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Comments

Comments are short papers which criticize or correct papers of other authors previously published in the **Physical Review.** *Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

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

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The location of Mn^{2+} ions in cubic ZnS is discussed. Discrepancies are found to exist between recent findings [H.-E. Gumlich, J. Lumin. **23**, 73 (1981)] and the model proposed by Zhou, Zhao, and Ning [Phys. Rev. B **43**, 3712 (1991); B **44**, 7770 (E) (1991)]. Contrary to their results, preference should be given to Mn^{2+} ions at metal T_d-symmetry sites in ZnS.

In a recent paper Zhou, Zhao, and Ning[1] reported results on zero-field-splitting calculations for Mn^{2+} ions in ZnS. The theoretical findings are correlated with the ZnS:Mn spectrum and conclusions on the Mn^{2+} location in ZnS are drawn on the basis of a crystal-field fitting with four variational parameters: Dq, B, C, and ζ. In their model, the authors claim that a unique fit can be obtained only with positive Dq values, corresponding to O_h site symmetry of the impurity surrounding. It is thus concluded that Mn^{2+} ions could occupy octahedral sites in cubic ZnS.

Since a similar topic was discussed most recently elsewhere[2] and the results reported there are at variance with those of Zhou, Zhao, and Ning,[1] we think it might be of interest to discuss the problem in more detail and to point out the differences.

Numerous calculations carried out on the ZnS:Mn spectrum,[3,4] seem to disprove the reliability of crystal-field theory, especially when studying fine-structure phenomena such as the spin-orbit or Jahn-Teller effects. As has been demonstrated by Parrot *et al.*,[4] simple crystal-field models fail to explain even qualitatively the Jahn-Teller coupling in ZnS:Mn. More elaborate covalent models, based on *metal-site coordination,* have been successfully used since then, to assess the Jahn-Teller coupling in this system.[5-7] Sophisticated quantum-chemical analyses[6,8] have also proved useful in locating the metal-site location of Mn^{2+} in ZnS.

In fact for zinc blende, the space group is T_d^2 (No. 216, $F\bar{4}3m$) with $Z=1$.[9] The sites available in this structure are $4T_d$ (1), C_{3v} (4), $2C_{2v}$ (6), C_3 (12), and C_1 (24).[10] There are no O_h sites and the Mn^{2+} ions can either substitute zinc ions and acquire T_d symmetry (see the x-ray data for $Zn_{1-x}Mn_xS$ cited in Ref. 8) or get into T_d-symmetry interstitial sites.

The main problem as to the geometry of the metal site arises in connection with the assignment of the five bands listed in Table II of Zhou, Zhao, and Ning.[1] These bands were not assigned by the same authors to electron transitions in the Mn^{2+} centers. We have performed the missing assignment with the Dq, B, and C values reported there.[1] The results obtained are given in Table I. They can be used to shed additional light on the model involved in these calculations on the basis of some recent findings.[3] No conflict arises from the assignment of the first three low-energy electronic transitions; it is the one generally accepted. The fourth and fifth bands in the ZnS:Mn spectrum so far have been assigned to a variety of electronic states (see, for example, Ref. 8). The interpretation of Zhou, Zhao, and Ning fits very well the ZnS:Mn^{2+} spectrum *numerically,* but it involves electronic transitions that are expected to be of low probability—sextet→doublet transitions $^6A_1\rightarrow{}^2T_2$, which correspond to a double spin flip. This problem is discussed in several papers.[9-11] It is generally accepted that the electronic spectra of Mn^{2+} are due to

TABLE I. Assignment of the electronic transitions of Mn^{2+} centers with $Dq=600\ \mathrm{cm}^{-1}$, $B=791\ \mathrm{cm}^{-1}$, and $C=2740\ \mathrm{cm}^{-1}$, $\zeta=0$. Transition energies [cm^{-1}] higher than 30 000 cm^{-1} are omitted, since they are not presented in the ZnS:Mn^{2+} spectrum.

Assignment in T_d	Transition energy (calculated)	Zero-phonon lines (experimental)
$^6A_1\rightarrow a\,^4T_1$	17 335[a]	17 891
$^6A_1\rightarrow a\,^4T_2$	20 430[a]	19 683
$^6A_1\rightarrow a\,^4E, {}^4A_1$	21 610[a]	21 237
$^6A_1\rightarrow a\,^2T_2$	23 376[a]	22 638
$^6A_1\rightarrow b\,^4T_2$	25 737[a]	25 297
$^6A\rightarrow b\,^4E$	27 147	
$^6A_1\rightarrow b\,^2T_2$	28 385	
$^6A_1\rightarrow b\,^4T_1$	28 448	

[a] Transitions for which the transition energies calculated by Zhou, Zhao, and Ning (Ref. 1) agree with experiment.

sextet→quartet transitions. In this connection, the parameters obtained by Zhou, Zhao, and Ning,[1] should be considered as a good numerical fit, but unrealistic as to the physical nature of the electronic transitions in ZnS:Mn^{2+}.

A further statement that the formation of cubic MnS domains in ZnS supports these authors' crystal-field model[1] is misleading. Cubic MnS crystallizes in the rocksalt structure corresponding to O_h coordination 6S+12Zn, which is obviously different from the 4Zn+6S coordination proposed by Zhou, Zhao, and Ning.[1] This latter coordination (with O_h crystal-field symmetry, but with T_d-point-group symmetry) could occur *only* if the Mn^{2+} ions are located at interstitial sites in cubic ZnS.[2] A moderate lattice relaxation is expected to occur around such centers resulting in a shift of the ZnS:Mn emission and absorption bands to lower energies.[2] Additional complication arises from the fact that another type of interstitial coordination (4S+6Zn) also exists and a fluxional behavior between the two virtual Mn^{2+} sites is expected.[2] We have demonstrated that Mn^{2+} ion can migrate easily ($\Delta E \sim 0.1$ eV) from 4Zn+6Se to 4Se+6Zn coordination in ZnSe, but trapping at the 4S+6Zn site should occur in ZnS, where the latter site is energetically preferred ($\Delta E \sim 3.5$ eV).[2] Thus, the location of Mn^{2+} at 4Zn+6S sites was predicted in our analysis to be of low probability.[12] It was finally concluded[2] that Mn^{2+} ions at interstitial sites cannot contribute noticeably to the ZnS:Mn spectrum.

The results reported by Zhou, Zhao, and Ning[1] throw additional light on this problem, but in our opinion they consider only a single possibility of the interstitial Mn^{2+} location in ZnS. Conversely, we think that recent findings[3] favor the T_d metal-site coordination of Mn^{2+} ions in ZnS.

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