

Direct-to-Indirect Crossover in Semiconductor Alloys: A First-Order Phase Transition?

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We study the direct-to-indirect gap crossover in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ alloys driven by Al addition, in analogy with temperature-induced phase transitions. The adopted real-space formalism incorporates occupational disorder in a realistic manner: different atomic configurations, accommodated in a supercell, are generated and solved independently. We perform a systematic study of the scaling of calculated gap properties of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ alloys with the cell size, and consider system sizes ranging from 64 to 8000 atoms. Extrapolation to infinite system size follows scaling laws appropriate for first-order phase transitions, and allows an accurate determination of the crossover composition x_c .

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The current development of electronic structure calculations allows for large systems to be treated and solved, in particular, taking into account surface effects, impurities, and disorder over relatively extended regions in space. It is well known that the finite size of a system produces systematic deviations from the macroscopic behavior, particularly around an order-disorder transition [1]. Knowledge and control over finite-size effects are powerful theoretical tools, since they allow nontrivial extrapolations of thermodynamic quantities toward their infinite system values. Such procedures, which are standard in statistical physics, have not yet been explored in electronic structure calculations.

In this Letter we consider a relevant problem both in fundamental and in applied semiconductor physics, namely, the direct-to-indirect band-gap transition in semiconductor alloys. $\text{Al}_x\text{Ga}_{1-x}\text{As}$ alloys are a prototype system for this transition. The optical gap remains direct up to x near 0.4, becoming indirect for larger Al concentrations. The most striking experimental signature of this transition is a sharp decrease of the luminescence intensity with composition around $x = 0.4$ [2]. Basic questions regarding this change in optical behavior remain open. Is it a critical transition, taking place at a well defined composition x_c , or a crossover over a finite range of compositions? If critical, is the luminescence intensity drop continuous or discontinuous at x_c ? These issues are hard to resolve experimentally, since temperature and sample imperfections always contribute to broaden the transition. We show that these questions may be investigated theoretically in close analogy with order-disorder transitions in statistical physics.

The binary constituents GaAs and AlAs crystallize in the zinc-blende structure and have nearly identical lattice parameters, which yield unstrained solubility in alloying over the whole composition range. The crystal structure consists of two equivalent fcc sublattices, one of which is occupied by As and the other one by the group-III element. In spite of their structural and electronic similarity,

GaAs is a light-emitting material, while AlAs is not. This is understood from their electronic band structures, since the top of the valence band wave functions correspond to Bloch wave vector $\vec{k} = 0$ (Γ) for both compounds, while the bottom of the conduction band wave functions correspond to $\vec{k} = \Gamma$ for GaAs and $\vec{k} = (\pi/a, 0, 0)$ (X) for AlAs. Optical transitions between Bloch states are allowed if $\Delta\vec{k} = 0$. Therefore they are allowed within the main gap in GaAs, but not in AlAs. In random alloys, translational symmetry is broken, \vec{k} is not a good quantum number, and such selection rule is not applicable. The usual Γ - X conduction band crossing criterion for alloys is based on *effective-potential-type* approximations [3], which presume or impose the zinc-blende symmetry of the constituents to the alloy environment. Interpolated band structures are thus obtained over the alloy's composition range.

We have recently studied the direct-to-indirect gap crossover in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ alloys through a real-space formalism—the small crystal approach—which provides clear identification of the transition without involving k -space special symmetry points assignment to the electronic states [4]. As the basic cluster size increases, the small crystal approach naturally provides a hierarchy of approximations for the treatment of disordered systems. In some cases, convergence of the results with the basic cluster size is very fast, and can be ascertained by simple inspection [5]. Around a crossover in physical behavior, however, finite-size effects are enhanced, and accurate identification of relevant physical quantities cannot be performed by inspection.

In the small crystal approach, a basic cluster is chosen, and different configurations are defined according to specified atomic occupations and periodic boundary conditions. Disordered $\text{A}_x^{\text{III}}\text{B}_{1-x}^{\text{V}}\text{C}^{\text{V}}$ alloy's properties are approximated by configurational averages over structures accommodated in the basic cluster of C sites [4,5]. This approximation becomes exact in the $C \rightarrow \infty$ limit. For finite C , averages are performed over an *ensemble* of

structures generated numerically according to the occupational probabilities of the sites in the group-III fcc sublattice. For random $\text{Al}_x\text{Ga}_{1-x}\text{As}$ alloys, these are $P(\text{Al}) = 1 - P(\text{Ga}) = x$.

The nature of the gap of a specified $\text{Al}_n\text{Ga}_m\text{As}_{m+n}$ compound (ℓ) is determined by the electric dipole moment of the minimum gap transition, $\vec{p}_\ell = \langle v_\ell | \vec{p} | c_\ell \rangle$, where $|v_\ell\rangle$ and $|c_\ell\rangle$ are the valence and conduction minimum gap states of the compound. Optical transitions are allowed if $\vec{p}_\ell \neq 0$. It is convenient to define a related scalar quantity, $\mathcal{O}_\ell = |\vec{p}_\ell|^2 / |\vec{p}_0|^2$, where \vec{p}_0 is the dipole moment for GaAs. Within the small crystal treatment, $\mathcal{O}(x)$ for an alloy of composition x is approximated by the ensemble average $\langle \mathcal{O}_\ell \rangle_C$ over values calculated for structures $\{\ell\}$ generated on a $C = 2(m+n)$ basic cluster. Note that $\mathcal{O}(x)$ decreases from 1 to 0 as x goes from 0 (GaAs) to 1 (AlAs). In analogy with order-disorder transitions, $\mathcal{O}(x)$ is identified to a scalar order parameter. The “ordered” (“disordered”) range corresponds to direct-gap (indirect-gap) alloys, and the transition is driven by increasing x , instead of the temperature, for example. Order-disorder transitions are always associated with some broken symmetry in the system. In the present case, this involves the *relative symmetry* of the gap-edge states, through the quantity $\langle v | \vec{p} | c \rangle$. For periodic potentials, wave function symmetry is naturally labeled by the Bloch wave vector \vec{k} , leading to the \vec{k} -conservation selection rule stated above. Such classification is not applicable to disordered materials. However, one may perform a spectral decomposition of the wave functions into zincblende symmetry components. The ordered range would correspond to a predominant Γ -symmetry spectral weight for both conduction and valence edge states while, in the disordered range, X character would dominate the conduction state.

The electronic properties of $\text{Al}_n\text{Ga}_m\text{As}_{m+n}$ ordered compounds are described within the tight-binding formalism. Calculations were performed on cubic basic clusters with L^3 conventional cubic unit cells of the fcc lattice, therefore with $C = 8L^3$ atomic sites. Electronic states are represented on a 5 orbitals per site (sp^3s^*) basis set [46]. Since full matrix diagonalization procedures become unnecessarily time consuming for large values of C , a new algorithm was developed within the small crystal approach for the determination of the relevant eigenstates of the Hamiltonian \mathcal{H} . The method consists in searching for the tight-binding wave function $|\Psi\rangle$ which minimizes the expectation value $\langle \Psi | (\mathcal{H} - \epsilon_{\text{ref}})^2 | \Psi \rangle$ [7]. This quantity is minimized by the energy eigenstate whose eigenvalue is closest to the reference energy ϵ_{ref} . By properly tuning ϵ_{ref} in the gap region, the band-edge states $|v_\ell\rangle$ and $|c_\ell\rangle$ are obtained. Minimizations are performed by a simple steepest descent algorithm.

Figure 1 presents results for $\mathcal{O}(x)$ calculated for basic cluster sizes $C = 64, 216,$ and 4096 . As C increases, the direct-to-indirect transition sharpens. The composition

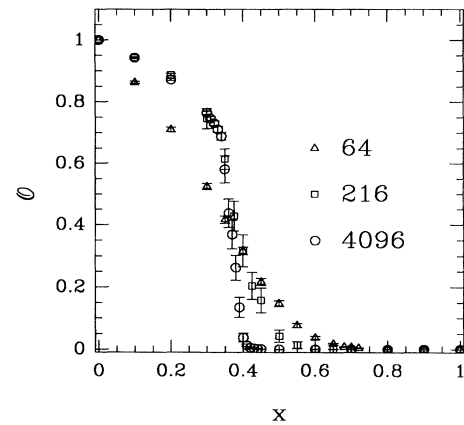


FIG. 1. Calculated order parameter versus composition for the indicated basic cluster sizes. For $C = 64$, each data point corresponds to an ensemble average over 400 randomly generated configurations for this basic cluster size, while larger sizes correspond to ensembles with 40 configurations.

dependence of \mathcal{O} for increasing C is quite similar to the temperature dependence of the order parameter (e.g., magnetization) in Monte Carlo simulations performed in lattices of increasing size [1]. The effect of the finite lattice is to “round” and shift the transition region. This occurs both for second-order transitions, when the order parameter goes continuously to zero at the transition temperature T_c , and for first-order transitions, which are characterized by a discontinuity of the order parameter at T_c . It is quite difficult to locate the transition accurately, or even to determine its order, based on Monte Carlo simulation results for the mean order parameter versus temperature. Higher moments of the order parameter distribution are needed to establish these features [8,9]. We proceed the analogy assuming a well defined x_c exists below which, in the $C \rightarrow \infty$ limit, \mathcal{O} appears spontaneously with a nonzero value.

A distinctive feature between continuous or discontinuous transitions is the absence or presence of phase coexistence at the transition point x_c . This allows the analytic nature of the transition to be inferred from the asymptotic behavior of the fourth-order reduced cumulant,

$$V_L(x) = 1 - \frac{M_L(4)}{3[M_L(2)]^2}, \quad (1)$$

where $M_L(n) = \langle \mathcal{O}^n \rangle_L$ is the n th moment of the order parameter distribution for systems of linear dimensions L . This quantity has a minimum at the effective transition composition, $x_c(L)$. In the infinite-lattice limit and at fixed x , $V_\infty = \frac{2}{3}$ except for a discontinuous transition at $x = x_c$. In this case,

$$V_\infty(x_c) = 1 - \frac{2}{3} \frac{\mathcal{O}_+^4 + \mathcal{O}_-^4}{(\mathcal{O}_+^2 + \mathcal{O}_-^2)^2}, \quad (2)$$

where \mathcal{O}_+ (\mathcal{O}_-) is the asymptotic value of the order parameter for x just above (below) x_c . Note that, for

$x > x_c$, \mathcal{O} and all of its moments tend to zero as L increases. Thus, for the disordered range, V_L is not well defined numerically in the $L \rightarrow \infty$ limit [10]. A simple way to overcome this difficulty is to rigidly shift the probability distribution of the order parameter away from zero, by adding a fixed constant to the calculated \mathcal{O} values.

Configuration *ensembles* generated for different system sizes and compositions yield order parameter distributions which were numerically analyzed. The statistics ranged from at least 20 samples for $L = 10$ up to at least 200 samples for $L \leq 6$, allowing us to represent within reliable accuracy the regions around the minima of V_L . Figure 2 presents results for the reduced fourth-order cumulant calculated for system sizes $L = 4$ to 10 ($C = 512$ to 8000). Note that a minimum is always present below $\frac{2}{3}$; it becomes narrower and seems to approach a nontrivial limit as L increases. This behavior of the cumulant reflects an order parameter probability distribution consisting of a superposition of two peaks. Analysis of our results confirms that this is the case. As illustrated by the inset in Fig. 2, the peaks correspond, respectively, to direct- and indirect-gap structures in the *ensemble*, which is the signature of phase coexistence, i.e., of the first-order character of the transition. For first-order phase transitions, finite-size scaling theory predicts shifts and broadening of anomalies to be inversely proportional to the volume, L^{-d} in d dimensions [8,9]. Following

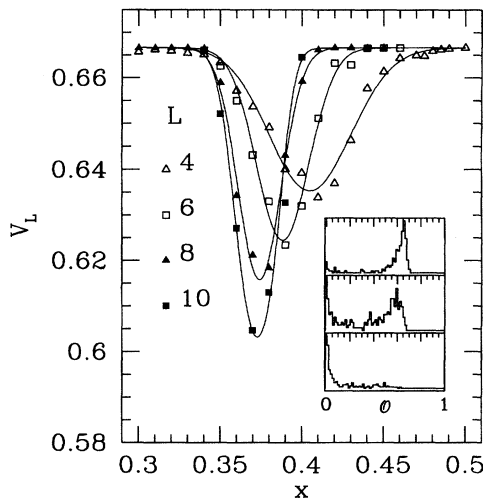


FIG. 2. Composition dependence of the fourth-order reduced cumulant around the critical composition, for the indicated system sizes (for clarity, odd values of L are omitted). Solid lines are guides to the eye. Away from the critical region, V_L approaches the trivial value $\frac{2}{3}$. The histograms in the inset are probability distributions of the order parameter for $L = 6$ as the composition ranges from values below to above the minimum (from top to bottom, $x = 0.36, 0.38, 0.40$). Note the double-peaked character of the distribution, with the indirect-gap peak overcoming the direct-gap one.

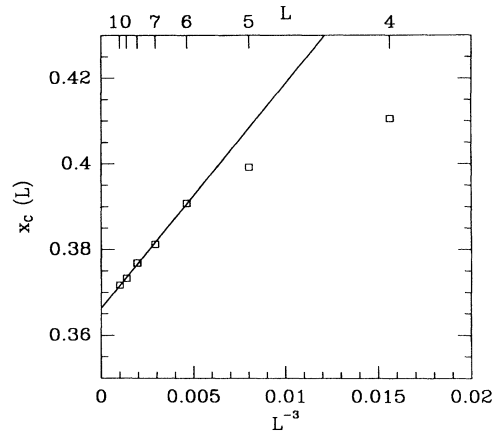


FIG. 3. Effective transition compositions versus L^{-3} .

the alloy analogy, we presume a L^{-3} dependence for the location of the minimum, $x_c(L)$, and present in Fig. 3 the variation of $x_c(L)$ with L^{-3} . Note that an excellent fit to this scaling law is attained for $L \geq 6$, up to the largest value considered, $L = 10$. These correspond to C values from 1728 to 8000. For smaller sizes, even for $C = 1000$, considerable deviations are found from the asymptotic scaling. The scaling of $x_c(L)$ confirms the assumption of a well defined x_c was correct. The $L \rightarrow \infty$ extrapolated value of the critical composition is $x_c = 0.366 \pm 0.004$.

Our results for the order parameter are summarized in Fig. 4. The asterisk gives the calculated infinite system behavior of the order parameter at x_c , with the discontinuity $\mathcal{O}_- = 0.69 \pm 0.01$ obtained from (2).

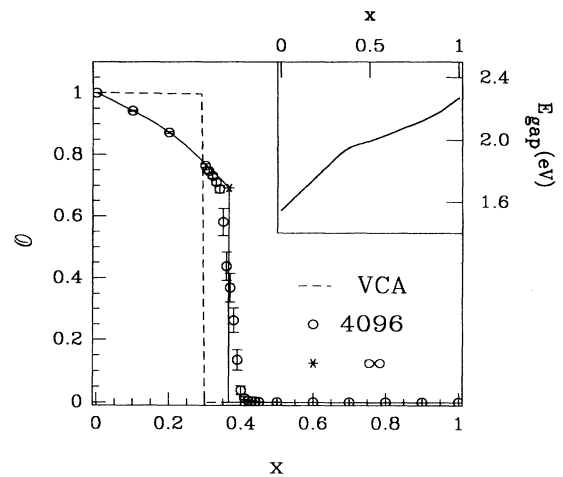


FIG. 4. Composition dependence of the order parameter in the virtual crystal approximation (dashed line) and in the small crystal approach for $C = 4096$ (circles) compared to the extrapolated ∞ -size crystal overall behavior (solid line). The asterisk gives the coordinates (x_c, \mathcal{O}_-) . The converged energy gap dependence with composition is presented in the inset.

The solid line indicates the overall extrapolated $\mathcal{O} \times x$ dependence. Comparison with results from $C = 4096$ shows that, even for this system size, finite-size deviations occur over a considerable range of compositions around x_c . If one adopts the same model Hamiltonian within the *virtual crystal approximation* (VCA), the resulting $\mathcal{O} \times x$ dependence is given by the dashed line in Fig. 4. The VCA predicts \mathcal{O} essentially constant up to the band-crossing composition $x_c^{\text{VCA}} = 0.3$, where it drops to zero.

Besides a discontinuous drop of the order parameter at T_c , first-order phase transitions are also characterized analytically by singularities or anomalies in related thermodynamic quantities, such as the specific heat and the susceptibility. The interpolated band-structure description of the alloy problem predicts a “kink” in the composition dependence of the energy gap, i.e., a discontinuity in the first derivative dE_{gap}/dx , occurring at x_c [3]. Previous theoretical studies have used this feature to identify x_c [11]. However, it is not possible to show that this derivative is proportional to the order parameter, or to any other function of the dipole moment matrix element. The fact that $\langle v|\hat{p}|c\rangle$ goes discontinuously to zero at x_c does not imply a kink in $E_{\text{gap}}(x)$ at this composition. For the system sizes considered here, results for the energy gap converge relatively fast with L for all x , and do not show a tendency to develop a kink at x_c as L increases. The result in the inset of Fig. 4 remains essentially unchanged for $5 \leq L \leq 10$. Contrary to the order parameter distributions, energy-gap distributions are single peaked. Qualitatively, E_{gap} increases linearly with x in the direct-gap region, and has a pronounced curvature in the indirect-gap region. These behaviors merge smoothly around x_c . Although a kink at x_c for $L = \infty$ cannot be ruled out, from the present convergence arguments its occurrence seems unlikely.

In conclusion, the composition-driven direct-to-indirect gap crossover in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ alloys presents close analogy with temperature-driven first-order phase transitions. The order parameter probes the relative symmetry of band-edge states in the main energy gap. Monte Carlo statistical mechanics techniques revealed the discontinuous character of the transition and allowed accurate determination of the transition composition and of the order parameter discontinuity at x_c . The value of x_c determined from a finite-size scaling *ansatz* for first-order transitions is in excellent agreement with experimental data recently

reported in the literature [12]. Finite-size scaling laws, developed in the context of considerably simpler statistical mechanics models, were shown to be applicable and valuable in electronic structure calculations. We propose this is a general point to be considered in alloy problems, where analogy to first- or second-order transitions may provide new tools and thus better understanding of different types of crossover in physical behavior.

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