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Lattice mismatch consequences for the intrinsic characteristics in the dilute (Zn, Se)O alloys

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Abstract

By means of *ab initio* pseudopotential calculations, we investigate the effect of lattice mismatch on the intrinsic properties in the dilute ZnO_xSe_{1-x} alloys. The substitution of isovalent elements having a large electronegativity and size mismatch with respect to the replaced atoms leads to strong nonlinear effects in the properties of the host crystal. From a detailed analysis of the bowing, we notice that the relative contribution of the three components (volume, charge exchange, and strain) shows that the most significant effect is caused by the structural relaxation.

1. Introduction

Current interest in the development of semiconductor alloys provides a strong motivation for fundamental studies of diluted III–V and II–VI alloys due to the unusual physical properties of these materials systems. Among them II–O–VI semiconductors, in which the group-VI element is partially replaced by oxygen, have recently attracted great attention [1–6]. It is found that the substitution of isovalent elements having a large electronegativity and size mismatch with respect to the replaced atoms leads to strong nonlinear effects in the electronic properties of the host crystal.

On the side of the II–VI compounds, O in ZnSe represents an interesting case. Very recently ZnSe_{1-x}O_x alloys having $x = (0.2-1.3)\%$ have been successfully grown by molecular beam epitaxy (MBE) in spite of the limited solubility of O in II–VI compounds [1–6]. From a technological point of view, the ZnSeO alloys have been proposed as very promising candidates for optoelectronic applications such as light emitting diodes and laser diodes.

The most important features observed in ZnSeO for typical oxygen concentrations ($x < 1\%$) are the following: (i) a strong decrease of the band gap, leading to the so-called ‘giant

optical band gap'; (ii) a reduced pressure coefficient; (iii) the response of ZnSeO to the temperature variation is the same as ZnSe, which is independent of the O concentrations. Due to the large difference in size, orbital energies, and electronegativity between O and Se, the oxygen atom has deep effects on the electronic properties of the resulting alloys. This scenario is similar to N in GaAs, GaP, GaSb, and InAs. It is well known that the band gap energy of GaAsN, GaPN, GaSbN, and InAsN alloy semiconductors has strong band gap bowing; that is, the band gap energy becomes much smaller than the conventional linear interpolation of the band gap of the binary compounds.

However, in spite of the ubiquitously observed optical properties of ZnSeO, there have been few theoretical calculations [7] regarding these unusual properties. In this work, we explore theoretically the O-induced electronic structure of dilute ZnSeO alloys using a large supercell of 64 atoms and a first principles pseudopotential approach. The rest of the paper is organized as follows. In section 2, we briefly describe the computational method used in this work. Results regarding the structural and electronic properties will be presented in section 3. A summary of the work will be proposed in section 4.

2. Method

The calculation is based on the density-functional theory in the local-density approximation (LDA) [8]. We use a plane wave expansion non-norm-conserving *ab initio* Vanderbilt pseudopotential [9] as implemented in the PWscf code [10]. The number of plane waves used for these calculations was determined by an energy cut-off of 30 Ryd. Accurate Brillouin zone integrations are performed using the standard special k point technique of Monkhorst and Pack (MP) [11]. We have used a $3 \times 3 \times 3$ mesh, corresponding to six k points. An energy cut-off of 30 Ryd and six k points turns out to be sufficient for the accuracy of the results (10 mRyd for total energy per cell and 5–10 meV for band gap energy).

A large 64 atom supercell representation is used in order to model the $\text{ZnO}_x\text{Se}_{1-x}$ alloy. More specifically, for the 64 atom $\text{Zn}_{32}\text{Se}_{32-n}\text{O}_n$ supercells which correspond to $2 \times 2 \times 2$ conventional cubic cells, a zinc-blende lattice is assumed. The forces acting on each atom are determined using a variation of the Hellmann–Feynman theorem [12, 13]. Given the forces at any configuration, atoms are geometrically relaxed by allowing them to move according to Newton's law in the presence of fictitious damping force. The system evolves until an equilibrium (zero force) geometry is obtained and the final atomic configuration is established.

3. Results

Figure 1 shows the calculated lattice constant as a function of oxygen fraction together with the Vegard's law [14] variation assuming linearity. The calculated lattice constant is larger than the predicted one from Vegard's law. This is in direct contrast with the composition variation of the lattice parameter for the conventional III–V and II–VI alloys. In these systems the deviation from Vegard's law is generally weak and negative. Recent experimental [15–18] studies have pointed out these deviations from Vegard's rule in alloys comprising atoms of very different sizes.

Figure 2 shows the calculated band structure of $\text{ZnO}_x\text{Se}_{1-x}$ for $x = 0.03125$. The main feature of this band structure is the splitting of the Γ conduction band into two sub-bands E_- and E_+ . According to the band anti-crossing model (BAC) [19], the dispersion of these bands is given by

$$E_{\pm}(\mathbf{k}) = \frac{1}{2}[E_M(\mathbf{k}) + E_O] \pm \sqrt{[E_M(\mathbf{k}) - E_O]^2 + 4xC^2}, \quad (1)$$

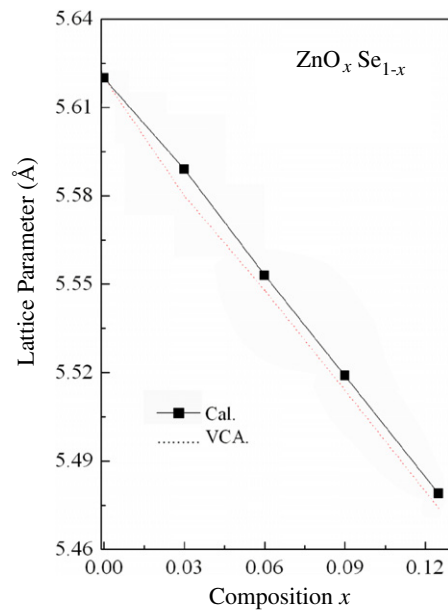


Figure 1. Comparison between Vegard's law (dotted line) and LDA (solid line) calculated lattice constants of $\text{ZnO}_x\text{Se}_{1-x}$.

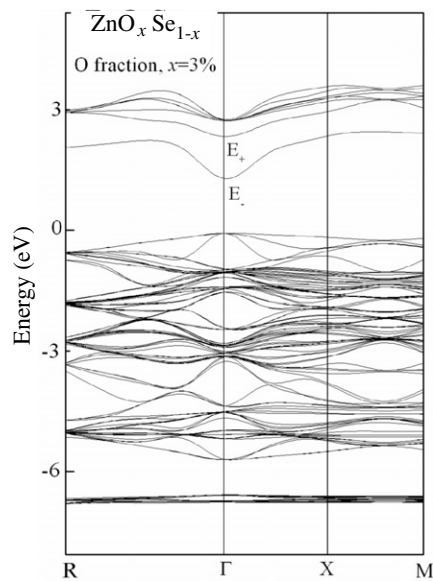


Figure 2. Band structure of $\text{ZnO}_x\text{Se}_{1-x}$ for $x = 0.03125$.

where E_O is the energy of the localized O level, $E_M(\mathbf{k})$ is the \mathbf{k} -vector-dependent energy of the conduction band states of ZnOSe, and C is the matrix element coupling the localized O state and the extended states of ZnSe.

The introduction of oxygen into ZnSe gives a narrow resonant oxygen band located in the conduction band edge. The interaction of the extended Γ states of the conduction band of the

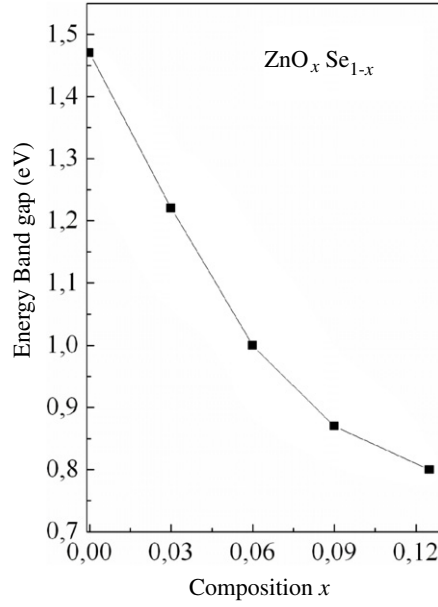


Figure 3. Variation of the energy band gap of $\text{ZnO}_x\text{Se}_{1-x}$.

host semiconductor with the localized O-induced resonant states results in the formation of the two non-parabolic sub-bands E_- and E_+ . The E_- band has mainly conduction-band-like character, whereas the E_+ band is due to E_O -like states.

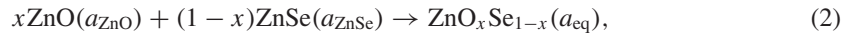
The calculated dependence of the conduction band energy on the alloy composition is shown in figure 3. The band gap decreases rapidly with increasing x , which is in agreement with the experimental results. ZnOSe shows an abnormal giant gap reduction; this behaviour is quite different from conventional semiconductors, where the band gap reduction is relatively small.

The calculated band gaps for a given oxygen composition are then used to obtain the bowing coefficient b of the optical band gap. The dependence of b is shown in figure 4. The optical band gap bowing is found to be strong and composition dependent. This is in contrast to the more typical II–VI semiconductor alloys, where it is relatively small and weakly composition dependent [20].

We found a bowing parameter b equal to 7.1 eV for $x = 0.03125$, and 5.1 eV for $x = 0.125$. We notice that even if the LDA calculations underestimate the energy gaps, the differences between the gaps used in the determination of the bowing parameter tend to be in good agreement with the recent measurement of Nabetani *et al* [3] (about 8 eV for $x < 1\%$).

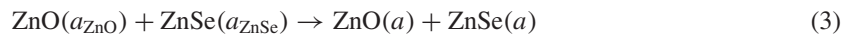
To understand the physical origins of this giant and composition-dependent optical band gap bowing, we decompose b into three physically distinct contributions [21]: (i) volume deformation (VD), (ii) charge exchange (CE), and (iii) structural relaxation (SR).

At a given average fraction x , the ternary alloy $\text{ZnO}_x\text{Se}_{1-x}$ obeys the formal reaction



where a_{ZnO} and a_{ZnSe} are the equilibrium lattice constants of the binary ZnO and ZnSe respectively. a_{eq} is the equilibrium lattice constant of the alloy at the average fraction x .

We decompose reaction (2) into three steps



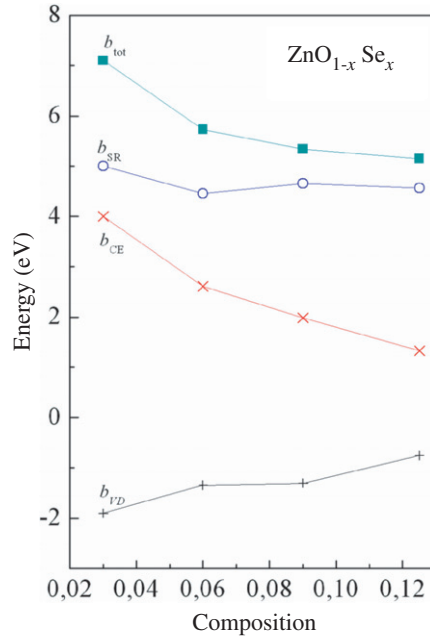


Figure 4. Composition dependence of the calculated total band gap bowing (b) with the three contributions b_{VD} , b_{CE} , and b_{SR} .

(This figure is in colour only in the electronic version)



The first step measures the volume deformation (b_{VD}) effect on the bowing. This term represents the relative response of ZnSe (ZnO) to hydrostatic pressure from its individual equilibrium lattice constant a_{ZnSe} (a_{ZnO}) to the alloy value $a = a(x)$. The second contribution, the charge exchange (CE) term, is related to a charge transfer in bringing ZnSe and ZnO to $a = a(x)$. The final step, the structural relaxation (SR) term, describes the change of the band gap upon passing from the unrelaxed to the relaxed alloy, i.e. $a(x) \rightarrow a_{\text{eq}}$. By construction, the total bowing is

$$b = b_{\text{VD}} + b_{\text{CE}} + b_{\text{SR}}. \quad (6)$$

The general representation of the composition-dependent band gap of the alloys in terms of the gaps of the binary compounds $E_{\text{ZnSe}}(a_{\text{ZnSe}})$ and $E_{\text{ZnO}}(a_{\text{ZnO}})$, and the total bowing b parameter, is

$$E_g(x) = xE_{\text{ZnO}}(a_{\text{ZnO}}) + (1-x)E_{\text{ZnSe}}(a_{\text{ZnSe}}) - bx(1-x). \quad (7)$$

This allows a division of the total bowing b into three contributions according to

$$b_{\text{VD}} = \frac{E_{\text{ZnO}}(a_{\text{ZnO}}) - E_{\text{ZnO}}(a)}{1-x} + \frac{E_{\text{ZnSe}}(a_{\text{ZnSe}}) - E_{\text{ZnSe}}(a)}{x} \quad (8)$$

$$b_{\text{CE}} = \frac{E_{\text{ZnO}}(a)}{1-x} + \frac{E_{\text{ZnSe}}(a)}{x} - \frac{E_{\text{ZnSe}_{1-x}\text{O}_x}(a)}{x(1-x)} \quad (9)$$

$$b_{\text{SR}} = \frac{E_{\text{ZnSe}_{1-x}\text{O}_x}(a) - E_{\text{ZnSe}_{1-x}\text{O}_x}(a_{\text{eq}})}{x(1-x)}. \quad (10)$$

All these energy gaps occurring in expressions (8)–(10) have been calculated for the indicated lattice constants. The three contributions b_{VD} , b_{CE} , and b_{SR} due to volume deformation, different atomic electronegativities and structural relaxation are plotted in figure 4. The following points are noticed.

- (i) The volume deformation term b_{VD} is relatively small and composition dependent.
- (ii) The charge exchange term b_{CE} is large and composition dependent; b_{CE} scales with the strong electronegativity mismatch of O and Se.
- (iii) The structural term b_{SR} is giant and strongly composition dependent, similar to the other III–V–N mixed anion semiconductor alloys [20, 22, 23]. Thus, the structural relation effect proportional to the Se–O atomic size difference appears to control the giant optical band gap bowing of ZnSeO alloy.

4. Summary

We have used first principles calculations to investigate the effects of lattice mismatch in the dilute ZnOSe alloys. Due to the large size mismatch between O and Se, the deviation of the lattice parameter variation is positive, which is in direct contrast with the composition variation of the lattice parameter for conventional III–V and II–VI alloys. Moreover, the optical band gap bowing is found to be strong and composition dependent as found for other mixed anion III–V–N systems. The stronger contribution is mainly due to the atomic bond relaxation effect.

References

- [1] Iwata K, Fons P, Yamada A, Shibata H, Matsubara K, Nakahara K, Takasu H and Niki S 2002 *Phys. Status Solidi b* **229** 887
- [2] Nabetani Y, Mukawa T, Okuno T, Ito Y, Kato T and Matsumoto T 2003 *Mater. Sci. Semicond. Process.* **6** 343
- [3] Nabetani Y, Mukawa T, Ito Y, Kato T and Matsumoto T 2003 *Appl. Phys. Lett.* **83** 1148
- [4] Shan W, Walukiewicz W, Ager J W III, Yu K M, Wu J, Haller E E, Nabetani Y, Mukawa T, Ito Y and Matsumoto T 2003 *Appl. Phys. Lett.* **83** 299
- [5] Polimeni A, Capizzi M, Nabetani Y, Ito Y, Okuno T, Kato T, Matsumoto T and Hirai T 2004 *Appl. Phys. Lett.* **84** 3304
- [6] Merita S, Krämer T, Mogwitz B, Franz B, Polity A and Meyer B K 2006 *Phys. Status Solidi c* **3** 960
- [7] Moon C-Y, Wei S-H, Zhu Y Z and Chen G D 2006 *Phys. Rev. B* **74** 233202
- [8] Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** 864
- [9] Vanderbilt D 1985 *Phys. Rev. B* **32** 8412
- [10] Baroni S, Dal Corso A, de Gironcoli S and Giannozzi P, <http://www.pwscf.org>
- [11] Monkhorst H J and Park J D 1976 *Phys. Rev. B* **13** 5188
- [12] Hellmann H 1937 *Einführung in die Quantumchemie* (Leipzig: Franz Deutsche)
- [13] Feynman R P 1939 *Phys. Rev.* **56** 340
- [14] Vegard L 1921 *Z. Phys.* **5** 17
- [15] Bauer M, Taraci J, Tolle J, Chizmeshya A V G, Zollner S, Smith D J, Mendez J, Hu C and Kouvetakis J 2002 *Appl. Phys. Lett.* **81** 2992
- [16] Fan W J, Yoon S F, Ng T K, Wang S Z, Loke W K, Liu R and Wee A 2002 *Appl. Phys. Lett.* **80** 4136
- [17] Fan W J, Yoon S F, Cheah W K, Loke W K, Ng T K, Wang S Z, Liu R and Wee A 2004 *J. Cryst. Growth* **268** 470
- [18] Reason M, Weng X, Ye W, Detting D, Hanson S, Obeidi G and Goldman R S 2003 *J. Appl. Phys.* **97** 103523
- [19] Shan W, Walukiewicz W, Ager J W III, Haller E E, Geisz J F, Friedman D J, Olson J M and Kurtz S R 1999 *Phys. Rev. Lett.* **82** 1221
- [20] Wei S-H and Zunger A 1996 *Phys. Rev. Lett.* **76** 664
- [21] Bernard J E and Zunger A 1987 *Phys. Rev. B* **36** 3199
- [22] Ferhat M 2004 *Phys. Status Solidi b* **241** R38
- [23] Belabbes A, Ferhat M and Zaoui A 2006 *Appl. Phys. Lett.* **88** 152109