Partial-ordering effects in In$_x$Ga$_{1-x}$P

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We present a theoretical study for the band-gap energy and structural properties of partially ordered In$_x$Ga$_{1-x}$P alloys. Partially ordered alloys are modeled through a statistical *ensemble* of *small crystal* structures defined in a 64-site periodic cell. Configurations are generated according to the degree of ordering. The dependence of calculated properties on the long-range-order parameter is found to follow simple functional relationships. Structural anisotropies scale accurately with the square of the order parameter.

In$_x$Ga$_{1-x}$P alloys have been extensively studied during the last few years due in great part to their adequacy as visible-light-emitting materials. A large direct band gap and a close lattice match to GaAs at $x = 0.5$ make this alloy an attractive alternative to Al$_x$Ga$_{1-x}$As in optoelectronic applications. Special attention has been given to the experimental observation of spontaneous ordering into a metastable structure and to the consequences of this ordering in the electronic properties of the material, especially the order-induced band-gap narrowing.

The band-gap energy (E_g) of In$_{0.5}$Ga$_{0.5}$P alloys grown on (001) GaAs substrates by metalorganic vapor-phase epitaxy[1–6] and atomic layer epitaxy[7] is found to depend strongly on the growth conditions. According to the growth parameters, values for E_g ranging from 1.78 to 1.92 eV at 300 K (Refs. 1, 2, and 7) and from 1.882 to 1.987 eV at 13 K (Ref. 6) have been measured. Gomyo *et al.*[1,2] qualitatively related this gap narrowing to the degree of ordering in the alloy's group-III sublattice. The reported ordered structure is the (GaP)$_1$/(InP)$_1$ monolayer superstructure along the [111] direction. Samples producing stronger superstructure spots in the electron-diffraction patterns also presented lower band-gap energies.[2] Polarized photoluminescence measurements[6,8] also related ordering to the band-gap reduction and to the valence-band crystal-field splitting.

Theoretically, band-structure calculations have focused on the (GaP)$_1$/(InP)$_1$ [111] monolayer superlattice,[9] and also on a few other GaInP$_2$-ordered compounds.[10,11] For the monolayer superlattice, E_g is found to be lower than the average of the binary compounds InP and GaP *at the Γ-point* by 0.33,[9] 0.46,[10] or 0.14 eV.[11] Alloy calculations[12,13] have addressed the composition dependence $E_g(x)$ for randomly disordered alloys.

Kurtz, Olson, and Kibbler[14] pointed out that the correlation between the degree of long-range order (LRO) in In$_{0.5}$Ga$_{0.5}$P and changes in the band-gap properties is not yet established in detail. They find samples with almost "normal" band gaps but still showing a significant degree of order in x-ray diffraction patterns. This is in contradiction with the assumption by Kanata *et al.*[6] that E_g decreases linearly with the LRO parameter in these alloys. Accurate determination of the LRO parameter is essential in the investigation of the mechanisms leading to ordering[15] as well as to establish the effect of different growth parameters in LRO.[5] In this work, partially ordered In$_x$Ga$_{1-x}$P is studied, and a clear correlation is established between local structural changes, gap reduction effects, and the degree of ordering.

The LRO parameter is defined in terms of site occupation probabilities in the group-III sublattice. This sublattice is divided into two sublattices α and β, which are occupied, respectively, by In and Ga in the perfectly ordered [111] monolayer superlattice. Four site occupation probabilities p_K^σ give the fraction of sites in sublattice $\sigma = \alpha$ or β which are occupied by species $K =$ In or Ga, respectively. In terms of these, the alloy composition is $x = (p_{In}^\alpha + p_{In}^\beta)/2 = 1 - (p_{Ga}^\beta + p_{Ga}^\alpha)/2$, and the LRO parameter is defined as $S = p_{In}^\alpha - p_{In}^\beta = p_{Ga}^\beta - p_{Ga}^\alpha$. The fully ordered structure corresponds to $x = 0.5$ and $S = 1$ while, for partially ordered configurations, $0 < S < 1$.

Alloys are treated within the *small crystal* formalism[16] using a 64-site cubic basic cluster, which contains eight conventional cubic cells of the diamond lattice.[17] Periodic boundary conditions are imposed. For the electronic properties, the *small crystal* approach yields the exact infinite-crystal spectrum of ordered compounds at selected symmetry points. It is conceptually different from *effective potential-type* alloy formalisms in which alloy properties are obtained from a configurationally averaged Hamiltonian[13] or Green's function.[12] These approximations cast the problem into a zinc-blende symmetry environment, where local correlations and LRO cannot be incorporated. In the present approach, Hamiltonians associated with different configurations accommodated in a relatively large basic cluster are determined and solved independently. A given alloy property is then identified to the average of the calculated values for this property over a representative set—statistical *ensemble*—of configurations. Occupational correlations within the basic cluster size are preserved. Partially ordered In$_x$Ga$_{1-x}$P alloys are simulated through a large number of small crystal configurations numerically generated according to the occupation probabilities of the 32 sites of the

group-III sublattice: $p_{In}^\alpha = (2x + S)/2 = 1 - p_{Ga}^\alpha$, $p_{In}^\beta = (2x - S)/2 = 1 - p_{Ga}^\beta$. This defines the statistical ensemble from which the physical properties of an alloy of composition x and LRO parameter S are calculated. The generated structures provide a realistic sampling of 64-atom cells extracted from the macroscopic system, in which local fluctuations are present. For the present study, $x = 0.5$, and 400 structures are generated for each value of S in the range [0,1].

The binary constituents of $In_xGa_{1-x}P$ present a bond-length mismatch of 7.6%, which results in a strained alloy. We determine the equilibrium atomic positions for each small crystal in the ensemble of configurations assuming the elastic energies are described by a Keating-type valence force field model.[18] Values of the model parameters appropriate for $In_xGa_{1-x}P$, namely, bond-stretching and bond-bending force constants and the unstrained bond lengths, are given in Ref. 9. The elastic energy was minimized using a molecular-dynamics algorithm,[19] allowing for unconstrained relaxation of all degrees of freedom within the basic cluster. Results from the equilibrium configurations are summarized in Fig. 1. There, the average nearest-neighbor distances along the [111] ordering direction (O) and along the lateral directions (L) are plotted versus S^2 for Ga–P and In–P bonds.[20] There are 128 inequivalent bonds per small crystal, all of which are allowed to relax towards equilibrium. Averages are thus obtained from 51 200 calculated bond lengths per LRO parameter value S. The distribution of bond lengths around the average may be quantified by the standard deviation, which is found to vary from 0.012 to 0.018 Å for different bond types and degrees of LRO.

Average values for the four types of bonds show an excellent quadratic fit for the dependence with the order parameter. In particular, the O-L bond shift may be written as

$$\Delta b(S) = \Delta b_{max}S^2 , \qquad (1)$$

with $\Delta b_{max} = -0.050$ Å for Ga–P bonds and 0.057 Å for In–P bonds. Bond lengths for the ordered ($S = 1$) system are in agreement with previous calculations.[9,11] O bonds are very close to the ideal unstrained length value for each bond type, while L bonds are shifted by Δb_{max} with respect to those. The calculated strain energy for this configuration is $U = 32.4$ meV/atom. As S decreases from 1 to 0, average O and L bond lengths merge into values which depend only on the species: 2.512 Å for In–P and 2.383 Å for Ga–P. This means that, instead of remaining confined essentially to L bonds, strain is shared among all bonds, reducing the elastic energy. The random ($S = 0$) alloy has an elastic energy lower than the ordered alloy by $\Delta U = 11.2\pm0.1$ meV/atom, confirming that the ordered bulk alloy configuration is not thermodynamically stable.[15] Our results for the increase of U with S are also well described by a quadratic relation: $U(S) = U(0) + \Delta U\, S^2$.

The electronic structure of each small crystal is obtained in the tight-binding approximation by directly solving for the Hamiltonian spectrum.[16,17] Matrix ele-
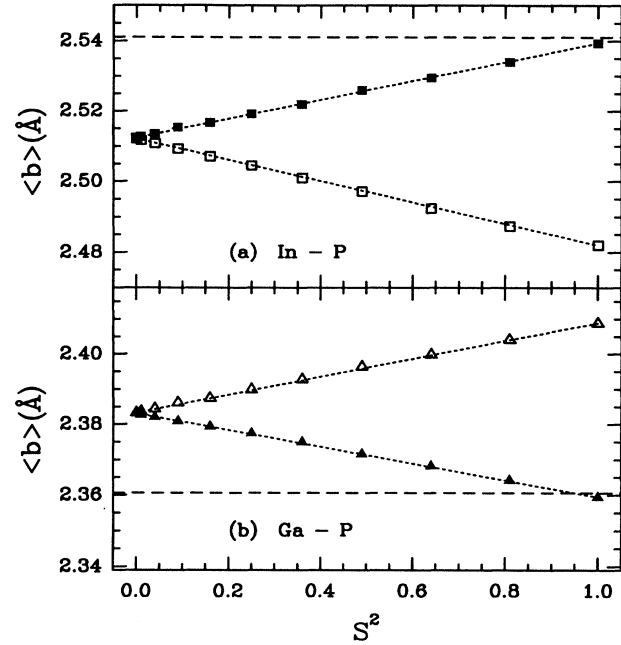

FIG. 1. Average calculated lengths of O bonds (solid symbols) and L bonds (open symbols) for (a) In–P, and (b) Ga–P bonds, vs the order paramenter squared. Statistical error bars are at most equal to symbol size. The corresponding unstrained bond length is given by a horizontal dashed line. Dotted lines indicate the quadratic dependence of average bond lengths with S.

ments, taken from the sp^3s^* parametrization in Ref. 21, are adapted to the present system environmental disorder. The GaP on-site elements are shifted downward with respect to those for InP by 0.05 eV to account for the band offset among these compounds.[22] Distortions due to stress are incorporated locally in each near-neighbor matrix element through a $(b_0/b_{ij})^2$ scaling,[23] where b_{ij} is the calculated equilibrium distance between atomic sites i and j and b_0 is the unstrained value of the corresponding bond. Figure 2 gives the ensemble average values for the main energy gap as a function of the order parameter S. As expected, E_g is a decreasing function of S, but, contrary to the structural parameters plotted in Fig. 1, a quadratic dependence alone does not describe the calculated trend accurately. Symmetry implies that $E_g(S) = E_g(-S)$; therefore, polynomial corrections are restricted to even powers of S. Addition of a small quartic term yields a satisfactory fit, indicated by the dotted line in Fig. 2. It corresponds to the form $E_g(S) = E_g(0) - \Delta E_g(S)$, where $\Delta E_g(S) = (0.13\,S^2 - 0.03\,S^4)$ eV, is the gap reduction of ordered samples with respect to the random alloy.

The gap for the ordered structure, $E_g(1) = 1.87$ eV, is lower than the average gap of the binary compounds at the Γ-point by 0.3 eV, in good agreement with Ref. 9. Previous calculations for the random alloy gap, 2.05 (Ref. 12) and 1.98 eV,[13] are comparable to our result $E_g(0) \simeq 1.97$ eV, which is also close to the experimental value 1.987 eV measured at 13 K.[6] All measured gap
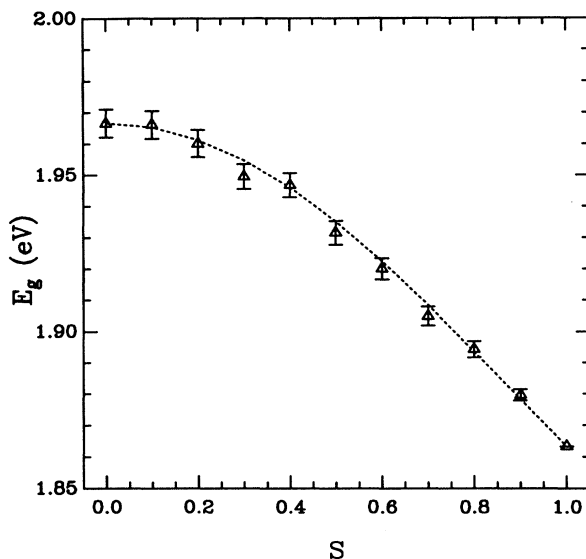
FIG. 2. Calculated low-temperature energy gap of $In_{0.5}Ga_{0.5}P$ vs order parameter. Each data point gives the ensemble average over 400 64-site small crystal structures. Statistical error bars are indicated. The dotted line is a fourth-order polynomial fit, described in the text.

values given in Ref. 6 for ordered samples fall within the range of our calculation. Assuming our calculated $E_g(S)$ dependence, those would correspond to S between 0.5 and 0.9. The order-parameter values estimated there are considerably smaller due to the presumed linear dependence of E_g with S, and also due to the value taken from Ref. 10 for $E_g(1) = 1.70$ eV, which seems to be too small.[11] The lowest value for E_g reported in the literature is 1.868 eV (at $T = 4$ K) for a sample grown by atomic layer epitaxy.[7] From our calculation, this sample would essentially correspond to $S \sim 1$.

The dependence of the gap with S obtained here explains the apparent contradiction described in Ref. 14 of samples with almost "normal" band gaps but still showing order in x-ray diffraction patterns. From Fig. 2 we note that for $S < 0.4$ the gap reduction effect is almost negligible (less than 1%), while values of $S \sim 0.4$ would still show superlattice diffraction spots in x-ray experiments.

Recently Tabor-Morris et al.[24] performed luminescence and polarized extended x-ray-absorption fine-structure (EXAFS) measurements in $In_xGa_{1-x}P$ samples. In this way, both the gap value and O-L bond shifts were obtained. For an ordered sample the measured O-L shift for Ga–P bonds was $\Delta b = (0.04 \pm 0.02)$ Å. From Eq. (1), $\Delta b = 0.04$ Å corresponds to the order parameter $S = 0.9$, leading to a gap narrowing $\Delta E_g(0.9) = 0.086$ eV at 0 K, which is consistent with the experimentally measured narrowing of 0.08 eV at 300 K.[24]

Our results indicate that local structural measurements provide essential information to establish the degree of ordering in $In_xGa_{1-x}P$ alloys. Electron diffraction[2] and x-ray diffraction[14] experiments show

great quantitative uncertainties, while photoluminescence spectra, from which E_g is usually obtained, present a strong and anomalous temperature dependence.[7] Therefore, diffraction spot intensities and band-gap values alone cannot give accurate estimates for the LRO parameter. On the other hand, the simple quadratic dependence of the O-L bond shifts with S obtained here might be used as a complementary measure for the degree of ordering of these alloys. Of course, O-L bond-shift measurements are also subject to uncertainties, caused in part by the disorder fluctuation effects discussed above which lead to line broadening, and by intrinsic accuracy limitations of the involved techniques. Trying to infer the absolute value of the order parameter from these experiments is subject to such inaccuracies, and must also be based on a precise knowledge of Δb_{max}. The accuracy of our bond-length calculations may be estimated by comparison with EXAFS measurements for the deviations of In–P and Ga–P bonds in the random $x = 0.5$ alloy with respect to the binary compound values.[25] The corresponding deviations in our calculation agree with those within the reported EXAFS experimental accuracy, from 0.005 to 0.01 Å. We estimate our value of Δb_{max} is also reliable within this range. Our calculated distribution of widths, about 0.02 Å, is also compatible with EXAFS experimental linewidth values.[26]

In conclusion, the small crystal formalism presented here is of general application to disordered or partially ordered alloys, and gives direct information about the dependence of different alloy properties on statistical parameters related to composition, long- or short-range order. Previous studies have mainly dealt with the composition dependence of elastic and electronic properties of semiconductor random alloys. Near-neighbor distances are usually found to follow a linear dependence with x.[25,26] Band gaps, however, show distinct "bowing" effects, and both linear and quadratic terms in x are present in fits to $E_g(x)$.[12] In the case of order, the simplest functional dependence of physical quantities on any order parameter S for which the system has $S \to -S$ symmetry is quadratic: no linear terms are allowed. For the particular system considered here, this is an excellent approximation for average near-neighbor distances, while gap properties require higher-order corrections. The situation is quite analogous to the composition dependence of these quantities, only that expansions are performed in powers of x in one case and in powers of S^2 in the other. Results for the energy gap might be refined by increasing the basic cluster size or by improving the tight-binding parametrization, but the qualitative behavior of the gap reduction effect obtained here is not expected to change. Note that the small crystal method could, in principle, be coupled to ab initio calculations for the structural properties. However, solving 400 64-atom basic cluster structures for each value of the LRO paramenter is far beyond the current computational limitations of such approaches. The agreement of our calculation with previous theoretical results for the fully ordered structure as well as with experimental data for partially ordered and random samples indicates that the present model accounts for the main features of these alloys.

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