

## LETTER TO THE EDITOR

### Theoretical Study of $\text{Mn}^{2+}$ Clustering in $\text{Zn}_{1-x}\text{Mn}_x\text{S}$ and $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$

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Communicated by J. W. Richardson, March 2, 1990

Total energy calculations have been performed for 17-atom ( $\text{MnS}(\text{Se})_4\text{Zn}_{12-y}\text{Mn}_y$ ) and 29-atom ( $\text{MnS}(\text{Se})_4\text{Zn}_{12-y}\text{Mn}_y\text{S}(\text{Se})_{12}$ ) clusters representing the first, second, and third neighbors of a central  $\text{Mn}^{2+}$  ion in  $\text{ZnMnS}$  and  $\text{ZnMnSe}$  lattices. The results show an energy gain for the Mn clustering as compared with the random impurity distributions. The electrostatic repulsion between the second neighbor ions was taken as a quantitative measure of the randomization effect and it was found to be of an order of magnitude lower than the effect produced by the clustering. The inclusion of the third neighbor's contribution is essential to the clustering effect. © 1990 Academic Press, Inc.

#### Introduction

The Mn-based semimagnetic semiconductors have been extensively studied in the past few years (1).  $\text{Zn}_{1-x}\text{Mn}_x\text{S}$  and  $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$  are among the most studied systems (2, 3). It is commonly thought that Vegard's law (4), which stipulates a random impurity distribution in the crystal lattice, should be obeyed also for semimagnetic compounds. However, in contrast to the low-doped  $\text{ZnS}:\text{Mn}$  and  $\text{ZnSe}:\text{Mn}$ , showing absorption and emission bands in the range  $16,000\text{--}28,000\text{ cm}^{-1}$  (2–3.5 eV), additional bands outside this spectral range have been observed for  $\text{ZnMnS}$

and  $\text{ZnMnSe}$  at high  $\text{Mn}^{2+}$  concentrations. As shown recently (3), the new IR, near IR, and UV bands of the two semimagnetics could not be assigned to transitions in the  $\text{Mn}^{2+}$  centers at regular  $T_d$  sites. Moreover, most of the bands in the absorption spectrum of  $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$  (wurtzite) are polarized and this phenomenon could also not be explained within the framework of a model that assumes a random  $\text{Mn}^{2+}$  ion distribution in the crystal (2).

Recently (5), we have applied semiempirical self-consistent field methods that neglect the differential overlap (NDO) between atomic orbitals (CNDO and INDO) to 17-atom clusters  $\text{MnS}_4\text{Zn}_{12-y}\text{Mn}_y$  that

represent the first ( $\text{MnS}_4$ ) and second ( $\text{MnZn}_{12}$ ) coordination spheres of a  $\text{Mn}^{2+}$  ion in  $\text{ZnS}$ . We have shown that minimal energies for the  $y \geq 2$  compositions were obtained with the  $\text{Mn}^{2+}$  ions located next to each other on the cluster's surface ( $\text{Zn}_{12-y}\text{Mn}_y$ ). Thus, clustering of  $\text{Mn}^{2+}$  ions in  $\text{Zn}_{1-x}\text{Mn}_x\text{S}$  was predicted on the basis of the energy factor. The results obtained were extended (5) to explain that the new spectral phenomena for this semimagnetic semiconductor is due to symmetry lowering or electron delocalization produced by the clustering.

The purpose of the present work is (i) to examine the clustering effect in  $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$  modeled by the 17-atom  $\text{MnSe}_4\text{Zn}_{12-y}\text{Mn}_y$  clusters and to compare the results obtained with those already known for  $\text{Zn}_{1-x}\text{Mn}_x\text{S}$  (5), and (ii) to assess the effect of an expanded coordination sphere by including the third neighbors (12 S(Se) anions) in the 29-atom  $\text{MnS(Se)}_4\text{Zn}_{12-y}\text{Mn}_y\text{S(Se)}_{12}$  cluster calculations.

The randomization effect is difficult to assess; entropy changes favor the most randomized structure but, at low temperatures, the entropy effect is negligible and the explanation for the observed irregularity in the spectral behavior should be searched for as an energy factor. Assuming that, for the most randomized structure, the ions with identical polarity must be separated as far away from each other as possible, one may argue that the Coulomb (potential) energy may be taken as a measure of randomization—the most randomized structure would have the lowest Coulomb energy. Consequently we have also tried to assess the potential energy differences between geometrical isomers of different  $\text{Mn}^{2+}$  ion configurations.

### Formulation of the Problem

We have explored 17-atom  $\text{MnSe}_4\text{Zn}_{12-y}\text{Mn}_y$  and 29-atom  $\text{MnS(Se)}_4\text{Zn}_{12-y}\text{S(Se)}_{12}$  clusters representing cubic  $\text{Zn}_{1-x}\text{Mn}_x\text{S(Se)}$ ,

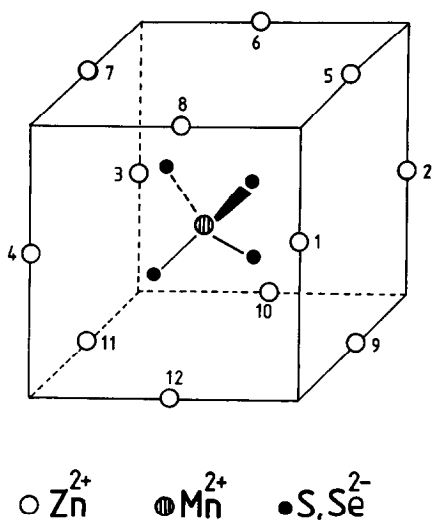
in which part of the second neighbor Zn ions of a central Mn ion are replaced by Mn ions. This is an attempt to expand the coordination cluster and thus to obtain a picture that is a more realistic model for the crystal environment of the impurity center.

It should be noted that  $\text{MnS(Se)}_4\text{Zn}_{12-y}\text{Mn}_y$  clusters can be correctly related to both the cubic (zinc blende) and hexagonal (wurtzite) lattices (7); however, 12 equidistant S(Se) anions as third neighbors exist only in the cubic phase [in wurtzite type  $\text{ZnS(Se)}$  there are 4 kinds of "third" neighbor anions—1 is closer to the second neighbor Zn ions, 9 anions are equidistant with the 12 third neighbors in the cubic compounds; there are also two other kinds of 6 and 9 anions farther away from the central ion]. Therefore, our clusters should be considered appropriate for cubic semimagnetics and probably are also valid for hexagonal lattices, since the 29-atom clusters differ only in the number and location of 3 third neighbor ions.

The  $y$  series considered here was truncated at  $y = 6$  since solid solutions of  $\text{ZnS(Se)}$  and  $\text{MnS(Se)}$  are obtained approximately up to 60% of  $\text{MnS(Se)}$  (2, 3), and therefore the  $y > 6$  values should reflect the picture of a Mn host with Zn guest ions which is of minor importance.

The  $\text{MnS(Se)}_4\text{Zn}_{12-y}\text{Mn}_y$  ( $y = 0$ ) cluster is presented in Fig. 1. The differently substituted clusters ( $y = 1, \dots, 6$ ) have been treated with interatomic distances equal to those in pure  $\text{ZnS}$  and  $\text{ZnSe}$ , thus neglecting the cluster relaxations and the  $M-L$  bond length scaling that are expected to occur as a function of  $y$  (2). No restrictions were imposed on the location of  $\text{Mn}^{2+}$  ions within the second sphere ( $\text{Zn}_{12-y}\text{Mn}_y$ ) and all combinations of Mn ions for a given  $y$ -value have been dealt with. Actually, the 12 second sphere sites for  $y = 1$  are equienergetic and the first series of geometrically (and energetically) inequivalent Mn compositions appear for  $y = 2$ .

The third neighbors ( $\text{S}^{2-}$  or  $\text{Se}^{2-}$ ) in the

FIG 1. The  $\text{MnS}(\text{Se})_4\text{Zn}_{12}$  cluster.

29-atom clusters  $\text{MnS}(\text{Se})_4\text{Zn}_{12-y}\text{Mn}_y\text{S}(\text{Se})_{12}$  are at a distance of  $a\sqrt{11}/4$  from the central Mn ion, where  $a$  is the cubic lattice constant (7). It should be mentioned that the 29-atom clusters possess a lower charge  $-6$  and provide better (closer to neutral) boundary conditions than the 17-atom clusters with total charge  $18+$ . Therefore, the results obtained from the 29-atom cluster analysis should be considered a more realistic approximation of the unit cell from the 17-atom clusters analysis, though the former are to some extent inapplicable to the wurtzite type semimagnetics already mentioned.

All calculations performed in this work use the self-consistent field CNDO/2 and INDO/2 methods with standard parametrization (6), in their unrestricted Hartree-Fock version. The  $\text{Mn}^{2+}$  ions were treated in their stable and well-separated ground state  ${}^6A_1$ . In the model thus described we neglect the spin exchange between the Mn ions but it is thought to play a minor role in the total energy determinations.

## Results and Discussion

For all clusters under consideration the  $\text{Zn}_{12-y}\text{Mn}_y$  (fixed  $y$ ) configurations with closest locations of the Mn ions were found to be of minimum energy. These minimum-energy configurations are denoted by the positions numbered in Fig. 1: (1,5), (1,5,8), (1,5,8,9), (1,5,8,9,12), and (1,2,5,8,9,12). The energy differences between the most clustered (MC) and the most randomized (MR)  $\text{Zn}_{12-y}\text{Mn}_y$  configurations with 17 and 29 atoms are presented in Table I.

The last two columns in Table I present the estimates of the electrostatic repulsion between the ions of different  $\text{Zn}_{12-y}\text{Mn}_y$  configurations. The Coulomb (potential) energy of a cluster built up from point charges could be expressed as

$$E = \sum_{i < j}^N \frac{q_i q_j}{d_{ij}}, \quad (1)$$

where  $N$  is the number of the ions in the cluster under consideration and  $d_{ij}$  is the distance between the point charges  $q_i$  and  $q_j$ .

Equation (1) can be rewritten by grouping the different ion interactions, and by calculating energy differences instead of absolute energies. Thus for any two different

TABLE I

ENERGY DIFFERENCES (eV)  $\Delta E = E_{\text{MC}} - E_{\text{MR}}$ :  $\Delta E_{\text{clustering}}$  (INDO)<sup>a</sup> AND  $\Delta E_{\text{random}}$  (Coulomb Energy Estimates) for 17-Atom [S(Se)17] and 29-Atom [S(Se)29] Clusters

y	$\Delta E_{\text{clustering}}$				$\Delta E_{\text{random}}$	
	S17	Se17	S29	Se29	ZnMnS	ZnMnSe
2	-1.12	-0.93	-1.31	-1.01	0.17	0.16
3	-3.09	-2.71	-3.70	-2.90	0.36	0.34
4	-4.80	-3.53	-5.22	-4.15	0.96	0.91
5	-6.07	-3.98	-4.45	-3.52	0.92	0.87
6	-6.28	-4.03	-3.61	-2.66	0.43	0.41

<sup>a</sup> CNDO and INDO produced similar results (energy differences less than 0.01 eV) and for this reason the values in the table are independent of the method employed.

Zn<sub>12-y</sub>Mn<sub>y</sub> configurations one could write

$$\Delta E = \Delta \sum_{i=1}^{N_{\text{Mn}}} \sum_{j=1}^{N_{\text{Zn}}} \left( \frac{q_i^{\text{Mn}} q_{i'}^{\text{Mn}}}{d_{i'i'}} + \frac{q_i^{\text{Mn}} q_j^{\text{Zn}}}{d_{ij}} + \frac{q_j^{\text{Zn}} q_{j'}^{\text{Zn}}}{d_{j'j'}} \right), \quad (2)$$

with  $i + j = 12$ . The terms with  $q^{\text{S}}$  or  $q^{\text{Se}}$  cancel being the same for the two configurations considered.

By adopting Eq. (2) (i) we ignore the interaction between the different clusters in the crystal and (ii) we assume equal interactions of the clusters with the remaining lattice. The latter could be easily demonstrated to hold for high-symmetry (e.g., cubic) crystals. In fact, the sums in Eq. (2) are infinite and, as usually done in calculating lattice energy, one can most profitably use the translational symmetry to get rid of these sums (8).

Setting  $\Delta E$  from Eq. (2) as  $\Delta E_{\text{random}}$  to calculate  $\Delta E$  we have assumed  $q^{\text{Mn}} = 1.36(7)$ ,  $q^{\text{Zn}} = 1.66(7)$  (obtained in our INDO calculations for ZnSe(S)), and  $d_{M-M}$  values for pure ZnS and ZnSe (7). The energy differences for the MC and MR clusters were found to be positive and a clearly expressed maximum in  $\Delta E_{\text{random}}$  vs  $y$  is observed at  $y = 4$  (one-third of the Zn ions replaced by Mn). This is rather unexpected since the substitution of a Zn ion ( $q = 1.66$ ) by a Mn ion ( $q = 1.36$ ) should produce a smooth increasing function of  $E_{\text{Coulomb}}$  vs  $y$ . The  $\Delta E_{\text{random}}$  are in the range 0.1–1.0 eV and differ only slightly (in contrast to the  $y$ -dependence) for the two environments (S or Se). This is obviously due to the similar ZnS and ZnSe lattice constants and to the charges of Mn and Zn ions in ZnMnS(Se) lattices. It should be noted, however, that the  $\Delta E$  values thus obtained (see Eq. (2)) are independent of the  $q^{\text{Mn}}/q^{\text{Zn}}$  ratio; as shown recently (9), the  $q^{\text{Mn}}$  and  $q^{\text{Zn}}$  values do not differ by more than 20%. Therefore, the  $\Delta E_{\text{random}}$  values are believed to be approximately 0.05 eV accurate.

There are several interesting points that emerge from Table I and should be commented upon.

First, all  $\Delta E_{\text{clustering}}$  values are negative, pointing out a considerable energy gain with the MC configurations. The stabilization energy varies roughly from 1 to 6 eV and increases with both the cluster size and  $y$ . The  $\Delta E_{\text{clustering}}$  vs  $y$  dependence however is complicated (vide infra). By comparing  $\Delta E_{\text{clustering}}$  and  $\Delta E_{\text{random}}$  it is seen that the former (in absolute value) are approximately of an order of magnitude larger. This finding suggests that the clustering effect should dominate over the electrostatic forces that tend to produce a random distribution of Mn<sup>2+</sup> ions in the crystals.

Second, by considering the  $\Delta E_{\text{clustering}}$  for 17-atom clusters as a function of  $y$  (first two columns of Table I) we find that  $\Delta E$  values decrease rapidly up to  $y = 4$  and then show a saturation trend at  $y \sim 5, 6$ . Further, the clustering effect is more pronounced for Zn<sub>1-x</sub>Mn<sub>x</sub>S than for Zn<sub>1-x</sub>Mn<sub>x</sub>Se. The same trends are also valid for the 29-atom clusters, but their energy dependence on  $y$  shows a clearly expressed minimum at  $y = 4$ . It should be pointed out that this is the influence of the third neighbors on the clustering effect. It is interesting to note that a maximum was found for  $\Delta E_{\text{random}}$  also at  $y = 4$ . Hence,  $y = 4$  (the second sphere of Zn ions replaced  $\frac{1}{3}$  by Mn ions) seemed to be a critical point in the process of building and clustering the Mn configurations under consideration.

Finally, by comparing the results obtained for different clusters it is seen that both approximations (17- and 29-atom) predict Mn<sup>2+</sup> clustering; the clustering effect is about 15–20% more pronounced for 29-atom structures with  $y$ -values up to the energy minimum. Thus the main conclusion that can be drawn from this work is that the inclusion of the longer-range interactions is essential for obtaining realistic values for

the energy gain produced by the  $Mn^{2+}$  clustering.

### Acknowledgments

This work was supported through MCSE Grants 152 and 912. K.K.S. thanks Professor Dr. H.-E. Gumlich for his hospitality in Berlin (West) and Drs. R. Parrot, D. Boulanger, C. Benecke, U. Pohl, Ch. Jung, and O. Goede for stimulating discussions.

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