

# Statistical aspects of electronic and structural properties in partially ordered semiconductor alloys

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We have investigated the statistical effects of spontaneous ordering on the electronic and structural properties of a semiconductor alloy as a function of order parameter using an empirical pseudopotential method in conjunction with a valence force field method in a supercell approach. The theoretical modeling yields valuable information on the statistical fluctuation of electronic properties, which includes the individual band edge as well as the band gap, for understanding the effects of ordering on various optical and transport measurements. The results on the average bond lengths and the statistical distributions of different types of bonds provide a guideline for the measurability of the effects of ordering in a partially ordered alloy in terms of the order parameter.

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## I. INTRODUCTION

When two crystalline materials  $A$  and  $B$  are mixed homogeneously, they form a random alloy  $A_xB_{1-x}$ , where  $x$  is the composition of  $A$ . Statistical fluctuation is inevitable for any alloys and has been an interesting subject for decades.<sup>1,2</sup> However, the focus of previous studies has mainly been on the issues related to random alloys. It is now well known that spontaneous ordering may occur in many semiconductor alloys during their epitaxial growth.<sup>3</sup> The purpose of this work is to study the statistical effects of spontaneous ordering for varying degrees of order on the electronic and structural properties of semiconductor alloys. We will take the  $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$  alloy, a most thoroughly investigated system,<sup>3,4</sup> as an example for demonstrating certain statistical effects which are expected to be ubiquitous for the phenomenon of ordering.

The frequently observed ordered structure, the so-called CuPt structure, is a monolayer superlattice with alternating Ga-rich and In-rich monolayers of  $\text{Ga}_{0.5+\eta/2}\text{In}_{0.5-\eta/2}\text{P}$  and  $\text{Ga}_{0.5-\eta/2}\text{In}_{0.5+\eta/2}\text{P}$  along one of the  $[111]$  directions, where the order parameter  $\eta$  can vary continuously from 0 to 1. A great deal of experimental and theoretical studies on spontaneous ordering have focused on the dependence of the ensemble average properties of the alloy on the order parameter: e.g., the band-gap reduction,<sup>4,5</sup> optical anisotropy,<sup>6</sup> valence-band splitting,<sup>7</sup> and average bond length.<sup>8</sup> In contrast, a fundamental aspect of spontaneous ordering relating to the statistical nature of the phenomenon has largely been ignored, except in Ref. 8 where the statistical fluctuation of the band gap was obtained from the configuration average of a 64-atom unit cell. Evidently, the investigation of statistical effects for partially ordered structures is more difficult in terms of sample quality (experimentally) or computation effort (theoretically) than that of ensemble average properties. Perhaps the most anticipated statistical effect of spontaneous ordering is a reduction in the effects of alloy fluctuation for a measurable physical property. Indeed, this effect has recently been experimentally confirmed in the observation of a con-

tinuous reduction of the exciton linewidth as a function of the order parameter.<sup>9</sup> Even for random alloys, the effects of statistical fluctuations on the electronic structure have rarely been specifically evaluated: only the statistical distribution of certain structural properties (for instance, the bond length or angle) have been studied.<sup>10-13</sup>

In this study, we will investigate the statistical effects of spontaneous ordering on both the electronic and structural properties of a semiconductor alloy as a function of order parameter  $\eta$ . Our results show how spontaneous ordering affects the statistical distribution of electronic states (including the valence band, conduction band, and the band gap) and of the structural properties (including the bond length and the local atomic occupation). The implications of our results with respect to the ability to measure these effects of ordering experimentally will be discussed.

## II. METHOD

We use a large supercell of nearly 3500 atoms to simulate the partially ordered  $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$  alloy for any given order parameter  $\eta$  ( $0 \leq \eta \leq 1$ ). Statistical effects are accounted for by averaging over 100 configurations for each value of  $\eta$ . Although the size of the supercell used here has been shown previously to be more than adequate for obtaining the correct statistics of the structural properties of random alloys,<sup>11-13</sup> we find that this size is necessary for producing accurate average band-structure parameters.<sup>14</sup> A modified empirical pseudopotential method is used for the band-structure calculations,<sup>15</sup> which has been shown to be able to give very accurate average band gap for the partially ordered alloy.<sup>14</sup> A valence force-field method<sup>16</sup> is used for determining the relaxed atomic configurations and the corresponding structural properties.

Since CuPt ordering occurs in the  $[111]$  direction with alternating Ga-rich and In-rich atomic planes, an orthorhombic supercell is built with three cell vectors  $\mathbf{a}_1$ ,  $\mathbf{a}_2$ , and  $\mathbf{a}_3$  along the  $x' \sim [11\bar{2}]$ ,  $y' \sim [\bar{1}10]$ , and  $z' \sim [111]$  directions, respectively. The basic cell with  $a_1 = \sqrt{3}/2a$ ,  $a_2 = \sqrt{2}a$ , and

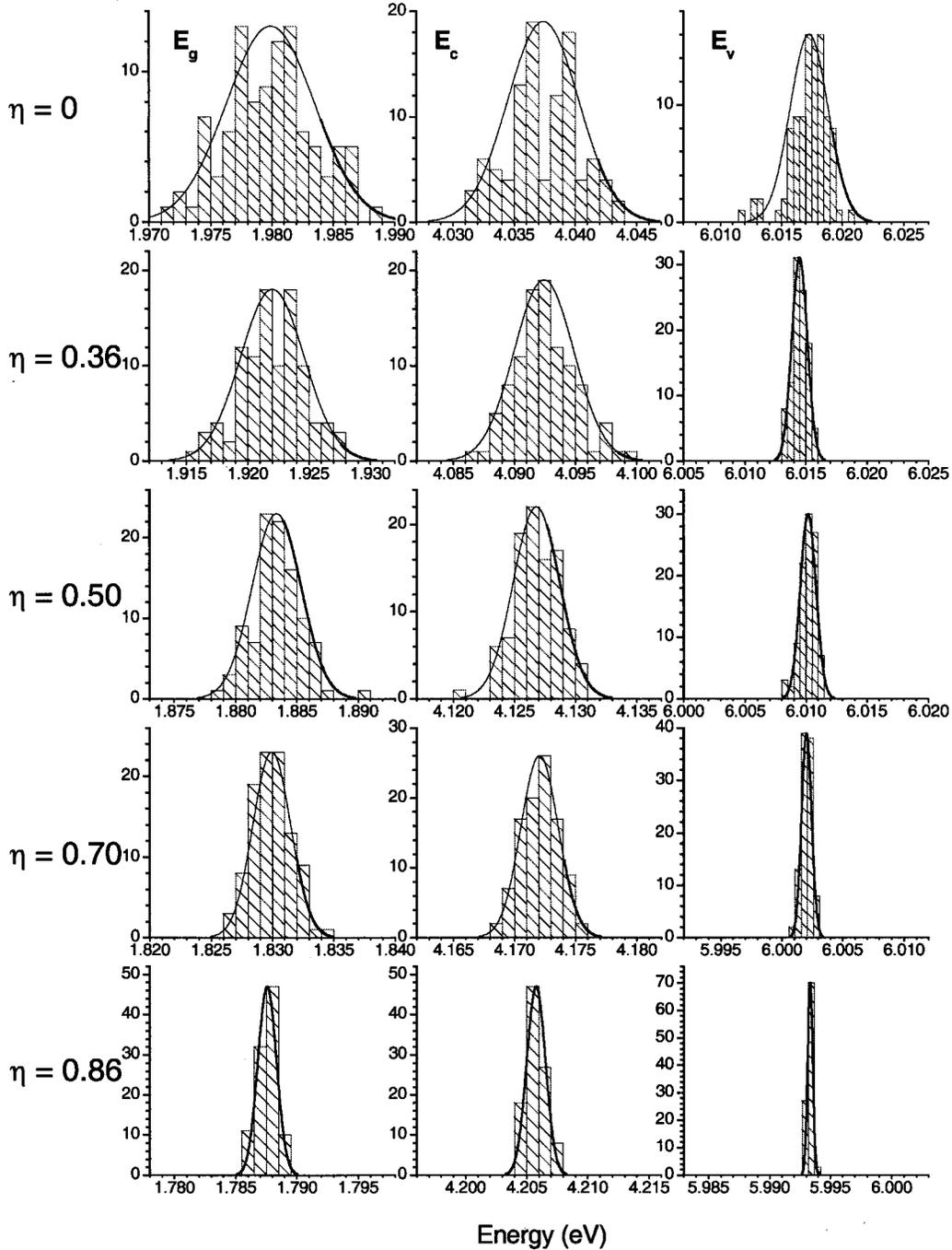


FIG. 1. Histogram plots of the energy distributions of the band gap ( $E_g$ ), conduction-band edge ( $E_c$ ), and valence-band edge ( $E_v$ ) for partially ordered  $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$  alloys with order parameter  $\eta=0, 0.36, 0.50, 0.70,$  and  $0.86$ .

$a_3=2\sqrt{3}a$  contains 24 atoms, where  $a$  is the lattice constant. The GaInP layer is assumed to be constrained by the substrate, resulting in a tetragonal film.<sup>17</sup> The standard supercell used to simulate the partially ordered GaInP alloy has a size of  $6a_1 \times 12a_2 \times 2a_3$ , which has 24 atomic planes along each direction and a total of 3456 atoms. For a partially ordered structure, each cation layer is randomly occupied by Ga or In with probabilities  $p_{\text{Ga}}=x+\eta/2$  for the Ga-rich plane and  $p_{\text{Ga}}=x-\eta/2$  for the Ga-poor plane, and the total number of Ga is constrained by the composition  $x=0.5$ .

### III. RESULTS AND DISCUSSIONS

Figure 1 shows the histogram plots for the band-edge energies of the valence band and conduction band as well as for the band gap of 100 randomly generated configurations. As expected, on increasing  $\eta$  the fluctuations of these quantities decrease. It is interesting to note that the main contribution to the band-gap fluctuation is from the conduction band for the GaInP alloy, which can be comprehended in terms of the fact that the major part of the band-gap difference between GaP and InP lies in their conduction band<sup>18</sup> and that the conduc-

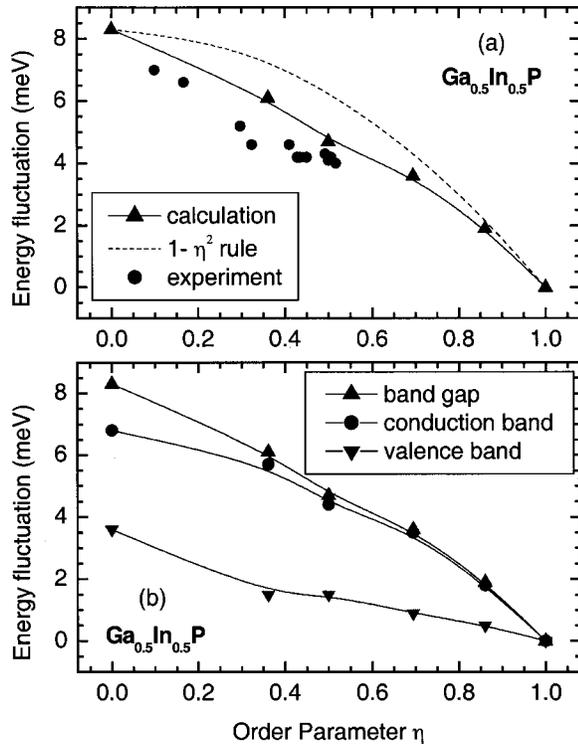


FIG. 2. Energy fluctuation of the band gap,  $W_{\text{gap}}(\eta)$ , of the conduction-band edge,  $W_c(\eta)$ , and of the valence-band edge,  $W_v(\eta)$ , for a partially ordered  $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$  alloy, measured by the full width at half maximum (FWHM) of the histogram plots (shown in Fig. 1), as a function of the order parameter  $\eta$ . (a) A comparison of the calculated  $W_{\text{gap}}(\eta)$  with the low-temperature photoluminescence linewidth  $W_{\text{ex}}(\eta)$  of Ref. 9 and a curve predicted by a simple  $\eta^2$  dependence. (b) Calculated  $W_c(\eta)$  and  $W_v(\eta)$  as well as  $W_{\text{gap}}(\eta)$ .

tion band has a smaller effective mass than that of the valence band. The information for the band-gap fluctuation is most relevant for various optical measurements (e.g., emission and absorption), but that for the individual band edge is most valuable for transport measurements related to either electrons or holes. Figure 2(a) shows the band-gap fluctuation  $W_{\text{gap}}(\eta)$  [measured by the full width at half maximum (FWHM) of the histogram plot], compared with the experimental data for the exciton linewidth  $W_{\text{ex}}(\eta)$ , as a function of  $\eta$ . Here  $W_{\text{gap}}(\eta)$  not only qualitatively agrees with but also quantitatively is rather close to the values of  $W_{\text{ex}}(\eta)$  for  $\eta < 0.55$  reported in Ref. 9. Nevertheless, one should notice that these two quantities are not exactly equivalent, but closely related to each other.<sup>19</sup> Figure 2(b) shows the fluctuation of the individual band edge:  $W_c(\eta)$  for the conduction and  $W_v(\eta)$  for the valence band. As indicated in Ref. 19, a proper modeling of the excitonic linewidth requires knowledge of all the three fluctuation parameters.

For a random alloy with only the substitutional fluctuation considered, the statistical fluctuation of a physical property  $P(x)$  from its average value  $P_0(x)$  is well known to be proportional to  $x(1-x)$ .<sup>1</sup> Applying the same argument to the partially ordered alloy, we find that the alloy fluctuation of a physical property will be proportional to  $(x-x^2-\eta^2/4)$  or

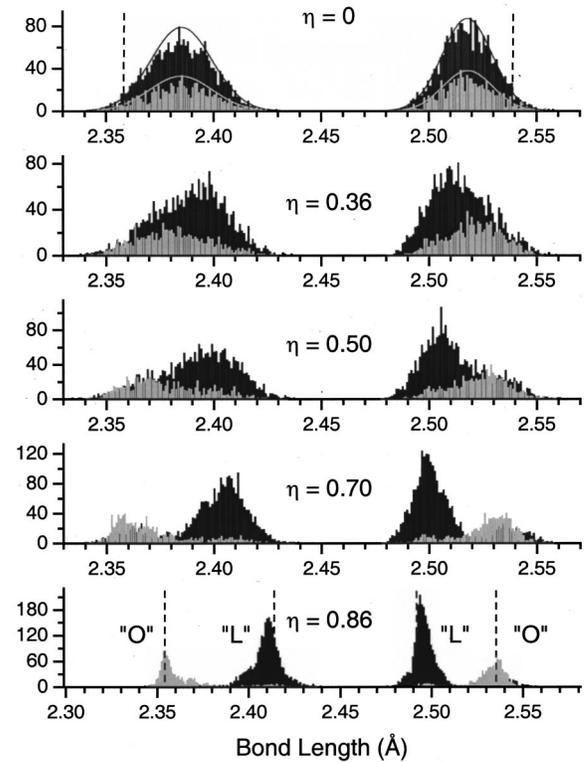


FIG. 3. Histogram plots of the bond length distributions of partially ordered  $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$  alloys with order parameter  $\eta = 0, 0.36, 0.50, 0.70$ , and  $0.86$ . Black: for the  $L$ -type bonds along the lateral directions. Gray: for the  $O$ -type bonds along the ordering direction. The dashed vertical lines denote the Ga-P and In-P bond lengths in the binaries on the  $\eta = 0$  panel (upmost) and in the fully ordered structure ( $\eta = 1$ ) on the  $\eta = 0.86$  panel (bottom).

simply  $1-\eta^2$  for  $x=0.5$ . As shown in Fig. 2, the band-gap fluctuation does not obey this  $1-\eta^2$  dependence. Although it was argued in Ref. 5 that the majority of physical properties would obey the  $\eta^2$  rule, here is another physical property for which this scaling is found to be invalid, besides the other example (i.e., the band-gap reduction) discussed in Ref. 14.

We next discuss the statistics of a few important structural properties. It has been shown experimentally that for the  $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$  random alloy there are two average bond lengths (the so-called bimodal behavior) that are close to those of Ga-P and In-P bonds in the binaries, respectively.<sup>20</sup> For a CuPt-ordered  $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$  alloy, the average bond length for both Ga-P and In-P has been found to be different for the bonds along the ordering direction ( $O$ ) and along the lateral direction ( $L$ ),<sup>8</sup> which in principle is detectable by polarized extended x-ray-absorption fine-structure (EXAFS) measurements.<sup>21</sup> Figure 3 shows the typical distributions of the  $O$  and  $L$ -type bonds for partially ordered  $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$  with different order parameter  $\eta$ . The results are obtained from “representative” configurations which yield the average band gaps for each  $\eta$  value. As expected, the number of  $O$  bonds is about 1/3 the number of  $L$  bonds. However, it is not expected *a priori* that the distributions for the two types of bonds strongly overlap with each other for  $\eta$  up to 0.5, which

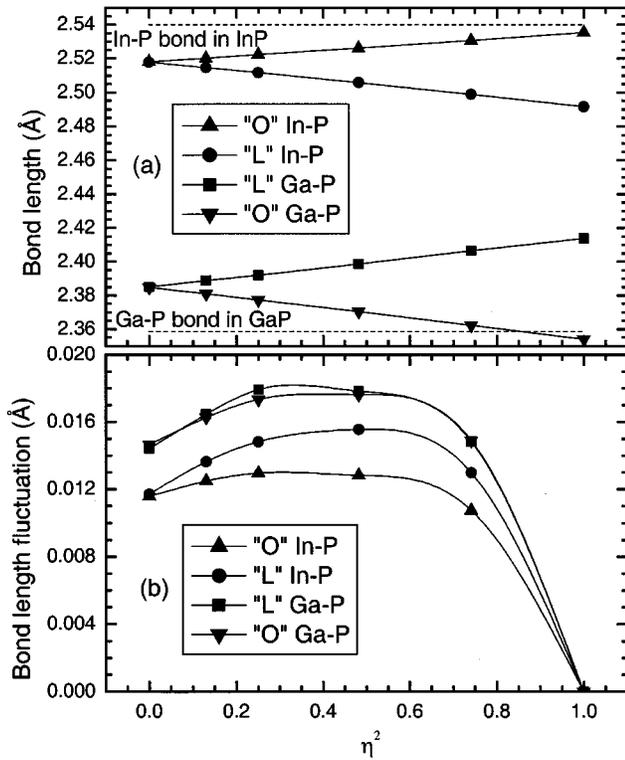


FIG. 4. (a) Average bond lengths for the four types of bonds in partially ordered  $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$  alloys vs  $\eta^2$  ( $O$ , along the ordering direction;  $L$ , along the lateral directions). (b) Bond length fluctuations vs  $\eta^2$  for the four types of bonds.

is about the order parameter for the strongest ordered samples currently available. Figure 4 shows the average bond lengths and their statistical fluctuations as functions of  $\eta^2$ . In agreement with the results of Ref. 8, the average bond length follows the  $\eta^2$  dependence very well, as shown in Fig. 4(a). However, as shown in Fig. 4(b), it is a surprise to find that the bond length fluctuation first increases from that for the random structure and, then, decreases after  $\eta > 0.7$ . Here we have taken the standard deviation of the average value as the measure of the fluctuation. This observation is counter-intuitive in that ordering should always reduce the random fluctuation. The phenomenon can be understood by considering how the average coordination numbers of Ga or In around P vary with the order parameter. For the random alloy, if counting the Ga coordination of the first nearest neighbor of a P atom, one will find the distribution to approximately follow the probability ratio of 1:4:6:4:1 for 0, 1, 2, 3, and 4 Ga atoms. Thus the average bond length for either Ga-P and In-P bond is largely determined by the most probable coordination of (2 Ga, 2 In). On increasing the order parameter, the most probable coordinations gradually be-

come (3 Ga, 1 In) and (1 Ga, 3 In), with Ga atoms being on the Ga-rich and In-rich planes, respectively. It is during this transition process that the enhancement in the fluctuation of the bond length occurs. For instance, for  $\eta < 1$ , there will always be a finite probability to find a (3 Ga, 1 In) coordination with the 3 Ga atoms in the In-rich plane. The Ga-P bond length for this coordination will be significantly different from that for the more probable coordination, i.e., the 3 Ga atoms being on the Ga-rich plane.

There are a few significant implications of the results shown in Figs. 3 and 4. First, as shown in Fig. 4(a), for  $\eta$  up to 0.5, the  $O$ - $L$  splitting is smaller than 0.2 Å, which is the typical experimental uncertainty of any EXAFS measurements.<sup>20-22</sup> Second, as shown in Fig. 3, the strong overlap between their distributions and the 1:3 ratio for the counts of bonds makes it unfeasible to distinguish the  $O$  and  $L$  bonds by using any unpolarized EXAFS techniques, unless the samples are very highly ordered. These two points might explain why only a single average Ga-P bond length was extracted from a recent XAFS measurement of partially ordered GaInP alloys.<sup>22</sup> Note that if not constrained by the instrumental resolution, for  $\eta \geq 0.5$ , an unpolarized XAFS technique may still resolve two average bond lengths for both Ga-P and In-P bonds, since the superposition of the distributions of the  $O$  and  $L$  bonds does show a two-peak distribution. However, the peak positions will not be the  $O$  and  $L$  bond lengths given in Fig. 4(a) and will not follow the  $\eta^2$  dependence.

#### IV. SUMMARY

In summary, we have investigated the statistical effects of spontaneous ordering in  $\text{Ga}_x\text{In}_{1-x}\text{P}$  alloys on the electronic and structural properties of the alloy, using an approach that can be extended to other semiconductor alloys in a straightforward manner. The calculated energetic fluctuations due to both chemical and positional disorder for the conduction and valence band as well as the band gap are expected to be very useful for understanding the ordering effects on various optical and transport measurements. The results on the bond length and its statistical distribution provide a guideline for the measurability of the ordering effects in the partially ordered alloy in terms of the order parameter.

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