Correlated Atomic Displacements in the Chemically Random $Ga_{1-x}In_xP$ Alloy

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Abstract. – Monte Carlo simulations of a chemically random Ga$_{1-x}$In$_x$P alloy are carried out. An interatomic potential has been parametrized to fit first-principle total-energy calculations of various ordered GaP/InP structures. Using this potential, good agreement between predicted and measured properties of the Ga$_{1-x}$In$_x$P alloy are obtained. This potential is then used to predict positions of atoms in Ga$_{1-x}$In$_x$P yielding for the phosphorous atomic-positions probability peaks at several distinct lattice locations which emerge from *correlated atomic displacements*. The evolution of these displaced positions with temperature is followed by molecular-dynamics calculations showing that the average thermal r.m.s. displacements $\bar{U}$ obey $\bar{U}_{\mathrm{In}} > \bar{U}_{\mathrm{P}} > \bar{U}_{\mathrm{Ga}}$.

Extended X-ray absorption fine-structure (EXAFS) experiments have demonstrated that in atomically random II-VI and III-V A$_{1-x}$B$_x$C semiconductor alloys [1] (*e.g.*, Ga$_{1-x}$In$_x$P) the nearest-neighbor A-C and B-C bond lengths are closer to their ideal values in the pure AC and BC compounds than to the virtual lattice average. Coupled with the fact that the *next*-nearest-neighbor distances A-A, B-B and A-B are close to the virtual lattice values [1], this discovery of a bimodal nearest-neighbor (A-C and B-C) bond length distribution suggests that, on average, the common sublattice C is displaced statically from its zincblende site. Such displacements were shown to affect profoundly the composition dependence of the alloy band gap [2], its mixing enthalpy [3, 4], and thermodynamic behavior [5, 6]. Since EXAFS measures the *average interatomic separations* rather than the *position distribution*, the nature of the atomic-scale structure that underlies the results of the EXAFS measurements remains hidden. In particular, one wonders what the principal directions of the static displacement are, whether such motions are spatially correlated, and what is the role of dynamic thermal motions on these atomic-displacement patterns.

To address these issues we have performed Monte Carlo (MC) and molecular-dynamics (MD) calculations on Ga$_{1-x}$In$_x$P using a modified form of the Keating [7] valence force field (VFF) interatomic potential, capable of handling ternary alloys (T-VFF). We have added 3 more parameters to the 3-body interaction [8] and fit them to a series of first-principle total-energy calculations on different GaP/InP superlattices [9]. This T-VFF potential is next tested via MC simulations to assess its ability to reproduce the measured temperature-composition phase diagram [10], the alloy mixing enthalpy [11] and the EXAFS values of the bond lengths in Ga$_{1-x}$In$_x$P [1]. Having established the validity of this T-VFF for thermodynamic and structural properties, we study the *static* displacement field via MC calculations, and the *dynamic* behavior via MD simulations. We find that even if one assumes

a perfectly random *distribution* of atoms, there exists a highly correlated static *position distribution* whereby the P atoms are displaced *deterministically* in certain high-symmetry directions. The unusual diffraction features observed[12] in nominally random bulk $Ga_{1-x}In_xP$ alloy could therefore reflect correlated atomic displacements, as suggested by Glas[13]. We further find that as the temperature is raised, the static (111)-type displacements are smeared out, while the (100) displacements persist. Dynamic simulations show that the root-mean-square (r.m.s.) displacement $\bar{U}$ obey $\bar{U}_{In} > \bar{U}_P > \bar{U}_{Ga}$. Interestingly, we find that although there is a considerable mass difference between the anions and the cations in the binary GaP and InP compounds, their vibration amplitudes are very close. We attribute this minor variation to the strong vibrational coupling between *anions* and *cations* resulting from the existence of strong bonds.

The excess configurational energy is modeled here by a modified Keating VFF[7] potential by adding three more parameters to the 3-body interaction term[8]. Their values have been determined by fitting the excess total energies of 25 superlattices $(GaP)_p/(InP)_q$ to those calculated by the first-principle density-functional formalism[9] using simulated annealing optimization. We find the following results:

  i) Figure 1a) shows the calculated average In-P and Ga-P nearest-neighbor bond lengths *vs.* composition, confirming the well-known[1] bimodal distribution. The average bond length change $\Delta_{AC} = R_{A-C}(x \to 1) - R_{A-C}(x \to 0)$ is found to be 0.036 and 0.050 Å for Ga-P and In-P, respectively. These values should be compared with the measured[1] values of 0.038 and 0.044 Å, and the tight-binding values[3] of 0.036 and 0.054 Å, respectively.

  ii) The mixing enthalpy $\Delta H_{mix}(x) = E(A_{1-x}B_xC) - (1 - x)E(AC) - xE(BC)$ of the ideally random alloy was calculated via structural relaxation of a 512-atom supercell averaged over 100 randomly selected configurations for each composition x. We find a maximum value with respect to x of $\Delta H_{mix}(x = 0.47) = (77.1 \pm 0.1)\,meV/(4\text{-atoms})$ or an «interaction parameter» $\Omega(x) = \Delta H_{mix}(x)/x(1 - x) = 3.7 - 0.8x\,kcal/mol$. This compares favorably with the averaged $\Omega(x = 1/2)$ value 3.3–3.6 kcal/mol deduced[11] from the measured phase diagram.
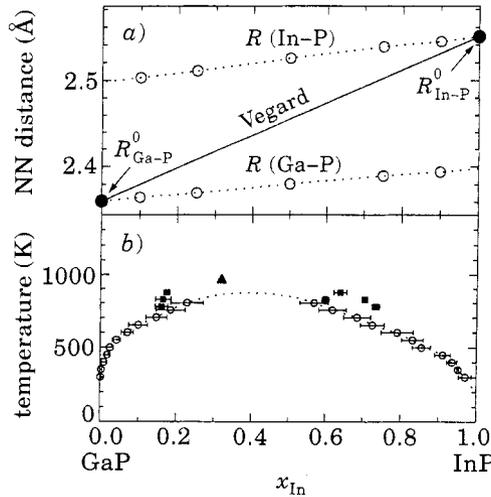
Fig. 1. – a) The average anion-cation nearest-neighbor distance of the random $Ga_{1-x}In_xP$ alloy. b) Calculated and measured[10] x-T phase diagram of the disordered $Ga_{1-x}In_xP$ alloy. The open circles denote results of our Monte Carlo simulations, and the dashed line is an interpolation of these results. The squares denote the experimental results[10], the filled circle and triangle denote the maximum miscibility-gap temperature of *ab initio* calculations of Marzari *et al.*[6] and Wei *et al.*[15].

iii) MC calculations of the temperature-composition phase diagram [14] gives (fig. 1*b*)) a maximum miscibility-gap temperature of $T_c = (870 \pm 20)$ K occurring at $x_c = 0.40 \pm 0.02$. These values should be compared to the recently calculated *ab initio* values of Marzari *et al.* [6] of $T_c = 820$ K and $x_c = 0.6$, and of Wei *et al.* [15] $T_c = 961$ K and $x_c = 0.32$.

The *average bond distances* (fig. 1*a*)) amenable to EXAFS measurements do not reveal the actual spatial distribution of the atoms in the alloy. In fact, if an atom of type α ($= $ P, Ga, In) can have a series of displaced sites $R_i^{(\alpha)}(x)$ with (normalized) probability $P_i^{(\alpha)}(x)$, the EXAFS measurement (and our calculation in fig. 1*a*)) would provide the average $\boldsymbol{R}^{(\alpha-\beta)}(x) = \sum_{ij} P_i^{(\alpha)}(x) P_j^{(\beta)}(x) |R_i^{(\alpha)}(x) - R_j^{(\beta)}|$ of the distribution and its width. Our calculation permits, however, to take a step «backwards» and to focus on the probability of finding an atom of type α in a given position on a crystalline plane. Figure 2 depicts this quantity for the anions (parts *a*) and *b*)) and cations (parts *c*) and *d*)) in the (001) projection of $Ga_{0.5}In_{0.5}P$ (the distributions of the In and Ga are almost identical, therefore we show only the distribution of the Ga). Each plot represents the average displacements over some 200 randomly selected samples, each relaxed to its minimum energy. We see that despite the fact that the lattice sites were initially occupied by Ga and In in a random manner, the relaxation process has led to a deterministic pattern of atomic displacements: while the undisplaced Ga, In and P zincblende sites have the highest probability (giving rise in reciprocal space to the usual Bragg diffraction peaks), there are nine distinct high-symmetry sites i for the anion. These displacements ($\Delta R_i^{(\alpha)} \sim 0.1$ Å) are highly correlated, and occur at specific positions at all compositions. As suggested by Glas [13] they could, therefore, lead to the distinct diffraction pattern observed [12] in nominally random bulk alloys. Figure 2 further shows that as the temperature is raised to 300 K, the four (111) peaks smear out while the peaks in the four soft directions along (100) persist.

The principal positions of the displaced atoms observed in our numerical simulations (fig. 2) can be analytically reproduced by a simple model. Assume that the mixed-cations
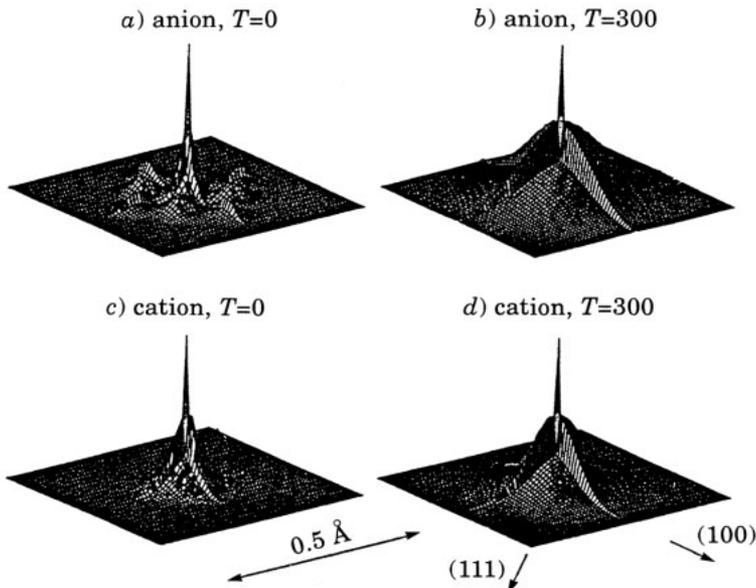
Fig. 2. – Three-dimensional plots of the (100) plane projection of the average probability of the atomic displacements in the chemically random $Ga_{0.5}In_{0.5}P$ alloy. The vertical axes represent the probability of the atoms to be in the specific location, while the horizontal axes represent the atomic locations. The $(0, 0)$ point is the zincblende site.

(Ga, In) reside on the ideal f.c.c. sites and that the P-centered $Ga_{4-n}In_n$ ($n = 0, ..., 4$) tetrahedra occur at composition x with the *random* Bernoulli probability

$$p^{(n)}(x) = \binom{4}{n} x^n (1 - x)^{4-n} . \tag{1}$$

There are fifteen positions that the P atom can take which are deduced from the geometries of the $Ga_{4-n}In_n$ tetrahedra. The P atom is assumed to deviate from its zincblende site toward the direction of the shorter bonds according to the specific nearest-neighbor cases. The above deviations determine the atomic locations, while their probabilities are determined by the Bernouilli distribution (eq. (1)). Figure 3 compares the plane projected deviations of the direct simulation for the $Ga_{0.5}In_{0.5}P$ random alloy at $T = 0$ with the projections of the model (after broadening the displacements by a Gaussian). It is clear that the simple model reproduces the essential physics. Thus, the static deviations of the P atoms are affected mostly by the nearest-neighbor geometries.

To calculate the *time-average* probability of the atomic displacements we apply an MD algorithm to our T-VFF potential. The time-averaged position probability obtained by MD calculations will have a *minimum* at the bottom of the potential surface, where the static displacements (obtained by energy minimization) have a *maximum* probability (fig. 2). $Ga_{1-x}In_xP$ samples of 512 atoms were used in the calculations and the initial In/Ga substitution was chosen randomly according to the required composition. Then, an MC algorithm was applied to equilibrate the atomic positions at a temperature $T = 300$ K using the T-VFF potential. The time evolution of the atomic coordinates was calculated using the Gear algorithm [16]. 500 MD cycles were used for initial equilibration and then the average displacements of the atoms were calculated for 2400 additional MD cycles. The r.m.s. average displacements defined as

$$\langle \Delta U \rangle_j = \sqrt{\frac{\sum_{i=1}^{n} [\bar{U}_j - U_j(t_i)]^2}{n}} \tag{2}$$

were calculated separately for each atom in the sample. Here $U_j(t_i)$ is the position of atom j at
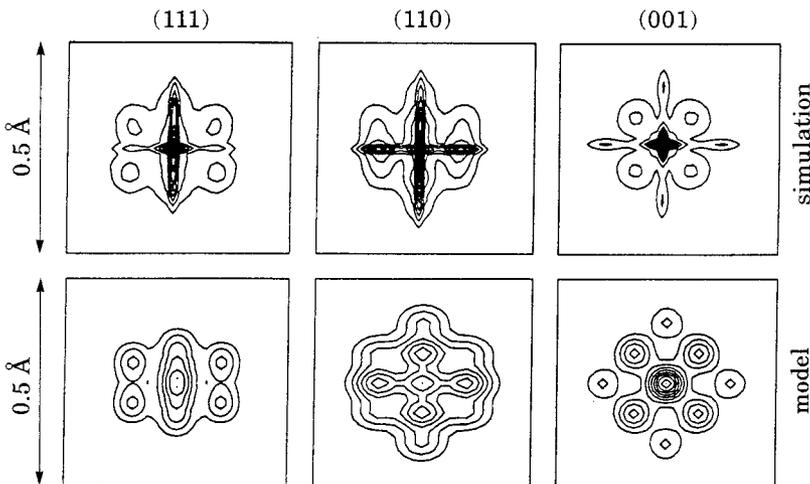
Fig. 3. – Comparison between the results of the MC simulations and the simple model for the displacements (at $T = 0$) of P atoms in a chemically random $Ga_{0.5}In_{0.5}P$ alloy. The displacements are presented in three *projections* (100), (110), and (111).

the instant $t_i = i \, \Delta t$, and $\bar{U}_j$ is the time-averaged position of atom j given by $\bar{U}_j = (1/n) \sum_{i=1}^{n} U_j(t_i)$. The above algorithm was applied for 100 different initial random atomic configurations and the average r.m.s. displacements for each species α were calculated. The MD results are shown in fig. 4. We observe the following:

i) In the pure GaP and InP binaries the anions and cations have similar mean-square dynamic displacements (MSDD) in agreement with Garbulsky and Ceder [17].

ii) The cation MSDD increases monotonically with In composition. This can be explained as follows: we saw in fig. 1*a*) that the Ga-P bond length in In-rich alloys is longer than the same bond in pure GaP, thus, in the alloy environment, the shorter of the two bonds (Ga-P) elongates, while the longer of the two (In-P) shortens. Since vibrational frequencies *decrease* with bond elongation, this means that *a*) bond relaxation *reduces* the frequency difference $\omega_{\text{In-P}} - \omega_{\text{Ga-P}}$ in the alloy relative to the pure binaries, *b*) the vibrational frequency of dilute alloys (*e.g.*, the Ga-P mode in In-rich alloys) is close to the vibrational frequency of the pure *complementary* compound (here pure GaP), as observed by Raman [18], and *c*) the decrease in the vibration frequency leads to an increase in the vibration amplitude (*i.e.* MSDD) and *vice versa*.

iii) While the *static* displacement map (fig. 3) shows that the *anion* has a larger probability than the *cation* to reside at off-center positions, the *dynamic* displacements (fig. 4) show $\bar{U}_{\text{In}} > \bar{U}_{\text{P}} > \bar{U}_{\text{Ga}}$. We might expect different vibrational modes (and different vibration amplitudes) to be related to the different static locations of the anions, however these cannot be observed in the MSDD representation as the probability of the different clusters is monotonic with x (eq. (1)).

As far as we know, no direct experimental results are available on the r.m.s. displacements of GaInP, so only comparison with related systems is possible.

Using ion channeling experiments, Haga *et al.* [19] have obtained a lattice average r.m.s. displacement of $\bar{U} = 0.07$ Å for $\text{Ga}_{0.47}\text{In}_{0.53}\text{As}$, a result which is very close to our predictions for GaInP. Comedi and Kalish [20] measured the r.m.s. displacements in CdZnTe. We have calculated $\langle U_\alpha \rangle$ for Z, Cd, and Te in the binaries ZnTe and CdTe using the standard VFF potentials [7, 21] in the same way as described above and could indeed reproduce the
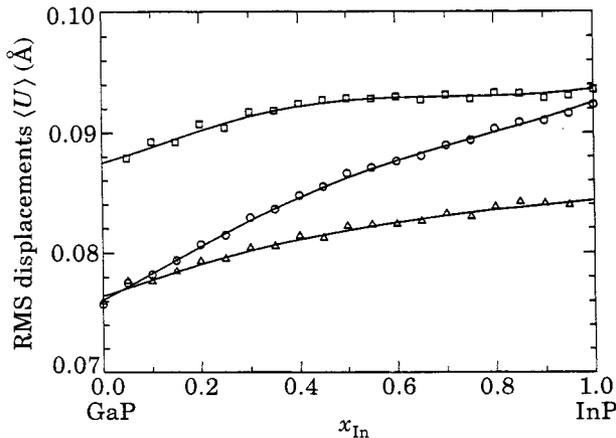
Fig. 4. – Molecular-dynamics results for the total root-mean-square (r.m.s.) displacements $\langle U \rangle$ of the In (squares), Ga (triangles), and P (circles) atoms in the random $\text{Ga}_{1-x}\text{In}_x\text{P}$ alloy at a temperature $T = 300$ K *vs.* In composition x_{In}. The solid lines are interpolations of the calculated results.

observed trend in the relations between the anion and cation r.m.s. displacements[1].

To summarize, we have developed a new method to extend the VFF potential which has allowed us to predict major off-site displacements of atoms in the $Ga_{1-x}In_xP$ random alloy. These atomic displacements are of the order of ~ 0.1 Å and should thus be amenable to measurements.

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[1] We obtained the following r.m.s. displacements for the binaries ZnTe and CdTe: $U_{Zn}(ZnTe) = 0.071$ Å, $U_{Te}(ZnTe) = 0.060$ Å, $U_{Te}(CdTe) = 0.065$ Å, and $U_{Cd}(CdTe) = 0.080$ Å. These should be compared with the experimental results of Comedi and Kalish $U_{Zn}(ZnTe) = (0.125 \pm 0.01)$ Å, $U_{Te}(ZnTe) = (0.095 \pm 0.01)$ Å, $U_{Te}(CdTe) = (0.135 \pm 0.01)$ Å, and $U_{Cd}(CdTe) = (0.155 \pm 0.01)$ Å. We observe that although there is a factor of about 2 between these experimental results and ours, the trend in the relations between the anions and cations is reproduced.

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