

Comparison of atomistic simulations and statistical theories for variable degree of long-range order in semiconductor alloys

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A direct atomistic quantum-mechanical theory is used for a comprehensive investigation on the applicability of a statistical theory based on cluster expansion to the electronic band structure of a semiconductor alloy with variable degree of long-range order. This study reveals that the applicability of the statistical theory depends on the modulation of the relevant wave function within the alloyed sublattice. This finding can be generalized beyond the prototype system—CuPt-ordered $\text{Ga}_x\text{In}_{1-x}\text{P}$ —to other alloys or other forms of long-range order and thus establishes a framework for understanding the effect of ordering in semiconductor alloys and the limitation of the cluster expansion approach for treating the electronic structure of alloys.

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I. INTRODUCTION

Spontaneous long-range ordering observed in many III–V semiconductor alloys $\text{A}_{1-x}\text{B}_x\text{C}$ provides not only unique opportunities for tailoring the material properties of these alloys for specific applications¹ but also an experimental environment for studying fundamental physical phenomena such as Anderson localization.² Temporal localization has recently been demonstrated in an effective three-dimensional (3D) system of cold atoms³ but a spontaneously ordered semiconductor alloy can offer a realistic 3D system with tunable degree of disorder.¹ It is thus of pivotal importance to understand how basic material properties of a partially ordered semiconductor alloy vary as functions of macroscopic parameters such as composition and order parameter.

Two diametrically different approaches have been used to understand alloy systems that are either disordered or partially ordered. One is a statistical approach that is often built on cluster expansion (CE).⁴ CE is widely used for describing order-disorder transformation in alloys⁵ and searching new structures with targeted material properties.^{6,7} The other approach is a direct quantum-mechanical computation using an atomistic theory. Besides obtaining quantitative results for the material system of interest, this approach can also provide qualitative insights as well as ultimate tests of the statistical theory and the assumptions adopted. However, to realistically model an alloy system, a very large structure is typically needed to correctly emulate the alloy statistics, which has prevented the direct atomistic calculation from being feasible for most situations.

The statistical theories based on CE are typically used for understanding ordering phenomena related to the change in structure and internal energy in alloys⁵ but the CE approach has also been extended to treat the electronic and optical properties in ordered semiconductor alloys.^{8,9} This extension could enhance greatly the usefulness of CE. However, the applicability of CE to the electronic structure of the alloy has not been rigorously and independently validated. In this work, an atomistic theory is applied to perform a systematic examination of the applicability and limitations of a generalized statistical model based on CE, using CuPt-ordered

$\text{Ga}_x\text{In}_{1-x}\text{P}$ as a prototype alloy system. The results of the atomistic theory provide a general understanding of the applicability of the statistical model to different alloy systems and forms of ordering.

II. THEORIES AND METHODS

A CuPt-ordered $\text{Ga}_x\text{In}_{1-x}\text{P}$ alloy can be defined as a (111) monolayer superlattice $\text{Ga}_{x+\eta/2}\text{In}_{1-x-\eta/2}\text{P}/\text{Ga}_{x-\eta/2}\text{In}_{1-x+\eta/2}\text{P}$, where η is the order parameter and has a maximum value $\eta_{\max}(x) = \min[2x, 2(1-x)]$. Full ordering can be achieved only at $x = X_\sigma = 0.5$. Note that the structural invariance of the mapping $\eta \rightarrow -\eta$ requires that any material property must be an even function of η . Previously, it has been shown^{8,9} that a physical property $P(x, \eta)$ can be described by

$$P(x, \eta) = P(x, 0) + [P(X_\sigma, 1) - P(X_\sigma, 0)]\eta^2, \quad (1)$$

when the property is determined primarily by *lattice-averaged pair interactions*. Two important features make Eq. (1) potentially very useful: it involves only one simple η^2 term and its prefactor is x independent and can be easily determined either experimentally or theoretically. However, in practice, it is unclear for a given alloy system as to which material property is expected to follow closely this elegant scaling rule or when the three-body or higher-order interactions are not negligible and when the statistical theory is simply not applicable, i.e., the expansion is nonconvergent. Although the elastic energy has been examined explicitly using a valence-force field (VFF) method, and found to obey nicely the η^2 rule stated above,⁸ the electronic bandgap seems to deviate significantly from this scaling rule for $\text{Ga}_x\text{In}_{1-x}\text{P}$ even at $x = 0.5$.¹⁰

First, using the CE approach,^{8,9} we develop a more general theory for the dependence of a physical property P on x and η . In this theory, the $P(x, \eta)$ is given by the sum over the contributions of different classes of figures (e.g., all the figures of nearest-neighbor pairs belong to one class):^{8,9}

$$P(x, \eta) = \sum_F O_F(x, \eta) p_F \bar{\Pi}_F(x, \eta), \quad (2)$$

where $O_F(x, \eta)$ is the number of figures of class F , p_F is the contribution of each figure of F , and $\bar{\Pi}_F(x, \eta)$ is the lattice-

averaged atomic correlation function for the class F . Note that Eq. (2) has adopted an important and a practical assumption, that is, the contribution of any given type of figure is always the same as p_F , independent of its location in the lattice. The atomic correlation function $\bar{\Pi}_F(x, \eta)$ is a product of pseudospin $S_i(x, \eta)$, which equals 1 if the site i is occupied by A or -1 if occupied by B. In this model, for a partially CuPt-ordered alloy, the lattice-averaged $S_i(x, \eta)$ is $(2x-1) + \eta \bar{S}_i(X_\sigma, \eta=1)$. Therefore, we have, for the single-site contribution

$$\bar{\Pi}_{\text{single}}(x, \eta) = (2x-1); \quad (3)$$

for the pair interaction

$$\bar{\Pi}_{\text{pair}}(x, \eta) = (2x-1)^2 + \eta^2 \bar{\Pi}_{\text{pair}}(X_\sigma, 1); \quad (4)$$

and for the nearest-neighbor triangle figures

$$\bar{\Pi}_{\text{ntri}}(x, \eta) = (2x-1)^3 + \eta^2(2x-1)[3\bar{\Pi}_{\text{ntri}}(X_\sigma, 1)], \quad (5)$$

where $\bar{\Pi}_F(X_\sigma, 1)$ is the atomic correlation of the fully ordered phase at X_σ . Because of the $\eta \rightarrow -\eta$ invariance, one can infer that in general the expansion of Eq. (2) can be expressed explicitly as

$$P(x, \eta) = P(x, 0) + \alpha[(2x-1)]\eta^2 + \beta[(2x-1)]\eta^4 + \gamma[(2x-1)]\eta^6 \dots, \quad (6)$$

that is, $P(x, \eta)$ is a series of η^2 , and the coefficients α , β , and γ are functions of $(2x-1)$. At $x=X_\sigma=0.5$, $\bar{\Pi}_F(0.5, \eta) = \eta^k \bar{\Pi}_F(X_\sigma, 1)$, thus, $\alpha[0]$, $\beta[0]$, and $\gamma[0]$ are determined by the averaged pair, four-body, and six-body atomic correlation functions of the fully ordered structure at X_σ , respectively. If only pair interactions are important, then $\alpha=[P(X_\sigma, 1) - P(X_\sigma, 0)]$ becomes x independent, and Eq. (6) reduces to Eq. (1). With the inclusion of the triangle and/or higher-order interactions, α should become x dependent. For this approach to be practically useful, the expansion of Eq. (6) has to converge quickly. If the expansion turns out to be nonconvergent, as illustrated in an example below, the CE approach is then inherently problematic.

Therefore, second, we test the convergence of Eq. (6), i.e., the importance of the high-order terms, using an accurate atomistic theory. We calculate explicitly the order-parameter dependences for a set of important properties: elastic energy, bandgap, conduction and valence-band-edge shifts, crystal-field splitting, and valence-band splitting for CuPt-ordered $\text{Ga}_x\text{In}_{1-x}\text{P}$ alloys with $0 < x < 1$ and $0 < \eta < \eta_{\text{max}}$. We discuss which of them follow a generalized η^2 rule (possibly with an x dependent coefficient), and which of them simply cannot be described by a convergent series of η^2 .

The electronic structure is calculated using an improved empirical pseudopotential method¹¹ with the use of a large (27,648-atom) supercell, which ensures that the statistical fluctuation for the energy levels of interest is within a few

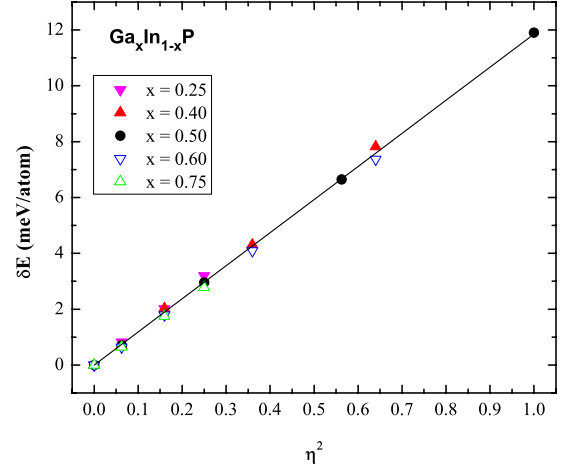


FIG. 1. (Color online) Elastic-energy change $\delta E(x, \eta)$ as a function of the square of order parameter η at different compositions of x .

meV. The supercell is relaxed by minimizing the VFF elastic energy.¹² Other computational details are given in previous publications.^{10,13}

III. RESULTS AND DISCUSSIONS

Elastic energy. Figure 1 shows the η dependence of the elastic energy for various x values. We find that this property indeed obeys the scaling rule of Eq. (1) quite well.⁸ By fitting all the data points together to $\delta E(x, \eta) = E(x, \eta) - E(x, 0) = \alpha\eta^2$, we get $\alpha = 11.85$ meV/atom, which agrees very well with the directly calculated value of $[E(X_\sigma, 1) - E(X_\sigma, 0)] = 11.91$ meV/atom. The reason for the good agreement is that the elastic energy is summed over the entire lattice and is largely determined by the effective pair interactions.

Bandgap. This is perhaps the most important property for semiconductor applications. The results for the bandgap reduction $\delta E_g(x, \eta) = E_g(x, \eta) - E_g(x, 0)$ are shown in Fig. 2, with $E_g(x, 0)$ from Ref. 13. For $x=0.5$, we find that the η^2

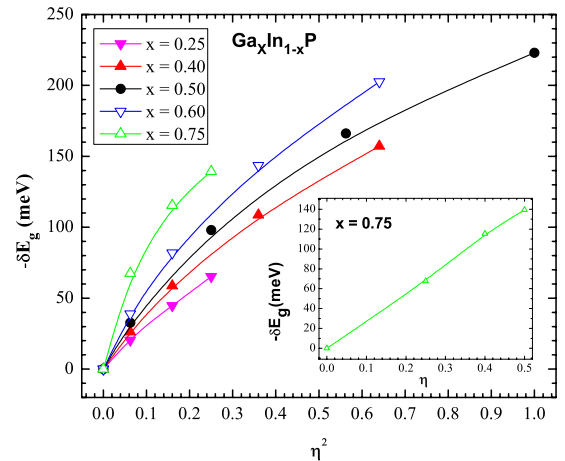


FIG. 2. (Color online) Dependence of the bandgap reduction on the square of order parameter η . The inset shows the linear dependence for $x=0.75$. The inset shows the linear plot for $x=0.75$.

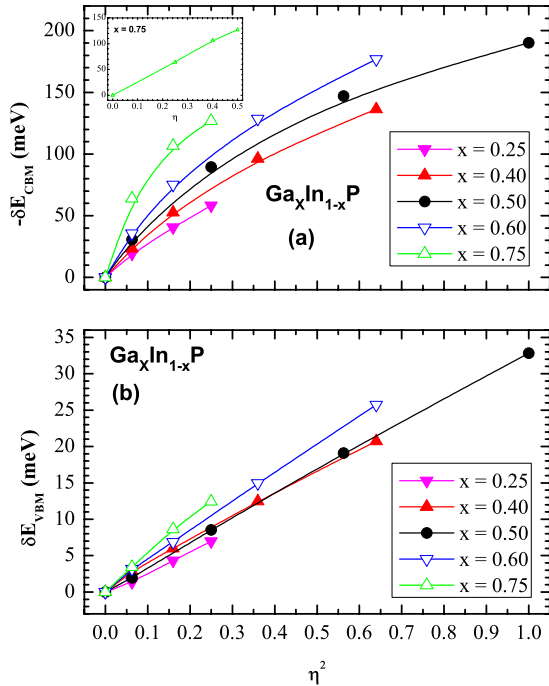


FIG. 3. (Color online) Shifts of the (a) conduction-band minimum and (b) valence-band maximum as a function of the square of the order parameter η . The inset shows the linear plot for $x=0.75$.

rule of Eq. (1) is inadequate to describe the variation of bandgap as a function of η . Nevertheless, $\delta E_g(x, \eta)$ can be fitted quite accurately with only the even-order terms up to η^6 . However, for $x=0.75$, δE_g surprisingly shows nearly a linear η dependence (or $|\eta|$ dependence), which implies that Eq. (6) is nonconvergent because $|\eta|$ is not an *analytic* function of η^2 . Because $\delta E_g(x, \eta) = \delta E_{\text{CBM}}(x, \eta) + \delta E_{\text{VBM}}(x, \eta)$, in the following we examine the individual variations in the valence-band maximum (VBM) and conduction-band minimum (CBM) states so as to reveal why the statistical theory fails.

Conduction band. CuPt ordering leads to a symmetry reduction from T_d to C_{3v} and the folding of the L_{111} state to the zone center. The level repulsion between the Γ and folded L point states results in the lowering of the CBM. Because the Γ -L energy separation, and thus the level repulsion and wave-function localization, depends strongly on x , one cannot expect that for the CBM, the shift $\delta E_{\text{CBM}}(x, \eta) = \delta E_{\text{CBM}}(0.5, \eta)$ as suggested by Eq. (1) will hold in a broad composition range. Indeed, our numerical calculations at $\eta = \eta_{\text{max}}$ show that $\delta E_{\text{CBM}}(0.25, 0.5) = -58$ meV and $\delta E_{\text{CBM}}(0.75, 0.5) = -130$ meV. The larger shift for the higher x is related directly to the smaller Γ -L separation. At $x=0.75$, it is the near degeneracy of the Γ and L states that leads to the near linear η dependence of δE_{CBM} , which could be understood qualitatively by applying a perturbation theory to the two degenerate states. The η dependences are plotted in Fig. 3(a) for different x values. Apparently Eq. (1) is in general not applicable. More significantly, any linear dependence will make Eq. (6) nonconvergent.

It is important to emphasize that the statistical theory employed to obtain Eq. (6) or Eq. (1) assumes that the physical

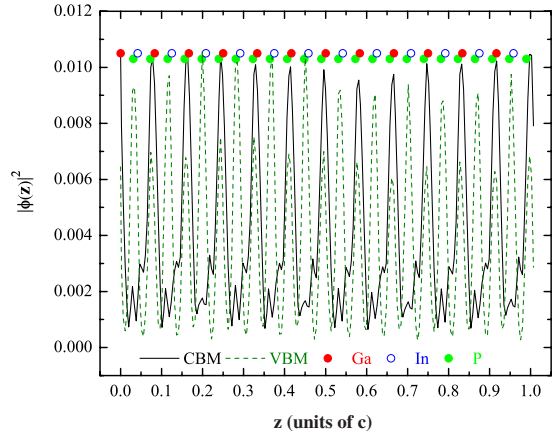


FIG. 4. (Color online) Charge distributions, represented by the squared wave functions, of the conduction-band minimum and valence-band maximum states along the ordering direction z for CuPt-ordered $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ with $\eta=0.5$. The z axis is normalized to the supercell period c in the ordering direction.

property $P(x, \eta)$ is obtained by unbiased averaging over the entire lattice with composition x , i.e., in Eq. (2) p_F is a constant throughout the whole structure for a given figure F . Therefore, if $P(x, \eta)$ is determined by a wave function localized in domains with composition $x' \neq x$, then this basic assumption is invalid. If $P(x, \eta)$ is indeed an analytical function of η^2 , one could in principle modify Eq. (2), for instance, by introducing different weights to configurations at different spatial locations with the weight determined by the local electronic wave-function intensity. However, because the wave function cannot be obtained before hand, such theory would not be practically very useful. For the situation where $P(x, \eta)$ is not an analytical function of η^2 , even the above mentioned modification to Eq. (2) cannot solve the nonconvergent difficulty of the CE method. For the current alloy system, because the CBM state is primarily derived from the cation states and ordering occurs in the cation sublattice in this common-anion alloy, when the ordering induces strong Γ -L coupling, the CBM wave function is expected to be highly nonuniform along the ordering axis. Figure 4 show the plan-averaged charge distribution of the CBM for $x=0.5$ and $\eta=0.5$ along the ordering direction. It indeed has a strong modulation between the Ga-rich and In-rich layers. This observation explains why the variation of the CBM and thus the bandgap, does not follow the statistical theory when the Γ -L coupling becomes strong. This type of failure of the statistical theory is expected for other materials or other forms of ordering whenever wave-function localization on a specific alloying component occurs.

Valence band. For each individual x , the shift $\delta E_{\text{VBM}}(x, \eta)$ of the VBM is found to be quite close to that of the η^2 dependence, although the magnitude of the shift varies slightly with x , as shown in Fig. 3(b). There are two possible sources for the x dependence: (1) the contribution of the triangle figures, Eq. (5), within the statistical theory and (2) the variation in the level repulsion between the VBM and the folded-in L_{3v} state, beyond the statistical theory. Because the VBM is largely derived from the common-anion p states, the effect of ordering is much weaker than that for the CBM

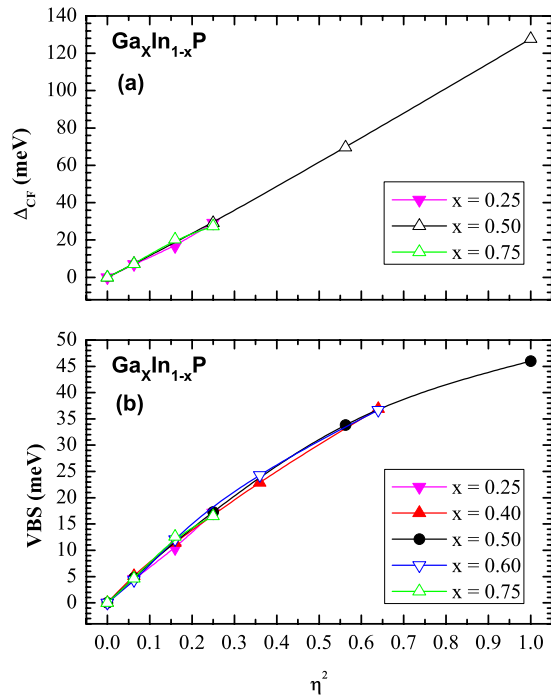


FIG. 5. (Color online) Dependences of (a) crystal-field splitting and (b) valence-band splitting on the square of order parameter η .

state. This is manifested as a much smaller VBM shift and a weaker modulation in the charge distribution of the VBM, as shown in Fig. 4. Owing to the weak wave-function modulation, the statistical theory is expected to be more accurate for the VBM than for the CBM. In general, we find that the statistical model is approximately valid for other valence-band-derived properties. For instance, for two important quantities originated from the ordering-induced symmetry reduction, the crystal-field splitting $\Delta_{CF}(x, \eta)$ is found to follow the η^2 rule quite well, as shown in Fig. 5(a) and the

valence-band splitting $VBS(x, \eta)$ is found to depend only weakly on x , as shown in Fig. 5(b), although not following the η^2 rule. Here the weak x dependence is due to the fact that the x dependences of the individual states are largely canceled out when evaluating the splitting. These observations are expected to be generally valid for common-anion alloys with similar valence-band electronic structures.

IV. CONCLUSIONS

In summary, using an accurate atomistic theory, we have provided an explicit test of the applicability of the cluster-expansion theory when it is used to describe the electronic properties of an ordered semiconductor alloy with varying composition and order parameter. We find that the generalized statistical theory given by Eq. (6) is converged for those electronic properties that are primarily associated with the atomic states of the nonmodulated sublattice (such as the valence-band states in the common-anion alloy), even though the lowest-order formula given by Eq. (1) might in general be inadequate. For any electronic property that is primarily derived from the atomic states that are localized on a particular alloyed sublattice (such as the CBM state in the mixed-cation alloy), the statistical theory is shown to either be nonconvergent or converge too slowly to be of practical use. This work, therefore, provides *a priori* principle about the applicability of the statistical approach based on the cluster expansion method to the description of the electronic structure of the semiconductor alloy.

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