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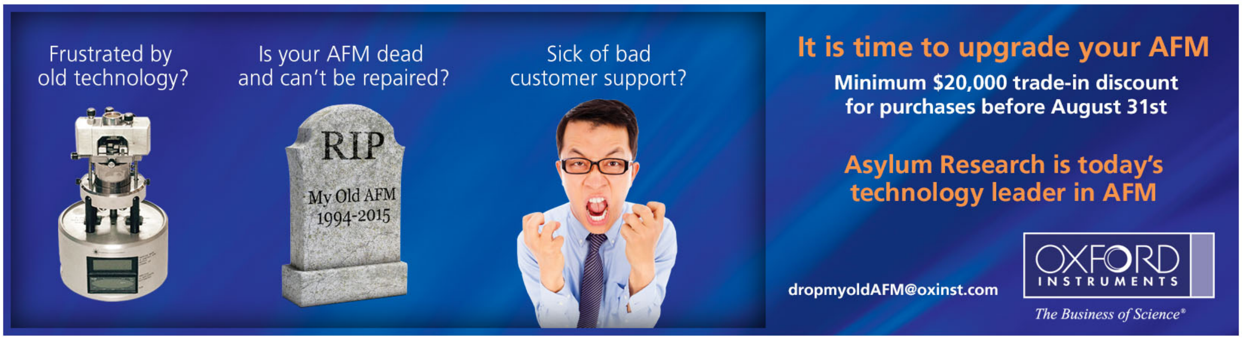
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Effects of atomic clustering on the optical properties of III-V alloys

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Self-consistent electronic structure calculations together with a structural model are used to study the effect of short-range atomic order on the optical properties of otherwise random $Al_{0.5}Ga_{0.5}As$, $Ga_{0.5}In_{0.5}P$, and $Al_{0.5}In_{0.5}As$ alloys. We find that clustering can reduce the direct band gap of these alloys by as much as 100 meV. Furthermore, sufficiently strong clustering is predicted to transform $Al_{0.5}Ga_{0.5}As$ into a direct gap material.

Pseudobinary $A_{1-x}B_xC$ semiconductor alloys generally exhibit deviations from perfect random arrangements of the A and B atoms on their fcc sublattice. These deviations take the form of long-range order (LRO), short-range order (SRO), or both. LRO in III-V alloys appears most frequently in the CuPt structure and is accompanied by a reduction in the band gap relative to the disordered phase.[1] This gap reduction reflects zone-folding and level-repulsion[2] and depends quadratically[3] on the degree η of LRO. In contrast, studies of the effects of SRO on alloy band gaps are scarce. The degree of SRO is generally quantified by the Warren-Cowley[4] parameter

$$\alpha_j = 1 - \frac{P_B(j)}{x_B}, \tag{1}$$

where $P_B(j)$ is the probability to find a B atom on the jth nearest-neighbor shell about A as an origin. In the perfect random alloy $P_B(j) = x_B$ and thus $\alpha_j = 0$ for all atomic shells. Preferred association of *like atoms* ("clustering") yields $\alpha_j > 0$, while association of *unlike atoms* ("anticlustering") is manifested by $\alpha_j < 0$. Direct measurements of SRO in tetrahedral semiconductor alloys were carried out by diffuse x-ray scattering,[5,6] transmission electron microscopy,[7] and scanning tunneling microscopy.[8] Indirect evidence for SRO comes from nuclear magnetic resonance,[9] resonant Raman scattering,[10] infrared reflectivity,[11] deep impurity photoluminescence,[12] and photoreflectance.[13] Many experiments[5–8,11,13] report clustering-type SRO ($\alpha > 0$), whereas anticlustering seems to be less frequently observed.[1,9] Despite these extensive studies, little is known about the effects of SRO on band gaps.[14,15] In this letter we report results of first-principles pseudopotential calculations on the band gaps of perfectly random ($\alpha = 0$) as well as clustered ($\alpha > 0$) models of $Al_{0.5}Ga_{0.5}As$, $Ga_{0.5}In_{0.5}P$, and $Al_{0.5}In_{0.5}As$ alloys. We find that local clustering can (i) reduce the band gap of III-V alloys to a similar extent as LRO does, (ii) transform the indirect-gap material $Al_{0.5}Ga_{0.5}As$ into a direct-gap one, and (iii) localizes the band edge wave functions preferentially on a particular type of cluster, which thus acts as a "local quantum-well." We will discuss the chemical trends for wave-function localization in the sequence Al/Ga/In.

The standard approach to the electronic structure of alloys—the virtual crystal approximation—does not distinguish A from B atoms irrespective of their chemical disparity. The single-site coherent potential approximation assumes that all A atoms (and separately, all B atoms) have the same charge transfer and bond sizes, irrespective of their local environments. A more realistic description would allow for a *distribution* of A and B atoms reflecting the existence of many distinct local atomic environments in the alloy. The most direct approach to this description would involve application of band theory to fictitious solids with huge ($\gtrsim$1000 atom) supercells[16–18] whose sites are occupied by A and B atoms according to a prescribed degree (zero or finite) of SRO. This "direct approach" has been implemented for random 1000–2000 atom models of $Al_{0.5}Ga_{0.5}As$ using empirical tight-binding[17] and empirical pseudopotentials in a plane-wave basis.[18] These studies showed that the results can be mimicked very well using much smaller unit cells (~10 atoms) but with *specially selected site occupations and cell geometries* ("special quasirandom structures," or SQS).[19] We find that the error of the SQS energy gaps relative to huge supercells is[18] ~20 meV. In this work we use these SQSs in the context of self-consistent nonlocal pseudopotential calculations within the local density approximation (LDA) to obtain the electronic energy bands of III-V alloys with and without SRO. The SRO assumed is of the clustering type in which the nearest-neighbor shell has $\alpha_1 > 0$ and all subsequent shells are random. We use 16-atom SQSs with the same computational parameters as described in Ref. 15. The atomic positions of $Ga_{0.5}In_{0.5}P$ and $Al_{0.5}In_{0.5}As$ in the SQSs were relaxed using a Keating-type valence force field,[20] while maintaining cubic symmetry for the cell-external degrees of freedom. We are interested in calculating alloy band gaps of a particular zinc-blende representation, e.g., Γ_{1c} or X_{1c}. We therefore average the eigenvalues $E_j(\bar{\mathbf{K}})$ of a few SQS states $|j\bar{\mathbf{K}}\rangle$, weighted with the spectral density of a zinc-blende-type state $|n\mathbf{k}\rangle$ of a given representation (n and j are band indices):

$$\langle E_n(\mathbf{k})\rangle_{\text{alloy}} = \frac{1}{W}\sum_{j,\bar{\mathbf{K}}} |\langle j\bar{\mathbf{K}}|n\mathbf{k}\rangle|^2 E_j(\bar{\mathbf{K}}), \tag{2}$$

where the sum runs over a few SQS states around a peak in the spectral density of the state $|n\mathbf{k}\rangle$, $\bar{\mathbf{K}}$ must differ from $\mathbf{k}$ by a reciprocal lattice vector of the SQS, and W is a normalization constant.

Table I summarizes our calculated [Eq. (2)] alloy band gaps[21] with and without SRO. We choose in this study a relatively large and positive SRO parameter of $\alpha = \frac{1}{6}$ in order to emphasize the effect of local clustering. (Note, however,

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TABLE I. LDA corrected band gaps in eV (measured from the top of the valence band) for three alloy systems at different states of order: perfect randomness ($\alpha=\eta=0$), clustering-type SRO ($\alpha=\frac{1}{6}$), and CuPt-type LRO ($\eta=1$). Here, $\bar{E}_g$ denotes the average gap of the binaries at their equilibrium volumes. Chemical symbols in parentheses denote the sublattice on which the VBM and CBM are localized, respectively, and D denotes that the state is delocalized.

System		$\bar{E}_g$	Random	SRO $\alpha=\frac{1}{6}$		LRO $\eta=1$	
$Al_{0.5}Ga_{0.5}As$	Γ_{1c}	2.27	2.22	2.13	(Ga/Ga)	1.86	(D/Ga)
	X_{1c}	2.18	2.17	2.16		2.10	
$Ga_{0.5}In_{0.5}P$	Γ_{1c}	2.16	2.06	1.93	(In/Ga)	1.57	(In/Ga)
$Al_{0.5}In_{0.5}As$	Γ_{1c}	1.78	1.65	1.56	(In/D)	1.49	(In/D)

that SRO parameters as large as the present one have been reported in the literature[5].) The table also gives the average band gaps of the binaries $\bar{E}_g=\frac{1}{2}[E_g(AC)+E_g(BC)]$ and the calculated gaps of CuPt ordered alloys ($\eta=1$). The optical bowing parameter b is defined by $E_g(x)=\bar{E}_g(x)-bx(1-x)$.

From the table we conclude the following: (i) The direct band gaps of the random alloys ($\alpha=\eta=0$) are reduced relative to $\bar{E}_g$ by 0.05, 0.10, and 0.13 eV for $Al_{0.5}Ga_{0.5}As$, $Ga_{0.5}In_{0.5}P$, and $Al_{0.5}In_{0.5}As$, respectively. This gives bowing parameters of 0.20, 0.40, and 0.52 eV, compared with the experimental results of 0.37 (Ref. 22), 0.70 (Ref. 23), and 0.74 eV (Ref. 24), respectively. (ii) LRO of the CuPt type ($\eta=1$) reduces the band gaps relative to $\bar{E}_g$ by 0.41, 0.59, and 0.29 eV, respectively. (iii) Local clustering with a SRO parameter $\alpha=\frac{1}{6}$ also reduces significantly the direct band gaps relative to $\bar{E}_g$, i.e., by 0.14, 0.23, and 0.22 eV for $Al_{0.5}Ga_{0.5}As$, $Ga_{0.5}In_{0.5}P$, and $Al_{0.5}In_{0.5}As$, respectively. In $Al_{0.5}Ga_{0.5}As$ the Γ_{1c}-like transition now lies *lower* in energy than the X_{1c}-like indirect transition. The latter seems to be almost unaffected by SRO. Thus we predict an indirect to direct band gap crossover in $Al_{0.5}Ga_{0.5}As$ with sufficient local clustering. This is in marked contrast to the findings of Fu *et al.* who find *negative* optical bowing upon clustering.[14] Magri *et al.* obtain the same sign of band gap modifications as we do, but a much smaller value due to the smaller SRO parameter assumed there.[15]

In order to understand the physical mechanism leading to the large gap reduction reported in Table I, we analyze the wave functions of the lowest conduction (CBM) and highest valence (VBM) states in the absence and then in the presence of SRO. We find that as SRO sets in, the wave functions at either the lowest conduction band edge ($Al_{0.5}Ga_{0.5}As$) or the highest valence band edge ($Al_{0.5}In_{0.5}As$) or both ($Ga_{0.5}In_{0.5}P$) strongly localize on clusters of one type of cations, while the corresponding states in the random alloys show no such tendency. This is illustrated by plotting contours of the wave functions squared in crystallographic planes intersecting these clusters (see right-hand side of Fig. 1). The wave functions are clearly segregated on a particular cation sublattice, indicated in the fourth column of Table I. The *degree* of segregation (i.e., localization) can be quantified by projecting the wave functions on atomic spheres belonging to a particular type of cation tetrahedron A_nB_{4-n}. We define a cluster weight as

$$w_n(j\bar{\mathbf{K}})=\frac{1}{N_n}\sum_{\mathbf{r}_i}|\langle\chi_\Omega(\mathbf{r}_i)|j\bar{\mathbf{K}}\rangle|^2, \tag{3}$$

where N_n is the number of clusters of type A_nB_{4-n}, the sum runs over all positions of A, B, and C atoms participating in such a cluster, and $\chi_\Omega(\mathbf{r}_i)$ is a characteristic function which is zero outside an atomic sphere of volume Ω centered at $\mathbf{r}_i$, and $1/\Omega$ inside the sphere. Histograms of the cluster weights w_n for the conduction band minimum of $Al_{0.5}Ga_{0.5}As$, $Ga_{0.5}In_{0.5}P$, and the valence band maximum of $Al_{0.5}In_{0.5}As$ are also shown in Fig. 1, demonstrating localization on particular "pure" clusters. (The CBM in $Al_{0.5}In_{0.5}As$ is weakly localized on In-rich clusters.)

The results of Fig. 1 imply that the clusters act as "impurity-like traps" for electrons or holes, very much like isoelectronic impurities which are known to bind carriers if the difference between their local potential and that of the host atom exceeds a critical value.[25] However, whereas an *isolated* Ga impurity is not strong enough to bind an electron in either a AlAs or InP host crystal,[26] the formation of clusters in the respective alloys spatially extends the range of the

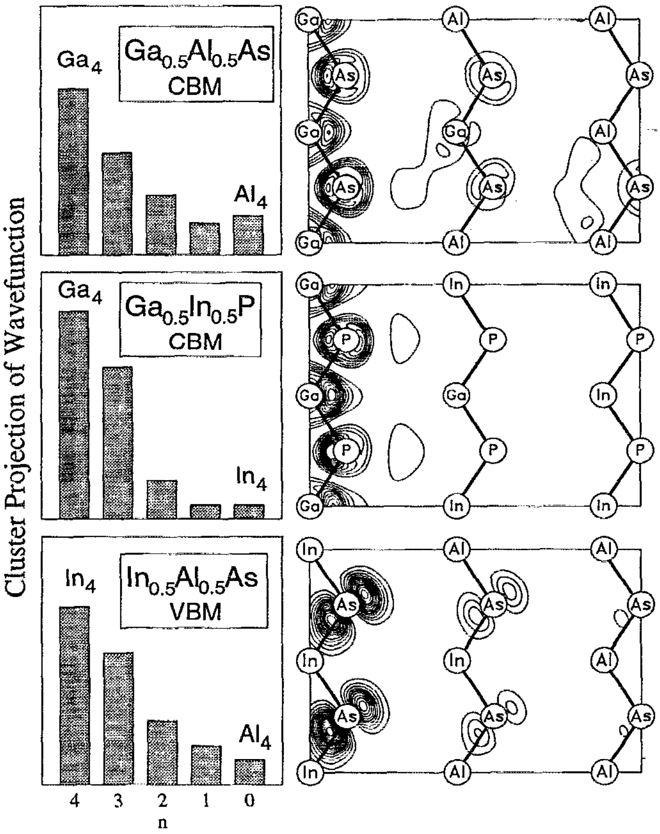

FIG. 1. The left-hand side histograms represent the weights [Eq. (3)] that CBM or VBM wave functions have on the A_nB_{4-n} clusters in the presence of clustering SRO. The atomic sphere volumes Ω used for the projections are equal to the average atomic volume in each alloy. In the right-hand side we show contour plots of the corresponding wave function squared on the (110) plane. The states are clearly segregated on one type of cluster.

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perturbing potential, thus enhancing its strength and leading to binding. Similarly, an isolated In impurity in GaP or AlAs will probably not bind a hole, but the corresponding clusters do. For sufficiently large cluster sizes we can rephrase the preceding argument in terms of band theory: The segregation of the band edge wave functions is dictated by the band offsets of the binary components taken at the alloy volume $\bar{V}=V(x=0.5)$. For example, whereas unstrained InP has a much smaller band gap than unstrained GaP, hydrostatic compression of the former and expansion of the latter to their common alloy volume $\bar{V}$ reverses the order of the lowest conduction states, so now Ga forms the conduction band edge. (The valence band maximum in compressed InP is only ~0.25 eV higher[27] than the one in expanded GaP.) Thus, the lowest conduction wavefunction in a clustered $Ga_{0.5}In_{0.5}P$ alloy should segregate on the Ga-rich clusters as found in the calculation (Fig. 1). For electrons, the observed trend follows the order of atomic s-orbital binding energies, which increase in the sequence Ga→In→Al (LDA values are −9.16, −8.46, and −7.83 eV, respectively). The hole localization, however, is less directly correlated with an atomic property of the cations alone, since the wavefunctions at the VBM are delocalized on the *anion sublattice*.

In summary, we have shown that local cation clustering in common-anion alloys can reduce the energy gap considerably with respect to the ideal random alloys. This is accompanied by localization of the band edge wave functions on clusters with lower potential energy. It would be interesting to study experimentally the band gaps of clustered III-V alloys. It is conceivable that intentional creation of SRO may be used as a tool for band gap engineering.

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