

“Majority Representation” of Alloy Electronic States

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Despite the lack of translational symmetry in random substitutional alloys, their description in terms of single Bloch states has been used in most phenomenological models and spectroscopic practices. We present a new way of analyzing the alloy electronic structures based on a “majority representation” phenomenon of the reciprocal space spectrum $P_i(\mathbf{k}, \mathbf{d})$ of the wave function. This analysis provides a quantitative answer to the questions: When can an alloy state be classified according to the crystal Bloch state symmetry, and under what circumstances are the conventional theoretical alloy models applicable. [S0031-9007(98)06043-8]

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Random substitutional $A_{1-x}B_x$ alloys lack translational symmetry both on the atomistic scale (due to random substitution of lattice sites by A and B atoms), and on the mesoscopic scale (due to statistical composition fluctuations leading to locally A -rich and B -rich regions). In semiconductor alloys, such loss of translational symmetry leads to scattering, manifested by a precipitous drop in carrier mobility [1], to exciton trapping, leading to the temperature dependence of photoluminescence (PL) lifetime and intensity [2–4], and to the appearance, in nominally indirect band-gap alloys, of direct transitions without phonon intervention [5]. Despite the formal illegitimacy of using physical concepts based on translational invariance when discussing random alloys, there is a strong tradition to do so in many phenomenological descriptions of alloy systems [6]. For example, reflectivity and PL peaks of alloys are routinely [7] classified in terms of Bloch-like van Hove singularities. Indeed, in many cases the identity of the translationally invariant states of pure crystals seems to be inexplicably preserved in random substitutional alloys. This point of view was carried out to its extreme in the widely used [6] “virtual crystal approximation” (VCA) [8–10], in which the symmetry of the alloy is assumed *identical* to the (higher) symmetry of the constituents. Thus, one needs to find a way to quantify the degree of translational symmetry in an alloy wave function. This will also help to classify different alloy systems according to this degree of translational symmetry and to judge the validity of various theoretical models (e.g., VCA, small supercells) that assume a certain level of translational symmetry.

If an alloy eigenfunction C_i were available, the extent of effective translational invariance could be quantified by expanding $C_i(\mathbf{r})$ in a complete set of Bloch functions $u_{n\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$ of band index n and computing the sum over bands of the projection at a given translationally invariant wave vector \mathbf{k} [which is inside the first Brillouin zone (BZ) of the constituent solid A and B]:

$$P_i(\mathbf{k}, \mathbf{d}) = \sum_{n>1} | \langle C_i(\mathbf{r}) | u_{n\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}} | \rangle |^2. \quad (1)$$

The alloy could be represented by a periodic supercell containing N atoms. The real alloy is then sought by increasing $N \rightarrow \infty$. For a given supercell, \mathbf{k} is the reciprocal lattice vector of the supercell. If the alloy state C_i were dominated by a single “majority representation” (MR) wave vector \mathbf{k}_{MR} , then $P_i(\mathbf{k}, \mathbf{d}) \neq 0$ and $P_i(\mathbf{k}, \mathbf{d})$ vs \mathbf{k} will have a δ -like peak at $\mathbf{k} = \mathbf{k}_{MR}$. In this case, the alloy wave function behaves essentially as a Bloch periodic state with wave vector \mathbf{k}_{MR} . “Composition fluctuation” [3,4], manifested by the localization of C_i in a real-space domain rich in the low potential alloy constituent, would then lead to a broadening of this δ peak in $P_i(\mathbf{k}, \mathbf{d})$. On the other hand, if no such majority representation wave vector \mathbf{k}_{MR} exists, we expect that $P_i(\mathbf{k}, \mathbf{d}) \approx 0$ for all wave vector \mathbf{k} 's for large supercells.

A direct answer to these questions requires knowledge of the explicit single-particle *eigenstate* $C_i(\mathbf{r})$ of the random alloy. Unfortunately, contemporary theories such as the “averaged Green’s function” [11] and the “coherent potential approximation” (CPA) [12], or “virtual crystal approximation” [8] and perturbation treatment based on it [13], provide only statistically averaged quantities, rather than explicit eigenstates. Indeed, a calculation of $C_i(\mathbf{r})$ requires a supercell that is large enough to capture localization due to composition fluctuation. For conventional semiconductor alloys, this entails $N \approx 10^3$ – 10^6 atoms. Because of advances in the computational algorithm for the electronic structure of large systems [14,15], it is now possible to calculate the band edge states for such large systems using atomistic screened pseudopotentials and plane wave basis functions [16].

We study substitutional binary semiconductor alloys made of zinc blende constituents: GaAs-AlAs, GaAs-InAs, GaAs-GaN, and GaP-GaN. The choice of these systems is based on the need to represent the major prototype behaviors: The lattice mismatch between GaAs and AlAs is very small (thus, the effect of atomic relaxation is negligible), while the lattice mismatch is significant in GaAs-InAs (7%) and huge in GaAs-GaN and GaP-GaN (20%). Furthermore, while GaAs-AlAs and GaAs-InAs represent mixing on the cation sublattice, GaAs-GaN and

GaP-GaN represent anion mixing. Also, $\text{GaAs}_{1-2x}\text{N}_x$ and $\text{GaP}_{1-2x}\text{N}_x$ have resonant or bound impurity states at $x \rightarrow 0$ and $x \rightarrow 1$ limits [17], while in the other alloys, there is no such impurity levels in the dilute limits.

To model a random alloy, we have used $3 \times 3 \times 3$ cubic supercells containing $N > 512$, 4096, and 32768 atoms for P_i calculation, and $N > 23$

TABLE I. Calculated projections $P_i \mathbf{s}_{\mathbf{k}_{\text{MR}}^d}$ [Eq. (1)] of alloy state \mathbf{c}_i . If $P_i \mathbf{s}_{\mathbf{k}_{\text{MR}}^d} \doteq \mathbf{1}$, the state has approximated translational symmetry. N is the number of atoms in the supercell. w_{MR} is the majority representation weight, which is calculated as the sum of $P_i \mathbf{s}_{\mathbf{k}}^d$ around \mathbf{k}_{MR} (dashed line box shown in Fig. 4) from the $N > 32\,768$ supercells. The $N > 512$ results

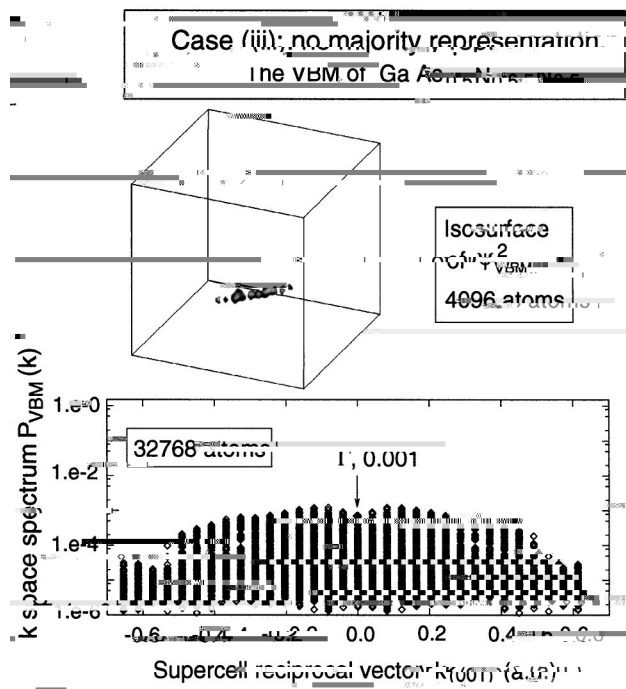


FIG. 3. Valence band maximum state of GaAs_{0.5}N_{0.5}. See caption of Fig. 1 for details.

“optical bowing.” In the case (ii) of weak majority representation, the states can still be classified according to k_{MR} . However, the VCA model clearly cannot be

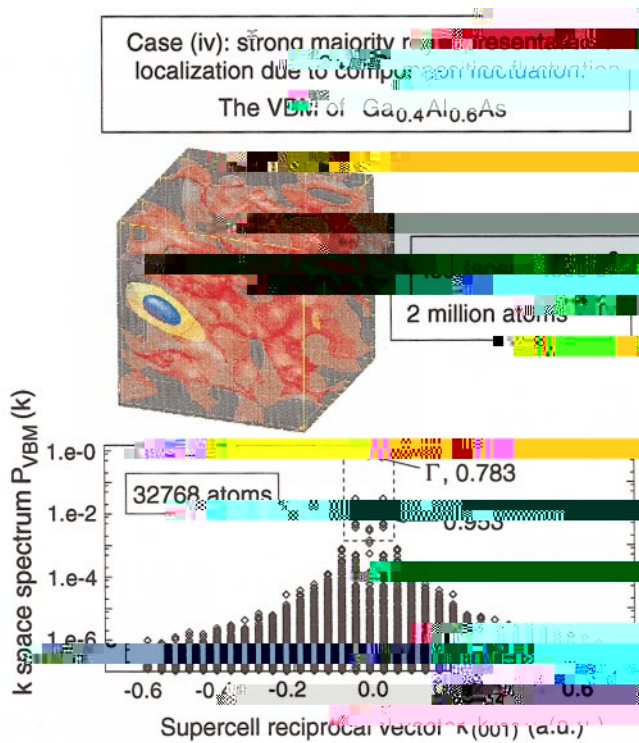


FIG. 4(color). Valence band maximum state of Ga_{0.4}Al_{0.6}As.