

Effects of disorder on the optical gap of (Zn,Mg)(S,Se)

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The electronic properties and optical gap of (Zn,Mg)(S,Se) wide-gap solid solutions are studied using *ab initio* techniques and starting from the previously determined atomistic structure of the alloy. Compositional disorder is shown to close the gap substantially with respect to the predictions of the virtual-crystal approximation. The bowing of the fundamental gap versus composition predicted by our calculations is in very good agreement with experiments available for the Zn(S,Se) pseudobinary alloy. At temperatures typical of molecular-beam epitaxy growth, the quaternary alloy displays a rather large amount of short-range order whose effect is to slightly but unmistakably open the gap. Our results agree well with recent experimental data for the quaternary alloy. © 1999 American Institute of Physics. [S0003-6951(99)02044-6]

In the last decade much effort has been devoted to the study of semiconducting materials capable of operating in the short wavelength optical range. The main goal of these efforts is the realization of light-emitting and laser diodes encompassing the entire visible-light window and, in perspective, the industrial-scale production of high-density storage optical disks and light sources for full-color displays. II–VI and nitride semiconductors are the most promising among these materials. Among II–VI semiconductors, ZnSe-based materials have a special importance,¹ and quaternary $Zn_yMg_{1-y}S_xSe_{1-x}$ alloys are commonly used as cladding layers in II–VI blue–green laser diodes. This system—which was introduced a few years ago²—has the desirable property that its lattice parameter a_0 and its fundamental band gap E_g can be tuned fairly independently by acting on the molar fractions x and y . In spite of the technological importance of this material, extensive experimental studies of its electronic and optical properties over a wide range of compositions and of their dependence on the structural and thermodynamic equilibrium properties are still lacking.

We recently reported³ on a theoretical study of the thermodynamical properties of this system, performed using *ab initio* methods. In that study the phase diagram of the quaternary alloy was determined, and the homogeneous alloy was found to be stable against segregation or the formation of ordered structures at temperatures typical of MBE growth (≈ 550 K). Nevertheless, a large amount of short-range order (SRO) characterized by the occurrence of Zn–Se and Mg–S clustering among first-nearest neighbors was found to occur and to persist even at very high temperatures (≈ 1700 K).

In this letter we report on an extensive theoretical study of the electronic and optical properties of (Zn,Mg)(S,Se) alloys both in the case of the experimentally well studied pseudobinary ZnS_xSe_{1-x} system, and for the quaternary solid solution in conditions of lattice matching to GaAs substrates. In the latter case the presence of the short range

correlations will be shown to slightly but significantly open the fundamental band gap.

Our work is based on density-functional theory (DFT) within the local density approximation (LDA), and the plane-wave pseudopotential method. All the technical details of our calculations are the same as in Ref. 3. DFT–LDA is known to underestimate electronic excitation energies, and many-body corrections should be considered, e.g., using the GW method.⁴ Notwithstanding, DFT–LDA usually yields quite accurate *occupied* (valence) energy levels, and also the shape of the *empty* (conduction) bands is predicted quite reasonably. Because of this, one commonly adopted semiempirical procedure to take into account many-body effects consists in simply shifting the conduction bands rigidly upwards with respect to valence bands. This method, known in the literature with the name of *scissor operator*,⁵ has been extensively used in a variety of applications.⁶

Ideally, the study of the electronic properties of an alloy should proceed in three steps: (i) the determination of the equilibrium structural properties of the system, including the relevant atomic correlations, as we obtained and discussed in Ref. 3; (ii) the calculation of the alloy band structure, taking into account the atomistic structure previously determined; (iii) the account of many-body corrections to the electronic band structure. It is still very hard to combine many-body calculations with a proper description of disorder, and in the following we assume that disorder and quasiparticle effects can be treated independently: we deal explicitly with compositional disorder at the LDA level, using a generalization of the *special quasirandom structures* approach,⁷ and we add semiempirically the many-body corrections by a simple linear interpolation of the scissor operators appropriate for the pure compounds.

Our main approximations are: (i) the assumption that disorder and many-body effects can be calculated independently of each other; and (ii) that the many-body corrections to the optical gap can be interpolated linearly as a function of composition, starting from the pure-compound end points. In order to assess the soundness of these approximations, we consider the case of the ZnS_xSe_{1-x} pseudobinary alloy whose optical properties are well known experimentally over

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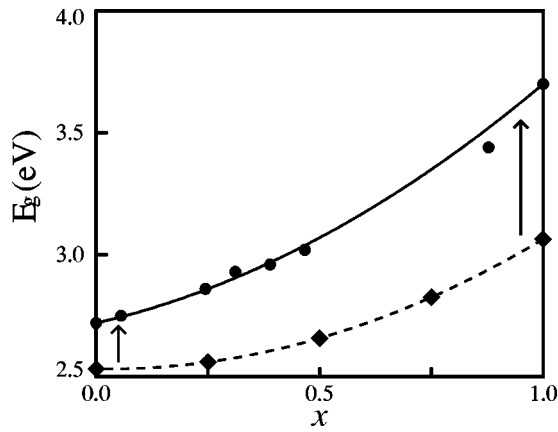


FIG. 1. Energy gap of the $\text{ZnS}_x\text{Se}_{1-x}$ pseudobinary alloy as a function of the ZnS molar fraction, x : (full dots) experimental data from Ref. 9; (diamonds) our theoretical results obtained neglecting many-body effects; (dashed line) quadratic interpolation to our theoretical results, (full line) theoretical results semiempirically corrected for quasiparticle effects.

a wide range of compositions.^{8,9} In Fig. 1 we display our results for the fundamental band gap of the alloy, as calculated for five different molar fractions, ($x=0, 0.25, 0.50, 0.75,$ and 1) and compare them with available experimental data.⁹ As previously discussed, LDA calculations systematically underestimate the optical gap. Adding a linear interpolation of the errors done at the pure-compound extremes, brings our theoretical predictions in very good agreement with experiments. This fact demonstrates that many-body corrections to the band gap can indeed be accounted for independently of disorder effects, and that they depend linearly upon composition. Upon this semiempirical correction, our theoretical results can be accurately described by the formula:

$$E_g(x) = E_g^{\text{ZnSe}}(1-x) + E_g^{\text{ZnS}}x - bx(1-x), \quad (1)$$

where the curvature, commonly known as *bowing parameter*, is $b \approx 0.56$ eV. Our result is in good agreement with experiments,^{8,9} according to which $0.41 \text{ eV} \leq b \leq 0.68 \text{ eV}$. One common adopted approximation to deal with solid solutions is the so called virtual crystal approximation (VCA) in which disorder effects are neglected. In the pseudopotential framework, such as used in the present study, this approximation amounts to replacing the alloy by a periodic crystal whose cationic and anionic pseudopotentials are compositional averages of those appropriate for the pure compounds. The value of the bowing parameter predicted by the VCA, $b_{\text{VCA}} \approx -0.1$ eV, is much smaller in magnitude than experimentally observed and with a wrong sign.

Having shown that our approximate treatment of many-body effects is accurate for the pseudobinary Zn(S,Se) alloy, we pass now to examine the quaternary case which displays a large amount of short-range order.³ Short-range order is measured by the atomic correlation functions, defined as

$$C_{XY}(\mathbf{r}) = \langle \xi(\mathbf{r}) \eta(0) \rangle - \langle \xi \rangle \langle \eta \rangle, \quad (2)$$

where $\xi(\mathbf{r})$ and $\eta(\mathbf{r})$ are integer random variables whose value is 1 if the atomic site at position \mathbf{r} is occupied by an atom of species X or Y, respectively, and 0 otherwise; $\langle \cdot \rangle$ indicates the average over disorder; and $\langle \xi \rangle$ and $\langle \eta \rangle$ are the molar fractions of the X and Y atomic species. Since atomic

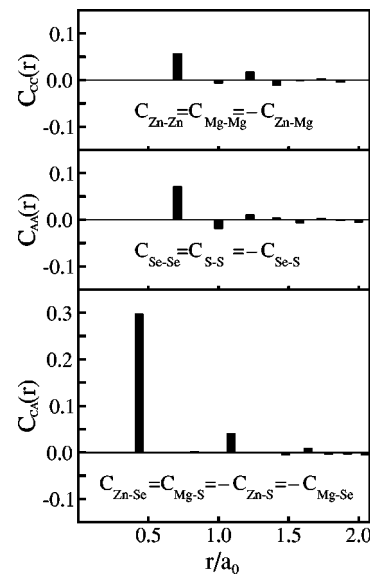


FIG. 2. Interatomic correlation functions in $\text{Zn}_{1/2}\text{Mg}_{1/2}\text{S}_{1/2}\text{Se}_{1/2}$ solid solutions [see Eq. (2)] as calculated in Ref. 3 for $T=550$ K.

disorder affects separately the cation and the anion sublattices, and no cation–anion intermixing is allowed in our study, out of the ten different correlation functions so defined (three cation–cation, three anion–anion and four mixed cation–anion correlation functions) only three of them—the cation–cation, the cation–anion, and the anion–anion—are actually independent. In Fig. 2 we display the atomic correlation functions calculated in Ref. 3 at a temperature of 550 K and for $x=y=\frac{1}{2}$. The large positive value of the Zn–Se and Mg–S first-nearest neighbor correlations indicates a strong tendency to form ZnSe and MgS local clusters. This kind of clustering acts to reduce the elastic energy of the system because ZnSe and MgS have lattice parameters similar to each other and to that of the alloy ($a_{\text{ZnSe}}=10.57$ a.u. and $a_{\text{MgS}}=10.79$ a.u.), but very different from those of ZnS and MgSe ($a_{\text{ZnS}}=10.09$ a.u. and $a_{\text{MgSe}}=11.32$ a.u.). This tendency also shows in the second-nearest neighbor correlations (first shell in the cation–cation and anion–anion correlations, upper panels of Fig. 2) which favor like cations and anions. All correlation functions rapidly decay with distance and the resulting order is very short ranged.

Starting from these structural data, we have calculated the electronic properties of the alloys using the *special quasirandom structures* approach.⁷ This method is based on the observation that—for any given composition—atomic disorder mainly affects the electronic properties of an alloy through the short-range atomic structure. A disordered solid solution can thus be mimicked by using reasonably small supercells that reproduce the alloy SRO in the first few (typically, four or five) shells of neighbors. We have generalized the original method to account for any given short-range order,¹⁰ arbitrary compositions, and double sublattice disorder. We have verified that atomic correlations beyond the fourth shell of neighbors affect only negligibly the band structure of the alloys presently studied. The supercell structures used in our simulations were thus obtained by a simulated-annealing procedure by which we searched among 64 atom simple-cubic structures the ones which give the most similar pair correlations up to the fourth shell of neigh-

TABLE I. Energy gap vs compositions in $\text{Zn}_y\text{Mg}_{1-y}\text{S}_x\text{Se}_{1-x}$.

y	x	VCA ^a	Random ^b	SRO ^c	Corrected SRO ^d	Expt ^e
0.50	0.50	2.96	2.57	2.64	3.52	3.56
0.75	0.13	2.68	2.48	2.50	3.00	3.00
0.84	0.00	2.55	2.43	2.44	2.78	2.82

^aTheoretical results obtained within the virtual-crystal approximation.

^bSuper-cell calculations for the random alloy.

^cSupercell calculations including SRO, but neglecting many-body effects.

^dAs above, but corrected for quasiparticle effects.

^eExperimental data from Ref. 11.

bors, as compared to those obtained from Monte Carlo simulations.³ The electronic structure of the quaternary alloy has been studied for three different molar fraction pairs along the line of lattice matching to GaAs (i.e., for pairs of molar fractions x and y such that the average lattice parameter of the alloy is the same as that of GaAs).

In Table I we report the values of the fundamental gap as calculated in the VCA, neglecting SRO correlations, and taking into account SRO, and we compare these results with recent experimental data.¹¹ Quasiparticle effects are taken into account by the same kind of semiempirical corrections described in the case of the pseudobinary alloy. In the present quaternary case, the values of scissor operators for the four pure compounds are bilinearly interpolated inbetween. Our calculated values for the energy gaps are in very good agreement with experiments (within 0.04 eV). As it was the case for the $\text{Zn}(\text{S},\text{Se})$ pseudobinary alloy, the predictions of the VCA are rather poor, resulting in too large a gap. The effect of SRO, as compared to the perfectly random solution, is to slightly open back the gap. The effect is small, but sizeable when disorder is maximum (i.e., for $x=y=\frac{1}{2}$). The effects of SRO on the alloy band structure can be understood qualitatively by considering the actual alloy as a perturbation with respect to the appropriate virtual crystal (VC), as done by Baldereschi and Maschke¹² in an early study of $\text{Ga}_x\text{In}_{1-x}\text{P}$:

$$V_{\text{alloy}}(\mathbf{r}) = V_{\text{VC}}(\mathbf{r}) + \Delta V(\mathbf{r}). \quad (4)$$

To second order in the perturbation, the alloy band structure is given by

$$\epsilon_n(\mathbf{k}) = \epsilon_n^0(\mathbf{k}) + \sum_{n',\mathbf{k}'} \frac{|\langle n, \mathbf{k} | \Delta V | n', \mathbf{k}' \rangle|^2}{\epsilon_n^0(\mathbf{k}) - \epsilon_{n'}^0(\mathbf{k}')}, \quad (5)$$

where $|n, \mathbf{k}\rangle$ are the VC eigenvectors with energy $\epsilon_n^0(\mathbf{k})$, for the given composition pair (x, y) . Since occupied (empty) states mostly interact with the other occupied (empty) states, that are closer in energy, the effect of the perturbation is to push the band edges in the gap region, thus reducing the VC gap, in agreement with our findings for $\text{Zn}_y\text{Mg}_{1-y}\text{S}_x\text{Se}_{1-x}$, as well as for $\text{ZnS}_x\text{Se}_{1-x}$ alloy. In the presence of SRO, this result can be generalized by showing that the magnitude of the gap reduction depends quadratically on the strength of the localized perturbations which transform the VC into the actual alloy, multiplied by the appropriate atomic correlation functions. From Fig. 2 it can be seen that the main difference between the correlated and the random alloy is that the former has a larger number of bond-length preserving Zn–Se and Mg–S nearest-neighbor pairs and a reduced number of

bond-stretching Zn–S and Mg–Se nearest-neighbor pairs relative to the random alloy. The former type of perturbation of the VC is probably weaker than the latter, thus explaining the smaller closure of the VC gap in the correlated alloy as compared to the random case.

In order to better characterize the optical gap of the alloy, we consider the spectral weight

$$A(E, \mathbf{k}) = \sum_n |\langle \psi_n | P(\mathbf{k}) | \psi_n \rangle|^2 \delta(E - \epsilon_n), \quad (6)$$

where ψ_n and ϵ_n are the wave functions and energy levels of the supercell, and $P(\mathbf{k})$ is the projector over the states of crystal quasimomentum \mathbf{k} . We have found that the alloy wave functions at the top of the valence and at the bottom of the conduction bands have a strong Γ character, thus indicating that the direct-gap nature of the pure materials is conserved also in the alloy. An analysis of the different atomic contributions to the density of states has been carried out by projecting the super-cell eigenfunctions onto the atomic-like localized orbitals. We found that the states at the top of the valence band have a strong anionic character (26% centered on S and 67% on Se). The anionic character of the top of the valence band is a direct consequence of the ionic character of the alloy, while the larger contribution of the Se atomic orbitals is consistent with Harrison's tight binding tables¹³ which indicate that the top of the valence band states of S compounds lies about 0.5 eV below the analogous states of the corresponding Se compounds. The low-lying conduction states are rather delocalized, with contributions from all the four atomic species and a slight prevalence of cationic character.

A more complete account of this work can be found in the Ph.D. thesis of one of us.¹⁴

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