Miscibility of Zinc Chalcogenides

Florian Janetzko and Karl Jug*

Theoretische Chemie, Universität Hannover, Am Kleinen Felde 30, 30167 Hannover, Germany

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Solid solutions in the system zinc sulfide/zinc selenide ($ZnS_{1-x}Se_x$) and in the system zinc oxide/zinc sulfide ($ZnO_{1-x}S_x$) were investigated using the cyclic cluster model within the semiempirical MSINDO method. Results of cyclic cluster calculations for the optimized lattice parameters, band gaps, and binding energies of the perfect zinc chalcogenides ZnO, ZnS, and ZnSe are presented and compared with the experimental data. The miscibility of zinc sulfide and zinc selenide over the complete range of $0 < x < 1$ was investigated by calculating the free enthalpy of mixing $\Delta_M G$ for different values of x. The variation of the lattice constant and the band gap in dependence of the composition of the solid solution was determined. The miscibility in the system $ZnO_{1-x}S_x$ was investigated for $x = 0.02$. The free enthalpy of mixing, the variation of the lattice parameters, and the cell volume were calculated. All data are compared with available experimental results.

1. Introduction

Since the development of the first blue-emitting laser diodes based on zinc selenide,[1] zinc chalcogenides have gained much interest as materials for the development of optoelectronic devices. The advantage of these compounds is the possibility of tuning their properties such as lattice parameters or band gaps by mixing different zinc chalcogenides ZnA and ZnB to obtain solid solutions of the composition $ZnA_{1-x}B_x$.

$$(1 - x)\mathrm{ZnA} + x\mathrm{ZnB} \rightarrow \mathrm{ZnA}_{1-x}\mathrm{B}_x \qquad (1)$$

The stability of such solid solutions depends on the free enthalpy of mixing $\Delta_M G$.

$$\Delta_M G = \Delta_M H - T\Delta_M S \qquad (2)$$

Here $\Delta_M H$ and $\Delta_M S$ denote the enthalpy and entropy of mixing, respectively, and T is the temperature. For $\Delta_M G < 0$ the solid solution will form, otherwise a miscibility gap is obtained. For isostructural compounds with anions of similar size like ZnS and ZnSe a miscibility over the complete range $0 < x < 1$ was found experimentally.[2−9] Both chalcogenides crystallize in the sphalerite structure at temperatures below 1000 °C. The dependence of the lattice parameter a for such systems is usually linear in x (eq 3) (Vegard's rule[10]) while the band gap E_g can show a quadratic behavior.

$$a(x) = (1 - x)a_{\mathrm{ZnA}} + xa_{\mathrm{ZnB}} \qquad (3)$$

$$E_g(x) = (1 - x)E_{g,\mathrm{ZnA}} + xE_{g,\mathrm{ZnB}} - b(1 - x)x \qquad (4)$$

where a_{ZnA}, a_{ZnB}, and $E_{g,\mathrm{ZnA}}$, $E_{g,\mathrm{ZnB}}$ are the lattice parameters and the band gaps of the isolated compounds, respectively, and b is the nearly composition-independent so-called optical bowing parameter.[11] For $ZnS_{1-x}Se_x$ bowing parameters of $0 \leq b \leq 0.63$ were measured experimentally,[2,4,5,7] indicating that $E_g(x)$ has a minimum. Bernard and Zunger[11] calculated a bowing parameter $b = 0.39$ for an ordered structure at $x = 0.5$ for the band gap in the ZnS/ZnSe system. They used a plane wave method on LDA level. Results of calculations by Gabrel'yan et al. using muffin-tin potentials within the virtual crystal approximation show an average bowing parameter $b = 0.50$.[12]

Zinc oxide crystallizes in the wurtzite structure. Furthermore, the difference in size between oxygen and sulfur is larger than between selenium and sulfur. Therefore, a miscibility gap is expected to occur in the system ZnO/ZnS. Recently, a solid solution $ZnO_{1-x}S_x$ with $x \leq 0.03$ was prepared experimentally[13] by laser ablation of a ZnS target during ZnO growth at about 700 °C. Furthermore, Binnewies and Locmelis[14] prepared ZnO/ZnS mixed crystals with a sulfur content up to 10% using a transport reaction at 900 °C. Because of difficulties in the preparation of solid solutions of the type $ZnO_{1-x}S_x$ due to the reactivity of sulfur to oxygen leading to intermediate phases such as $ZnSO_4$ or SO_2, this system is experimentally less investigated.

The purpose of this paper is to investigate the miscibility in the system ZnS/ZnSe and in the system ZnO/ZnS using the cyclic cluster model (CCM) within the semiempirical MSINDO method.[15−17] After a short review of the CCM and the MSINDO method we present the results for the optimized lattice parameters, band gaps, and binding energies of the perfect ZnO, ZnS, and ZnSe. The miscibility in the system ZnS/ZnSe was investigated by calculating the free enthalpy of mixing for different contents x of selenium. The calculated variation of the optimized lattice parameter and the band gap for $0 \leq x \leq 1$ is compared with experimental data. Finally, the solid solution $ZnO_{1-x}S_x$ was investigated for $x = 0.02$. The changes of the hexagonal lattice parameters and of the cell volume of the ZnO were calculated and are discussed together with experimental results.

2. Models and Computational Method

All quantum chemical calculations presented in this work were performed using the semiempirical SCF-MO method MSINDO[15] which is an improved version of the SINDO1 method.[18] The CCM for the description of bulk and surface properties of solids was recently implemented in the MSINDO

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code.[16] In the CCM periodic boundary conditions (PBC) are directly applied to a fragment (cluster) which represents the perfect or defective solid under consideration. This cluster corresponds to a large or extended unit cell (supercell), and its translation vectors $\{\mathbf{A}_i\}$ can be obtained from the primitive cell vectors $\{\mathbf{a}_i\}$ by applying a transformation matrix $\mathbf{L} = (l_{ij})$.

$$\mathbf{A}_i = \sum_{j=1}^{3} l_{ij}\mathbf{a}_j \tag{5}$$

The cluster consists of $l = \det \mathbf{L}$ primitive unit cells. All interactions for each atom I of the cluster were calculated within an interaction region around that atom which corresponds to its Wigner−Seitz cell. At most two-center integrals are taken into account in MSINDO. Therefore, the introduction of PBC has been achieved by averaging the two-center integrals of the overlap, the nuclear attraction, and the electron repulsion between the atom I and the atoms at the border of its Wigner−Seitz cell. The proper symmetry of the system is retained. The CCM has been extended to the description of ionic systems[17] where long-range Coulombic interactions play an important role. This has been achieved by embedding of the cyclic cluster in an infinite field of point charges using the Ewald summation technique. The CCM within the MSINDO method has been successfully applied to calculations of bulk and surface properties of perfect and defective metal oxides.[17,19] Details of the implementation of the CCM and the embedding procedure can be found elsewhere.[16,17]

3. Modeling of Perfect ZnO, ZnS, and ZnSe

Zinc oxide (ZnO) crystallizes in the hexagonal wurtzite structure (space group $P6_3mc$). Each zinc and each oxygen atom has four neighbors of the opposite type, three at a distance[20] of r_1(Zn−O) = 1.976 Å and one at a distance of r_2(Zn−O) = 1.991 Å. The cell parameters[20] are $a = 3.253$ Å and $c = 5.213$ Å, the internal parameter determining the oxygen position is $u = 0.382$. Newer experimental values for the lattice parameters ($a = 3.248\,98$ Å and $c = 5.205\,35$ Å) were measured by Zeuner et al.[21] The experimental heat of atomization is $\Delta_aH_{298} = 728$ kJ/mol.[22] It has been obtained by the experimental heat of formation of the solid ZnO and the heats of formation of the corresponding atoms Zn and O in the gas phase. The experimental band gap of zinc oxide is $E_g = 3.44$ eV.[23]

The stable modification of zinc sulfide and zinc selenide at room temperature is the cubic zinc blende or sphalerite structure (space group $F\bar{4}3m$). All atoms are tetrahedrally surrounded by the opposite atom type. The cubic lattice parameter a and the resulting bond length $r = \sqrt{3}/4a$ are $a = 5.410$ Å and r(Zn−S) = 2.343 Å for ZnS[24] and $a = 5.668$ Å and r(Zn−Se) = 2.454 Å for ZnSe.[24] The experimental heat of atomization for zinc sulfide is $\Delta_aH_{298} = 615$ kJ/mol,[22] the experimentally obtained value for the band gap is $E_g = 3.85$ eV.[25] The corresponding values for the selenide are $\Delta_aH_{298} = 522$ kJ/mol[26] and $E_g = 2.82$ eV.[25]

For the simulation of the perfect ZnO bulk we chose cyclic clusters which can be obtained from the primitive unit cell by the following transformation matrix.

$$\mathbf{L} = \begin{pmatrix} n_1 & -n_1 & 0 \\ n_1 & 2n_1 & 0 \\ 0 & 0 & n_2 \end{pmatrix}; \quad l = \det \mathbf{L} = 3{n_1}^2 n_2 \tag{6}$$

Here n_1 and n_2 denote positive integers. For $n_1 = n_2 = 2$ one obtains the $Zn_{48}O_{48}$ cyclic cluster which is shown in Figure 1a.

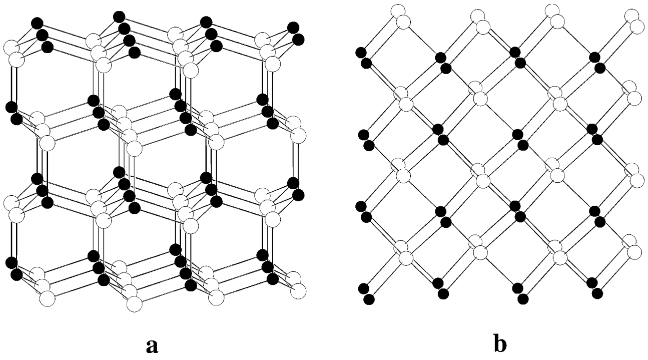

Figure 1. Cyclic clusters for zinc chalcogenides: (a) $Zn_{48}O_{48}$, (b) $Zn_{32}X_{32}$ (X = S, Se), ○ chalcogen, ● zinc.

It consists of $l = 24$ primitive unit cells. The cubic sphalerite structure was modeled by using cyclic clusters generated by the transformation matrix.

$$\mathbf{L} = \begin{pmatrix} -n & n & n \\ n & -n & n \\ n & n & -n \end{pmatrix}; \quad l = \det \mathbf{L} = 4n^3 \tag{7}$$

Here n denotes again a positive integer. The $Zn_{32}X_{32}$ cyclic cluster (X = S, Se) is shown in Figure 1b and can be obtained from eq 7 for $n = 2$.

For the description of the bulk properties of the zinc chalcogenides under consideration some of the MSINDO parameters had to be adjusted. First, properties of the ZnSe and Zn_2Se_2 molecules were added to the set of molecules for the parametrization of selenium. The calculated bond length r(Zn−Se) = 2.159 Å by the G2 method with the Gaussian 98 program,[27] the experimental heat of formation[28] Δ_fH_{298}(ZnSe) = 237.2 kJ/mol for the ZnSe molecule, and the G2 value of the heat of formation $\Delta_fH_{298}(Zn_2Se_2)$ = 175.6 kJ/mol for the Zn_2Se_2 molecule were included in the optimization of the selenium parameters. In a second step selected parameters of zinc, sulfur, and selenium were chosen, and a parametrization under inclusion of the $Zn_{48}O_{48}$, the $Zn_{32}S_{32}$, and the $Zn_{32}S_{32}$ cyclic clusters was performed. Especially the screening factors K_{SC}[29] for the 3d orbitals of sulfur, zinc, and selenium and the screening factors for the 4s and 4p orbitals for zinc were refined.

Then the bulk properties of the perfect ZnO, ZnS, and ZnSe were calculated using the optimized parameters. First, the convergence of the binding energy per formula unit with increasing cluster size was investigated. The chosen cluster was fully optimized within the corresponding crystal symmetry using a quasi-Newton method. The calculated binding energy corresponds to the experimental heat of atomization. They differ by the contributions of the vibrations which are not included in the calculation of the binding energy. Table 1 shows the binding energy E_B for different cyclic clusters of the three zinc chalcogenides. The energy of the $Zn_{48}O_{48}$ is already converged with respect to the cluster size in the case of the hexagonal zinc oxide, and the calculated value of E_B^{MSINDO}(ZnO) = 731.8 kJ/mol compares well with the experimental heat of atomization[22] Δ_aH_{298}(ZnO) = 728 kJ/mol. The $Zn_{32}X_{32}$ (X = S, Se) cyclic clusters are converged within less than 2 kJ/mol compared to the larger cluster in the case of the cubic zinc sulfide and selenide. Again, the calculated values E_B^{MSINDO}(ZnS) = 615.0 kJ/mol and E_B^{MSINDO}(ZnSe) = 521.6 kJ/mol agree well with the experimental[22,26] data (Δ_aH_{298}(ZnS) = 615 kJ/mol, Δ_aH_{298}(ZnSe) = 522 kJ/mol).

Table 2 compares the MSINDO-optimized lattice parameters, bond lengths, and band gaps of the $Zn_{48}O_{48}$ and the two $Zn_{32}X_{32}$

TABLE 1: Calculated Binding Energies E_B^{MSINDO} and Experimental Heats of Atomization $\Delta_a H_{298}$ per Formula Unit (kJ/mol) for MSINDO-CCM Calculations of ZnO, ZnS, and ZnSe Using Different Cyclic Clusters (n_1,n_2) and (n) (see eqs 6 and 7)

cluster	n_1	n_2	n	E_B^{MSINDO}
$Zn_{48}O_{48}$	2	2		731.8
$Zn_{108}O_{108}$	3	2		731.8
$Zn_{162}O_{162}$	3	3		731.7
$\Delta_a H_{298}$ (ZnO)[a]				728
$Zn_{32}S_{32}$			2	615.0
$Zn_{108}S_{108}$			3	616.3
$Zn_{256}S_{256}$			4	616.4
$\Delta_a H_{298}$ (ZnS)[a]				615
$Zn_{32}Se_{32}$			2	521.6
$Zn_{108}Se_{108}$			3	523.2
$Zn_{256}Se_{256}$			4	523.2
$\Delta_a H_{298}$ (ZnSe)[b]				522

[a] Reference 22. [b] Reference 26.

TABLE 2: MSINDO-CCM Results for Lattice Parameters a and c (Å), Internal Parameter u (Dimensionless), Bond Lengths r (Å), and Band Gap E_g (eV) for the $Zn_{48}O_{48}$, $Zn_{32}S_{32}$, and $Zn_{32}Se_{32}$ Cyclic Clusters; Experimental Data in Parentheses

cluster	structure parameters	band gap
$Zn_{48}O_{48}$	$a = 3.198$ (3.253, 3.24898)[a,b] $c = 5.185$ (5.213, 5.20535)[a,b] $u = 0.378$ (0.382)[a] r_1(Zn−O) = 1.951 (1.976)[a] r_2(Zn−O) = 1.962 (1.991)[a]	3.67 (3.44)[c]
$Zn_{32}S_{32}$	$a = 5.372$ (5.410)[d] r(Zn−S) = 2.326 (2.343)	3.48 (3.85)[e]
$Zn_{32}Se_{32}$	$a = 5.832$ (5.668)[d] r(Zn−Se) = 2.525 (2.454)	3.34 (2.82)[e]

[a] Reference 20. [b] Reference 21. [c] Reference 23. [d] Reference 24. [e] Reference 25.

(X = S, Se) cyclic clusters with the experimental data. The calculated lattice constants and bond lengths for the zinc oxide are slightly too short compared with the experimental values, but the maximum error is less than 1.6%. The calculated band gap of $E_B^{MSINDO} = 3.67$ eV using the improved virtual orbital approximation (IVO) of Huzinaga and Arnau[30] for the unoccupied orbitals compares well with the experiment of Hümmer[23] ($E_g = 3.44$ eV). The calculated properties of ZnS and ZnSe are also in good agreement with the corresponding experimental data (Table 2). The lattice parameter a and therefore also the bond length r(Zn−S) in the sulfide are slightly underestimated, while the values for the ZnSe are slightly too long. The band gaps of both systems differ at most by 0.52 eV from the experiment.

Summing up, the results of the MSINDO-CCM calculations show a good agreement with the experimental data concerning the structural and electronic properties of the zinc chalcogenides ZnO, ZnS, and ZnSe.

4. Miscibility of ZnS and ZnSe

We used the $Zn_{32}X_{32}$ cyclic cluster to investigate the miscibility in the $ZnS_{1-x}Se_x$ system. The free enthalpy of mixing $\Delta_M G$ was calculated according to eq 2. We calculated $\Delta_M S$ and $\Delta_M H$ in the following way:

$$\Delta_M S = -R(1-x)\ln(1-x) - Rx\ln(x) \tag{8}$$

$$\begin{aligned}\Delta_M H &= \Delta_M E_0 \\ &= E_0(\mathrm{ZnS}_{1-x}\mathrm{Se}_x) - (1-x)E_0(\mathrm{ZnS}) - xE_0(\mathrm{ZnSe})\end{aligned} \tag{9}$$

Here R denotes the ideal gas constant. For $\Delta_M S$ we used the standard formula for the ideal solution of eq 8. This approximation is justified since the system ZnS/ZnSe shows an almost ideal behavior.[9] $\Delta_M H$ is approximated by the reaction energy ΔE_0 which can be calculated from the total energies of the mixed system $ZnS_{1-x}Se_x$ and the total energies of the perfect ZnS and ZnSe according to eq 9. In eq 8 the temperature dependence and in eq 9 the zero-point energy and the temperature dependence are neglected.

Starting from the perfect zinc sulfide cluster $Zn_{32}S_{32}$ we introduced selenium by substituting the S atoms stepwise by Se atoms. The first substitution leads to the $Zn_{32}S_{31}Se$ cyclic cluster corresponding to a solid solution $ZnS_{1-x}Se_x$ with $x = {}^1/_{32} = 0.0313$. The cluster was optimized, that is, all atoms and the lattice parameter were allowed to relax. This was done by performing first a Cartesian geometry optimization of the atoms of the cyclic cluster keeping the lattice parameter a fixed. Then the fractional coordinates of the atoms with respect to the lattice vectors were kept constant and the length of a was optimized. This procedure was repeated until self-consistency was reached. The reaction energy in this case was calculated as follows:

$$\Delta_M E_0 = \frac{1}{32}[E_0(\mathrm{Zn}_{32}\mathrm{S}_{31}\mathrm{Se}) - (1 - 0.0313)E_0(\mathrm{Zn}_{32}\mathrm{S}_{32}) - 0.0313E_0(\mathrm{Zn}_{32}\mathrm{Se}_{32})] \tag{10}$$

$E_0(Zn_{32}S_{31}Se)$, $E_0(Zn_{32}S_{32})$, and $E_0(Zn_{32}Se_{32})$ are the total energies obtained from the quantum chemical calculations of the mixed $Zn_{32}S_{31}Se$ cluster and the two $Zn_{32}S_{32}$ and $Zn_{32}Se_{32}$ clusters, respectively.

Due to symmetry there are five possibilities for the substitution of the second sulfur atom by selenium. The energetically most favorable configuration for two Se atoms in the $Zn_{32}S_{30}Se_2$ cluster is the substitution of two S atoms which are 5.372 Å apart in the unsubstituted cluster. Substituting nearest-neighbor sulfur atoms (3.798 Å apart in the perfect ZnS cluster) by selenium would lead to a configuration which is about 13.6 kJ/mol higher in energy. Therefore, for higher amounts of selenium substitution patterns were chosen where the substitution of nearest-neighbor S atoms is kept to a minimum. For each value of x only one configuration was taken into account. Bernard and Zunger[11] used the tetragonal CuAuI structure (space group $P\bar{4}m2$) to model the $x = 0.5$ mixture. Their optimization of the tetragonal lattice parameters a and c led in this case to a ratio $c/a = 1.004$ which indicates that the cubic symmetry is retained. Therefore, all our cyclic clusters were optimized by relaxation of all atoms and the lattice parameter a in the cubic symmetry.

For each cluster $\Delta_M S$ and $\Delta_M E_0$ were calculated according to eqs 8 and 9. Then $\Delta_M G$ was obtained by eq 2 at $T = 1000$ K. The results are shown in Table 3. The calculated $\Delta_M G$ values are negative for all clusters. This indicates a miscibility without a gap in the $ZnS_{1-x}Se_x$ system for all compositions $0 < x < 1$ in line with the experiments.[2−9] This observation can be explained by the similar size of the lattice parameter of ZnS (5.41 Å) and ZnSe (5.67 Å).

We found an almost linear dependence of the lattice constant a on the amount x of selenium, shown by a small bowing factor $b = 0.13$ when fitting the calculated $a(x)$ values according to eq 3 (Figure 2). For $x = 0.5$ our optimized lattice parameter a is about 0.6% smaller than the average value of our calculated lattice parameters of the perfect ZnS and ZnSe. This is in line

TABLE 3: MSINDO-CCM Results for the Entropy of Mixing $\Delta_M S$ (J/(K·mol)), Energy and Free Enthalpy of Mixing $\Delta_M E_0$ and $\Delta_M G$ (kJ/mol) for the Mixed Crystals $ZnS_{1-x}Se_x$[a]

x	$\Delta_M S$	$\Delta_M E_0$	$\Delta_M G$
0.00000	0.0	0.0	0.0
0.03125	1.2	−1.3	−2.5
0.06250	1.9	−2.8	−4.8
0.09375	2.6	−4.3	−6.9
0.12500	3.1	−5.9	−9.0
0.15625	3.6	−7.7	−11.3
0.18750	4.0	−8.6	−12.6
0.21875	4.4	−9.4	−13.8
0.25000	4.7	−11.5	−16.2
0.28125	4.9	−12.4	−17.3
0.31250	5.2	−13.0	−18.2
0.34375	5.3	−13.8	−19.2
0.37500	5.5	−15.0	−20.5
0.40625	5.6	−15.7	−21.3
0.43750	5.7	−16.5	−22.2
0.46875	5.7	−17.2	−23.0
0.50000	5.8	−18.4	−24.2
0.53125	5.7	−17.6	−23.4
0.56250	5.7	−17.3	−23.0
0.59375	5.6	−16.6	−22.2
0.62500	5.5	−16.3	−21.8
0.65625	5.3	−15.3	−20.6
0.68750	5.2	−14.9	−20.0
0.71875	4.9	−14.4	−19.4
0.75000	4.7	−13.9	−18.5
0.78125	4.4	−11.3	−15.6
0.81250	4.0	−10.4	−14.4
0.84375	3.6	−9.5	−13.1
0.87500	3.1	−7.3	−10.5
0.90625	2.6	−5.4	−8.0
0.93750	1.9	−3.6	−5.5
0.96875	1.2	−1.7	−2.8
1.00000	0.0	0.0	0.0

[a] The $\Delta_M G$ values correspond to $T = 1000$ K.

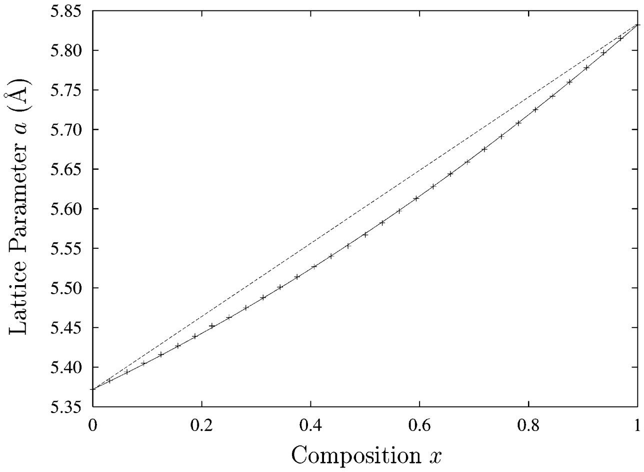

Figure 2. Variation of the lattice parameter a (Å) with the composition x in $ZnS_{1-x}Se_x$, + calculated values; (dashed curve) linear dependence (Vegard's rule), (solid curve) quadratic fit.

with the results of Bernard and Zunger[11] who found a small deviation from linearity for the lattice parameter a in the tetragonal structure different from Vegard's rule.

In contrast to the almost linear dependence of the lattice constant we found a pronounced nonlinear dependence of the band gap E_g (Figure 3). We obtained an optical bowing parameter $b = 0.55$ by fitting our $E_g(x)$ values to expression 3, in good agreement with the experimental values $0 \leq b \leq 0.63$.[2,4,5,7]

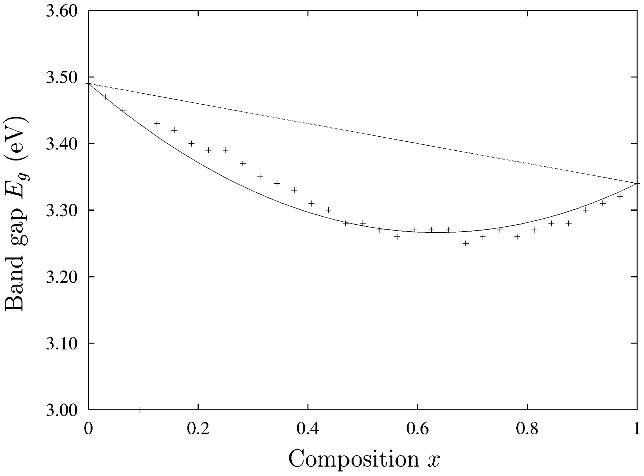

Figure 3. Variation of the band gap E_g (eV) with the composition x in $ZnS_{1-x}Se_x$, + calculated values; (dashed curve) linear dependence, (solid curve) quadratic fit.

TABLE 4: MSINDO-CCM Results for Lattice Parameters a and c (Å) and Cell Volume V (Å^3) (Change with Respect to the Unsubstituted Cluster in Parentheses), Entropy of Mixing $\Delta_M S$ (J/(K·mol)), Energy and Free Enthalpy of Mixing $\Delta_M E_0$ and $\Delta_M G$ (kJ/mol) Using the $Zn_{48}O_{47}S$ Cyclic Cluster ($x = 0.0208$)

lattice parameter	$a = 3.208$ (+0.3%) $c = 5.204$ (+0.4%) $V = 46.376$ (+1.0%)
cell volume	$\Delta_M S = +0.84$
thermodynamic properties	$\Delta_M E_0 = +1.76$ $\Delta_M G$ (1000 K) = +0.92

5. Miscibility of ZnO and ZnS

To investigate the miscibility of zinc oxide and zinc sulfide we chose the $Zn_{48}O_{48}$ cyclic cluster as the model. One oxygen atom was substituted by one sulfur atom which corresponds to a sulfur content of $x = 0.0208$. The resulting $Zn_{48}O_{47}S$ cluster was optimized following the procedure described in the previous section. The results for the optimized lattice parameters a and c, the cell volume V, and the thermodynamical properties $\Delta_M S$, $\Delta_M E_0$, and $\Delta_M G$ ($T = 1000$ K) are shown in Table 4. $\Delta_M S$ was calculated according to eq 8. $\Delta_M E_0$ was obtained as follows:

$$\Delta_M E_0 = \frac{1}{48}[E_0(Zn_{48}O_{47}S) - (1 - 0.0208)E_0(Zn_{48}O_{48})] - \frac{0.0208}{32}E_0(Zn_{32}S_{32}) \quad (11)$$

The two calculated lattice parameters and the calculated cell volume show an increase by 0.3%, 0.4%, and 1.0%, respectively. This is qualitatively in agreement with the observations of Binnewies and Locmelis,[14] although their experimental results show smaller changes of 0.03%, 0.04%, and 0.1% for the corresponding values. Yoo et al.[13] obtained experimentally an increase for a by 0.5% for a mixed $ZnO_{1-x}S_x$ crystal with $x = 0.01$ while c decreased for these crystals. For a higher content of sulfur ($x = 0.03$) they found an increase of both the lattice parameter and the cell volume without specifying the exact values.

Our calculated free enthalpy of mixing $\Delta_M G = 0.92$ kJ/mol at $T = 1000$ K is positive indicating a miscibility gap at $x = 0.0208$. A miscibility gap is expected due to the large difference of lattices parameters a of ZnO (3.25 Å) and ZnS (5.41 Å). Of course, miscibility increases at higher temperatures due to the entropy term in eq 2. We find a negative $\Delta_M G$ value for $x = 0.0208$ only at about 2000 K, whereas the experiments predict miscibility already at 1000 K.[14] On the other hand, our value for $\Delta_M G$ is quite small. Here the zero-point energy and the temperature dependence for $\Delta_M H$ and $\Delta_M S$, which were both neglected in our present calculation, could be important. They should cause a small lowering of $\Delta_M G$. These contributions are not important in the system ZnS/ZnSe because the system shows a continuous mixing already without these small corrections due to the similar size lattice parameters. The inclusion of such effects by using molecular dynamic simulations is planned in future work.

6. Conclusion

MSINDO calculations in the cyclic cluster model for bulk properties of the perfect zinc chalcogenides ZnO, ZnS, and ZnSe are in good agreement with the experimental data from the literature. The investigation of the mixed crystals $ZnS_{1-x}Se_x$ with the cyclic cluster model shows a complete miscibility. The calculated lattice parameter depends almost linearly on the content of selenium indicated by a small calculated bowing parameter. In contrast, the band gap E_g exhibits a quadratic behavior resulting in a calculated optical bowing parameter which is in good agreement with experimental results from the literature. The results of calculations for the substitution of oxygen by sulfur in zinc oxide show an increase of the lattice parameter a and c as well as for the cell volume V for a sulfur content of about 2%. We found miscibility of ZnO and ZnS feasible at higher temperatures than by experiments. We suspect that this discrepancy is due to the lack of inclusion of the zero-point energy and the temperature dependence of $\Delta_M H$ and $\Delta_M S$. Therefore molecular dynamics simulations are planned for the future.

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