeta = 0$ but $B \neq 0$ and $C \neq 0$; and they reduce to 42 (including an occasional twofold degeneracy level) if $\zeta = 0$ but $B \neq 0$, $C \neq 0$, and $Dq \neq 0$. This shows the matrices are exactly correct.

The third step is to check the Dq dependence of the parameter a . It is known that Powell, Gabriel, and Johnston¹³ (PGJ) obtained an $a \sim Dq$ relation as shown in Table I and that the method used is just the one used in the work of GJP.⁹ Our result is that, if the values of B , C , and ζ used by PGJ¹³ are used in our matrices, the $a \sim Dq$ relation obtained will be just identical with the $a \sim (-Dq)$ relation of PGJ (cf. Table I). Therefore, if Dq and ζ are written as Dq' and ζ' in our matrices and Dq''

TABLE I. Dependences of cubic ZFS $3a$ (in 10^{-4} cm^{-1}) of d^5 - $6S$ ions on the cubic field parameter Dq , with $B=900$, $C=3300$, and $\zeta=400$ (in cm^{-1}).

Dq (cm^{-1})	This work	Powell, Gabriel, and Johnston (Ref. 13)
1200	117.0	80.2
1000	63.59	42.1
800	34.42	21.1
600	17.65	9.45
400	7.860	3.06
200	2.401	0.178
0	0	0
-200	0.1778	2.4
-400	3.063	7.86
-600	9.453	17.7
-800	21.18	34.4
-1000	42.06	63.6
-1200	80.26	117

and ζ'' in the PGJ method, one can see that

$$\zeta' = \zeta'' \quad \text{and} \quad Dq' = -Dq''$$

$$\text{or} \quad \zeta' = -\zeta'' \quad \text{and} \quad Dq' = Dq'' ,$$

in consideration that a simultaneous changing of the signs of Dq and ζ does not change the splittings calculated for d^5 systems. This shows, on the one hand, the phase relationship between Dq and ζ in our matrices is different from that in PGJ method, on the other hand, our matrices are as correct as the PGJ formulas as long as such a phase relationship is left aside. However, the phase relationship is very important here so that we must make clear which one is correct, PGJ's or ours. In our matrices the usual definition of Dq and ζ is adopted, i.e.,

$$10Dq = E(e_g) - E(t_{2g}) , \quad (2)$$

$$\zeta = \int_0^\infty R_{nd}^2 \xi(r) r^2 dr , \quad (3)$$

where

$$\xi(r) = \frac{-e}{2m^2c^2} \left[\frac{1}{r} \frac{\partial V(r)}{\partial r} \right] . \quad (4)$$

Therefore, in calculating the energies of electron systems, we have $Dq > 0$ for octahedral crystal fields and $Dq < 0$ for tetrahedral fields whereas $\zeta > 0$ for both cases; while in calculating energies of hole systems, we have $Dq < 0$ for octahedral fields and $Dq > 0$ for tetrahedral fields whereas $\zeta < 0$ for both cases. If the signs of both Dq and ζ are changed, the eigenvalues of the matrices will remain unchanged. This reflects the fact that a d^5 system can be regarded as either five electrons (electron model) or five holes (hole model). All these results are consistent with the standard viewpoint. Thus we can conclude that the phase relationship between Dq and ζ in our method is correct and that in PGJ's is incorrect. This conclusion is

strengthened by the fact that Kuang and Cheng¹⁴ recently found, by diagonalizing a complete weak-field matrix, that the sign of Dq in the PGJ method is incorrect. This was later confirmed by Yu.¹⁰

The fourth step is to calculate the spectrum and the a value of ZnS:Mn^{2+} . At first we adopted the values of Dq (negative), B , and C used by Pohl, Gumlich, and Busse⁶ and Kushida, Tanaka, and Oka⁷ in their spectral analysis based on a tetrahedral model of the Mn^{2+} ions. We adjusted the value of ζ but kept it smaller than that of ζ_0 (347 cm^{-1}) of a free Mn^{2+} ion. The result showed that the calculated a values are much smaller than the observed value of $7.97 \times 10^{-4} \text{ cm}^{-1}$, as shown by the curves II and III in Fig. 1. Then we adjusted all the parameters ζ (still keeping $\zeta < \zeta_0$), B , C , and Dq but still keeping $Dq < 0$ (i.e., tetrahedral symmetry). But we were unable to make simultaneously the spectrum and the a value consistent with the observed results. If the spectrum was made to agree with the observed result, the a value would be much smaller than the observed value, unless the sign of Dq was reversed, as shown in Fig. 1 (cf. curve I). Finally, we determined (in cm^{-1})

$$B = 791, \quad C = 2740, \quad Dq = +600, \quad \zeta = 343 . \quad (5)$$

From this, the calculated spectrum and the a value are in very good agreement with the observed result, as can be seen in Table II.

However, as indicated above, the result $Dq > 0$ and $\zeta > 0$ means the crystal field surrounding the Mn^{2+} ions is an octahedral one produced by 6 negative ligands. Of course, a tetrahedral field produced by 4 positive coordination ions is also possible, because it is identical to the former in determining the energy order of d orbitals. We can conclude that the Mn^{2+} ions seem to be coordinated by a double shell of $4\text{Zn} + 6\text{S}$ ions but do not replace the Zn ions, as shown in Fig. 2. Such a crystal field seems to have some distortion, making the number of fine structures of the observed absorption bands much larger than

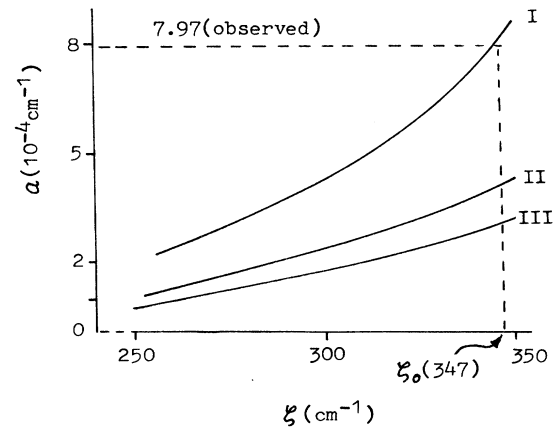


FIG. 1. Dependences of the cubic zero-field splitting parameter a on the spin-orbit-coupling parameter ζ . I: $B=791$, $C=2740$, $Dq=+600$ (this paper). II: $B=630$, $C=3040$, $Dq=-600$ (Ref. 7). III: $B=405$, $C=3437$, $Dq=-575.2$ (Ref. 6).

TABLE II. The spectrum (cm^{-1}) and the parameter a (10^{-4}cm^{-1}) of $\text{ZnS}:\text{Mn}^{2+}$.

Calc. ^a	Observed 1 ^b	Observed 2 ^c
E'' 17259	17914 (17891)	18631
U' 17288	17926	
U' 17351	17999	
E' 17401	18205	
	18257	
	18297	
E'' 20305	19693 (19683)	20083
U' 20372	19782	
E' 20492	19870	
U' 20499	19989	
	20032	
	20078	
	20116	
	20161	
	20239	
	20259	
	20282	
	20369	
U' 21593	21244 (21237)	21454
E'' 21601	21327	
E' 21615	21416	
U' 21617	21432	
	21540	
	21622	
	21711	
	21803	
	21843	
	21933	
	22143	
E'' 23039	22638 (22638)	23390
U' 23569	22724	
	22803	
	22977	
	23030	
	23107	
	23213	
	23280	
	23410	
U' 25535	25297 (25297)	25648
E' 25570	25383	
U' 25830	25644	
E'' 25943	25775	
	25896	

$$a = 7.84$$

$$a = 7.97^d$$

^a $B = 791$, $C = 2740$, $Dq = +600$, $\zeta = 343$ (cm^{-1}).

^bAt $T = 77$ K with $\text{ZnS}:\text{Mn}$ (0.8%). The values in the parentheses are zero-phonon absorptions.

^cAt room temperature with $\text{ZnS}:\text{Mn}$ (3%).

^dBy Walsh (Ref. 5).

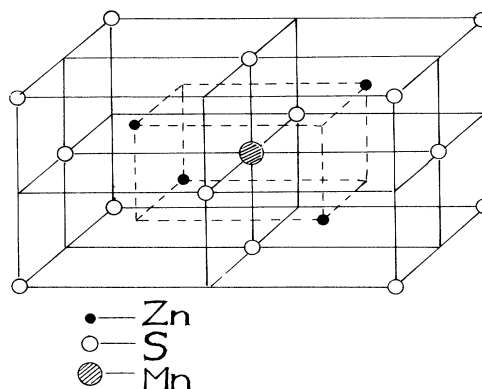


FIG. 2. A possible site of the Mn^{2+} ions in ZnS .

the one permitted by our matrices (cf. Table II).

Now, we have reached a unified explanation for the spectrum and the cubic ZFS of $\text{Mn}^{2+}:\text{ZnS}$ by the crystal-field theory. The optical and magnetic properties can both be attributed to the synthetic effect of the distorted twofold crystal field and the spin-orbit coupling of the Mn^{2+} ions within the d^5 configuration.

Of course, the conclusion of the doubly coordinated site of the Mn^{2+} must be examined by further experiments. Since the strictness of our calculation leaves no room for compromise between various coordination structures, such an examination will perhaps be a decisive one for the effectiveness of the crystal-field theory.

It is interesting to note that similar situations have been found in our recent investigations for $\text{ZnS}:\text{Cr}^{2+}$ and $\text{CdS}:\text{Cr}^{2+}$. The results will be published elsewhere.

It is especially worthwhile to indicate that Goede *et al.*^{15,16} have recently found that pure MnS can have either a tetrahedral or octahedral coordination structure, depending on the crystallizing temperature, and that heat treatment can lead to a transition from the tetrahedral to octahedral phase. Again they have indicated¹⁶ that MnS occurs as a stable octahedral structure in rocksalt and that tetrahedrally coordinated MnS can be obtained only by low-temperature growing techniques. We think this is strong support to our twofold crystal-field model for Mn^{2+} in ZnS .

As for why GJP⁹ have been unable to explain the cubic ZFS of d^5 S ions, it is just due to the incorrect phase relationship between Dq and ζ in the PGJ method,¹³ which is adopted in their calculation. This incorrectness makes their method reflect neither hole nor electron model in treating practical problems. That is to say, a significant error has existed in their method all along. For example, they had determined, by fitting the observed spectrum and ZFS, that

$$B = 900, \quad C = 3300, \quad \zeta = 400, \quad Dq = -600 \quad (\text{cm}^{-1})$$

for $\text{Mn}^{2+}:\text{ZnS}$,

$$B = 900, \quad C = 3300, \quad \zeta = 400, \quad Dq = +1050 \quad (\text{cm}^{-1})$$

for $\text{Mn}^{2+}:\text{MgO}$,

where ζ is unusually larger than that for free Mn^{2+} ions.

It can be seen from the sign and magnitude of the values of Dq that they regarded the crystal-field symmetry as tetrahedral for $Mn^{2+}:ZnS$ and octahedral for $Mn^{2+}:MgO$. However, since the relative phase relationship between the phase factors of their Dq and ζ is incorrect, the practical symmetries reflected by the two sets of parameter values are just the opposite ones. Therefore, this example shows, exceeding PGJ's expectation, that the site symmetry of the Mn^{2+} ions is octahedral with negative ligands or tetrahedral with positive ligands

instead of tetrahedral with negative ligands, and thus agrees with our point of view.

As for the difficulty of Yu¹⁰ mentioned above, it can be attributed to the incorrect tetrahedral model that he suggested for the Mn^{2+} ions.

The authors are indebted to Associate Professor Zheng Wen-Chen for helpful discussions. This project was supported by National Natural Science Foundation of China.

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