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Reply to "Comment on 'Cubic zero-field splitting and site symmetry of Mn^{2+} in ZnS'"

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Six different numerically best-fitting sets of assignments of both the spectrum and the cubic zero-field splitting of Mn^{2+} in ZnS are given and compared. It is shown that among them, only the one previously adopted in the work of Zhou, Zhao, and Ning, which is being commented upon here, is physically reasonable. The difficult problem of the low-probability transition ${}^6A_1 \rightarrow {}^2T_2$ is resolved by use of the spin-orbit coupling mechanism. Thus the twofold-crystal-field model of Zhou, Zhao, and Ning is again shown to be reasonable, while the conjecture of the 4Zn+6S coordination model is not similarly supported and should be further examined by direct experiments. The simple spectral fitting scheme with use of pure quartets by Stavrev, Kynev, Nikolov, and Dyakovitch is shown to be unsuccessful.

It should be emphasized that in the method of Zhou, Zhao, and Ning[1] the crystal field in the Hamiltonian is expressed by an irreducible tensor operator $V(A_1)$, which describes only the symmetry feature of the field but not the coordination details of the ligands. Thus the surrounding symmetry of the Mn^{2+} ions deduced from the results $\zeta > 0$ and $Dq > 0$ is intended only for the crystal field, not for the coordination. As Zhou, Zhao, and Ning[1] indicated, the calculation results $\zeta > 0$ and $Dq > 0$ show that the crystal field surrounding the Mn^{2+} ions is an octahedral one produced by negative charges, a tetrahedral one produced by positive charges, or a superposition of these two. Therefore a model of twofold-crystal field, i.e., an octahedral negative field plus a tetrahedral positive field, is proposed. Such a field is equivalent to an octahedral field with a negative sign in determining the energy order of d orbitals. Any information on the detailed arrangement of the ligands that produce the twofold field, say 4Zn+6S coordination, can only be taken as conjecture, as we have done. But the twofold-crystal-field model seems to be supported by the paper of Goede *et al.*,[2] also cited by Zhou, Zhao, and Ning,[1] since the authors indicated that MnS in the rock-salt structure occurs as an octahedral structure. Though the authors of the preceding comment stressed that the coordination in this case is 6S+12Zn instead of 4Zn+6S, the feature of the effective field in both the two cases are the same, i.e., an octahedral field with a negative sign.

Whether a Mn^{2+} ion in ZnS can be located at a 4Zn+6S interstitial site should be resolved by further experiments. The authors of the preceding Comment concluded, according to the calculation by Stavrev, Ivanov, and Nikolov[3] (cited in the Comment) that the location of Mn^{2+} at 4Zn+6S sites was predicted, however to have a lower probability than at 4S+6Zn sites. We think this conclusion may not be necessarily reliable, since too many assumptions and approximations have been made in the course of the calculations of Stavrev, Ivanov, and Nikolav.[3] Moreover, some mistakes are found in their paper.[3] For example, they stated at the end of the text[3] that "the crystal-field splitting in the case ($MnZn_4S_6$) is T_d for the nearest neighbors but O_h for the next-nearest neighbors,... it would be effectively a T_d site." But it is well known that a T_d field of $4Zn^{2+}$ is equivalent to an O_h field with a negative sign, similar to 6S, in splitting d orbitals. Thus the field of 4Zn+6S would effectively be an O_h one (with a negative sign).

An important problem stressed by the authors of the preceding Comment is connected with the low-probability transition ${}^6A_1 \rightarrow {}^2T_2$. Our explanation is as follows. The ground state of d^5 in a cubic field, owing to spin-orbit coupling, will no longer be ${}^6A_1$ but instead a state $E''(1)$, formed by a mixture of the sextet, the quartets, and the doublets. The ${}^2T_2$ state will be mixed with the ${}^6A_1$, the quartets, and other doublets to form two other states $E''(5)$ and $U'(8)$. The transition ${}^6A_1 \rightarrow {}^2T_2$ will be replaced by the transitions $E''(1) \rightarrow E''(5)$ and $E''(1) \rightarrow U'(8)$, which include sextet→sextet, quartets→quartets, and doublets→doublets transitions and can thus have higher probability.

Because the result of a parameter-fitting method in general may not be unique, we have recently made use of a computer program for minimization of a function with several variables to find all possible numerically best-fitting results of the spectrum of ZnS:Mn^{2+}. The function constructed in our case is

$$F(B,C,Dq)=\left[\sum_j (E_j-\mathcal{E}_j)^2/\mathcal{E}_j^2\right]^{-1/2},$$

where E_j and $\mathcal{E}_j$ are the jth calculated and observed bands, respectively. We obtained six results, as listed in Table I. The values of spin-orbit coupling coefficient ζ which fit the zero-field splitting in each case are also given in the table. Among these results, only the first one, i.e., the first column of the table, is physically reasonable. It is close to, but better than, the result of Zhou, Zhao, and Ning.[1] The other five sets of assignments are not reasonable, because the values of ζ are larger than the value 347 of a free Mn^{2+}. Moreover, values for the ratio C/B in the third and fourth sets (7.29) and in the fifth and sixth sets (2.33) deviate far from the generally accepted value (~ 4). According to the relation $B=N^4B_0$ and $C=N^4C_0$ given by Curie, Barthon, and Canny,[4] we have

TABLE I. Six different sets of candidate numerically best-fitting assignments of the spectrum and zero-field splitting parameter a of Mn^{2+} in Zns.

	Calculated[a]						observed
bands (cm^{-1})	$17127(^4T_1)$	$17127(^4T_1)$	$17763(^4T_1)$	$17763(^4T_1)$	$18192(^4T_1)$	$18192(^4T_1)$	17891
	$20105(^4T_2)$	$20105(^4T_2)$	$19755(^4T_2)$	$19755(^4T_2)$	$19885(^4T_2)$	$19885(^4T_2)$	19683
	$21184\begin{bmatrix}{}^4A_1\\{}^4E\end{bmatrix}$	$21184\begin{bmatrix}{}^4A_1\\{}^4E\end{bmatrix}$	$21267\begin{bmatrix}{}^4A_1\\{}^4E\ 2\end{bmatrix}$	$21267\begin{bmatrix}{}^4A_1\\{}^4E\end{bmatrix}$	$20110\begin{bmatrix}{}^4A_1\\{}^4E\end{bmatrix}$	$20110\begin{bmatrix}{}^4A_1\\{}^4E\end{bmatrix}$	21237
	$23142(^2T_2)$	$23142(^2T_2)$	$23342(^4T_2)$	$23342(^4T_2)$	$23461(^4T_1)$	$23461(^4T_1)$	22638
	$25331(^4T_2)$	$25331(^4T_2)$	$24473(^4E)$	$24473(^4E)$	$26165(^4T_2)$	$26165(^4T_2)$	25297
a ($10^{-4}cm^{-1}$)	7.969	7.938	7.958	7.971	7.982	7.984	7.97
	Values of fitting parameters (in cm^{-1})						
B	783.5	783.5	458.0	458.0	929.5	929.5	
C	2670.0	2670.0	3337.5	3337.5	2163.0	2163.0	
Dq	+571.5	−571.5	+581.5	−581.5	+281.0	−281.0	
ζ	343.5	403.0	375.0	444.4	422.5	739.3	

[a] The spectral bands are calculated with $\zeta=0$, while the parameter a is calculated with $\zeta\neq0$. Only the first and second sets involve the sextet→doublet transition.

$$C/B=C_0/B_0=3325/960=3.46\ ,$$

which is just the value determined by Zhou, Zhao, and Ning.[1]

Stavrev *et al.*[5] (also cited in the preceding Comment) tried to account for the absorption spectrum of ZnS:Mn^{2+} by pure quartet transitions with a T_d crystal-field model. The values adopted for their $B(461)$ and $C(3325)$ are almost just the same as those in our fourth set in Table I, and likewise unreasonable. The problem would be much worse if one were to fit the zero-field splitting and the spectrum simultaneously: An unusually large value of $\zeta(\sim444)$ would be obtained. This shows that their explanation with use of pure quartets is unsuccessful.

In conclusion, the parameter-fitting result of Zhou, Zhao, and Ning[1] for the absorption spectrum and the zero-field splitting and the twofold-crystal-field model of Mn^{2+} in ZnS are again shown to be physically reasonable, while the 4Zn+6S coordination model which can only be taken as a conjecture, must be examined by further experiments.

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