Gap properties of Al$_n$Ga$_{8-n}$As$_8$ ordered compounds

Belita Koiller

Departamento de Física, Pontifícia Universidade Católica do Rio de Janeiro,
Caixa Postale 38071, 22452 Rio de Janeiro RJ, Brazil

Roberto Osório*

Departamento de Física, Universidade de Brasília, 70910 Brasília, Brazil

L. M. Falicov

Department of Physics, University of California, Berkeley, California 94720
and Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

The small-crystal approach with a 16-site basic cluster is used to determine the electronic structure of 16 inequivalent ordered structures of Al$_n$Ga$_{8-n}$As$_8$ compounds. The energy gaps and oscillator strengths for the main gap transitions are calculated, and different results are obtained for different structures of the same composition n, which illustrates the role of compositional ordering in the electronic properties of alloys. Average values of these quantities are used as an attempt to describe Al$_x$Ga$_{1-x}$As alloys. Important features of our results are (a) a positive curvature in the averaged gap versus x dependence for small x and (b) a smooth featureless decrease of the averaged oscillator strength with x. This last feature implies that the direct-indirect gap crossover in the alloy system cannot be genuinely obtained by any sort of averaging among Al$_n$Ga$_{8-n}$As$_8$ ordered compounds.

Among the isovalent ternary semiconductor alloys of type $A_x^{III}B_{1-x}^{III}C^V$, the Al$_xGa_{1-x}$As series[1] has been playing a leading role in technological applications, including high-speed electronic and optoelectronic devices. The interplay between compositional ordering in such alloys and their electronic properties has become an important theme of investigation since the discovery[2] of spontaneous formation of [001]-oriented Al$_x$Ga$_{1-x}$As superlattices.

The dependence of the energy gap E_g of these compounds on the concentration x and the direct-to-indirect gap transition that occurs near $x = 0.4$ have been the object of numerous experimental[3-7] and theoretical[8-11] studies. Most experimental results display a positive curvature (i.e., $d^2 E_g / dx^2 > 0$), especially in the low-x direct-gap range, but these results usually disagree quantitatively from one another. It has been suggested[11] that different degrees of compositional short-range order (SRO) of the samples, caused by different growth processes and temperatures of preparations, are an additional source of the discrepancies among the reported $E_g(x)$ values, beyond the known technical limitations in the precise determination of the alloy composition.

Theoretical studies of the influence of different degrees of SRO on the gap and other electronic properties of alloys are limited by the difficulties found in simulating an infinite crystal with a given degree of SRO. Sophisticated electronic-structure calculations[10] usually rely on the accurate determination of properties of a small number of periodic structures that are suitably averaged to simulate a disordered alloy. Additional insight on the role of compositional ordering can be gained by studying the properties of *all* possible arrangements of a *small crystal*, subject to Born–von Karman periodic boundary conditions, whose Hamiltonian can be solved exactly without recourse to disordered-alloy approximations, such as the virtual-crystal or the coherent-potential approximation.

The small-crystal approach[12] is equivalent, for ordered systems, to a sampling of a small number of points in the Brillouin zone of the infinite, periodic lattice. In the present work, we use a tight-binding scheme for semiconductors, with matrix elements taken from the semiempirical parametrization of Vogl, Hjalmarson, and Dow.[13] The method uses an $sp^3 s^*$ basis, where the excited s^* state gives improved results for the conduction bands, and therefore to the energy gap. In a previous work,[14] this approach was introduced and discussed in detail for a 16-site small crystal of diamond structure, and applied to calculate the total electronic energies of some semiconductor compounds. Related previous work[10,15-17] includes the discussion of the band-gap energies of a number of periodic structures of III-V and II-VI pseudobinary alloys.

The 16-site basic cluster accommodates 16 equivalent ordered structures of Al$_n$Ga$_{8-n}$As$_8$ compounds. The Hamiltonian, written in the tight-binding approximation with five orbitals per site, becomes an 80×80 matrix whose elements are defined in Ref. 14. The spectrum, obtained by direct diagonalization of this matrix, corresponds to the exact energy eigenvalues of the (infinite) crystal at eight special points of the fcc Brillouin zone: the Γ point, the three X points, and the four L points. The on-site and off-site matrix elements are taken from the parametrizations suggested for GaAs and AlAs in

Ref. 13; therefore values of E_g fitted to experiment are readily obtained for the binary compounds ($n = 0$ and 8, respectively). In order to account for the valence band-edge discontinuity,[18] the on-site elements of AlAs are shifted downward with respect to those for GaAs by 0.47 eV.

We have determined the spectrum of all 16 ordered $Al_nGa_{8-n}As_8$ compounds, and the value of the energy gap is associated with the energy difference between the topmost occupied and the lowest empty energy levels. Given that the number of electrons in the 16-site small crystal is 64,

$$E_g(S_\xi) = \mathscr{E}_{33}(S_\xi) - \mathscr{E}_{32}(S_\xi) , \qquad (1)$$

where $\mathscr{E}_i(S_\xi)$ is the ith eigenvalue of the Hamiltonian corresponding to structure S_ξ.

Values of E_g calculated from (1) for the $Al_nGa_{8-n}As_8$ compounds, according to the notation for the structures in Ref. 14, are given in Fig. 1. The horizontal axis gives the composition in terms of $x = n/8$, which is the Al concentration relative to the total of group-III species. We also present an average $E_g(x)$, which is obtained by weighting $E_g(S_\xi)$ by the degeneracy of the S_ξ structure, given in Ref. 14, multiplied by the concentration probability $(x)^n(1-x)^{8-n}$. Note that $E_g(x)$ increases monotonically with x: The low-x region is characterized by a small positive curvature, whereas above $x = 0.5$ the curvature becomes larger and negative.

The direct-to-indirect gap transition is usually attributed in the literature[19] to the concentration at which the conduction-band minimum at Γ becomes higher than the minimum at X. This is a perfectly valid criterion for the ordered, stoichiometric binary compounds, since the top

of the valence band is always at Γ, and optically dipole-allowed transitions must satisfy $\Delta k = 0$. However, this rule is not applicable to disordered alloys, since these systems lack the complete translational symmetry of the constituents, and therefore k ceases to be a good quantum number.

Even for the ternary ordered compounds used in interpolation schemes for the study of alloys, the zinc-blende special k points map (fold) into different symmetry points of the other structures. For example, in the five $A_nB_{4-n}C_4$ ternary compounds, studied in Ref. 10, it has been shown that many of the zinc-blende X, L, and W states fold into Γ states of the Brillouin zone of the lower-symmetry structures.

The above criterion concerning the nature of the gap can only be understood in some sort of virtual-crystal scheme, in which the alloy Hamiltonian is averaged into one with zinc-blende symmetry, and then diagonalized. One could also think of linearly averaging the full spectrum of the binary constituents according to the alloy composition. However, the result in Fig. 1, as well as previous studies[10,11] of the gap versus composition, shows that local ordering, which is expected to occur in alloys, usually produces fluctuations with strong deviations from the average, which means that any sort of crossover behavior in alloys is difficult to define in terms of the crossing of two *sharp* functions of composition.

The relevant parameter to establish whether the gap of a material is direct or not is the dipole selection rule for a transition from the top of the valence band to the bottom of the conduction band of the system. This is conveniently established by the dimensionless oscillator strength[20]

$$f_{v,c} = \frac{2}{m} |\langle v|\mathbf{p}|c \rangle|^2 /(\mathscr{E}_c - \mathscr{E}_v) , \qquad (2)$$

where $|v\rangle$ and $|c\rangle$ are the valence- and conduction-band eigenstates, respectively. This quantity is easily calculated within the small-crystal approach, in which each eigenfunction $|e\rangle$ is specified by its expansion coefficients $a_{i\mu}^e$ in the tight-binding basis set $\{|i\mu\rangle\}$, where i is the site index and μ identifies the orbital. Thus,

$$\langle v|\mathbf{p}|c\rangle = \sum_{\substack{i,\mu \\ j,\nu}} a_{i\mu}^{v*}a_{j\nu}^c \langle i\mu|\mathbf{p}|j\nu\rangle . \qquad (3)$$

The dipole matrix elements may be written in terms of the Hamiltonian H and the position $\mathbf{r}$ operators matrix elements in the tight-binding basis set as[21]

$$\langle i\mu|\mathbf{p}|j\nu\rangle = \frac{im}{\hbar}\langle i\mu|H|j\nu\rangle(\langle j\nu|\mathbf{r}|j\nu\rangle - \langle i\mu|\mathbf{r}|i\mu\rangle) . \qquad (4)$$

The term in parenthesis on the right-hand side of (4) may be approximated by $\mathbf{d}_{ij} = \mathbf{r}_j - \mathbf{r}_i$, the relative position vector of sites i and j.

We have calculated the oscillator strength of the main gap transition for the 16 ordered structures of the 16-site small crystal. Results are presented in Fig. 2, normalized to the value of the oscillator strength obtained for GaAs, $f(S_1)$. As in Fig. 1, the average $f(x)$, obtained by
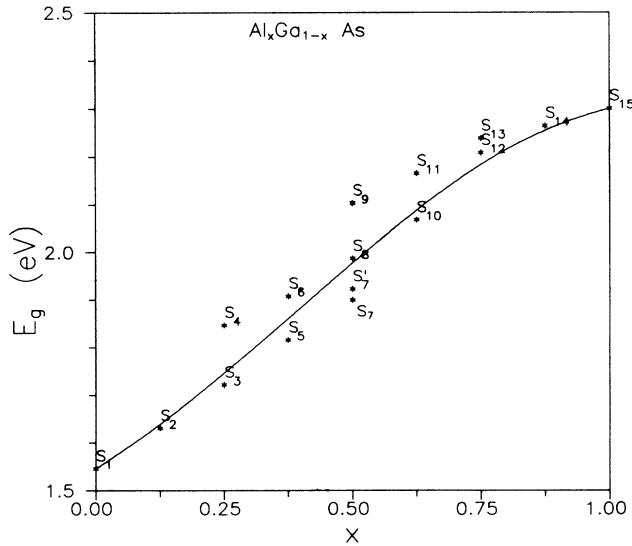

FIG. 1. Asterisks give the calculated values of the main energy gap. $E_g(S_\xi)$, for ordered $Al_xGa_{1-x}As$ compounds. The labels correspond to the structures S_ξ given in Ref. 14. Solid curve gives the average $E_g(x)$ calculated as described in the text.
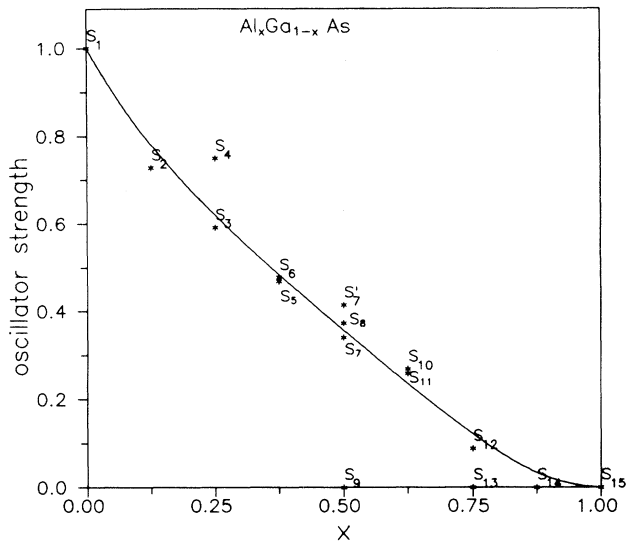
FIG. 2. Asterisks give the calculated oscillator strength of the main gap transition, normalized to the GaAs value, $f(S_\xi)/f(S_1)$, for ordered $Al_xGa_{1-x}As$ compounds. The labels correspond to the structures S_ξ given in Ref. 14. Solid curve gives the average $f(x)/f(S_1)$ calculated as described in the text.

weighting each $f(S_\xi)$ by the degeneracy of the S_ξ structure multiplied the concentration probability, is also given.

From Fig. 2, we notice that the average oscillator strength decreases smoothly from $x=0$ to $x=1$. Except for the appearance of a few indirect-gap compounds above $x=0.5$, no indication of a global transition in the gap nature of alloys within any range is identified from these results.

The increase in energy gap as a function of x, and the small positive curvature in the GaAs-rich region are in agreement with experimental[1,7] data. On the other hand, results concerning the nature of the gap, with their smooth mean change but with large fluctuations in the AlAs-rich region, indicate that values averaged over a relatively small number of ordered structures may produce unsatisfactory results as simulations of random alloys.

It has been found[14] that the fraction of Al-Ga second neighbors (first neighbors in the fcc cation sublattice) is the most relevant parameter for the distinction among formation energies (ΔE) of $Al_nGa_{8-n}As_8$ ordered compounds. Therefore a *cluster expansion* of ΔE in terms of on-site energies and fcc–first-neighbor pairwise interac-

tions may be a good approximation for the alloy.[22] In contrast, a similar cluster expansion is expected to converge much more slowly for gap properties. For example, structures S_7 and S_7' have the same composition and several identical short-range environmental characteristics (in fact, their first distinct correlation function is a four-site term) and are practically degenerate in ΔE,[21,22] but present clearly separated main gaps and oscillator strengths (see Figs. 1 and 2).

Attempts to correlate the gap magnitude with the oscillator strength also lead to inconsistencies. One would think that, for a given concentration, structures with larger gaps approach somehow the AlAs character, and should have a smaller oscillator strength. Although this is usually the case (e.g., structures S_{12} and S_{13}), inversions occur, as for structures S_3 and S_4 which show just the opposite behavior.

Although charge-transfer and lattice-mismatch effects have not been included in our tight-binding calculations, the relative results for the different ordered structures are believed to be reasonably accurate. No mechanism is apparent that would cause the mentioned effects to modify our conclusions concerning the dispersion of the total gap and oscillator strength at a given composition.

In summary, we have calculated the value and optical nature of the main gap of the 16 ordered compounds $Al_nGa_{8-n}As_8$ obtained by periodic repetition of all atomic arrangements of a 16-site crystal. A considerable dispersion, which cannot be explained in terms of short-range pairwise correlations, has been found in both the main gap and the oscillator strengths of different structures at most n values. Gap properties are clearly sensitive not only to composition, but also to the compound's symmetry. The present example illustrates this rule through a combination of effects due to the different periodicities of the ordered compounds and to the dissimilar optical nature of the binary constituents. Disordered $Al_xGa_{1-x}As$ alloys should then be studied with caution, since knowledge of only the composition x is probably too little information to determine its gap properties, and averaging among a few ordered structures may lead to an incomplete or even wrong description.

*Present address: Solar Energy Research Institute, Golden, CO 80401.

[1]S. Adachi, J. Appl. Phys. **58**, R1 (1985).

[2]T. S. Kuan, T. F. Kuech, W. I. Wang, and E. L. Wilkie, Phys. Rev. Lett. **54**, 201 (1985).

[3]B. Monemar, K. K. Shih, and C. D. Petit, J. Appl. Phys. **47**,

2604 (1976).

[4]N. C. Miller, S. Zenon, G. P. Weber, and W. Powazinik, J. Appl. Phys. **57**, 512 (1985).

[5]D. E. Aspnes, S. M. Kelso, R. A. Logan, and R. Bhat, J. Appl. Phys. **60**, 754 (1986).

[6]T. F. Kuech, D. J. Wolford, R. Potenski, J. A. Bradley, K. H.

Kelleher, D. Yan, J. P. Farrell, P. M. S. Lesser, and F. H. Pollak, Appl. Phys. Lett. **51**, 505 (1987).

[7]C. Bosio, J. L. Stachli, M. Guzzi, G. Burri, and R. A. Logan, Phys. Rev. B **38**, 3263 (1988).

[8]A. B. Chen and A. Sher, Phys. Rev. B **23**, 5360 (1981).

[9]J. E. Hasbun, V. A. Singh, and L. M. Roth, Phys. Rev. B **35**, 2988 (1987).

[10]S. -H. Wei and A. Zunger, Phys. Rev. B **39**, 3279 (1989).

[11]Y. Fu, K. A. Chao, and R. Osório, Phys. Rev. B **40**, 6417 (1989).

[12]See, for example, L. M. Falicov, in *Recent Progress in Many-Body Theories,* edited by E. Pajanne and R. F. Bishop (Plenum, New York, 1988), Vol. 1, p. 275.

[13]P. Vogl, H. P. Hjalmarson, and J. D. Dow, J. Phys. Chem. Solids **44**, 365 (1983).

[14]B. Koiller, M. A. Davidovich, and L. M. Falicov, Phys. Rev. B **41**, 3670 (1990); **42**, 3194(E) (1990).

[15]M. F. Ling and D. J. Miller, Phys. Rev. B **34**, 7388 (1986).

[16]P. Boguslawski and A. Baldereschi, Solid State Commun. **70**, 1085 (1989).

[17]J. E. Bernard and A. Zunger, Phys. Rev. B **36**, 3199 (1987).

[18]C. G. Van de Walle and R. M. Martin, J. Vac. Sci. Technol. B **4**, 1055 (1986); S. Massidda, B. I. Min, and A. J. Freeman, Phys. Rev. B **35**, 9871 (1987); A. D. Katnani and R. S. Bauer, *ibid.* **33**, 1106 (1986).

[19]H. C. Casey and M. B. Panish, *Heterostructure Lasers* (Academic, New York, 1989), Part A; J. C. M. Henning and J. P. Ansems, Semicond. Sci. Technol. **2**, 1 (1987).

[20]W. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980).

[21]L. Brey and C. Tejedor, Solid State Commun. **48**, 403 (1983).

[22]R. Magri and A. Zunger, Phys. Rev. **43**, 1584 (1991).