

First-principles calculation of the order-disorder transition in chalcopyrite semiconductors

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We describe the polymorphic order-disorder transition in the chalcopyrite-type semiconductor $\text{Cu}_{0.5}\text{In}_{0.5}\text{Se}$ through a Monte Carlo simulation of a generalized Ising Hamiltonian whose interaction energies are determined from *ab initio* total-energy calculations. The calculated transition temperature ($T_c = 1125 \pm 20$ K) compares well with experiment ($T_c = 1083$ K). Unlike the analogous ordering in isovalent III-V alloys, we find that the transition is dominated by electronic compensation between donor and acceptor states, leading to strong correlations in the disordered phase, and a decrease in the optical band gap upon disordering.

Recent theory¹⁻³ and observations^{4,5} of spontaneous long-range order in isovalent III-V semiconductor alloys created interest in the theoretical implications on self-organization in random systems³ and in the technologically attractive possibility of changing the optical band gaps of random alloys at fixed composition through ordering.^{5,6} The relatively weak interactions between the isovalent atoms in such III-V alloys lead, however, to a small enthalpy difference between the disordered and ordered bulk phases⁷ ($\delta H < 0.5$ kcal/mole), so the driving force for the transition is dominated by surface energetics.² This leads to imperfect ordering⁴ and irreversibility^{4,5} that complicates the study of the transitions. There is, however, a large class of tetrahedrally bonded semiconductors—the $A^{\text{I}}B^{\text{III}}C^{\text{VI}}_2$ chalcopyrites⁸—where the stronger interactions between the nonisovalent $A^{\text{I}}B^{\text{III}}$ atoms (reflected in much larger latent heat⁹ δH of 2-3 kcal/mole) leads to reversible order-disorder transitions observable at conveniently higher temperatures even in bulk crystals. These ternary $A^{\text{I}}B^{\text{III}}C^{\text{VI}}_2$ chalcopyrites (e.g., CuInSe_2) undergo as a function of temperature a first-order phase transition between the high-temperature disordered zinc-blende-like (ZB) phase and the ordered chalcopyrite (CH) structure. Depending on the system, the disordering transition occurs in the temperature range⁸⁻¹⁰ $T_c \sim 800$ -1300 K, is accompanied by an abrupt disappearance of the zinc-blende-forbidden x-ray-diffraction peaks,¹¹ a large (0.1-0.5 eV) reduction in the semiconducting band gaps¹²⁻¹⁴ and marked changes in the short-range order seen in NMR studies.¹³ Since the disordered phase contains cross substitutions between nonisovalent $A^{\text{I}}B^{\text{III}}$ atoms, it manifests donor-acceptor electronic compensation. It then appears that experimental and theoretical studies of the physical factors controlling the polymorphic order-disorder transition in chalcopyrites can be used to gain insights into (i) the analogous (but weaker) transformations in isovalent alloys, and (ii) the physics of compensation in highly concentrated donor-acceptor systems.

In this work we describe an *ab initio* theoretical study of the microscopic origins of the order-disorder transitions in the prototype chalcopyrite system $\text{Cu}_{0.5}\text{In}_{0.5}\text{Se}$. Similar but less detailed results are also presented for the “III-V analog”⁸ $\text{Zn}_{0.5}\text{Sn}_{0.5}\text{P}$. Despite the fact that the transition temperature in these systems is high (relative to the melt-

ing temperature), the energy differences involved are rather fine (on the scale of *ab initio* calculations). Indeed, while the measured¹⁵ cohesive energy of CuInSe_2 is 13.5 eV and its formation enthalpy is 2.8 eV, the enthalpy difference between the disordered and ordered phases at T_c is⁹ only 0.02 eV/atom. This subtlety of the energy balance had focused previous theories on studying the qualitative relations between the transition temperature and structural^{10,16,17} or optical¹⁸ parameters. In the present study we combine sufficiently precise *ab initio* total-energy calculations with statistical mechanics calculations of the phase transition. This provides a quantitative microscopic description of this order-disorder transformation in terms of the electronic structure, permitting comparisons with the isovalent case.

Our calculations consists of three steps. First (“energetics”) we conduct $T=0$ quantum-mechanical total-energy calculations on a variety of ordered superstructures of CuSe/InSe , mapping the results onto a generalized Ising Hamiltonian. The excess energy of a configuration σ of A and B atoms on the fcc lattice

$$\Delta E_{\text{LDA}}(\sigma, V, x) = E_{\text{LDA}}(\sigma, V, x) - E_{\text{LDA}}^0(V, x) \quad (1)$$

is computed at constant volume (V) and composition (x) in the local-density approximation (LDA) with respect to a reference energy E^0 . This calculation is repeated for N_s ordered superstructures. Independently, we construct a cluster expansion (CE) of the excess energy of arbitrary configurations in terms of a series of effective interactions $J_{k,m}(V, x)$ within clusters consisting of k atoms separated by up to m neighbors:

$$\Delta E_{\text{CE}}(\sigma, V, x) = \sum_k \sum_m D_{k,m} \bar{\Pi}_{k,m}(\sigma) J_{k,m}(V, x). \quad (2)$$

Here, $\bar{\Pi}_{k,m}(\sigma)$ are lattice-averaged spin products⁷ of cluster (k, m) in configuration σ , and $D_{k,m}$ are appropriate⁷ degeneracy factors. Mapping the LDA calculations for N_s configurations $\{s\}$ onto the Ising model (2)

$$\sum_s |\Delta E_{\text{LDA}}(s) - \Delta E_{\text{CE}}(s)| = \text{Min} \quad (3)$$

then yields a set of $N_J \leq N_s$ effective interaction energies $\{J_{k,m}\}$. The practical completeness of the expansion is then examined by the ability of this set $\{J_{k,m}\}$ to predict through Eq. (2) the energies $\Delta E_{\text{LDA}}(s')$ of other structures $s' \neq s$, not used in Eq. (3). Sufficient long-range in-

teraction terms are included in (2) to assure a “prediction error” of less than a given tolerance.

In the *second* step (“ground-state search”) the converged set of interaction energies $\{J_{k,m}\}$ are used to find through Eq. (2) the lowest-energy $T=0$ structure among the many ($\gg N_s$) configurations attainable by different occupations of the fcc lattice by As' and Bs' . This examines the ability of the LDA-derived cluster expansion to identify the correct ground-state phase.

In the *third* step (finite-temperature statistics) we use the set $\{J_{k,m}\}$ to solve the generalized Ising Hamiltonian (2) using the Monte Carlo method, finding as a function of temperature the various thermodynamic quantities of the ground state and other phases, and, hence, the transition temperature. The basic difference between this approach and the more traditional phenomenological Ising models¹⁹ is that we define the type of interactions (two-, three-, four-body), their range (first, second, etc., neighbors), and their absolute magnitudes directly in terms of the quantum-mechanical electronic structure. This enables analysis of the statistical and thermodynamic quantities obtained in step three (T_c , δH , short-range order, correlations) in terms of the electronic structure formulated in step one (e.g., atomic relaxations, charge compensation, band structures).

The ordered structures used in step one are $(AC)_p(BC)_p$ superlattices of repeat periods $p=1,2$ and various orientations G . We sample a range of superlattice layer orientations, i.e., $G=[001]$ ($p=1,2$ are termed CA and Z2, respectively), $G=[111]$ ($p=1,2$ are termed CP and Y2, respectively), $G=[110]$ ($p=1$ is again CA while $p=2$ is termed Y2), $G=[201]$ ($p=1$ is CA and $p=2$ is CH), and $G=[113]$ ($p=1,2$ are termed CP and W2, respectively). These structures contain all possible C-centered A_nB_{4-n} cation tetrahedra ($0 \leq n \leq 4$), as shown in Table I. The LDA equations are solved scalar relativistically through the linear-augmented plane-wave (LAPW) method²⁰ using the Ceperley-Alder exchange-correlation potential, as parametrized by Perdew and Zunger.²¹ To assure a high precision of 5 meV/atom, we use a large basis set consisting of 110 LAPWs per atom

TABLE I. LAPW calculated relaxed excess energies [Eq. (1)] of $\text{Cu}_{0.5}\text{In}_{0.5}\text{Se}$ in various structures defined in the text. Fitting these to Eq. (3) using six interaction energies (see text) gives the results shown in parentheses. All results are in meV/(4 atoms) and are given relative to equivalent amounts of CuSe and InSe in the zinc-blende structure at the molar volume of $\text{Cu}_{0.5}\text{In}_{0.5}\text{Se}$. The last column gives the type of tetrahedra in each of the structures.

Structure	ΔE	Tetrahedra type
CA	-2318(-2318)	A_2B_2
CH	-2326(-2326)	A_2B_2
CP	-2113(-2113)	$\frac{1}{2}A_3B + \frac{1}{2}AB_3$
Z2	-1774(-1774)	$\frac{1}{4}A_4 + \frac{1}{2}A_2B_2 + \frac{1}{4}B_4$
Y2	-2113(-2113)	$\frac{1}{2}A_3B + \frac{1}{2}AB_3$
Y2	-1655(-1655)	$\frac{1}{4}A_4 + \frac{1}{4}AB_3 + \frac{1}{4}A_3B + \frac{1}{4}B_4$
W2	-2220(-2220)	$\frac{1}{4}A_3B + \frac{1}{2}A_2B_2 + \frac{1}{4}AB_3$

and a set of Brillouin zone \mathbf{k} points that samples all structures equivalently (folded from ten special \mathbf{k} points in the fcc lattice). All calculations are done at a fixed (experimental) molar volume of the ordered phase, neglecting the¹⁴ $\leq 0.08\%$ volume expansion upon disordering and (unless otherwise mentioned) the $< 1\%$ noncubic axial deformation.⁹ The total energy of each ordered structure is minimized at constant volume with respect to all of the cell-internal structural degrees of freedom. Initial guesses for the geometry obtained by a LAPW-parametrized valence force field model are subsequently refined iteratively using the recently developed all-electron quantum-mechanical force minimization.²² To examine the effect of the neglected external deformation, we have calculated it for a single structure (the CH phase), finding $c/a=1.008$, compared with the observed value⁹ of 1.004. The energy lowering [< 3 meV/(4 atoms)] was, however, negligible. For the chalcopyrite phase of CuInSe_2 we obtain the equilibrium lattice constant $a=5.736$ Å (observed:⁹ 5.784 Å) and the internal distortion parameter 0.214 (observed:⁹ 0.224). We find that cell-internal structural relaxations lower the total energies enormously (e.g., by 440 and 610 meV per four atoms in chalcopyrite and the Y2 structures, respectively). Table I gives the relaxed excess energies $\Delta E_{\text{LDA}}(\sigma, V, \frac{1}{2})$ for seven ordered superstructures; the arbitrary reference energy E_{LDA}^0 (which does not affect T_c) is taken as the energy of an equivalent amount of hypothetical zinc blende $AC+BC$.

The mapping of the LDA energies onto a cluster expansion [Eqs. (2) and (3)] is done using an extended set of cluster interactions $\{J_{k,m}\}$. These include (i) the “empty figure” $(k,m)=(0,0)$, (ii) the first four pair ($k=2$) interactions (2,1), (2,2), (2,3), and (2,4) between first through fourth fcc neighbors, and (iii) the lowest-order four-body interaction $(k,m)=(4,1)$. Note that because of the symmetry of the $x=\frac{1}{2}$ structures studied here the coefficients $\bar{\Pi}_{k,m}$ vanish for all odd-body $k=1,3,\dots$ terms, so T_c at $x=\frac{1}{2}$ is unaffected by them. Table I shows that mapping $N_s=7$ structures to these six interaction parameters gives a perfect fit (shown in parentheses). Omission of any of the structures from the basis set and a subsequent prediction of its energy from the cluster expansion produces a “prediction error” $\delta E_{\text{LDA}}(s')$ of less than the underlying error of the LAPW itself. Hence we can use this cluster expansion to predict the energies of arbitrary lattice configurations and their thermodynamic properties.

Using the converged interaction energies $\{J_{k,m}\}$, we solved in step-three the spin- $\frac{1}{2}$ fcc generalized Ising model using Monte Carlo simulations with single-spin flip kinetics and a periodic supercell. Five hundred spin-flip attempts per site are used to reach steady state before starting to collect data at a chemical potential $\mu=0$. The data are averaged in each block of 40 flips per site; this is repeated 60 times to calculate the global averages and standard deviations. Size effects were investigated by increasing the number of fcc sites from $8^3=512$ to $12^3=1728$ and to $16^3=4096$. We found that the cell with 1728 fcc sites is generally sufficient. In order to reduce hysteresis effects near T_c we used a starting sample that is half chalcopyrite and half random. Vibrational degrees of freedom

are neglected.

Our results are summarized as follows:

a. Electronic compensation. While the ordered chalcopyrite ABC_2 structure contains but the C-centered A_2B_2 tetrahedra, the disordered $A_{0.5}B_{0.5}C$ phase contains also a statistical mix of $AB_3 + A_3B$, as well as the $A_4 + B_4$ tetrahedra. To assess the effective interactions between these complimentary clusters, we consider the total-energy difference $\delta_{1,3} = E(CP) - 1/2[E(L1) + E(L3)]$ between the periodic $A_2B_2C_4$ CP structure that contains both AB_3 and A_3B tetrahedra (Table I), and the average energies of the Luzonite structures A_3BC_4 (L1) and AB_3C_4 (L3), each containing a *single* type of tetrahedron. In *isovalent* alloys *all* cation tetrahedra are electronically closed shell so the (constant volume) interaction $\delta_{1,3}$ is very weak [e.g.,⁷ $\delta_{1,3} = 17$ meV/(4 atoms) in $Cd_{0.5}Zn_{0.5}Te$ and 8 meV/(4 atoms) in $Ga_{0.5}In_{0.5}P$]. In contrast, in nonisovalent systems such as $Cu_{0.5}In_{0.5}Se$ the Se-centered Cu_3In cluster is electron deficient while the $CuIn_3$ cluster has excess electrons. Indeed, we find that the periodic Luzonite structures Cu_3InSe_4 and $CuIn_3Se_4$ are both metallic, exhibiting, respectively, holes in the valence band and electrons in the conduction band. Consequently, these uncompensated clusters have a very high electronic energy. When they are allowed to couple, they form an insulating donor-acceptor complex (e.g., the CP structure) with a significant energy stabilization [$\delta_{1,3} = -670$ meV/(4 atoms)] attendant upon charge transfer. Similar results are found when the Cu_4 and In_4 clusters condense into the Z2 structure. The existence of such a strong electronic compensation is the main distinguishing feature between the order-disorder transition in nonisovalent versus isovalent ternary semiconductors. Indeed, when the electronic compensation is neglected (using in step one periodic structures containing isolated, *uncompensated* clusters) we find (in step three) a very high transition temperature of $T_c > 3000$ K, compared with the observed value⁸ for $Cu_{0.5}In_{0.5}Se$ of $T_c = 1083$ K.

b. Ground-state structures. The mapping of the LDA energies of the compensated structures onto the cluster expansion yields the interaction energies (in meV)

$$\begin{aligned} J_{2,1} &= 70.6, & J_{2,2} &= 2.6, \\ J_{2,3} &= 0.8, & J_{2,4} &= 0.7, & J_{4,1} &= 6.6. \end{aligned} \quad (4)$$

They show that (i) all pair interactions are antiferromagnetic (attractive) so, unlike the isovalent case,⁷ the ensuing low-temperature bulk ground state will be ordered, (ii) while the nearest-neighbor pair interaction $J_{2,1}$ is dominant, the remaining interactions in (4) are non-negligible (see the effect on T_c discussed below). We find, however, that the higher pair interactions are an order of magnitude smaller than the fourth pair energy, and that their effect on T_c is negligible.

A global ground-state search⁷ of the Hamiltonian (2) with the interaction energies of (4) reveals that the chalcopyrite structure has the lowest $T=0$ energy of all possible fcc configurations. *The result remains unchanged even if the chalcopyrite structure is excluded from the set of structures used to determine $\{J_{k,m}\}$.* Note, however, that the energy of CuAu-I-like structure (CA) is only slightly above that of the chalcopyrite. We found that the small

tetragonal distortion in the CA and CH structures does not change this result. This has an interesting implication on the finite-temperature correlation functions (see below).

c. Transition temperatures and latent heats. Figure 1 shows the probability $\rho(A_2B_2)$ of finding an A_2B_2 tetrahedron [Fig. 1(a)] and the mixing enthalpy $\Delta H(T)$ [Fig. 1(b)] for $Cu_{0.5}In_{0.5}Se$. We see that the phase transition is first order. The calculated order-disorder transition temperatures T_c is 1125 K, with a Monte Carlo error of ± 20 K. Due to the uncertainty in our $T=0$ LDA total-energy calculations, we estimate that the total uncertainty in the calculated T_c is about 100 K. Our calculated T_c is in very good agreement with the experimentally observed⁸ value $T_c = 1083$ K, considering that the calculation is parameter-free. Note the role of interactions beyond first neighbors: In an fcc lattice with only nearest-neighbor antiferromagnetic pair interaction the exact transition temperature¹⁹ is $k_B T_c = 1.766 J_{2,1}$ where k_B is the Boltzmann constant. For $Cu_{0.5}In_{0.5}Se$, the neglect of the interactions beyond the nearest-neighbor pair gives $T_c = 1447$ K. The calculated latent heats of transition δH is 1.2 kcal/mole [Fig. 1(b)]. This is too small compared with the measured⁹ differential thermal analysis value of ~ 1.9 kcal/mole. We cannot explain this discrepancy. We suspect that it may arise in part from the neglect of the excess vibrational entropy and from the fact that in the measurement δH was not obtained at T_c , but rather integrated in a temperature range around it.

d. Spatial correlations. We find that the disordered phase exhibits significant short-range order. For a perfectly random alloy at composition $A_{0.5}B_{0.5}C$ the probability to find AB pairs $\rho(AB)$ is 0.5. The calculated values just above T_c are 0.61, 0.38, 0.47, and 0.47, respectively, for first- to fourth-nearest-neighbor pairs, showing CH-like fingerprints [the respective $\rho(AB)$ for CH structure

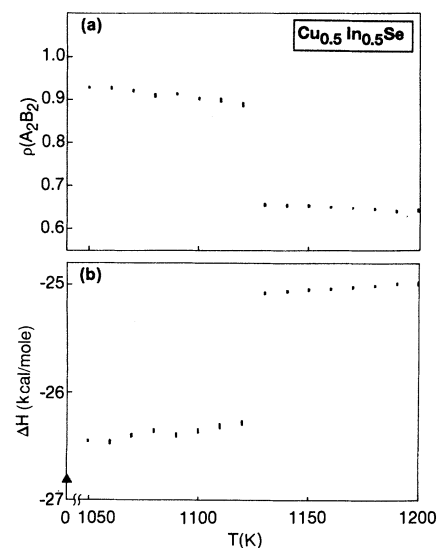


FIG. 1. Monte Carlo calculation of (a) tetrahedron probability $\rho(A_2B_2)$ and (b) excess enthalpy ΔH as a function of temperature at $x = \frac{1}{2}$. The dots or bars have sizes equal or larger than the standard deviations. $\Delta H(T=0) = \Delta H(CH)$ is also given (solid triangle) for reference.

are 0.66, 0.33, 0.33, and 0.66]. Furthermore, the electronic compensation between donor and acceptor clusters also lead to strong spatial correlations, as follows: A random $A_{0.5}B_{0.5}C$ alloy contains the clusters A_4 , A_3B , A_2B_2 , AB_3 , and A_4 in the percentage ratios 6.25:25:37.5:25:6.25; we find for disordered $\text{Cu}_{0.5}\text{In}_{0.5}\text{Se}$ the tetrahedron probabilities 0:17:66:17:0. This strong suppression of all $n \neq 2$ clusters is qualitatively analogous to what was found for size-mismatched *isovalent* alloys,⁷ except that there the driving force was the lowering in elastic strain energy in A_2B_2 , while here it is the greater degree of electronic compensation in A_2B_2 . Consequently, the clustering effect is several fold stronger in the nonisovalent systems. This is consistent with the complete absence of the A_4 and B_4 clusters noted in NMR chemical shift¹³ experiments on the related alloy $\text{Zn}_{0.5}\text{Sn}_{0.5}\text{P}$, and with the absence of $\text{Se}(\text{Cu}_4)$ or $\text{Se}(\text{In}_4)$ signatures in diffused scattering measurements on²³ $\text{Cu}_{0.5}\text{In}_{0.5}\text{Se}$. Our calculated probabilities do not support the hypothesis of Garbato, Ledda, and Rucci⁹ that CH disorders into a phase built exclusively from differently oriented pure A_2B_2 tetrahedra. The latent heat for a transition into such a disordered phase will be very small; we further calculate $T_c < 100$ K for this model.

e. Metastable phases. The similarity in the $T=0$ total energies of CH and CA (Table I) persists to finite temperatures. We find at low temperature a mix of CA-like and CH-like correlation functions. This suggests that growth below T_c (e.g., vapor phase epitaxy) could result in "trapping" into metastable mixture of CH-like and CA-like modifications, hence to a different short-range order than that obtained in growth above T_c (e.g., melt growth).

f. Ordering-induced band-gap increase. A cluster ex-

pansion of the direct band gap,²⁴ [analogous to the total-energy expansion of Eq. (2)] reveals that upon ordering the direct band gap *increases* by 0.35 ± 0.1 eV. We find two contributing factors: (i) All ordered or disordered adamantine alloys exhibit a reduction in the band gaps relative to a linear average of the band gaps of the constituents ("bowing"). This level repulsion effect^{6,25} increases in the series $\text{CH} \rightarrow \text{random} \rightarrow \text{CP}$. Since most isovalent semiconductor alloys exhibit CP ordering,⁵ they show ordering-induced band-gap *narrowing*^{5,6} relative to the random alloy. The CH phase shows instead an increase of the gap relative to the random alloy. (ii) In nonisovalent systems, the disordered phase exhibits donorlike (CuIn_3) and acceptorlike (Cu_3In) bands inside the parent band gap. Ordering the alloy into the chalcopyrite structure eliminates these states, hence it further *increases* the band gap. This effect is absent in isovalent alloys.

To examine the generality of our method we have carried out analogous calculations for the $\text{Zn}_{0.5}\text{Sn}_{0.5}\text{P}$ alloy. The results are very similar except that the cutoff error in the cluster expansion is slightly larger. We find a transition temperature of 1080 ± 20 K, compared with the measured value⁸ of 993 K, and a latent heat of 1.3 kcal/mole (we are unaware of experimental values for this system). The band gap increases upon ordering by 0.4 ± 0.1 eV, close to the measured value^{12,13} of 0.39 eV.

We conclude that the LDA, in conjunction with the Monte Carlo simulation is able to provide a detailed description of "strong" order-disorder transitions in ternary chalcopyrites. The calculation reveals the dominant effect of electronic compensation and the ensuing strong correlations and band-gap reduction in the disordered phase.

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