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Dependence of the band structure on the order parameter for partially ordered $Ga_xIn_{1-x}P$ alloys

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An empirical pseudopotential method is demonstrated for realistically and accurately calculating the band structure of partially CuPt ordered $Ga_xIn_{1-x}P$ alloys. A sufficiently large supercell of ~3500 atoms, with all atomic positions relaxed by applying a valence force field method, is used to simulate the (Ga,In) distribution in the partially ordered alloy with the order parameter η varying from 0 to 1. While agreeing very well with experimental data in the experimentally verifiable region $\eta<0.5$, our results illustrate that a commonly accepted *interpolation* scheme (i.e., the η^2 rule) is grossly inaccurate for determining certain primary band structure parameters (e.g., the band gap) between $\eta=0$ and $\eta=1$.

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Spontaneous ordering has been regularly observed in $Ga_xIn_{1-x}P$ and other III-V alloys during epitaxial growth by metal-organic chemical-vapor deposition. The most frequently observed form of ordering is the so-called CuPt structure, i.e., a spontaneously generated monolayer superlattice with alternating Ga-rich and In-rich layers of $Ga_{x+\eta/2}In_{1-x-\eta/2}P$ and $Ga_{x-\eta/2}In_{1-x+\eta/2}P$, respectively, along one of the [111] directions, where η is the *order parameter* that varies from 0 to $\min[2x,2(1-x)]$. Beside the crystal structure change,[1] spontaneous ordering brings about changes in many experimentally observable electronic and optical properties: band-gap reduction,[1] valence band splitting,[2,3] optical anisotropy,[2] pyroelectricity,[4] birerefringence,[5] second-harmonic generation,[6] conductivity anisotropy,[7] and reduction of the alloy fluctuation.[8] The dependence of these phenomena on the strength of the ordering has also been extensively investigated.[8–12] Concurrently, various techniques or approaches have been used to calculate the band structure of the ordered alloy with $\eta=1$ and $x=0.5$: LAPW-LDA (linearized augmented-plane-wave with the local-density approximation),[13–17] TB (tight-binding) method,[18,19] first-principles PM-LDA (pseudopotential method),[20] and EPM (empirical pseudopotential method).[21,22] The results of these calculations display a considerable scatter. The calculated band-gap reduction (δE_g) ranges from 100 to 900 meV.[13–22] Since only partial ordering has been achieved in real samples, an *interpolation* scheme has been proposed for determining the order parameter. Such an interpolation scheme supposedly allows one to obtain the value of a property $P(x,\eta)$ through the two end-point values of $P(x,\eta=0)$ and $P(x,\eta=1)$ by using a η^2 rule: $P(x,\eta)=P(x,0)+\eta^2[P(x,1)-P(x,0)]$.[23] For almost a decade, this scheme has been extensively used by experimentalist for determining the order parameter and by theorists for interpolating the properties of partial ordered structures.[9,15,22] Only quite recently, was a reasonably reliable x-ray technique used to directly measure the order parameter.[12] The most strongly ordered Ga-In-P samples have been found to have an order parameter η of about 0.5 ($\eta^2\approx0.25$), and the *extrapolation* to $\eta=1$ using the η^2 rule yielded $\delta E_g(x=0.52,\eta=1)=498\pm27$ meV or $E_g(0.52,1)=1.508\pm0.027$ eV.[12] The theoretical values of Ref. 20 ($\delta E_g=490$ meV) and Ref. 22 ($E_g=1.54$ eV) appeared to agree with these *extrapolated* values very well. However, the applicability of the interpolation scheme to the band structure parameters has never been thoroughly examined. In general, making a judgment as to whether or not a physical quantity $P(x,\eta)$ should follow the η^2 rule is not trivial without actually performing the calculation. An obvious problem with such a generalization is because of the fact that not all physical properties are linearly related to each other, especially when the ordering effect is not necessarily very weak. Although the η dependences for $\delta E_g(0.5,\eta)$ were given in a TB calculation and an EPM calculation (with the virtual crystal approximation),[19,21] the results significantly either underestimated or overestimated the band-gap reduction in the experimentally tested range of $\eta<0.55$.[12] Nevertheless, the result of Ref. 19 showed that the η^4 term gave a roughly 20% correction to the η^2 term.

In this work, we apply a modified empirical pseudopotential method to directly calculate the band structure of partially ordered Ga-In-P for any given order parameter η ($0\leqslant\eta\leqslant1$), in a supercell approach with a relaxed atomic configuration. We find that the calculated $\delta E_g(x,\eta)$ for $\eta<0.5$ agrees with the experimental data excellently, but, for higher η values, it strongly deviates from values extrapolated using the widely used η^2 rule.

Empirical pseudopotentials for bulk GaP and InP are obtained separately by fitting to the experimentally determined (if available and if reliable) or theoretically calculated electronic properties at their equilibrium conditions. These properties include energies, deformation potential, effective masses at different critical points,[24] and valence band offsets.[25] The fitting results for those most important parameters are given in the ''output'' columns of Table I where they are compared to the corresponding ideal values given in

TABLE I. The empirical pseudopotential fit for GaP and InP.

Properties \ Materials	GaP		InP	
	Input	Output	Input	Output
$E_{g\Gamma}$ (eV)	2.896	2.903	1.424	1.421
E_{gL} (eV)	2.640	2.601	2.030	2.021
E_{gX} (eV)	2.350	2.352	2.380	2.412
E_{SO} (eV)	0.08	0.080	0.108	0.110
$a_{g\Gamma}$ (eV)	−8.56	−8.154	−6.6	−7.597
a_{gX} (eV)	1.27	1.259	1.0	1.375
a_v (eV)	−0.58	−0.578	−0.41	−0.403
b_v (eV)	−1.40	−1.409	−1.55	−1.456
$E_{v\Gamma}$ (eV)[a]	−0.47	−0.470	−0.360	−0.356

[a]The top of the GaAs valence band is taken as a reference, i.e., $E_{v\Gamma}=0$ eV.

the ''input'' columns. In most cases, the pseudopotentials can reproduce the input parameters very well. The pseudopotential contains a local part and a nonlocal spin-orbit interaction part.[26] To better account for the local atomic environment in the combined system of the two binaries, we have made two modifications to the conventional EPM. First, the pseudopotential for the common anion (P) is taken as a weighted average according to the number of Ga and In on the four nearest-neighbor cation sites. Second, the functional form chosen for the pseudopotential $v(q)$ includes a strain parameter (a_4): $v(q,\epsilon)=a_0[(q^2-a_1)/(a_2e^{a_3q^2}-1)][1+a_4\ \mathrm{Tr}(\epsilon)]$, where $\mathrm{Tr}(\varepsilon)$ is the trace of the local strain. This modification not only imposes a constraint on the pseudopotential but also allows the pseudopotential to be adjusted for the local atomic distance which might be different from that in the bulk.[26] All atoms in the supercell are allowed to be relaxed so as to minimize the strain energy, using the valence force field method.[27] The Ga-In-P layer is assumed to be constrained by the substrate, resulting in a cubic or tetragonal film.[15] The average lattice constant is assumed to obey Vegard's rule: $a(x)=xa(1)+(1-x)a(0)$.

Since CuPt ordering occurs in the [111] direction, 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 $a_1=\sqrt{3/2}a$, $a_2=\sqrt{2}a$, and $a_3=2\sqrt{3}a$ contains 24 atoms. The standard supercell used to mimic the partially ordered Ga-In-P alloy has a size of $6a_1\times12a_2\times2a_3$ that 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 $p_{\mathrm{Ga}}=x+\eta/2$ for the Ga-rich plane and $p_{\mathrm{Ga}}=x-\eta/2$ for the Ga-poor plane, and the total number of Ga is constrained by the composition x. For the random alloy with $x=0.5$, the average of 100 configurations yields a band gap $E_g=1.980$ eV with a residual valence band splitting $E_{\mathrm{vbs}}=2.3$ meV (because the supercell does not have the zinc-blende symmetry). The same calculation for a 432 atom cell (a factor of 2 smaller along each direction) gives $E_g=1.971$ eV and $E_{\mathrm{vbs}}=6.8$ meV. A check for a single 27648 atom cell results $E_g=1.979$ eV and $E_{\mathrm{vbs}}=1.5$ meV. Thus, the size of the working cell appears quite adequate. The calculations are performed for $\eta=0$, 0.36, 0.5, 0.7, 0.86, and 1, and for $x=0.5$ (assumed in all previous theoretical calculations) and $x=0.52$ (the composition lattice matched to GaAs substrate for which the experimental data were normally calibrated to). The results presented are 100 configurations averaged for $x=0.5$ and 20 configurations averaged for $x=0.52$. To solve the Schrödinger equation for the large systems involved, a folded spectrum method is used.[28] A plane-wave basis is used to expand the electronic wave function. The kinetic-energy cutoff is 7 Ry.

Figure 1 shows the calculated band gap reduction $\delta E_g(0.5,\eta)$ and crystal-field splitting parameter $\Delta_{\mathrm{CP}}(0.5,\eta)$. Our result of $\delta E_g(0.5,1)=223$ meV is larger than the TB results of 100–140 meV,[19,18] but smaller than the LAPW-LDA results of 320–430 meV,[15–17] and the PM-LDA result 490 meV.[20] The most important aspect of our result is that $\delta E_g(0.5,\eta)$ strongly deviates from the proposed η^2 rule,[23] contrary to the conclusion of Ref. 23. A fit to the numerical results yields the following empirical form:

$$\delta E_g(0.5,\eta)=484.5\eta^2-435.4\eta^4+174.4\eta^6. \quad (1)$$

A slightly better fit can be obtained with η^3 and η^5 terms included:

$$\delta E_g(0.5,\eta)=525.8\eta^2+114.5\eta^3-1431.8\eta^4+1566.3\eta^5-551.7\eta^6. \quad (2)$$

If plotting either Eq. (1) or Eq. (2) alongside the experimental data in Ref. 12 and using only the leading term (i.e., the η^2 term), one will find a good fit with the experimental data, and the η^2 term would extrapolate to the same value ~500 meV as obtained in Ref. 12 for $\eta=1$ (the perfectly ordered structure). However, there are two points to note: (1) The good fit in the range $\eta<0.5$ occurs because the cumulative contribution of the higher-order terms in Eq. (1) or Eq. (2) is negligible. (2) As Fig. 1 indicates, the true $\eta=1$ band gap reduction is only ~230 meV. Use of the full Eq. (1) or Eq.

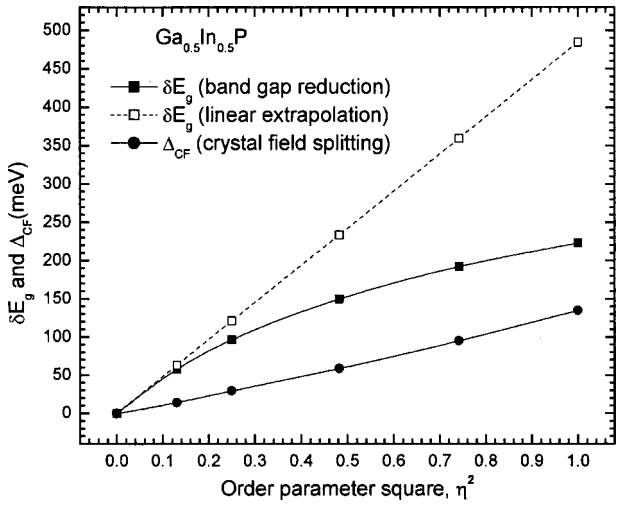

FIG. 1. Band-gap reduction (δE_g) and crystal-field splitting parameter (Δ_{CF}) as functions of the square of the order parameter (η^2) for partially ordered $Ga_{0.5}In_{0.5}P$ alloys. $E_g(0.5,0)=1.980$ eV.

(2) in the region $\eta > 0.5$ gives a strong nonlinear dependence on η^2. The large fluctuation for $\delta E_g(0.5,1)$ among the previous calculations is partially due to the uncertainty in choosing the reference point $E_g(x=0.5,\eta=0)$ for the random alloy (1.97–2.2 eV), from the ''binary average,'' [14] random configuration average of a 64-atom cell,[19] ''special quasirandom structure,'' [20] and virtual crystal approximation.[21] Our result for the random configuration average of the 3456-atom cell is $E_g(0.5,0)=1.980$ eV. However, the major contribution to the fluctuation lies in the value $E_g(x=0.5,\eta=1)$: 1.3–2.03 eV.[14,18–22] Our result of 1.757 eV is lower than the TB values but higher than the first-principles values. As regards the valence band splitting, our calculated result is $\delta E_{\rm vbs}(0.5,1)=46$ meV, which is slightly smaller than the previous results, 56 meV (Ref. 15) or 54 meV (Ref. 16). By applying a quasicubic model to the valence band splitting,[29,14–16] we extract a crystal-field splitting parameter $\Delta_{\rm CF}(0.5,1)=135$ meV. Indeed, $\Delta_{\rm CF}(0.5,\eta)$ follows the η^2 rule reasonably well, as shown in Fig. 1.

The η^2 rule (importance of only the η^2 term) had been proposed and utilized based on the assumption that only the pair interactions were sufficient for adequately describing the physical properties under consideration.[23] This assumption may be valid for those properties (e.g., elastic energy[23] and bond length[19]) which depend on the relatively short-range pair interactions, but is not always valid for those properties which are associated with long-range interactions (such as the band gap and the conduction band effective mass). In general, if a band structure parameter involves a strong coupling among different bands, its dependence on η is unlikely to be as simple as η^2. In fact, the η^2 rule is already known to be invalid for a few other parameters: e.g., the valence band splitting,[15] the effective masses of the light hole and spin-orbit split-off band,[30] and the interband transition matrix elements involving the light hole and spin-orbit split-off band.[10] The heavy hole effective mass[30] and the crystal-field splitting parameter are amongst the few exceptions that approximately obey the η^2 rule. Since the repulsion between the conduction band Γ point and folded L point is considered to be the major contribution to the band-gap reduction,[13] the perturbation scheme gives $\delta E_c \propto |\langle c,L|\Delta V|c,\Gamma\rangle|^2/(E_{cL}-E_{c\Gamma})$, assuming the perturbation potential for the ordering ΔV is relatively weak. If the matrix element $|M_{L\Gamma}| = |\langle c,L|\Delta V|c,\Gamma\rangle| \propto \eta$, we will have $\delta E_c \propto \eta^2$. However, to achieve the large band-gap reduction of ~400 meV calculated in Refs. 16, 20, 22, the coupling required would be too strong ($|M_{L\Gamma}| \sim 370$ meV) for this perturbation scheme to be valid, considering the fact that $\delta E_{L\Gamma}=E_{cL}-E_{c\Gamma}$ is ~350 meV for the random alloy.[31] At the Γ point, a simple generalized two-level model yields $\delta E_c = -\delta E_{L\Gamma}/2 + \sqrt{\delta E_{L\Gamma}^2+4|M_{L\Gamma}|^2}/2$.[32] Using this equation and the data shown in Fig. 1, we find that $|M_{L\Gamma}|=307$ meV for $\eta=1$, and $|M_{L\Gamma}(\eta)|=470\eta-162\eta^2$ (meV). Thus, there will naturally be a significant contribution from higher-order terms beyond η^2 for δE_g. Finally, we would like to point out that because of the strong $\Gamma-L$ coupling, the conduction band effective masses are also not expected to have the η^2 dependence which was the assumption made in order to obtain the masses for $0<\eta<1$.[33]

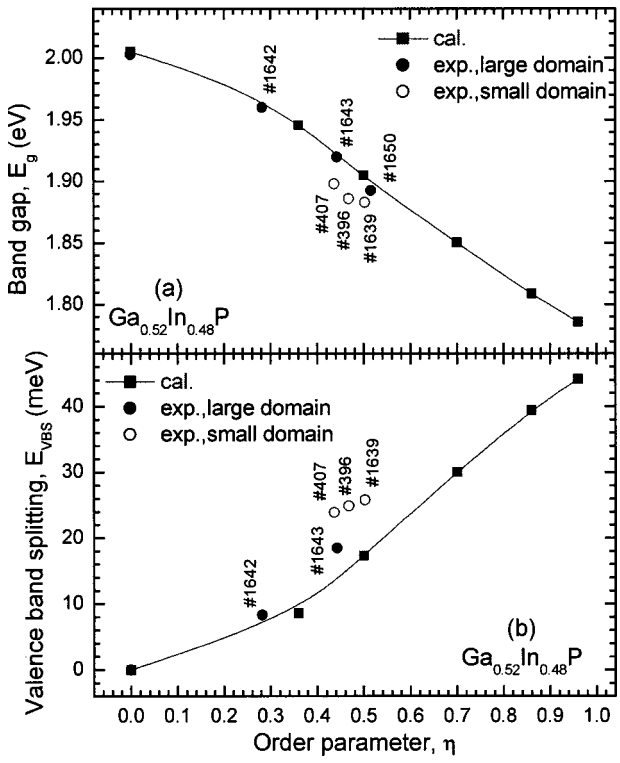

FIG. 2. Band-gap (E_g) and valence band splitting ($E_{\rm VBS}$) as functions of order parameter η for partially ordered $Ga_{0.52}In_{0.52}P$ alloys. Labels next to experimental data points are sample numbers used in Ref. 12. For sample 1650; $E_{\rm VBS}$ could not be determined in Ref. 12.

Figure 2 shows a comparison between our calculated results and the experimental data of Ref. 12 for the band-gap energies and valence band splittings at $x=0.52$. For the random alloy, our result of 2.005 eV agrees very well with the experimental results: 2.010, 2.007, and 2.003 eV for $x=0.52$.[34,9,11] For partially ordered samples, as shown in Fig. 2(a), the calculated band gaps agree very well with those for three samples (1642, 1643, and 1650, shown as solid circles) that were found to have relatively large crystalline domains but less well with those for the other three samples (407, 396, and 1639, shown as open circles) that were found to have relatively small crystalline domains.[12] The situation is similar for the valence band splitting, as shown in Fig. 2(b). It is now understood that the existence of the crystalline defects (e.g., antiphase domain boundaries) will reduce the order parameter evaluated using the simplified model of Ref. 12 which did not take into account the defects.[35] For instance, for sample 1639 shown in Fig. 2(a) with $E_g=1.883$ eV, one can now estimate the order parameter to be $\eta=0.57$, instead of 0.50.[12] Figure 2 can now be used for obtaining the order parameter of any partially ordered Ga-In-P alloys much accurately than before.

In summary, we have shown that the widely used but never thoroughly justified η^2 rule for describing band-structure parameters (e.g., band gap, effective mass, etc.) is grossly inaccurate for partially ordered $Ga_xIn_{1-x}P$ alloys. We have demonstrated an accurate and effective method for realistically modeling partially ordered as well as random

alloys. The band gap of a fully ordered Ga-In-P CuP structure is predicted to be ~1.76 eV, which is significantly higher than the roughly 1.55 eV predicted by previous calculations. In the experimentally verifiable region, our results agree very well with available data in terms of the absolute band gap energy. In the light of these results, the conclusions of many previous studies have to be re-examined.

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