SOLID STATE PHYSICS, VOLUME 46

Band Offsets in Semiconductor Heterojunctions

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ISBN 0-12-607746-0

I. Introduction

Investigations concerning the physics and applications of semiconductor heterojunctions have resulted in tremendous progress since the initial theoretical proposals of Gubanov,[1–3] Shockley,[4] and Kroemer[5] over 30 years ago. The use of heterojunctions in the design and fabrication of semiconductor devices has yielded dramatic improvements in the performance attainable with existing semiconductor device concepts[5–8] and has led to the development of a wealth of new structures that could not have been realized using simple homojunction technology.[9–18]

Among the most important physical parameters for a given heterojunction system are the conduction- and valence-band offsets; indeed, the quality and even the feasibility of heterojunction device concepts often depend crucially on the values of these band offsets. As shown in Fig. 1, the band offset is defined simply as the discontinuity in the band edge at the interface between two semiconductors. Current epitaxial crystal growth techniques such as molecular-beam epitaxy (MBE) are capable of producing abrupt, atomically sharp heterojunction interfaces; in addition, theoretical calculations indicate that the electronic structure in each layer of a heterojunction becomes very nearly bulklike even a single atomic layer away from the interface, lending credence to the idealized notion of an abrupt band-edge discontinuity. Figure 1 also shows the effects of electrostatic band bending that occurs because of charge redistribution near a heterojunction interface. Figure 2 shows the various types of band alignments that can arise in semiconductor interfaces: type I, type II staggered, type II broken-gap (or misaligned), and

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[1] A. I. Gubanov, *Zh. Tekh. Fiz.* **21**, 304 (1951).

[2] A. I. Gubanov, *Zh. Eksp. Teor. Fiz.* **21**, 721 (1951).

[3] A. I. Gubanov, *Zh. Tekh. Fiz.* **22**, 729 (1952).

[4] W. Shockley, U.S. Patent 2,569,347 (1951).

[5] H. Kroemer, *Proc. IRE* **45**, 1535 (1957).

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[13] D. L. Smith, T. C. McGill, and J. N. Schulman, *Appl. Phys. Lett.* **43**, 180 (1983).

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[16] F. Capasso, *Annu. Rev. Mater. Sci.* **16**, 263 (1986).

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[18] D. L. Smith and C. Mailhiot, *J. Appl. Phys.* **62**, 2545 (1987).

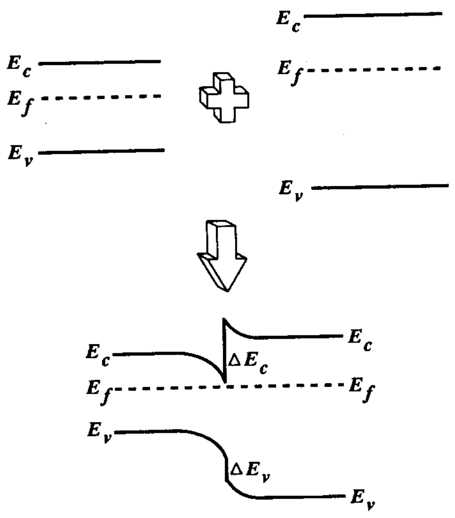

FIG. 1. Conduction- and valence-band offsets in a semiconductor heterojunction. E_c and E_v are the conduction- and valence-band edges, respectively, and E_f is the Fermi level. The band offsets ΔE_c and ΔE_v are abrupt discontinuities in the band edges at the heterojunction interface. Electrostatic band bending also occurs because of charge redistribution near the heterojunction interface.

type III. A type I alignment, in which the band gap of one semiconductor lies completely within the band gap of the other, occurs in a large number of heterojunction systems, e.g., GaAs/$Al_xGa_{1-x}As$ and GaSb/AlSb. A type II staggered alignment occurs when the band gaps of the two materials overlap but one does not completely enclose the other, and it is characteristic of interfaces such as ZnSe/ZnTe and CdSe/ZnTe. A type II broken-gap alignment occurs when the band gaps of the two materials do not overlap at all in energy, as occurs in the InAs/GaSb heterojunction. A type III alignment occurs in heterojunctions containing a semimetallic compound such as HgTe or α-Sn, with HgTe/CdTe being the most extensively studied type III heterojunction system. The device concepts that can be implemented successfully in a given heterojunction system will depend very strongly on the type of band alignment characteristic of that heterojunction, and heterojunction device performance will often depend critically on the exact values of the band offsets.

One would like to have a reliable yet relatively simple way to obtain accurate band offset values for a wide variety of heterojunction systems to help determine their suitability for various device applications. A number of theoretical approaches and empirical rules for calculating band offsets have been developed, beginning with the electron affinity rule proposed by

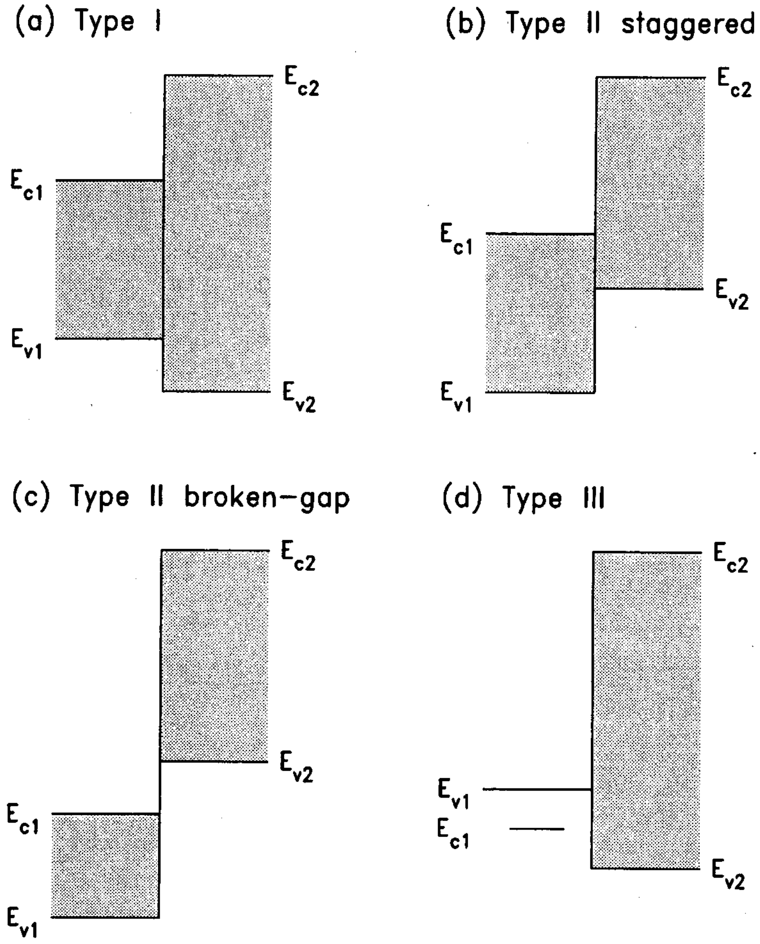

FIG. 2. Possible types of band alignments at a semiconductor interface. Conduction- and valence-band-edge positions for each material have been labeled E_c and E_v, respectively, with the shaded regions indicating the energy band gap in each material.

Anderson[19] in which the conduction-band offset was assumed to be given simply by the difference in the electron affinities of the two heterojunction constituents. The central concept of the Anderson model was that properties of a semiconductor interface could be deduced from the properties of free semiconductor surfaces; other empirical models have been proposed in which

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[19] R. L. Anderson, *Solid-State Electron.* **5**, 341 (1962).

band offset values are related to experimentally measured properties of semiconductor-metal[20] or other semiconductor-semiconductor interfaces.[21] Several purely theoretical methods have also been developed. In these models, band offset values are obtained using approaches such as calculations of bulk band structure on an absolute energy scale,[22–24] calculations of effective "midgap," "pinning," or "charge neutrality" reference energy levels in each semiconductor that align at an interface,[25–32] or actual *ab initio* calculations of electronic structure for each semiconductor interface.[33–43]

Despite this wealth of theoretical work, a thorough and precise understanding of the physics of band offsets has yet to be attained. Tremendous progress has been made beyond the earliest notions, such as the electron affinity rule,[19] but substantial work remains to be done—a testament to the extraordinary difficulty and complexity of the problem of accurately calculating the electronic structure of semiconductor interfaces. Current theories are often able to confirm experimentally determined band offset values to within approximately ±0.05–0.10 eV, and in some cases, such as HgTe/CdTe, qualitatively correct predictions of unexpected experimental results have been made.[28] However, the ability to predict band offset values reliably and consistently for heterojunctions in which the band offset has not already been measured experimentally has yet to be demonstrated. To be of use in the quantitative evaluation and design of a semiconductor heterostructure

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[20] J. O. McCaldin, T. C. McGill, and C. A. Mead, *Phys. Rev. Lett.* **36**, 56 (1976).

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[31] A. Zunger, *Solid State Phys.* **39**, 275 (1986).

[32] J. M. Langer and H. Heinrich, *Phys. Rev. Lett.* **55**, 1414 (1985).

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[40] N. E. Christensen, *Phys. Rev. B* **37**, 4528 (1988).

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[42] W. R. L. Lambrecht and B. Segall, *Phys. Rev. Lett.* **61**, 1764 (1988).

[43] W. R. L. Lambrecht, B. Segall, and O. K. Andersen, *Phys. Rev. B* **41**, 2813 (1990).

device, a band offset must typically be known to an accuracy of approximately ± 0.10 eV or better; however, predicted band offset values for many heterojunctions of current interest extend over a range of 1 eV or more, rendering them of limited use in determining the viability of various device structures in these material systems.

The large discrepancies among theoretically predicted band offset values for many heterojunction systems make apparent the need for reliable experimental determinations of band offsets. Such measurements provide valuable data crucial to the development of a satisfactory theoretical understanding of band offsets and are currently the only way to obtain trustworthy band offset values for novel, previously unstudied heterojunction systems. A large number of experimental techniques have been used to measure band offsets for various heterojunction systems.[44–56] However, the technical difficulty and often indirect nature of these measurements have been at least partially responsible for sizable discrepancies in measured band offset values. Despite several years of research, the value of the valence-band offset even for the extensively studied and supposedly well-understood $GaAs/Al_xGa_{1-x}As$ heterojunction system remained a subject of considerable controversy[44–52,57–64] until the middle 1980s. In addition to the complexity

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[45] R. Dingle, A. C. Gossard, and W. Wiegmann, *Phys. Rev. Lett.* **34**, 1327 (1975).

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inherent in these measurements, evidence exists that the actual value of a heterojunction band offset can depend on the detailed conditions under which the interface was prepared.[65–69] An understanding of these effects could provide insight into the factors that are most relevant in determining band offset values and might also allow band offset values to be adjusted, within limited ranges, to optimize various aspects of heterostructure device performance. However, such dependences can also severely complicate interpretations of band offsets in certain material systems. Despite these difficulties, experimental measurements have yielded fairly reliable band offset values for a large set of semiconductor heterojunction systems.

In this article, we present an overview of the various theoretical approaches and experimental measurement techniques for determining band offset values and then discuss experimental and theoretical data reported for a number of specific heterojunction systems. An attempt is made to evaluate the credibility and accuracy of the experimental measurements and to provide a tabulation of reliable band offset values for as many heterojunctions as possible, as Kroemer[70] had done for a much more restricted set of heterojunctions and before the full complexity of the problem was realized, even for the $GaAs/Al_xGa_{1-x}As$ heterojunction; from these measurements we attempt to extract some general trends that seem to be especially relevant in governing band offset values. We also address some issues that are specific to particular interfaces, such as strain in lattice-mismatched heterojunctions and diffusion and chemical reactivity in heterovalent semiconductor interfaces. Our approach has been to undertake a critical examination of both experimental and theoretical approaches to the subject of band offsets and to attempt to blend these into a balanced perspective one might refer to as "enlightened empiricism." From the work that has been reported to date we draw some general conclusions regarding the observed theoretical and experimental trends, discuss some effects that now seem to be well understood, and present some issues that remain unresolved and provide possibilities for further investigation.

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[70] H. Kroemer, *J. Vac. Sci. Technol. B* **2**, 433 (1984).

II. Theories and Empirical Rules

We have divided the various theoretical treatments of semiconductor heterojunction band offsets into three categories. The first consists of empirical rules based on experimentally determined properties of semiconductor–vacuum, semiconductor–metal, or semiconductor–semiconductor interfaces. In the second category are theoretical calculations of semiconductor band structure that inherently treat the band offset as a bulk parameter independent of the detailed structure of a specific interface, and that therefore effectively assume the electronic states in every semiconductor can be placed on a single common energy scale. The third category comprises theories that include both heterojunction constituents in a single calculation, thereby yielding explicitly the electronic structure of each heterojunction considered and allowing the influence of variables such as strain and crystal orientation to be studied. Our theoretical overview is not intended to be completely exhaustive, but it does include most of the more widely quoted theories that have been proposed.

1. EMPIRICAL RULES

a. *Electron Affinity Rule*

The earliest attempts to describe band offsets theoretically assumed that band offset values were determined by the intrinsic properties of each individual semiconductor, and therefore attempted to place the electronic levels in every material on a single absolute energy scale. Band offsets were then determined by the relative position of each material on this absolute energy scale. The first such model was the so-called electron affinity rule[19,71] postulated by Anderson, which states that the conduction-band offset ΔE_c is given simply by the difference in the electron affinities of the two heterojunction constituents. Experimentally determined electron affinities are used to obtain values for conduction-band offsets.

Because the electron affinity is an experimental measure of the energy of the conduction-band edge in a semiconductor relative to the vacuum level, the essential assumption of the electron affinity rule is that the vacuum level serves as a valid common energy reference level for all materials. A major conceptual weakness of this rule is that electron affinities reflect potential shifts arising from surface electronic structure, rather than shifts that are due to charge redistribution at an actual interface. A more practical consideration

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[71] A. G. Milnes and D. L. Feucht, "Heterojunctions and Metal–Semiconductor Junctions," Academic Press, New York, 1972.

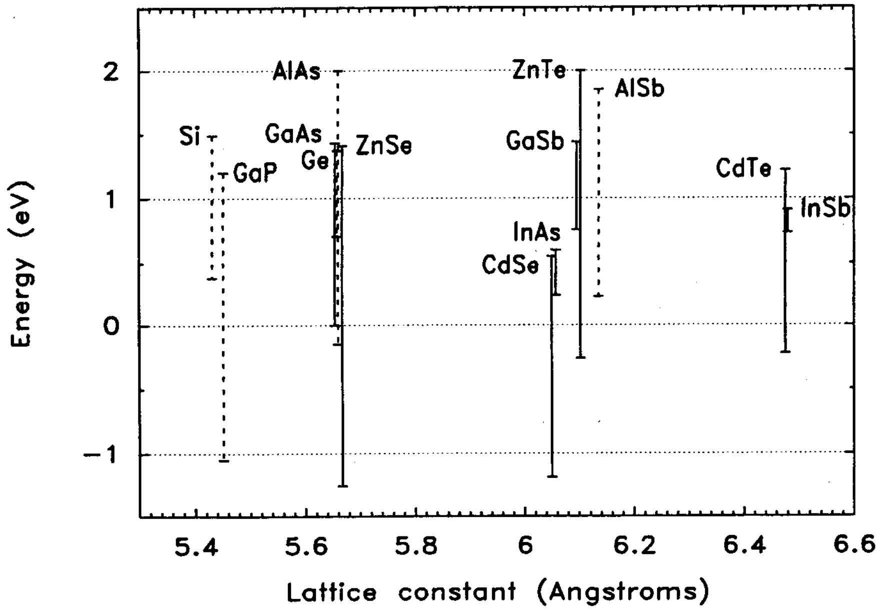

FIG. 3. Energy band gaps of selected semiconductors plotted as a function of lattice constant on an absolute energy scale as determined by the electron affinity rule. Electron affinity data were taken from the compilation of Ref. 71. The origin of the energy scale is taken to be the valence-band edge of GaAs. Direct band gaps are indicated by solid vertical lines, indirect gaps by dashed lines. Conduction- and valence-band offsets can be determined directly from the figure.

is that large uncertainties in experimental electron affinity values for many materials produce correspondingly large ambiguities in predicted band offset values.

Figure 3 shows the energy band gaps of several semiconductors plotted as a function of lattice constant on the absolute energy scale given by the electron affinity rule. Such a diagram ref. 71a allows one to examine heterojunction pairs based on considerations of both lattice match and band alignment simultaneously. Electron affinity data used to produce Fig. 3 were taken from the compilation of Ref. 71. The origin of the energy scale is taken to be the valence-band edge of GaAs. For each material, the position of the energy band gap is indicated by a vertical line, with solid lines representing direct band gaps and dashed lines representing indirect gaps. The conduction- and valence-band edges are indicated by horizontal bars. The conduction- and valence-band offsets given by the electron affinity rule can be determined directly from this figure. We will use diagrams of this type to summarize the predictions of a number of band offset theories. An implicit

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[71a] R. H. Miles, J. O. McCaldin, and T. C. McGill, *J. Cryst. Growth* **85**, 188 (1987).

assumption of these diagrams is that band offsets are transitive; i.e., for three semiconductors labeled A, B, and C, the following rule should be obeyed:

$$\Delta E_v(\mathrm{A/B}) + \Delta E_v(\mathrm{B/C}) + \Delta E_v(\mathrm{C/A}) = 0. \tag{1.1}$$

This rule has been verified experimentally and theoretically for a number of material systems; however, for heterojunction systems in which interfacial reactions occur, and for unusual materials such as CuBr, the transitivity rule may not necessarily be valid.

b. *Common Anion Rules*

In addition to the electron affinity rule, a number of other semiempirical rules have been proposed as at least qualitative guides for predicting band offset values. Among the more widely quoted of these have been the so-called common anion rules, proposed originally by McCaldin, McGill, and Mead[20] with a modified form later postulated by Menéndez *et al.*[72] The physical motivation for the original common anion rule arises from theoretical evidence that, in compound semiconductors, the valence-band states are derived predominantly from *p*-like atomic orbitals of the anion.[70] One might then expect that the position of the semiconductor valence-band edge on an absolute energy scale would be determined principally by the energies of the outermost (valence) electrons of the anion. In their original paper, McCaldin *et al.* pointed out that the Schottky barrier height for a large number of III–V and II–VI semiconductors depended primarily on the electronegativity of the anion. It was later proposed[22] that this correlation might extend to valence-band offset values as well, leading to the postulate that, for a large number of compound semiconductors (materials containing Al being a notable exception), the valence-band offset in a heterojunction should depend only on the difference in anion electronegativity for the two constituent materials. Early theories of band offsets, such as those of Harrison[24] and of Frensley and Kroemer,[22,23] were in general agreement with the common anion rule, even for compounds such as AlAs for which the common anion rule was not claimed to be valid. Wei and Zunger[73] have performed calculations suggesting that deviations from the common anion rule arise largely from cation *d*-orbital contributions to the valence-band structure, which were generally omitted in early theoretical studies of band offsets. Figure 4 shows the energy band gaps of several semiconductors plotted as a function of lattice constant using valence-band-edge positions determined by the common anion rule.

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[72] J. Menéndez, A. Pinczuk, D. J. Werder, J. P. Valladares, T. H. Chiu, and W. T. Tsang, *Solid State Commun.* **61**, 703 (1987).

[73] S.-H. Wei and A. Zunger, *Phys. Rev. Lett.* **59**, 144 (1987).

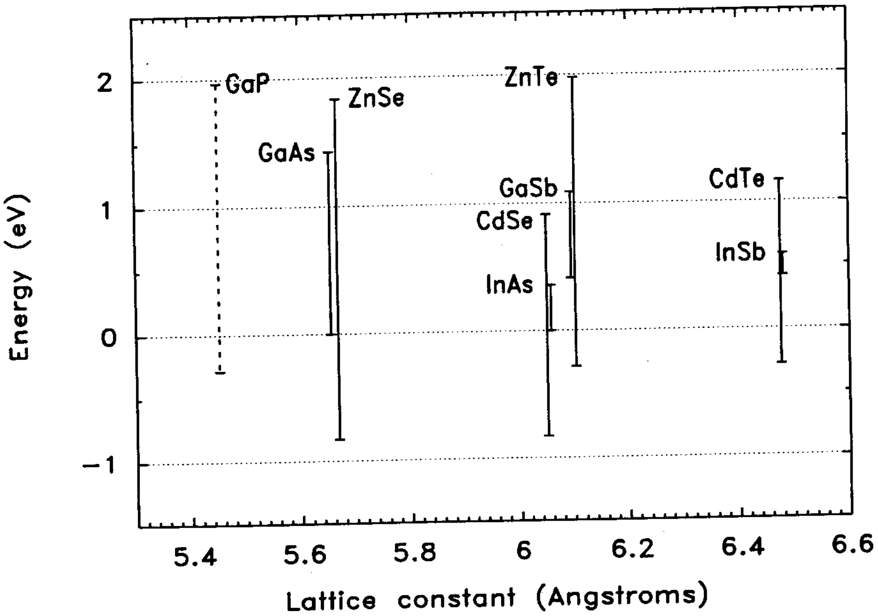

FIG. 4. Energy band gaps of selected semiconductors plotted as a function of lattice constant on an absolute energy scale determined by anion electronegativity, as postulated by the common-anion rule of McCaldin *et al.*[20] Compounds containing Al have been omitted from the plot. The origin of the energy scale is taken to be the valence-band edge of GaAs. Direct band gaps are indicated by solid vertical lines, indirect gaps by dashed lines. Conduction- and valence-band offsets can be determined directly from the figure.

The modified version of the common anion rule proposed by Menéndez *et al.*[72] states that the valence-band offset in a heterojunction system in which the constituents share a common anion is determined primarily by the two cations. This rule was proposed on the basis of experimental evidence for the GaAs/$Al_xGa_{1-x}As$ and GaSb/$Al_xGa_{1-x}Sb$ heterojunctions and the theoretical predictions of Tersoff[27,28] for these heterojunctions and for the GaP/InP, GaAs/InAs, and GaSb/InSb material systems. Unfortunately, considerations of lattice match severely limit the number of heterojunction systems for which this rule can be tested: substitutions of Al for Ga in III–V compounds or Hg for Cd in II–VI semiconductors are the only cation changes that preserve the lattice constant. In lattice-mismatched heterojunctions, strain effects will most likely overwhelm any potential intrinsic deviation from the modified common anion rule of Menéndez. However, the approximate validity of this rule for the GaAs/$Al_xGa_{1-x}As$ and GaSb/$Al_xGa_{1-x}Sb$ heterojunctions might provide some useful insight into the basic physics of band offsets.

c. *Empirical Compilation of Katnani and Margaritondo*

A more recent attempt to relate band offset values to empirical data was made by Katnani and Margaritondo,[21,74] who measured band offsets for a large number of heterojunctions formed by depositing Si or Ge on various semiconductor substrates. It was hoped that these measurements would yield reliable valence-band-edge energies, relative to the Si and Ge valence-band edges, for a large number of semiconductors. The results of these measurements were combined with other experimental band offset values to produce a set of valence-band-edge energies optimized to give the best agreement with the available experimental data. This scheme is somewhat analogous to the earlier semiempirical electron affinity and common anion rules, except that experimental data for semiconductor–semiconductor interfaces, rather than metal–semiconductor or vacuum–semiconductor interfaces, were used to provide a common energy reference for all materials. As acknowledged by the authors, however, this compilation was obtained simply by optimizing agreement with the experimental data available at the time and therefore provides limited insight in the physical basis responsible for determining band offset values. Figure 5 shows the energy gaps of several selected semiconductors plotted as a function of lattice constant using valence-band-edge energies proposed by Katnani and Margaritondo on the basis of the experimental data available to them.

2. BAND OFFSETS CALCULATED AS BULK PARAMETERS

It has long been recognized[75] that, at least from a purely theoretical perspective, one would like to be able to calculate band offset values directly from the properties of each heterojunction constituent, rather than rely upon quantities determined experimentally for semiconductor–vacuum, semiconductor–metal, or semiconductor–semiconductor interfaces. A number of theories relating band offset values to the calculated electronic properties of bulk semiconductors have been proposed. In theories that extract band offset values simply from electronic properties of bulk semiconductors, the bulk band structure of each material is typically obtained relative to a reference level, determined in various theories by factors such as atomic potentials or cancellation of interfacial dipoles. A suitable alignment of the reference levels in each semiconductor then yields values for the band offsets.

[74] A. D. Katnani and G. Margaritondo, *J. Appl. Phys.* **54**, 2522 (1983).

[75] H. Kroemer, *Crit. Rev. Solid State Sci.* **5**, 555 (1975).

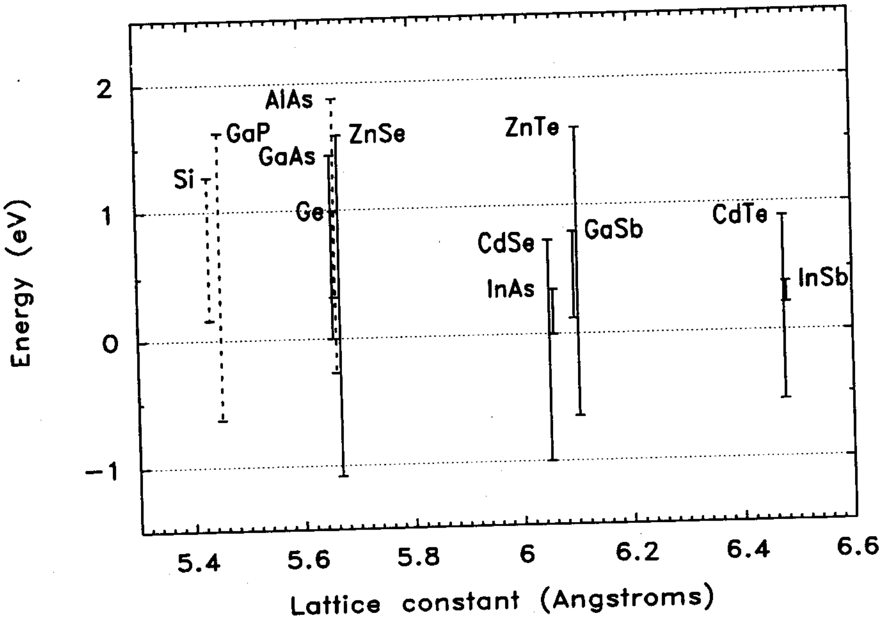

FIG. 5. Energy band gaps of selected semiconductors plotted as a function of lattice constant using valence-band-edge energies proposed by Katnani and Margaritondo.[21] The origin of the energy scale is taken to be the valence-band edge of GaAs. Direct band gaps are indicated by solid vertical lines, indirect gaps by dashed lines. Conduction- and valence-band offsets can be determined directly from the figure.

a. *Pseudopotential Theory of Frensley and Kroemer*

The first attempt to calculate band offset values without the use of experimental data for vacuum–semiconductor or metal–semiconductor interfaces was the pseudopotential theory of Frensley and Kroemer.[22,23] In this theory, a pseudopotential calculation was used to obtain the bulk band structure of each semiconductor, with a self-consistency condition enforced for the electrostatic potential and the charge density calculated from valence-band wave functions. Once the bulk band structure was obtained for each individual semiconductor, the band offsets in a heterojunction could be obtained by matching the energies of the interstitial potentials for the two heterojunction constituents.

This theory was subsequently refined to include an approximate correction to account for heterojunction dipoles induced by charge redistribution near the interface.[23] An approximate calculation of heterojunction dipole effects was made by estimating the effective charge on atoms near the interface using the electronegativities of each atom and its nearest neighbors. This scheme leads to an effective "electronegativity potential" for each semiconductor. The correction to the band offsets for heterojunction dipole effects was then taken to be simply the difference in the electronegativity potential for the two heterojunction constituents.

A consequence of this result is that, even when corrections for heterojunction dipole effects are included, band offset values are still predicted to obey the transitivity rule, Eq. (1.1). Although the validity of this rule is obvious for treatments such as the common anion and electron affinity rules, which do not include any effects specific to a particular interface, it is not as obvious that band offsets should be transitive when the detailed properties of each heterojunction interface are taken into account. The theory of Frensley and Kroemer, and in particular the ability to define an effective electronegativity potential for each material that accounts for interfacial dipole effects, suggested that the concept of band offsets as quantities determined primarily by properties of bulk semiconductors may be physically sound.

Figure 6a and b show the band gaps of several semiconductors plotted using valence-band-edge energies determined by the Frensley-Kroemer pseudopotential theory. Corrections arising from heterojunction dipole effects have been neglected in Fig. 6a, and included in Fig. 6b. As discussed by Frensley and Kroemer,[23] the dipole correction for most lattice-matched heterojunction pairs is typically a few tenths of an electron volt or less. For lattice-mismatched heterojunctions, the apparent dipole corrections can be much larger; however, the dipole corrections were not claimed to be valid for lattice-mismatched heterojunctions, and the applicability of Frensley and Kroemer's electronegativity potential in lattice-mismatched heterojunctions is probably questionable.

b. *LCAO Theory of Harrison*

Another early theory of heterojunction band offsets was the linear combination of atomic orbitals (LCAO) theory of Harrison.[24] In Harrison's approach, the electronic states in a semiconductor are constructed as a superposition of individual atomic orbitals. It is claimed that an adequate description of the relevant electronic structure in each material can be obtained using four orbitals—a single atomic *s* state and three atomic *p* states—for each of the two atoms in the zincblende primitive cell. The position of the valence-band edge is then given by[24,76]

$$E_{\mathrm{v}} = \frac{\varepsilon_p^{\mathrm{c}} + \varepsilon_p^{\mathrm{a}}}{2} - \left[\left(\frac{\varepsilon_p^{\mathrm{c}} - \varepsilon_p^{\mathrm{a}}}{2}\right)^2 + V_{xx}^2\right]^{1/2}, \qquad (2.1)$$

[76] D. J. Chadi and M. L. Cohen, *Phys. Status Solidi (B)* **68**, 405 (1975).

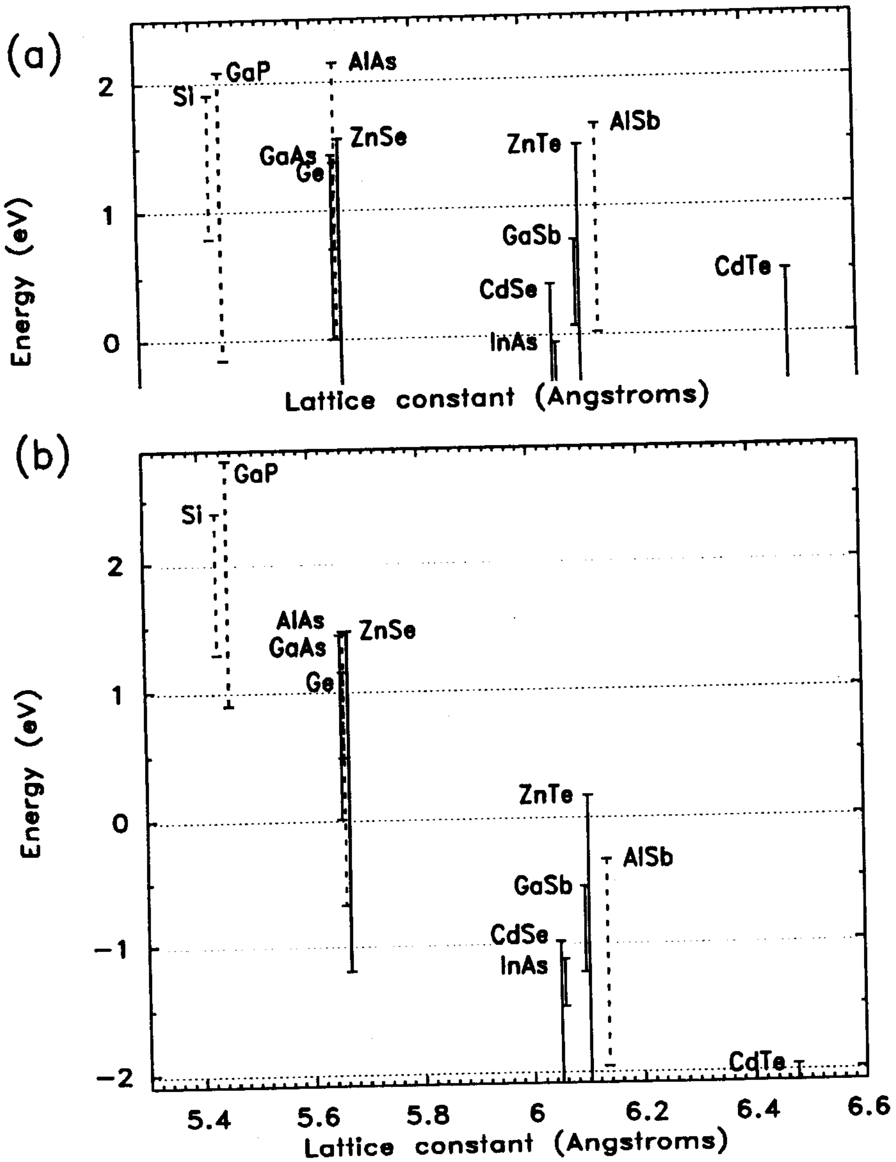

FIG. 6. Energy band gaps of several selected semiconductors plotted as a function of lattice constant using valence-band-edge energies determined by the Frensley-Kroemer pseudopotential theory.[22,23] The two plots have been constructed (a) neglecting and (b) including the electronegativity potential, which provides an approximate correction for effects arising from the formation of heterojunction dipoles.

where ε_p^c is the on-site energy of the cation p state and ε_p^a is the on-site energy of the anion p state, both taken from calculated atomic values. V_{xx} is a matrix element between atomic p states for adjacent atoms and is given approximately by[24]

$$V_{xx} = 2.16\hbar^2/md^2, \tag{2.2}$$

where m is the free electron mass and d the bond length; the numerical coefficient was chosen to agree with values obtained by Chadi and Cohen[76] to fit the true bands of Si and Ge. The valence-band-edge energies obtained using the LCAO approach are therefore automatically given on the common energy scale determined by the individual atomic state energies, and valence-band offsets are computed simply by taking the difference between the valence-band-edge energies on this common energy scale for the two heterojunction materials. Conduction-band offsets can be determined from the valence-band offset and experimental band gaps for each material. As was the case for the early semiempirical rules and the original theory of Frensley and Kroemer, Harrison's LCAO theory does not include any correction for heterojunction dipole effects.

Figure 7 shows the energy band gaps of several semiconductors plotted as a function of lattice constant on the common energy scale determined by Harrison's LCAO theory. The values shown in the figure were calculated by Harrison using atomic p state energies taken from the calculations of Herman and Skillman.[77] Harrison later modified his theory by adding excited s states to his basis set and adjusting the interatomic matrix elements.[78] These modifications and the use of Hartree–Fock atomic energies yielded a better description of the conduction-band structure and allowed both dielectric and elastic properties to be described using a single set of parameters, which had not been possible in the earlier version of his theory. Kraut[79] recalculated the valence-band-edge energies using Harrison's LCAO theory of band offsets in conjunction with Hartree–Fock neutral atom ionization energies computed by Mann.[80] However, valence-band offsets obtained in this way were found by Kraut to be in poorer agreement with available experimental results than

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[76] D. J. Chadi and M. L. Cohen, *Phys. Status Solidi (B)* **68**, 405 (1975).

[77] F. Herman and S. Skillman, "Atomic Structure Calculations," Prentice Hall, Englewood Cliffs, NJ, 1963.

[78] W. A. Harrison, *Phys. Rev. B* **24**, 5835 (1981).

[79] E. A. Kraut, *J. Vac. Sci. Technol. B* **2**, 486 (1984).

[80] J. B. Mann, "Atomic Structure Calculations, I: Hartree–Fock Energy Results for Elements Hydrogen to Lawrencium," Clearing House for Technical Information, Springfield, VA, 1967.

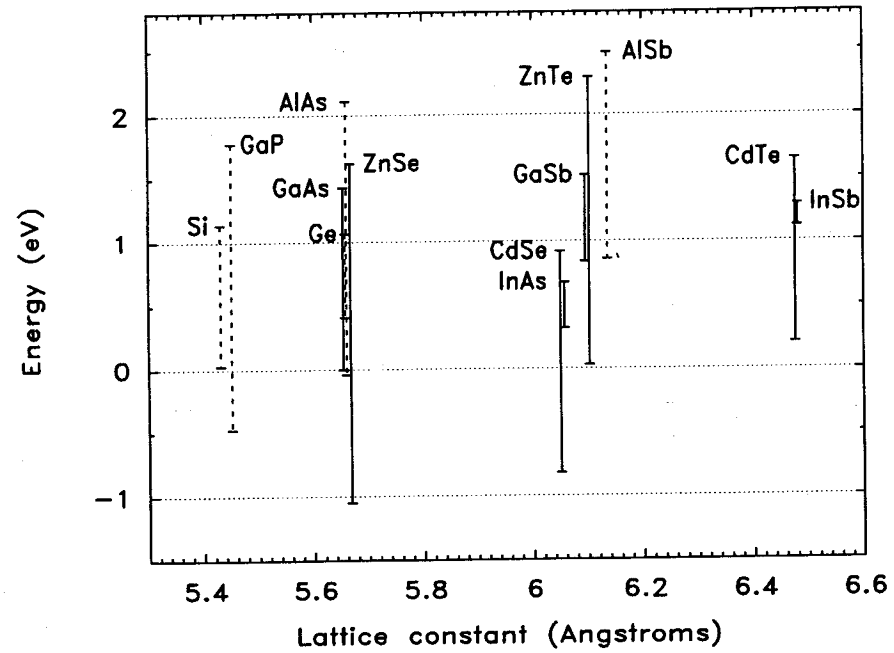

FIG. 7. Energy band gaps of selected semiconductors plotted as a function of lattice constant on the energy scale calculated using the LCAO theory of Harrison.[24] The origin of the energy scale is taken to be the valence-band edge of GaAs. Direct band gaps are indicated by solid vertical lines, indirect gaps by dashed lines. Conduction- and valence-band offsets can be determined directly from the figure.

the original calculations of Harrison using the Herman–Skillman atomic energies.

c. *Interface Dipole Theories*

A number of more recent theories, such as those of Tersoff[27,28] and of Harrison and Tersoff,[29] have argued that interfacial dipoles, rather than bulk semiconductor energy levels, are the dominant factor in determining band offset values. The physical principle underlying these theories is that the alignment of the energy gaps at a semiconductor heterojunction will be such that the interface dipole is minimized. It is argued that by analyzing the band structure of each individual semiconductor, a midgap, pinning, or charge neutrality reference energy level at which evanescent states in the band gap are composed equally of conduction-band-like and valence-band-like states can be determined for each material. Band offsets are then determined by an appropriate alignment of the midgap energies of each material at a heterojunction interface, a procedure that effectively minimizes the electrostatic dipole formed at the interface.

The basic concept of a charge neutrality energy level was proposed by Tejedor *et al.*[81] for calculating Schottky barrier heights in metal-semiconductor interfaces. This idea was later extended[25,26] to the calculation of band offsets in semiconductor heterojunctions. The influence of interfacial dipoles, and the relevance of the charge neutrality level, is perhaps most easily understood by first considering the case of a metal-metal junction.[28] At a metal-metal interface, a misalignment of the work functions, or equivalently of the electronegativities, of the two metals will induce a charge transfer, resulting in the formation of a dipole. However, the essentially infinite dielectric constant of metal will screen any discontinuity in the electronegativity and yield a simple alignment of the Fermi level across the interface.

For semiconductors, Tersoff[27,28,82] argued for the existence of an effective midgap energy level corresponding to the energy in the band gap at which a surface, interface, or defect state induced in the band gap would contain equal conduction- and valence-band character; despite its name, this effective midgap energy very rarely coincides with the actual midpoint of the energy band gap. A discontinuity in the effective midgap energy would induce charge transfer and the formation of a dipole at the interface; discontinuities in the effective midgap energy would therefore be screened by the dielectric constant of the semiconductors. As a result, the band offsets at a semiconductor heterojunction should be within an energy V/ε of the offsets determined by a rigorous alignment of the effective midgap energies, where V is the discontinuity in the midgap energy corresponding to theories in which interfacial dipoles are neglected. Because typical values of V were on the order of 0.5 eV or less, it was argued that with dipole effects included the effective midgap energies should be aligned to within $\sim$0.05 eV for typical values of semiconductor dielectric constants.

The ability to determine an effective midgap energy for each individual semiconductor, independent of the material with which it is to form an interface, is again equivalent to placing the energy gaps of each material on a single common energy scale, although the common energy scale in this case is not determined by any external reference energy as was the case in, for example, Harrison's LCAO theory. The theories of Tersoff[27,28] and of Harrison and Tersoff,[29] which differ principally in the method used to calculate the effective midgap energy, therefore provide theoretical evidence

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[81] C. Tejedor, F. Flores, and E. Louis, *J. Phys. C* **10**, 2163 (1977).

[82] J. Tersoff, *Phys. Rev. Lett.* **52**, 465 (1984)

that even when heterojunction dipole effects are taken into account, and in fact are assumed to be the dominant factor in determining band offset values, the transitivity condition given by Eq. (1.1) should remain valid. Figure 8a and b show the energy gaps of several selected semiconductors plotted using the valence-band-edge alignments determined by the theories of Tersoff[28] and Harrison and Tersoff,[29] respectively.

Cardona and Christensen[39] have proposed a model in which band offset values are determined by an approximate alignment of the dielectric midgap energy (DME)—the midpoint between the conduction and valence energies at the Penn gap—calculated for each material; the deviation from an exact alignment of the dielectric midgap energies is due to finite screening with an effective dielectric constant, obtained by averaging the long-wavelength dielectric constants for each material:

$$\Delta E_v(\mathrm{A/B}) = E_v^{\mathrm{B}} - E_v^{\mathrm{A}} - (E_{\mathrm{D}}^{\mathrm{B}} - E_{\mathrm{D}}^{\mathrm{A}})\left(\frac{\bar{\varepsilon} - 1}{\bar{\varepsilon}}\right), \tag{2.3}$$

where E_v^{A} and E_v^{B} are the valence-band-edge energies in materials A and B, respectively, $E_{\mathrm{D}}^{\mathrm{A}}$ and $E_{\mathrm{D}}^{\mathrm{B}}$ are the dielectric midgap energies, and $\bar{\varepsilon}$ is the effective dielectric constant. A reasonable approximation to the band offset values predicted by this model can be obtained by assuming $\bar{\varepsilon} = 3.5$ for all materials;[26,39] this approximation then allows a common energy scale to be defined for all materials. Figure 9 shows the energy gaps of several selected semiconductors plotted using valence-band offsets predicted by the model of Christensen and Cardona.

An empirical correlation noted by Langer and Heinrich[32] and by Zunger[30,31] has been shown[83] to be related to the concept of the effective midgap energy alignment. It was pointed out by Langer and Heinrich and by Zunger that alignment of transition-metal impurity levels in compound semiconductors appeared to yield fairly accurate values for valence-band offsets in isovalent (i.e., III–V on III–V or II–VI on II–VI) heterojunctions. Model calculations of Tersoff and Harrison[83] indicate that, for cation-substitutional impurities, requiring charge neutrality in the impurity *d* shell yields a correlation, for a given transition-metal impurity, of the impurity level with a characteristic energy level in the semiconductor very close to the effective midgap energy as defined by Harrison and Tersoff.[29] Alignment of the effective midgap energy at a heterojunction should therefore also produce an approximate alignment of the transition-metal impurity levels across the interface.

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[83] J. Tersoff and W. A. Harrison, *Phys. Rev. Lett.* **58**, 2367 (1987).

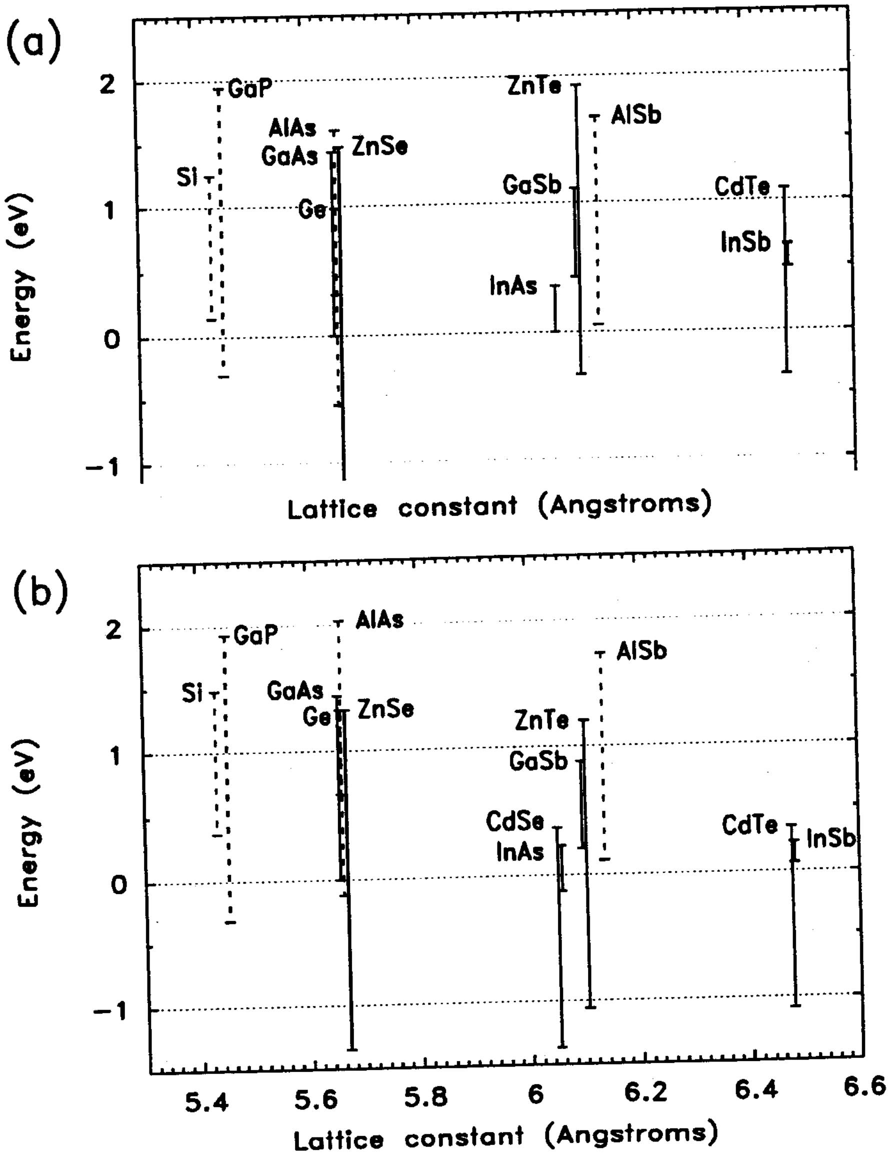

FIG. 8. Energy band gaps of several selected semiconductors plotted as a function of lattice constant using the valence-band-edge alignments determined by the interface dipole theories of (a) Tersoff[28] and (b) Harrison and Tersoff.[29] The origin of the energy scale is taken to be the valence-band edge of GaAs. Direct band gaps are indicated by solid vertical lines, indirect gaps by dashed lines. Conduction- and valence-band offsets can be determined directly from the figure.

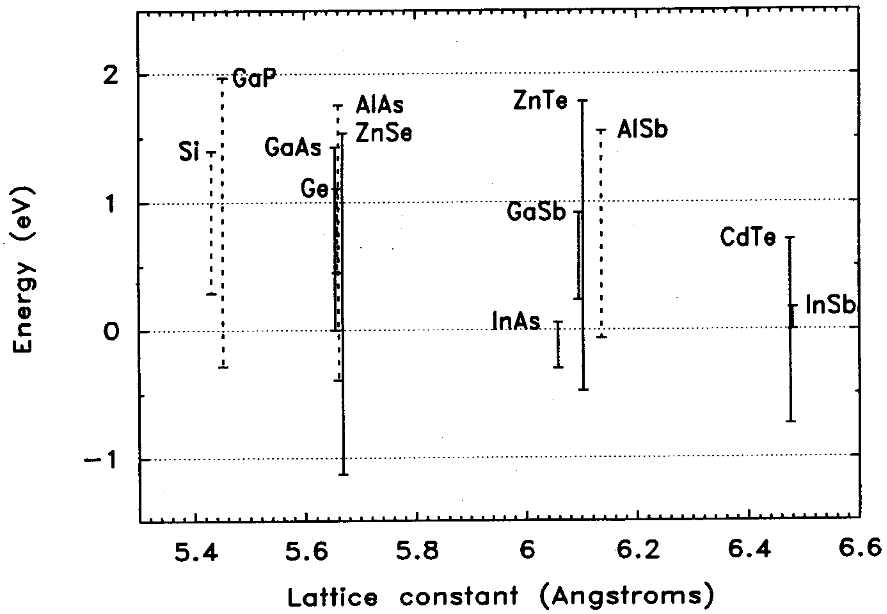

FIG. 9. Energy band gaps of selected semiconductors plotted as a function of lattice constant using band offsets corresponding to the screened dielectric midgap energy alignment proposed by Cardona and Christensen.[39] The origin of the energy scale is taken to be the valence-band edge of GaAs. Direct band gaps are indicated by solid vertical lines, indirect gaps by dashed lines. Conduction- and valence-band offsets can be determined directly from the figure.

3. SELF-CONSISTENT CALCULATIONS FOR SPECIFIC INTERFACES

A number of theories have also been developed that include effects arising from the detailed electronic structure of the specific semiconductor interface under consideration. The typical approach is to calculate the electronic band structure for a so-called supercell geometry, essentially a superlattice with a unit cell consisting of n monolayers of one semiconductor followed by n monolayers of the other. Because the electronic structure in each layer becomes bulklike very rapidly as one moves away from the interface,[33,34,37,38] it is possible to determine the position of the valence-band edge in each layer, and therefore the value of the band offset, in structures with only 5–10 monolayers of each material in the supercell.

The first approaches of this type were reported by Baraff, Appelbaum, and Hamann[33,34] and by Pickett, Louie, and Cohen.[35,36] Baraff *et al.* and Pickett *et al.* calculated the electronic structure of the GaAs/Ge interface and obtained valence-band offsets of ~0.9 eV and 0.35 eV, respectively. Presumably at least in part because of the prohibitive amount of computation that would have been required, neither group applied its methods to a large number of other heterojunctions.

A number of investigators subsequently developed more comprehensive band offset theories based on supercell calculations for specific semiconductor interfaces. The information obtained from full calculations for a large number of specific heterojunction systems is often used to develop or justify simpler, more intuitive model theories for band offset values, often based primarily on bulk semiconductor properties. Van de Walle and Martin[37,38,84,85] have calculated band offset values by using a self-consistent local density functional theory and *ab initio* pseudopotentials to compute the electronic structure in each layer of a superlattice. The calculations of Van de Walle and Martin were also the first to incorporate the effects of strain in lattice-mismatched heterojunctions, with the Si/Ge heterojunction being considered as a prototypical lattice-mismatched material system. On the basis of their self-consistent local density functional calculations for Si/Ge and other heterojunction systems, Van de Walle and Martin proposed a model solid theory of band offsets.[84–86]

In their model solid theory, an absolute electrostatic potential is computed for each material by constructing the solid as a superposition of neutral atoms. The atomic potentials can be placed on an absolute energy scale common to all materials, and an average electrostatic potential relative to the atomic potentials can be defined in the solid. This procedure was found[84–86] to yield good agreement with the results of the full self-consistent interface calculations. The bulk band structure relative to the average electrostatic potential within the solid is calculated using *ab initio* pseudopotentials. It is then possible to define the position of the valence-band edge in each material on the common energy scale given by the atomic potentials and consequently to derive band offset values for various heterojunctions. The relatively good agreement between the results of the model solid theory and the fully self-consistent calculations suggests that band offsets can be considered, at least approximately, to be determined primarily by characteristics of the bulk constituent materials. Van de Walle[86] has also calculated absolute deformation potentials using the model solid approach, allowing band offsets in

[84] C. G. Van de Walle and R. M. Martin, *Phys. Rev. B* **35**, 8154 (1987).

[85] C. G. Van de Walle and R. M. Martin, *J. Vac. Sci. Technol. B* **4**, 1055 (1986).

[86] C. G. Van de Walle, *Phys. Rev. B* **39**, 1871 (1989).

strained heterojunctions to be predicted. Figure 10 shows the energy gaps of several selected semiconductors plotted using valence-band offsets given by the model solid theory of Van de Walle and Martin.[86]

Christensen[40,41] and Lambrecht *et al.*[42,43] have also performed self-consistent calculations of band offsets for superlattice geometries, using linear muffin-tin orbital (LMTO) methods rather than *ab initio* pseudopotentials. Christensen used the results of his calculations to argue in favor of the dielectric midgap energy model proposed by Cardona and Christensen.[39] For a large number of heterojunctions, Christensen found that interfacial dipoles did indeed tend to drive band offsets toward the values predicted by alignment of dielectric midgap energies, although the presence of interface states for certain heterojunctions tended to produce band offsets in disagreement with the dielectric midgap energy model.

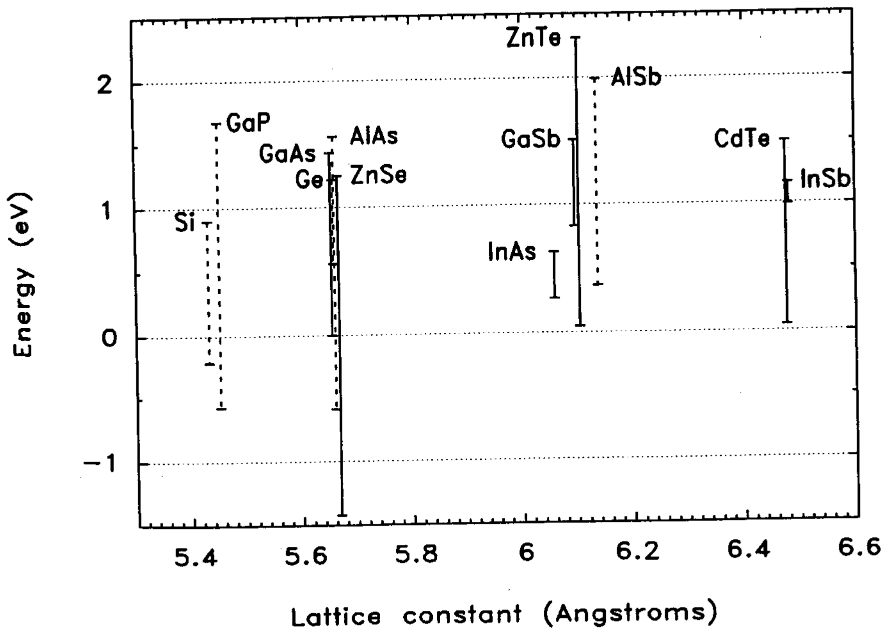

FIG. 10. Energy band gaps of selected semiconductors plotted as a function of lattice constant using valence-band-edge energies corresponding to the model solid theory of Van de Walle and Martin.[86] The origin of the energy scale is taken to be the valence-band edge of GaAs. Direct band gaps are indicated by solid vertical lines, indirect gaps by dashed lines. Conduction- and valence-band offsets can be determined directly from the figure.

Lambrecht and Segall used the results of their self-consistent dipole calculations to develop their interface bond polarity model.[42,87] In this model, the bulk electronic structure in each material is first calculated with respect to an average reference potential using LMTO methods. Band offsets are obtained by calculating the difference between the average reference potentials for each material and applying a screened dipole correction to account for bond polarity and charge transfer at the heterojunction interface. An analysis of their self-consistent dipole calculations indicated that a relatively simple and accurate approximation for the screened dipole correction could be obtained by estimating the charge transfer in bonds formed between the two materials from bond polarities and calculating the resulting dipole potential with screening given by the long-wavelength dielectric constant. The resulting band offset values do not rigorously obey the transitivity relation, Eq. (1.1), and this model therefore does not allow all materials to be placed on a single energy scale. For most heterojunctions, the interface bond polarity model was found to agree reasonably well with the fully self-consistent LMTO calculations of Christensen[40,41] and the self-consistent dipole calculations of Lambrecht *et al.*[42,43]

4. COMPARISONS AMONG THEORIES

Despite the extensive theoretical efforts discussed in the previous sections, band offsets in novel heterojunction systems cannot yet be reliably predicted to a high degree of accuracy by any existing theory. Figure 11 shows valence-band offsets calculated using several different theories for the AlAs/GaAs, GaP/Si, and ZnSe/Ge heterojunctions. The shaded regions indicate the approximate range of experimental values thought to have been valid at the time each theory was developed. Until the middle 1980s, band offsets were thought to be fairly well understood, both theoretically and experimentally.[70] Reliable band offset measurements were apparently available for several material systems, including GaAs/$Al_xGa_{1-x}As$, InAs/GaSb, and Ge/GaAs/ZnSe, and these experimental values were in good agreement with the predictions of Harrison's LCAO theory.[24]

Renewed interest in band offsets in the middle 1980s was inspired largely by the unexpected discovery that the AlAs/GaAs valence-band offset was much larger than had previously been thought. The correct value of the AlAs/GaAs valence-band offset was in disagreement with the prediction of

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[87] W. R. L. Lambrecht and B. Segall, *Phys. Rev. B* **41**, 2832 (1990).

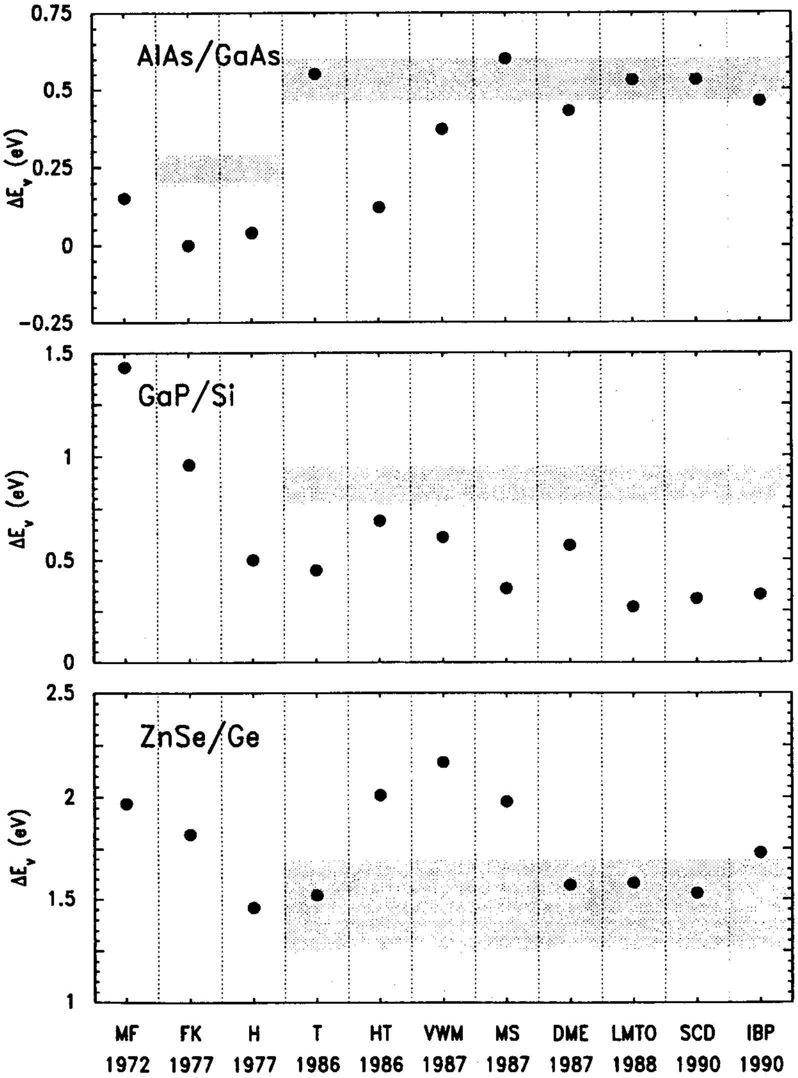

FIG. 11. A comparison of theoretical and experimental band offset values for the AlAs/GaAs, GaP/Si, and ZnSe/Ge heterojunctions. Different theories are plotted in approximately chronological order, and the range of experimental values thought to have been valid at the time each theory was developed has been shaded. For extensively studied systems such as AlAs/GaAs, recent theories agree well with experiment. Agreement between theory and experiment, and even among theoretical values, is poorer for less studied systems such as GaP/Si and ZnSe/Ge. Theoretical predictions are from the following sources; MF 1972, Ref. 71; FK 1977, Ref. 23; H 1977, Ref. 24; T 1986, Ref. 28; HT 1986, Ref. 29; VWM 1987, Ref. 84; MS 1987, Ref. 84; DME 1987, Ref. 39; LMTO 1988, Ref. 40; SCD 1990, Ref. 43; IBP 1990, Ref. 87.

Harrison,[24] as shown in Fig. 11. Several new theories have since appeared, most of which, as shown in the figure, are in close agreement with the experimental AlAs/GaAs valence-band offset. For less extensively studied heterojunctions, however, the agreement between experiment and theory, and even among different theoretical treatments, is considerably worse. For GaP/Si, the values predicted by the more recent theories (starting with Tersoff[28] in 1986) differ by as much as 0.38 eV. These theories predict values much smaller than the few experimentally measured values that have been reported. For the ZnSe/Ge heterojunction, the recent theoretical values encompass a range of approximately 0.64 eV, and agreement with even the very wide range of reported experimental values, indicated by the shaded region in the bottom graph of Fig. 11, is tenuous.

Figure 11 illustrates a general observation that for heterojunctions that are well understood experimentally, theories can reproduce experimental band offset values quite accurately. For more complicated or less extensively studied material systems, however, theoretical band offset values are probably best used as qualitative guides rather than accurate quantitative predictions. The widely disparate physical principles underlying current band offset theories, which nevertheless often yield rather similar band offset values, are probably also an indication that much remains to be understood about the electronic structure of semiconductor interfaces.

III. Experimental Techniques

The capabilities of current theoretical treatments of band offsets are such that consistently reliable theoretical predictions of band offset values in novel semiconductor heterojunctions cannot yet be obtained; band offsets must therefore be determined experimentally for each new material system of interest. Various methods have been devised to measure band offsets in semiconductor heterojunctions. These techniques can be divided into three categories: optical spectroscopy, in which optical absorption, photoluminescence, or photoluminescence excitation spectra from quantum-well or superlattice structures are analyzed with the band offsets as fitted parameters; various types of electron spectroscopy, such as x-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), or synchrotron photoemission spectroscopy, that provide a direct measure of the valence-band offset; and electrical (device-like) techniques, in which either the conduction - or the valence-band offset is extracted from measurements, such as C-V or I-V characteristics, on electrical device structures. An overview of several common band offset measurement techniques is presented in this section.

5. OPTICAL SPECTROSCOPY

One of the earliest methods used to measure band offsets to a high degree of precision was optical spectroscopy performed on quantum wells and superlattices. These measurements have remained in widespread use despite the considerable care required to avoid well-known pitfalls of the technique. The extraction of band offsets from optical spectra was first performed for the GaAs/$Al_xGa_{1-x}As$ heterojunction, and the pioneering efforts of Dingle *et al.*[44–46] in this area, while providing the basis for much subsequent work, also illustrate the weaknesses and potential dangers of the technique.

Analysis of optical absorption spectra from $Al_xGa_{1-x}As$/GaAs/$Al_xGa_{1-x}As$ quantum-well heterostructures by Dingle *et al.*[44–46] yielded what was for several years the most widely accepted value for the GaAs/$Al_xGa_{1-x}As$ band offsets: $\Delta E_c \approx 0.85\ \Delta E_g$ and $\Delta E_v \approx 0.15\ \Delta E_g$, where ΔE_g is the difference between the GaAs and $Al_xGa_{1-x}As$ energy band gaps. In this technique, calculated quantum-well bound-state energies are fitted to the observed structure in the quantum-well absorption spectrum, with the band offset as an adjustable parameter. Unfortunately, the calculated bound-state energies for these structures depend quite strongly on parameters such as the well width and carrier effective mass, as well as on the band offset. Subsequent photoluminescence experiments on parabolic quantum wells,[47,58] in which the bound-state energies are more sensitive to the band offset values, demonstrated the importance of using accurate material parameters, such as effective masses, and yielded a conduction-band offset $\Delta E_c \approx 0.57\ \Delta E_g$, in closer agreement with the currently accepted values. However, considerable care was required in the growth of the parabolic quantum-well samples. Because control of the Al flux during growth was not sufficient to yield truly parabolic compositional profiles,[63] an effective parabolic potential was synthesized by deposition of alternating layers of GaAs and $Al_xGa_{1-x}As$; the widths of the $Al_xGa_{1-x}As$ layers were increased quadratically with distance from the center of the quantum well, and the GaAs layer widths were correspondingly reduced. Optical techniques have also been applied, with somewhat mixed results, to other material systems, including InP/$In_{0.53}Ga_{0.47}As$[88,89] and $Ga_{0.47}In_{0.53}As/Al_{0.48}In_{0.52}As$.[90]

A related technique, in which a light-scattering method is used to determine conduction-band offsets, has been developed by Menéndez and coworkers and applied to a number of heterojunctions, including

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[88] B. I. Miller, E. F. Schubert, U. Koren, A. Ourmazd, A. H. Dayem, and R. J. Capik, *Appl. Phys. Lett.* **49**, 1384 (1986).

[89] R. Sauer, T. D. Harris, and W. T. Tsang, *Phys. Rev. B* **34**, 9023 (1986).

[90] D. F. Welch, G. W. Wicks, and L. F. Eastman, *J. Appl. Phys.* **55**, 3176 (1984).

GaAs/$Al_xGa_{1-x}As$[56] and GaSb/$Al_xGa_{1-x}Sb$.[72] Backscattering spectra obtained from photoexcited carriers in multiple-quantum-well structures were found to contain peaks arising from inelastic light scattering, with energy shifts corresponding to transition energies between bound states in the quantum wells.[91] Values for the conduction-band offset in these multiple quantum wells were obtained by fitting the observed transition energies to a theoretical model for quantum-well bound-state energies, with the conduction-band offset as an adjustable parameter. Band offsets obtained using this technique for the GaAs/$Al_xGa_{1-x}As$ and GaSb/$Al_xGa_{1-x}Sb$ heterojunctions were found to be in fairly good agreement with other reported results.

The GaAs/$Al_xGa_{1-x}As$ valence-band offset has also been measured by studying the pressure dependence of photoluminescence from GaAs/$Al_xGa_{1-x}As$ quantum wells and superlattices.[51] This technique exploited the proximity in energy of the Γ-point and X-point conduction-band minima in $Al_xGa_{1-x}As$; by applying hydrostatic pressure to GaAs/$Al_xGa_{1-x}As$ heterostructure samples, the GaAs quantum-well confined states were shifted above the X-point conduction-band minimum in the $Al_xGa_{1-x}As$ barriers, resulting in a sharp reduction in photoluminescence intensity from the Γ-confined quantum-well states. By analyzing the pressure dependence of the $Al_xGa_{1-x}As$ energy band gap and of the photoluminescence energies for pressures $\lesssim 60$ kbar, a GaAs/$Al_xGa_{1-x}As$ valence-band offset $\Delta E_v = (0.32 \pm 0.02)\,\Delta E_g^\Gamma$ was deduced, in reasonable agreement with currently accepted values. As stated by the authors in the original study,[51] an assumption made in this experiment was that the valence-band edges of GaAs and $Al_xGa_{1-x}As$ move together with pressure, i.e., that the valence-band offset is approximately independent of pressure. Later measurements by Lambkin *et al.*[92] indicated that the GaAs/AlAs valence-band offset increased slightly with pressure, $d(\Delta E_v)/dP \approx 1$ meV/kbar. This dependence would yield only a relatively small shift of the GaAs/AlAs valence-band offset of approximately 0.06 eV over the range of pressures studied by Wolford *et al.* For other material systems, however, the valence-band offset has been found to depend more strongly on pressure. Magneto-optical studies of InAs/GaSb superlattices[93] indicated that the InAs/GaSb valence-band offset varies considerably with pressure; the separation between the InAs conduction-band edge and the GaSb valence-band edge was found to decrease at a rate of 5.8 meV/kbar. Given an increase in the InAs energy band gap of 10 meV/kbar,[93] this yields a valence-band offset that increases with pressure at a rate of 4.2 meV/kbar.

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[91] A. Pinczuk, J. Shah, A. C. Gossard, and W. Wiegmann, *Phys. Rev. Lett.* **46**, 1341 (1981).

[92] J. D. Lambkin, A. R. Adams, D. J. Dunstan, P. Dawson, and C. T. Foxon, *Phys. Rev. B* **39**, 5546 (1989).

[93] L. M. Claessen, J. C. Maan, M. Altarelli, P. Wyder, L. L. Chang, and L. Esaki, *Phys. Rev. Lett.* **57**, 2556 (1986).

6. XPS AND RELATED TECHNIQUES

Various types of electron spectroscopies have been used to measure band offsets in a large number of material systems. In particular, x-ray photoelectron spectroscopy has been used to measure band offsets in several heterojunction systems. The basic XPS method, illustrated in Fig. 12, requires first

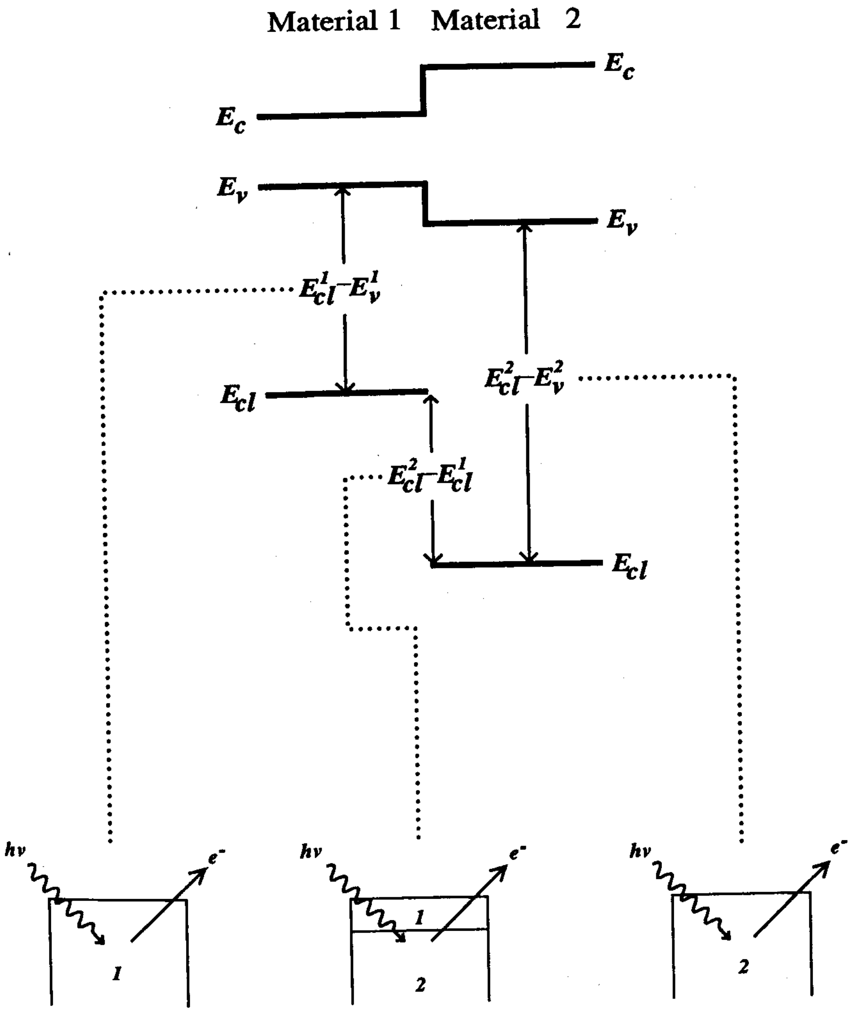

FIG. 12. A schematic energy band diagram illustrating the basic principle of the XPS band offset measurement. Reference core-level binding energies are measured in thick films of each material, and the separation between the two reference core levels is measured in heterojunction samples. These three quantities can then be combined to yield a value for the valence-band offset.

the measurement of reference core-level binding energies, e.g., the Ga $3d$ core level in GaAs or the Al $2p$ level in AlAs, relative to the valence-band edge in two semiconductors. Heterojunctions consisting of a thin (~ 25 Å) layer of one material deposited on the other are then grown in which the separation between the reference core levels in each material is measured; the separation between the reference core levels can be translated directly into a value for the valence-band offset using the previously measured core-level to valence-band-edge binding energies:

$$\Delta E_v(1/2) = (E^1_{\mathrm{cl}} - E^1_v) + (E^2_{\mathrm{cl}} - E^1_{\mathrm{cl}}) - (E^2_{\mathrm{cl}} - E^2_v). \tag{6.1}$$

Related techniques, such as the direct measurement of valence-band separations using ultraviolet photoelectron spectroscopy (UPS) or synchrotron photoemission, which are characterized by higher energy resolution but greater surface sensitivity, have also been reported. Unlike many optical and electrical methods for determining band offsets, photoemission techniques provides a direct measurement of the band offset value, so interpretation of the experimental results is fairly straightforward. In addition, the XPS method is well suited to the study of novel material systems because the structures required are quite simple. XPS measurements can also provide valuable information regarding issues such as interface reactions and commutativity (independence of growth sequence).

The primary source of uncertainty in XPS measurements of band offsets arises from the need to determine accurately (to within approximately ± 0.05 eV) the position of the valence-band edge in the XPS spectrum. Kraut, Grant, Waldrop, and Kowalczyk[53,54] developed the high-precision analysis techniques that allow band offsets to be measured by XPS to a high degree of accuracy and pioneered the use of these techniques to study band offsets in heterojunctions such as Ge/GaAs,[69,94] GaAs/AlAs,[57,95] and InAs/GaAs.[96] In addition, XPS has been used to measure valence-band offsets for the nearly lattice-matched ZnSe/GaAs/Ge material system,[65,97] the InAs/GaSb heterojunction,[98] and the GaSb/AlSb heterojunction.[99] Band offset measure-

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[94] R. W. Grant, J. R. Waldrop, and E. A. Kraut, *J. Vac. Sci. Technol.* **15**, 1451 (1978).

[95] J. R. Waldrop, S. P. Kowalczyk, R. W. Grant, E. A. Kraut, and D. L. Miller, *J. Vac. Sci. Technol.* **19**, 573 (1981).

[96] S. P. Kowalczyk, W. J. Schaffer, E. A. Kraut, and R. W. Grant, *J. Vac. Sci. Technol.* **20**, 705 (1982).

[97] F. Xu, M. Vos, J. P. Sullivan, Lj. Atanasoska, S. G. Anderson, J. H. Weaver, and H. Cheng, *Phys. Rev. B* **38**, 7832 (1988).

[98] G. J. Gualtieri, G. P. Schwartz, R. G. Nuzzo, R. J. Malik, and J. F. Walker, *J. Appl. Phys.* **61**, 5337 (1987).

[99] G. J. Gualtieri, G. P. Schwartz, R. G. Nuzzo, and W. A. Sunder, *Appl. Phys. Lett.* **49**, 1037 (1986).

ments for the HgTe/CdTe heterojunction[100] and the CdTe/HgTe/ZnTe material system[101] have also been reported, although in the latter work strain effects were neglected despite the large lattice mismatch (~6.5%) of CdTe and HgTe with ZnTe.

The XPS technique has also been extended to the study of strain-dependent band offsets in the Si/Ge (001) material system.[102–105] To measure strain-dependent band offset values, effective deformation potentials must be determined either theoretically[103] or experimentally[104,105] for the strain-induced shifts between atomic core levels and the valence-band edge in bulk material and between core levels in different materials in strained heterojunctions. Alternatively, the positions of the conduction- and valence-band edges relative to the Fermi level in undoped Si and $Si_{1-x}Ge_x$ can be monitored in strained, heavily doped samples and core-level energies subsequently measured in undoped heterostructures.[102]

Interface reactions in certain heterojunction systems can also be studied by XPS. The sensitivity of XPS core-level binding energies to different chemical bonding states can produce shifted peak components in core-level XPS or synchotron photoemission spectra obtained from heterojunctions in which an intermediate, chemically reacted layer is present at the interface.[105–107] Studies of core-level peak intensity as a function of overlayer coverage can also yield information regarding the abruptness of heterojunction interfaces.[108] Additional studies of band offsets in a variety of heterojunctions using XPS will be discussed in relation to specific material systems in Sections IV through VII.

7. Electrical Measurements

Various electrical measurement techniques have been used to determine band offset values. Thermionic emission across a single barrier has been used

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[100] S. P. Kowalczyk, J. T. Cheung, E. A. Kraut, and R. W. Grant, *Phys. Rev. Lett.* **56**, 1605 (1986).

[101] T. M. Duc, C. Hsu, and J. P. Faurie, *Phys. Rev. Lett.* **58**, 1127 (1987).

[102] W.-X. Ni, J. Knall, and G. V. Hansson, *Phys. Rev. B* **36**, 7744 (1987).

[103] G. P. Schwartz, M. S. Hybertsen, J. Bevk, R. G. Nuzzo, J. P. Mannaerts, and G. J. Gualtieri, *Phys. Rev. B* **39**, 1235 (1989).

[104] E. T. Yu, E. T. Croke, T. C. McGill, and R. H. Miles, *Appl. Phys. Lett.* **56**, 569 (1990).

[105] E. T. Yu, E. T. Croke, D. H. Chow, D. A. Collins, M. C. Phillips, T. C. McGill, J. O. McCaldin, and R. H. Miles, *J. Vac. Sci. Technol. B* **8**, 908 (1990).

[106] W. G. Wilke and K. Horn, *J. Vac. Sci. Technol. B* **6**, 1211 (1988).

[107] W. G. Wilke, R. Seedorf, and K. Horn, *J. Vac. Sci. Technol. B* **7**, 807 (1989).

[108] K. J. Mackey, P. M. G. Allen, W. G. Herrenden-Harker, R. H. Williams, C. R. Whitehouse, and G. M. Williams, *Appl. Phys. Lett.* **49**, 354 (1986).

to measure band offsets in a number of heterojunctions.[48,49,59,60,109,110] The thermionic current density J at temperature T over a single barrier is given approximately by

$$J \approx A^*T^2 \exp(-\phi/k_B T), \tag{7.1}$$

where A^* is the effective Richardson constant, k_B is the Boltzmann constant, and ϕ is the barrier height, given by $[\Delta E_v + (E_f - E_v)]$ for holes and $[\Delta E_c + (E_c - E_f)]$ for electrons. By analyzing the temperature dependence of current–voltage characteristics in single-barrier heterostructures, it is possible to determine the barrier height and therefore the band offset values. This technique has been applied with considerable success to, among others, the $GaAs/Al_xGa_{1-x}As$[48,49,59,60] and HgTe/CdTe[110] material systems.

Capacitance–voltage measurements have also been applied to the determination of band offset values. Kroemer *et al.*[55] showed that it is possible, by performing C–V profiling through a heterojunction, to extract a value for the band offset in that heterojunction. This technique has been used to determine band offsets in a number of heterojunction systems, including $GaAs/Al_xGa_{1-x}As$,[55,61,62] lattice-matched InGaAsP/InP,[111,112] and $In_xAl_{1-x}As/In_{0.53}Ga_{0.47}As$.[113,114] A number of investigators have also applied a somewhat simplified version of the C–V profiling technique to the measurement of band offsets. For structures in which the doping level is constant in each heterojunction layer, a plot of $(1/C^2)$ as a function of V should yield a straight line. The intercept voltage V_{int} should then yield the total built-in voltage of the heterojunction and consequently the band offset value, assuming that the doping level in each layer is known. This technique has been used to determine band offsets in several heterojunction systems, including InAs/AlSb,[115] $InAs_{0.95}Sb_{0.05}/GaSb$,[116] and CdS/InP.[117,118]

A charge transfer method has also been used to determine band offset values. In this technique, the sheet density is measured in the two-dimensional carrier gas formed at a heterojunction interface; a method has been

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[109] A. C. Gossard, W. Brown, C. L. Allyn, and W. Wiegmann, *J. Vac. Sci. Technol.* **20**, 694 (1982).

[110] D. H. Chow, J. O. McCaldin, A. R. Bonnefoi, T. C. McGill, I. K. Sou, and J. P. Faurie, *Appl. Phys. Lett.* **51**, 2230 (1987).

[111] S. R. Forrest and O. K. Kim, *J. Appl. Phys.* **52**, 5838 (1981).

[112] S. R. Forrest, P. H. Schmidt, R. B. Wilson, and M. L. Kaplan, *Appl. Phys. Lett.* **45**, 1199 (1984).

[113] R. People, K. W. Wecht, K. Alavi, and A. Y. Cho, *Appl. Phys. Lett.* **43**, 118 (1983).

[114] P. Z. Lee, C. L. Lin, J. C. Ho, L. G. Meiners, and H. H. Wieder, *J. Appl. Phys.* **67**, 4377 (1990).

[115] A. Nakagawa, H. Kroemer, and J. H. English, *Appl. Phys. Lett.* **54**, 1893 (1989).

[116] A. K. Srivastava, J. L. Zyskind, R. M. Lum, B. V. Dutt, and J. K. Klingert, *Appl. Phys. Lett.* **49**, 41 (1986).

[117] J. L. Shay, S. Wagner, K. J. Bachmann, and E. Buehler, *J. Appl. Phys.* **47**, 614 (1976).

[118] J. L. Shay, S. Wagner, and J. C. Phillips, *Appl. Phys. Lett.* **28**, 31 (1976).

developed[50,119] to estimate the band offset value from the measured sheet carrier density. This method has been used to measure the valence-band offset in GaAs/AlAs (100)[50] and GaAs/$Al_xGa_{1-x}As$ (100)[119] heterojunctions; the orientation dependence of the GaAs/Al_xGa_{1-x} valence-band offset has also been studied[120] by this technique, with no measurable difference found between the valence-band offsets in the (100) and (311) orientations.

Finally, internal photoemission measurements have been used to determine band offsets for the GaAs/$Al_xGa_{1-x}As$ material system. In these experiments, threshold photon energies determined from photocurrent measurements in p^+-GaAs/n^--$Al_xGa_{1-x}As$ heterojunctions[52,121] or in a GaAs/$Al_xGa_{1-x}As$ heterojunction combined with a Mo-GaAs Schottky barrier[122] were used to obtain values for the conduction-band offset. GaAs/$Al_xGa_{1-x}As$ conduction-band offset values have also been derived from measurements of photocurrents[52] and photovoltages[123] arising from internal photoemission from the two-dimensional electron gas in GaAs/$Al_xGa_{1-x}As$ heterostructures.

IV. III–V Material Systems

In reviewing the available experimental data on band offsets, we have divided the various heterojunction systems for which data are available into a number of categories: lattice-matched III–V heterojunctions, lattice-matched II–VI heterojunctions, lattice-mismatched heterojunctions, and heterovalent material systems. By doing so we hoped to isolate to some degree chemical trends within each group of isovalent heterojunctions, effects arising from strain, and effects that are due to chemical reactivity at heterovalent interfaces. We begin with a review in this section of the available experimental band offset data for lattice-matched III–V heterojunctions.

8. GAAS/ALAS

a. *Experimental Data*

Any discussion of heterojunction band offset measurements begins most naturally with the GaAs/AlAs interface. The GaAs/$Al_xGa_{1-x}As$ heterojunction system is currently the most important technologically, and has therefore

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[119] W. I. Wang, E. E. Mendez, and F. Stern, *Appl. Phys. Lett.* **45**, 639 (1984).

[120] W. I. Wang, T. S. Kuan, E. E. Mendez, and L. Esaki, *Phys. Rev. B* **31**, 6890 (1985).

[121] M. A. Haase, M. A. Emanuel, S. C. Smith, J. J. Coleman, and G. E. Stillman, *Appl. Phys. Lett.* **50**, 404 (1987).

[122] M. Heiblum, M. I. Nathan, and M. Eizenberg, *Appl. Phys. Lett.* **47**, 503 (1985).

[123] K. W. Goossen, S. A. Lyon, and K. Alavi, *Phys. Rev. B* **36**, 9370 (1987).

been the subject of by far the most extensive experimental investigation. Despite these efforts, there existed for some time considerable controversy regarding the actual value of the GaAs/$Al_xGa_{1-x}As$ valence-band offset and its possible dependence on substrate orientation and growth sequence.

For several years the value of the GaAs/$Al_xGa_{1-x}As$ valence-band offset was thought to have been well established. A 1974 experiment in which Dingle *et al.*[44–46] measured optical absorption spectra from $Al_xGa_{1-x}As$/GaAs/$Al_xGa_{1-x}As$ quantum-well heterostructures with $x = 0.2 \pm 0.01$ yielded a conduction-band offset $\Delta E_c = 0.85\ \Delta E_g$, corresponding to a valence-band offset $\Delta E_v = 0.15\ \Delta E_g$, where ΔE_g is the difference in band gap between GaAs and $Al_xGa_{1-x}As$. Several other experiments seemed to confirm this measurement. Gossard *et al.*[109] obtained a conduction-band offset $\Delta E_c \approx 0.85\ \Delta E_g$ from current-voltage (J–V) measurements performed on GaAs/$Al_xGa_{1-x}As$ single barrier heterostructures with square, triangular, and sawtooth-shaped barriers. People *et al.*[113] measured a conduction-band offset $\Delta E_c = (0.88 \pm 0.04)\ \Delta E_g$ by capacitance-voltage (C–V) profiling, and Welch *et al.*[90] obtained GaAs/$Al_xGa_{1-x}As$ quantum-well photoluminescence spectra consistent with $\Delta E_c = 0.85\ \Delta E_g$. Confidence in the so-called 85 : 15 rule was such that in experiments in which substantially smaller conduction-band offsets were observed,[55,125] the authors attributed the discrepancy to compositional grading at the GaAs/$Al_xGa_{1-x}As$ heterojunction during crystal growth, rather than considering the possibility that their band offset value might be more correct than that given by the 85 : 15 rule.

Subsequent experiments, however, provided strong evidence that the 85 : 15 rule is indeed incorrect and that the GaAs/$Al_xGa_{1-x}As$ valence-band offset is substantially larger than had been thought at first. A number of these experiments also provided detailed data relating the GaAs/$Al_xGa_{1-x}As$ band offset to alloy composition x and energy gap difference ΔE_g over the entire range of alloy compositions $x \in [0, 1]$. The early experiments supporting the 85 : 15 rule were conducted for only a limited range of alloy compositions, typically $x \lesssim 0.45$. Several of the more recent band offset measurements reported for the GaAs/$Al_xGa_{1-x}As$ heterojunction are shown in Fig. 13, and experimental measurements for the GaAs/$Al_xGa_{1-x}As$ valence-band offset are summarized in Table I.

The first indication that the 85 : 15 rule might be incorrect was provided by photoluminescence measurements on parabolic quantum wells reported by Miller, Gossard, Kleinman, and Munteanu.[47] Earlier measurements of band offsets using quantum-well photoluminescence or optical absorption techniques utilized data obtained from square quantum wells; in square quantum-well structures, the energies of the bound states depend quite

[125] C. M. Wu and E. S. Yang, *J. Appl. Phys.* **51**, 2261 (1980).

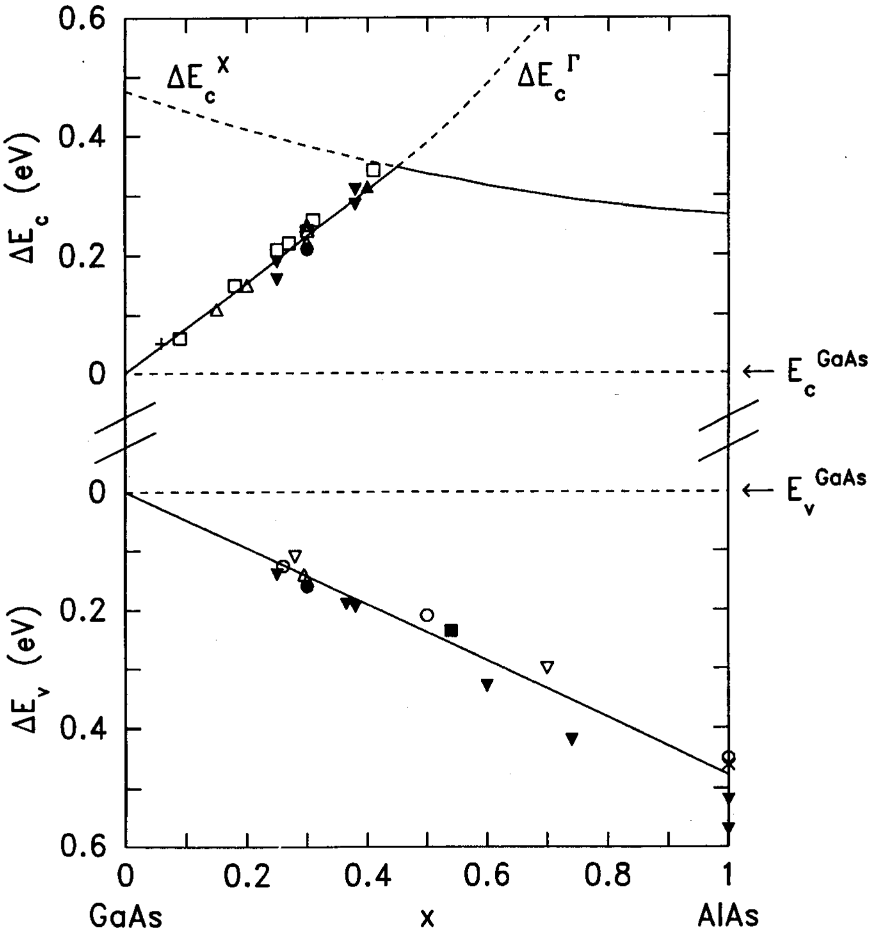

FIG. 13. Summary of experimental band offset data for the GaAs/Al$_x$Ga$_{1-x}$As heterojunction. Data are from Miller *et al.*[58] (●); Wang *et al.*[50,119,120] (○); Arnold *et al.*[60] (■); Okumura *et al.*[61] (□); Hickmott *et al.*[59] (▲); Watanabe *et al.*[62] (△); Batey and Wright[48,49] (▼); Wolford *et al.*[51] (▽); Menéndez *et al.*[56] (+); and Yu *et al.*[64] (×).

sensitively on parameters such as the quantum-well width and carrier effective mass as well as on the band offset. For parabolic wells, the bound-state energies depend more strongly on the band offset values than for square wells; however, controlling the sample growth to ensure that the wells are indeed parabolic is quite difficult. The data obtained by Miller *et al.* indicated that the conduction-band offset was smaller than had previously been thought, $\Delta E_c \approx 0.50\,\Delta E_g$. A subsequent analysis of exciton transitions in

TABLE I. EXPERIMENTAL VALENCE-BAND OFFSET VALUES FOR GaAs/$Al_xGa_{1-x}As$

SOURCE	HETEROJUNCTION	ΔE_v^a (expt.)	ΔE_c^a (expt.)
Dingle *et al.* (1974)[44–46]	GaAs/$Al_{0.20}Ga_{0.80}As$	$[(0.15 \pm 0.03)\Delta E_g]$	$[(0.85 \pm 0.03)\Delta E_g]$
Kroemer *et al.* (1980)[55]	GaAs/$Al_{0.3}Ga_{0.7}As$	—	$0.66\Delta E_g$
Wu and Yang (1980)[125]	GaAs/$Al_{0.35}Ga_{0.65}As$	—	$0.64\Delta E_g$
Gossard *et al.* (1982)[109]	GaAs/$Al_xGa_{1-x}As$	—	$[0.85\Delta E_g]$
People *et al.* (1983)[113]	GaAs/$Al_{0.3}Ga_{0.7}As$	$[(0.12 \pm 0.04)\Delta E_g]$	$[(0.88 \pm 0.04)\Delta E_g]$
Welch *et al.* (1984)[90]	GaAs/$Al_{0.33}Ga_{0.67}As$	$[0.15\Delta E_g]$	$[0.85\Delta E_g]$
Miller *et al.* (1984)[58]	GaAs/$Al_xGa_{1-x}As$	$0.43\ \Delta E_g$	$0.57\Delta E_g$
Arnold *et al.* (1984)[60]	GaAs/$Al_xGa_{1-x}As$	$0.35\ \Delta E_g$	—
Wang *et al.* (1985)[50,119,120]	GaAs/$Al_{0.26}Ga_{0.74}As$	0.126 ± 0.04 eV	—
	GaAs/$Al_{0.5}Ga_{0.5}As$	0.21 ± 0.03 eV	—
	GaAs/AlAs	0.45 ± 0.05 eV	—
Okumura *et al.* (1985)[61]	GaAs/$Al_xGa_{1-x}As$	—	$0.67\Delta E_g$
Hickmott *et al.* (1985)[59]	GaAs/$Al_{0.6}Ga_{0.6}As$	—	$0.63\Delta E_g$
Watanabe *et al.* (1985)[62]	GaAs/$Al_xGa_{1-x}As$	—	$0.62\Delta E_g$
Batey and Wright (1985)[48,49]	GaAs/$Al_{0.30}Ga_{0.70}As$	$0.38\ \Delta E_g$	—
Wolford *et al.* (1986)[51]	GaAs/$Al_xGa_{1-x}As$	$0.55x$ eV	—
Menéndez *et al.* (1986)[56]	GaAs/$Al_xGa_{1-x}As$	$(0.32 \pm 0.02)\Delta E_g^\Gamma$	—
Dawson *et al.* (1986)[126]	GaAs/$Al_{0.06}Ga_{0.94}As$	—	$0.69\Delta E_g$
Katnani and Bauer (1986)[128]	$Al_{0.37}Ga_{0.63}As$/AlAs	0.342 ± 0.004 eV	—
Waldrop *et al.* (1987)[57]	GaAs/AlAs	0.38 eV	—
Yu *et al* (1988)[64]	GaAs/AlAs	0.36-0.46 eV	—
Hirakawa *et al* (1990)[129]	GaAs/AlAs	0.46 ± 0.07 eV	—
		0.44 ± 0.05 eV	—

[a] Values in square brackets are in disagreement with currently accepted values.

both square and parabolic quantum wells by Miller, Kleinman, and Gossard[58] yielded a conduction-band offset $\Delta E_c \approx 0.57\ \Delta E_g$.

The results of Miller *et al.* led to renewed interest in the determination of the GaAs/$\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ band offset, and a large number of subsequent measurements[48–51,56,59–62,119,120,126,127] yielded GaAs/$\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ band offset values consistent with the results of Miller *et al.* rather than those of Dingle *et al.* Wang *et al.*,[50,119,120] using a charge transfer technique, reported valence-band offset values of 0.126 ± 0.04 eV, 0.21 ± 0.03 eV, and 0.45 ± 0.05 eV for the GaAs/$\mathrm{Al}_{0.26}\mathrm{Ga}_{0.74}\mathrm{As}$, GaAs/$\mathrm{Al}_{0.5}\mathrm{Ga}_{0.5}\mathrm{As}$, and GaAs/AlAs heterojunctions, respectively, corresponding to $\Delta E_v \approx 0.28\text{–}0.39\ \Delta E_g$. Arnold *et al.*[60] used current-voltage measurements as a function of temperature to deduce a valence-band offset $\Delta E_v = 0.35\ \Delta E_g$ over a range of alloy composition $x \in [0.3, 1.0]$. Okumura *et al.*[61] obtained a conduction-band offset $\Delta E_c = 0.67\ \Delta E_g$ for $x < 0.42$ from capacitance-voltage measurements. Hickmott *et al.*[59] combined C–V and J–V measurements to obtain a conduction-band offset $\Delta E_c = 0.63\ \Delta E_g$ for $x = 0.4$. Watanabe *et al.*[62] used C–V measurements to determine the conduction- and valence-band offsets independently and obtained values $\Delta E_c = 0.62\ \Delta E_g$ for $x \in [0.15, 0.30]$ and $\Delta E_v = 0.38\ \Delta E_g$ for $x = 0.30$. Batey and Wright[48,49] used J–V techniques to measure the GaAs/$\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ valence-band offset as a function of alloy composition x and obtained $\Delta E_v = 0.55x$ for $x \in [0, 1]$. Wolford *et al.*[51] studied quantum-well photoluminescence in GaAs/$\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ heterostructures as a function of pressure; from an analysis of the critical pressure for crossing in energy of the Γ-like bound states in GaAs and the X-like states in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ for various alloy compositions, a valence-band offset $\Delta E_v = 0.32 \pm 0.02\ \Delta E_g^{\Gamma}$ was deduced for $x \approx 0.28$ and 0.70. Menéndez *et al.*[56] used a light-scattering method to obtain $\Delta E_c = 0.69\ \Delta E_g$ for $x = 0.06$. Photoluminescence measurements by Dawson *et al.*[126] yielded evidence of a staggered band alignment corresponding to $\Delta E_v = 342 \pm 4$ meV in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$/AlAs heterostructures with $x = 0.37$, and data for other compositions[127] were consistent with $\Delta E_v = 0.55x$. In all cases, measurements indicated that the energy gap difference was divided more equally between the conduction- and valence-band offsets than indicated by the 85 : 15 rule. Most of these experiments were conducted for GaAs/$\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ heterojunctions in which the band gap of $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ was still direct, i.e., $x \lesssim 0.4\text{–}0.45$, and yielded conduction- and valence-band offsets $\Delta E_c \approx (0.55\text{–}0.65)\ \Delta E_g$ and $\Delta E_v \approx (0.35\text{–}0.45)\ \Delta E_g$. For heterojunctions involving $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ layers with direct band gaps, the conduction- and valence-band offsets could be measured independently; the requirement that $\Delta E_c + \Delta E_v = \Delta E_g$ then provided convincing confirmation that the band offset measurements were indeed valid.

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[126] P. Dawson, B. A. Wilson, C. W. Tu, and R. C. Miller, *Appl. Phys. Lett.* **48**, 541 (1986).

[127] B. A. Wilson, P. Dawson, C. W. Tu, and R. C. Miller, *J. Vac. Sci. Technol. B* **4**, 1037 (1986).

The variation of the GaAs/$Al_xGa_{1-x}As$ valence-band offset with alloy composition x was also a subject of some debate. The initial approach was to assume that the conduction-band offset was proportional to the energy gap difference at the heterojunction, even though the measurements of Dingle *et al.* were carried out at only a single alloy composition. Arnold *et al.*[60] measured current-voltage characteristics for p^+-GaAs/ $Al_xGa_{1-x}As$/ p^--GaAs capacitor structures and deduced a valence-band offset $\Delta E_v = 0.35\Delta E_g^\Gamma$ for $x \in [0.3, 1.0]$. Because the direct band gap difference ΔE_g^Γ is not linear in x, this result was taken to imply a nonlinear dependence of ΔE_v on x. In contrast, measurements by Batey and Wright[48,49] of current-voltage characteristics as a function of temperature yielded a GaAs/$Al_xGa_{1-x}As$ valence-band offset linear in alloy composition, $\Delta E_v \approx 0.55x$. Uncertainties and inconsistencies in the actual band offset values obtained by various investigators, however, render the exact form of this dependence a secondary issue.

Additional complications can arise from characteristics such as substrate orientation and interface quality. Using x-ray photoelectron spectroscopy, Waldrop *et al.*[57,95] observed a dependence of the valence-band offset on both substrate orientation and growth sequence. For samples grown on (100) substrates, valence-band offsets of 0.46 eV and 0.36 eV were measured for AlAs grown on top of GaAs (AlAs–GaAs) and GaAs grown on top of AlAs (GaAs–AlAs), respectively. For samples grown on (110) subtrates, valence-band offsets of 0.55 eV and 0.42 eV were reported for the AlAs–GaAs and GaAs–AlAs growth sequences, respectively. These data were contradicted, however, by photoemission measurements of Katnani and Bauer[128] on heterojunctions involving GaAs, AlAs, and Ge. Katnani and Bauer did not observe any dependence of the GaAs/AlAs valence-band offset on growth sequence, obtaining a value of 0.39 ± 0.07 eV for both GaAs–AlAs and AlAs–GaAs heterojunctions. Measurements of Yu *et al.*[64] and of Hirakawa *et al.*[129] also provided evidence that, for interfaces of sufficiently high quality, the GaAs/AlAs band offset is commutative. In addition, band offset measurements for GaAs/$Al_{0.26}Ga_{0.74}As$ (100) and (311) heterojunctions[120] and for GaAs/AlAs (100), (110), and (111) *B* heterojunctions[129] failed to show any dependence of band offset values on substrate orientation.

For ideal, abrupt interfaces, one would expect that band offset values should not exhibit any dependence on growth sequence; that band offsets should be independent of growth sequence is referred to as the commutativity property. The dependence of the valence-band offset on growth sequence observed by Waldrop *et al.*[57,95] was thought to result from detailed microscopic differences in epitaxial growth on various semiconductor surfaces. A dependence on growth sequence of band offset values in a given material

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[128] A. D. Katnani and R. S. Bauer, *Phys. Rev. B* 33, 1106 (1986).

[129] K. Hirakawa, Y. Hashimoto, and T. Ikoma, *Appl. Phys. Lett.* 57, 2555 (1990).

system large enough to affect device properties, as the effects observed by Waldrop *et al.* were, could have significant implications for the analysis and design of heterojunction devices in that material system. Such a dependence could also provide insight into the properties of an interface that are most relevant in determining band offset values. In light of the confirmation of commutativity by other investigators,[64,128,129] however, it would appear that noncommutativity of the band offset is not an inherent feature of the GaAs/AlAs material system but is instead a consequence of insufficient control over interface quality.

Figure 13 summarizes several of the experimentally measured conduction- and valence-band offsets that have been reported for GaAs/$Al_xGa_{1-x}As$ heterojunctions. Assuming that the valence-band offset is a linear function of composition x, a least-squares fit to the data yields $\Delta E_v = 0.48x$ eV, as shown in the figure. The corresponding conduction-band offsets, for both the Γ and X valleys in $Al_xGa_{1-x}As$, are also shown in the figure. The Γ-point (direct) and X-point (indirect) band gaps for $Al_xGa_{1-x}As$ as a function of alloy composition x have been taken from the review of Adachi.[130]

b. *Comparison with Theory*

Theoretical predictions for the GaAs/AlAs band offset extend over a wide range of values. The early band offset theories generally predicted small values for the valence-band offset, the physical justification being that, near the valence-band edge, the valence-band wave functions were derived primarily from *p*-like atomic orbitals of the anion. Because the anion in GaAs and AlAs is the same, it was thought that the valence-band edges in the two materials should be at approximately the same position in energy. For all cases in which a nonzero valence-band offset was predicted, the AlAs valence-band edge was correctly predicted to be lower in energy than the GaAs valence-band edge. Predictions of several of the more widely quoted band offset theories are summarized in Table II. Figure 11 contains a graphical comparison of theoretically predicted valence-band offsets with the currently accepted experimental values for the GaAs/AlAs heterojunction.

The electron affinity rule[19] in conjunction with the electron affinity data of Milnes and Fuecht[71] yielded a valence-band offset of 0.15 eV, while the LCAO theory of Harrison[24] predicted a valence-band offset of 0.04 eV. Frensley and Kroemer,[22,23] using a pseudopotential band structure calculation, obtained a valence-band offset of 0 eV without interfacial dipole corrections and an offset of 0.69 eV with their dipole correction included. With the exception of the dipole-corrected value of Frensley and Kroemer, these predictions were all in general agreement with the value measured by Dingle *et al.* The common anion rule of McCaldin *et al.*[20] is often erroneously cited as predicting a very small GaAs/AlAs valence-band offset;

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

TABLE II. THEORETICAL PREDICTIONS FOR THE GaAs/AlAs VALENCE-BAND OFFSET

SOURCE	ΔE_v(theor.) (eV)
Electron affinity rule (1972)[71]	0.15
Frensley and Kroemer (1977)[23]	0.00
Frensley and Kroemer (1977)[23] (with dipole correction)	0.69
Harrison (1977)[24]	0.04
Tersoff (1986)[28]	0.55
Harrison and Tersoff (1986)[29]	0.12
Van de Walle and Martin (1987)[84] (self-consistent supercell)	0.37
Van de Walle and Martin (1987)[84] (model solid theory)	0.60
Cardona and Christensen (1987)[39] (dielectric midgap energy model)	0.43
Christensen (1988)[40]	0.53
Lambrecht *et al.* (1990)[43] (self-consistent dipole)	0.53
Lambrecht and Segall (1990)[87] (interface bond polarity model)	0.46

because Schottky barriers on AlAs and AlSb did not follow the behavior of the other materials studied, compounds containing Al were not included in the data on which the rule was based and the rule was not claimed to be valid for Al compounds.

Following the experimental realization that Dingle's result was substantially in error, a number of new theories predicting generally larger valence-band offsets were developed. Theories based on interface dipoles were developed by Tersoff[27,28] and by Harrison and Tersoff;[29] these theories predicted valence-band offsets of 0.55 eV and 0.12 eV, respectively. The dielectric midgap energy model of Cardona and Christensen[39] yielded a valence-band offset of 0.43 eV, and the interface bond polarity model of Lambrecht and Segall[87] predicted $\Delta E_v = 0.46$ eV. A number of calculations taking into account the electronic structure at specific interfaces were also developed. A self-consistent interface calculation based on *ab initio* pseudopotentials was developed by Van de Walle and Martin[85] and predicted a valence-band offset of 0.37 eV; the model solid theory[86] derived from these calculations yielded a valence-band offset of 0.60 eV. Self-consistent theories based on linear muffin-tin orbital (LMTO) calculations were developed and applied to the GaAs/AlAs heterojunction by Christensen[40] and by Lambrecht and Segall,[42] with both calculations yielding valence-band offsets of 0.53 eV. These more recent theories are all in relatively good agreement with the currently accepted experimental band offset values. As discussed in the previous section, Waldrop *et al.*[57,95] observed a dependence of the GaAs/AlAs valence-band offset on substrate orientation. In contrast, measurements by Wang *et al.*[120] and by Hirakawa *et al.*[129] did not reveal any dependence of the GaAs/AlAs valence-band offset on substrate orientation. Such a dependence might at first seem fairly plausible, given the variations in atomic structure and chemical bonding for different interface orientations. However, theoretical calculations in which the detailed structure of specific, albeit ideal, interfaces is taken into account generally predict a very small dependence of the band offset value on substrate orientation.[37,41,84]

9. INGAAS/INALAS/INP

Much effort has been devoted to the measurement of band offsets in the lattice-matched $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As/InP$ material system. $In_{0.53}Ga_{0.47}As$ has a room-temperature band gap of 0.74 eV (1.67 μm), close to the 1.55-μm wavelength needed to minimize attenuation in optical fiber transmissions; the effective energy for optical absorption and emission can be increased considerably by quantum confinement effects. The $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As$ and $In_{0.53}Ga_{0.47}As/InP$ heterojunctions, from which $In_{0.53}Ga_{0.47}As$ quantum wells can be fabricated, are therefore of considerable technological interest. A number of measurements have been made of band offsets for lattice-matched $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As$, $In_{1-x}Ga_xAs_{1-y}P_y/InP$, and $In_{0.52}Al_{0.48}As/InP$ heterojunctions. A summary of selected experimentally measured band offsets for the $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As/$ InP material system is given in Fig. 14, and

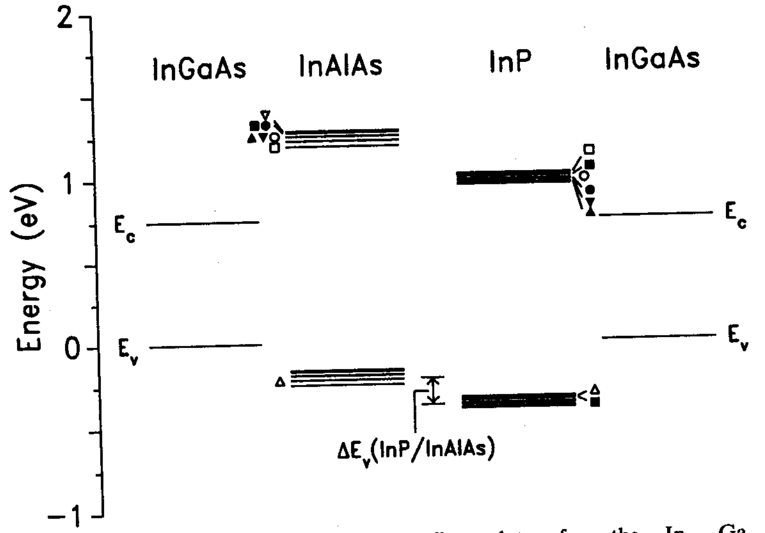

FIG. 14. Summary of experimental band offset data for the $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As/InP$ material system. For the $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As$ heterojunction, data are from Morgan *et al.*[149] (●); People *et al.*[150] (○); Welch *et al.*[90] (■); Weiner *et al.*[151] (□); Wagner *et al.*[152] (▼); Sugiyama *et al.*[153] (▽); Lee *et al.*[114] (▲); and Waldrop *et al.*[141] (△). For the $In_{0.53}Ga_{0.47}As/InP$ heterojunction, data are from Forrest *et al.*[111,112] (●); Miller *et al.*[88] (○); Lang *et al.*[136] (■); Westland *et al.*[137] (□); Haase *et al.*[140] (▲); Waldrop *et al.*[141] (△); and Cavicchi *et al.*[139] (▼). The $In_{0.52}Al_{0.48}As/InP$ valence-band offset is from the measurement of Waldrop *et al.*[158] Consistency of the experimental data with band offset transitivity can be seen in the figure.

theoretical band offset values are plotted in Fig. 15. The available experimental and theoretical band offset values are also summarized in Tables III and IV, respectively.

a. *InGaAs/InP*

For the $In_{0.53}Ga_{0.47}As/InP$ material system, band offset values ranging from $\Delta E_c = 190 \pm 30$ meV $\approx 0.32\,\Delta E_g$ to $\Delta E_c = 600$ meV $\approx \Delta E_g$ have been reported.[88,89,111,112,131–143] The more widely accepted measurements for this heterojunction typically yield $\Delta E_c \approx 0.4\,\Delta E_g$. Figure 14 shows the band alignments given by several of these measurements, and the available experimental data are summarized in Table III. Forrest *et al.*[111,112] used the capacitance–voltage technique to measure the conduction-band offset in lattice-matched $In_{1-x}Ga_xAs_{1-y}P_y/InP$, and found $\Delta E_c = 0.39\,\Delta E_g$ over the entire compositional range of $In_{1-x}Ga_xAs_{1-y}P_y$ alloys lattice-matched to InP. Miller *et al.*[88] measured photoluminescence energies in $In_{0.53}Ga_{0.47}As/InP$ quantum wells as a function of quantum-well width and obtained results generally consistent with $\Delta E_c \approx 0.40\,\Delta E_g$, although for certain well widths the experimental results could be modeled theoretically using conduction-band offsets ranging from 20 to 50% of the total band gap difference. Lang *et al.*[136] measured both the conduction- and the valence-band offset for the $In_{0.53}Ga_{0.47}As/InP$ heterojunction by using admittance spectroscopy to analyze *p–n* junctions containing $In_{0.53}Ga_{0.47}As/InP$ superlattices and obtained $\Delta E_v = 0.346 \pm 0.010$ eV and $\Delta E_c = 0.250 \pm 0.010$ eV $= 0.42\,\Delta E_g$. The sum of these measured conduction- and valence-

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[143] J. R. Waldrop, R. W. Grant, and E. A. Kraut, *J. Vac. Sci. Technol. B* **7**, 815 (1989).

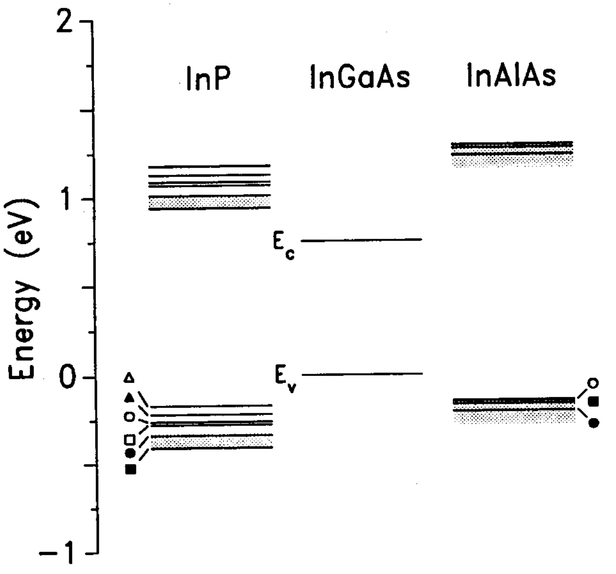

FIG. 15. Summary of theoretical band offset values for the $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As/InP$ material system. For the $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As$ heterojunction, calculated values are from the model solid theory of Van de Walle and Martin[84] (●); Cardona and Christensen[39] (○); and Hybertsen[163] (■). For the $In_{0.53}Ga_{0.47}As/InP$ heterojunction, calculated values are from the model solid theory of Van de Walle and Martin[84] (●); Cardona and Christensen[39] (○); Hybertsen[161,162] (■); the common-anion rule of McCaldin *et al.*[20] (□); self-consistent dipole calculations of Lambrecht *et al.*[43] (▲); and the interface bond polarity model of Lambrecht and Segall[87] (△). The theories shown here all obey the transitivity rule to within ±0.01 eV. The shaded regions indicate the approximate range of commonly accepted experimental band offset values.

band offsets yields a total band-gap discontinuity $\Delta E_g = 0.596 \pm 0.015$ eV, in excellent agreement with the independently measured band-gap difference[136] of 0.613 eV at 4.2 K and 0.600 ± 0.010 eV at 300 K. The consistency of these results is a reassuring indication of the validity of the measurements reported in Ref. 136. Cavicchi *et al.*[139] used the same technique to measure the conduction-band offset for $In_xGa_{1-x}As$ grown on InP and obtained $\Delta E_c = 0.21 \pm 0.02$ eV for $x = 0.53$. Measurements of optical absorption in $In_{0.53}Ga_{0.47}As/InP$ multiple-quantum-well structures by Westland *et al.*[137] yielded a conduction-band offset $\Delta E_c \approx 0.45\,\Delta E_g$. Optical absorption measurements by Skolnick *et al.*[138] yielded a lower bound for the $In_{0.53}Ga_{0.47}As/InP$ conduction-band offset (based on the lack of absorption features at photon energies above ~1.075 eV) of 0.235 ± 0.020 eV, or $\Delta E_c \geq (0.38 \pm 0.03)\,\Delta E_g$. Internal photoemission measurements by Haase *et al.*[140] yielded a conduction-band offset $\Delta E_c = 0.203 \pm 0.015\text{ eV} = 0.34\,\Delta E_g$ at

TABLE III. EXPERIMENTAL BAND OFFSET VALUES FOR $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As/InP$

SOURCE	HETEROJUNCTION	ΔE_v (expt.) (eV)	ΔE_c (expt.) (eV)
Forrest *et al.* (1981, 1984)[111,112]	$InP/In_{0.53}Ga_{0.47}As$	—	$0.39\ \Delta E_g = 0.23 \pm 0.02$
Miller *et al.* (1986)[88]	$InP/In_{0.53}Ga_{0.47}As$	—	$0.40 \Delta E_g = 0.24$
Lang *et al.* (1987)[136]	$InP/In_{0.53}Ga_{0.47}As$	0.346 ± 0.010	0.250 ± 0.010
Westland *et al.* (1987)[137]	$InP/In_{0.53}Ga_{0.47}As$	—	$0.45\ \Delta E_g = 0.27$
Skolnick *et al.* (1987)[138]	$InP/In_{0.53}Ga_{0.47}As$	—	$>0.235 \pm 0.020$
Haase *et al.* (1989)[140]	$InP/In_{0.53}Ga_{0.47}As$	—	0.203 ± 0.015
Cavicchi *et al.* (1989)[139]	$InP/In_{0.53}Ga_{0.47}As$	—	0.21 ± 0.02
Waldrop *et al.* (1991)[141]	$InP/In_{0.53}Ga_{0.47}As$	0.34	—
Chin *et al.* (1979)[131]	$InP/In_{0.53}Ga_{0.47}As$	—	$0.67\ \Delta E_g = 0.40$
Guldner *et al.* (1982)[132]	$InP/In_{0.53}Ga_{0.47}As$	—	0.53
Brunemeier *et al.* (1985)[133]	$InP/In_{0.53}Ga_{0.47}As$	—	$0.65\ \Delta E_g = 0.39$
Sauer *et al.* (1986)[89]	$InP/In_{0.53}Ga_{0.47}As$	—	$0.60\ \Delta E_g = 0.36$
Morgan *et al.* (1982)[149]	$In_{0.52}Al_{0.48}As/In_{0.53}Ga_{0.47}As$	—	$0.72\ \Delta E_g = 0.52$
People *et al.* (1983)[150]	$In_{0.52}Al_{0.48}As/In_{0.53}Ga_{0.47}As$	—	0.50 ± 0.05
Welch *et al.* (1984)[90]	$In_{0.52}Al_{0.48}As/In_{0.53}Ga_{0.47}As$	—	$0.7\ \Delta E_g = 0.52$
Weiner *et al.* (1985)[151]	$In_{0.52}Al_{0.48}As/In_{0.53}Ga_{0.47}As$	0.29	0.44
Wagner *et al.* (1985)[152]	$In_{0.52}Al_{0.48}As/In_{0.53}Ga_{0.47}As$	0.2	0.5
Sugiyama *et al.* (1986)[153]	$In_{0.52}Al_{0.48}As/In_{0.53}Ga_{0.47}As$	—	0.53 ± 0.05
Lee *et al* (1990)[114]	$In_{0.52}Al_{0.48}As/In_{0.53}Ga_{0.47}As$	—	0.50
Waldrop *et al.* (1991)[141]	$In_{0.52}Al_{0.48}As/In_{0.53}Ga_{0.47}As$	0.22	—
Caine *et al.* (1984)[156]	$InP/In_{0.52}Al_{0.48}As$	0.40	0.52
Aina *et al.* (1988)[157]	$InP/In_{0.52}Al_{0.48}As$	0.29	0.39
Waldrop *et al.* (1990)[158]	$InP/In_{0.52}Al_{0.48}As$	0.16	—

TABLE IV. THEORETICAL BAND OFFSET VALUES FOR $InP/In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As$

SOURCE	HETEROJUNCTION	ΔE_v (theor.) (eV)
McCaldin *et al.* (1976)[20]	$InP/In_{0.53}Ga_{0.47}As$	0.28
Van de Walle and Martin (1987)[84] (model solid theory)	$InP/In_{0.53}Ga_{0.47}As$	0.34
Cardona and Christensen (1987)[39] (dielectric midgap energy model)	$InP/In_{0.53}Ga_{0.47}As$	0.26
Lambrecht *et al.* (1990)[43] (self-consistent dipole)	$InP/In_{0.53}Ga_{0.47}As$	0.22
Lambrecht and Segall (1990)[87] (interface bond polarity model)	$InP/In_{0.53}Ga_{0.47}As$	0.17
Hybertsen (1990)[161,162]	$InP/In_{0.53}Ga_{0.47}As$	0.41
Van de Walle and Martin (1987)[84] (model solid theory)	$In_{0.52}Al_{0.48}As/In_{0.53}Ga_{0.47}As$	0.21
Cardona and Christensen (1987)[39] (dielectric midgap energy model)	$In_{0.52}Al_{0.48}As/In_{0.53}Ga_{0.47}As$	0.15
Hybertsen (1991)[163]	$In_{0.52}Al_{0.48}As/In_{0.53}Ga_{0.47}As$	0.17
Van de Walle and Martin (1987)[84] (model solid theory)	$InP/In_{0.52}Al_{0.48}As$	0.13
Cardona and Christensen (1987)[39] (dielectric midgap energy model)	$InP/In_{0.52}Al_{0.48}As$	0.11
Hybertsen (1991)[163]	$InP/In_{0.52}Al_{0.48}As$	0.25

room temperature for the $In_{0.53}Ga_{0.47}As/InP$ heterojunction. In addition, Haase *et al.* measured a temperature dependence of the conduction-band offset $\partial(\Delta E_c)/\partial T = -0.2 \pm 0.1$ meV/K. Finally, Waldrop *et al.*[141] used XPS to measure the valence-band offset for the $In_{0.53}Ga_{0.47}As/InP$ heterojunction, obtaining $\Delta E_v = 0.34$ eV $= 0.57\ \Delta E_g$. In an earlier study, Waldrop *et al.*[142,143] used XPS to measure band offsets for the lattice-mismatched GaAs/InP and InAs/InP heterojunctions and interpolated those results to obtain a valence-band offset $\Delta E_v = 0.42\ \Delta E_g$, corresponding to a conduction-band offset $\Delta E_c = 0.58\ \Delta E_g$, for the lattice-matched $In_{0.53}Ga_{0.47}As/InP$ system. However, the ability to measure an effective "unstrained" valence-band offset value for a lattice-mismatched heterojunction by the XPS method is somewhat questionable, and the interpolated $In_{0.53}Ga_{0.47}As/InP$ valence-band offset obtained by Waldrop *et al.*, which does not agree with the value measured directly, should be viewed with some caution.

A number of other measurements have been reported that yield band offsets differing considerably from the currently accepted values. In many cases, however, these discrepancies appear to arise from complications in experimental interpretation and are indicative of the difficulty of performing accurate band offset measurements rather than an actual variation in band offset values. Forrest and Kim[144] and Ogura *et al.*[145] claimed on the basis of C–V measurements that the $In_{0.53}Ga_{0.47}As/InP$ conduction-band offset dropped sharply and approached zero as the temperature was decreased, behavior they both attributed to the filling of interface trap levels with electrons at low temperature. Subsequently, Kazmierski *et al.*[146] pointed out the importance of accounting for trap levels in the actual interpretation of C–V measurements and claimed that in their measurements on $In_{0.53}Ga_{0.47}As/InP$ heterojunctions the apparent conduction-band offset was in reality attributable to the presence of interface traps and that the actual conduction-band offset was nearly zero; however, their calculations incorrectly assumed[147] that donor trap levels were only partially filled at low temperature and completely filled at high temperature. A later analysis by Leu and Forrest[147] of the effects of temperature and measurement frequency on C–V profiles finally appeared to explain the apparent reduction in the conduction-band offset at low temperature. Assuming that e_t, the rate of emission for charge in a trap, is proportional to a Boltzmann occupation factor, $e_t \propto \exp(-E_t/k_B T)$, Leu and Forrest deduced that for frequencies $\omega \ll e_t$ the measured value of ΔE_c was nearly independent of the interface trap

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density and therefore very close to the value measured in the absence of interface traps, whereas for high frequencies $\omega \gg e_t$ the measured conduction-band offset decreased with increasing trap density. It was therefore postulated that the apparent drop in the measured conduction-band offset at low temperature was actually a transition from the low-frequency to the high-frequency measurement regime induced by the temperature dependence of the Boltzmann factor in the trap response rate e_t.

Several other types of experiments have also been reported in which band offset values inconsistent with the currently accepted values were obtained. Chin *et al.*[131] analyzed photoluminescence and laser spectra from $In_{0.87}Ga_{0.13}As_{0.29}P_{0.71}/InP$ quantum wells grown by liquid phase epitaxy and obtained a conduction-band offset $\Delta E_c \approx 0.67\ \Delta E_g$. Brunemeier *et al.*[133] later used the same technique and obtained $\Delta E_c \approx 0.65\ \Delta E_g$ over the entire compositional range of lattice-matched $In_{1-x}Ga_xAs_{1-y}P_y/InP$ heterojunctions. These two results, however, should be viewed with some caution in light of the fact that this technique was also used to obtain a valence-band offset $\Delta E_v = 0.15\ \Delta E_g$ for the $GaAs/Al_xGa_{1-x}As$ heterojunction,[148] which is now known to be a clear underestimation of the size of the valence-band offset or, equivalently, an overestimation of the conduction-band offset. Guldner *et al.*[132] deduced a conduction-band offset of 0.53 eV from Shubnikov–de Haas and cyclotron resonance measurements on the two-dimensional electron gas at the $In_{0.53}Ga_{0.47}As/InP$ interface. Temkin *et al.*[134] used optical absorption and photoluminescence spectra to deduce that the conduction-band offset was larger than the valence-band offset for the $In_{0.53}Ga_{0.47}As/InP$ heterojunction, and Sauer *et al.*[89] analyzed photoluminescence excitation spectra and obtained $\Delta E_c \approx 0.60\ \Delta E_g$. However, the difficulty of obtaining reliable band offset values from analyses of optical spectra has been clearly demonstrated for the case of $GaAs/Al_xGa_{1-x}As$,[47,58] and the same considerations are a factor in determining band offsets in other heterojunction systems, including $In_{0.53}Ga_{0.47}As/InP$.

b. *InGaAs/InAlAs*

Band offsets in lattice-matched $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As$ and $In_{0.53}Ga_{0.48}As/In_{0.52}(Ga_{1-x}Al_x)_{0.48}As$ heterojunctions have been measured by a number of techniques. The experimental data are summarized in Fig. 14 and Table III. Morgan *et al.*[149] measured the temperature dependence of current–voltage characteristics in $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As$ heterostructures and obtained a conduction-band offset $\Delta E_c = 0.72\ \Delta E_g = 0.52$ eV.

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People *et al.*[150] used the C–V profiling technique to measure the $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As$ conduction-band offset and at room temperature (297 K) obtained $\Delta E_c = (0.50 \pm 0.05)$ eV $= (0.71 \pm 0.07)\,\Delta E_g$. Welch *et al.*[90] analyzed photoluminescence spectra from $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As$ single quantum wells and obtained a conduction-band discontinuity $\Delta E_c \approx 0.7\,\Delta E_g \approx 0.52$ eV. Weiner *et al.*[151] measured optical absorption spectra at room temperature in $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As$ multiple quantum wells; using both the conduction- and valence-band offsets as adjustable parameters to fit a theoretical model to the observed absorption spectra, Weiner *et al.* obtained a conduction-band offset $\Delta E_c = 0.44$ eV $= 0.60\,\Delta E_g$ and a valence-band offset $\Delta E_v = 0.29$ eV. Wagner *et al.*[152] measured photoluminescence excitation spectra at low temperature (5–30 K) for $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As$ quantum wells and obtained conduction- and valence-band discontinuities $\Delta E_c \approx 0.5$ eV $\approx 0.7\,\Delta E_g$ and $\Delta E_v \approx 0.2$ eV. Sugiyama *et al.*[153] analyzed the temperature dependence of current–voltage characteristics in $In_{0.52}Ga_{0.48}As/In_{0.52}(Ga_{1-x}Al_x)_{0.48}As$ single-barrier heterostructures and obtained a conduction-band offset $\Delta E_c = (0.53 \pm 0.05)x$ eV $= (0.72 \pm 0.07)\,\Delta E_g(x)$; in other studies[154,155] the energy band gap of $In_{0.52}(Ga_{1-x}Al_x)_{0.48}As$ quaternary alloys had been found to depend linearly on the composition x. Lee *et al.*[114] measured conduction-band offsets in $In_xAl_{1-x}As/In_{0.53}Ga_{0.47}As$ heterojunctions for $x \in [0.47, 0.52]$ using C–V profiling and obtained $\Delta E_c = 0.50$ eV $= 0.70\,\Delta E_g$ for the lattice-matched composition, $x = 0.52$. Finally, Waldrop *et al.*[141] used XPS to measure the $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As$ valence-band offset, with their measurements yielding $\Delta E_v = 0.22$ eV $= 0.32\,\Delta E_g$, corresponding to $\Delta E_c = 0.68\,\Delta E_g$.

These measurements appear to converge on values of $0.70\,\Delta E_g \approx 0.50$ eV for the conduction-band offset and $0.30\,\Delta E_g \approx 0.20$ eV for the valence-band offset. The relative sizes of the conduction- and valence-band offsets appear therefore to be fairly close to those found in the GaAs/AlGaAs material system, with the fraction of the total band gap discontinuity found in the conduction-band offset being slightly greater in the $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As$ heterojunction.

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c. *InAlAs/InP*

Relatively few measurements of band offset values have been performed for the $In_{0.52}Al_{0.48}As$/InP heterojunction. The available experimental data are summarized in Table III. Caine *et al.*[156] measured bias-tunable luminescence from lattice-matched p-$In_{0.52}Al_{0.48}As$/n-InP heterojunctions and obtained conduction- and valence-band offsets of 0.52 eV and 0.40 eV, respectively. Aina *et al.*[157] measured photoluminescence from $In_{0.52}Al_{0.48}As$/InP multiple quantum wells and single heterojunctions, from which they deduced a staggered band alignment with an effective band gap for the single heterojunction of 1.06 eV, corresponding to conduction- and valence-band offsets of 0.39 eV and 0.29 eV, respectively. Waldrop *et al.*[158] used XPS to measure the valence-band offset in lattice-matched $In_{0.52}Al_{0.48}As$/InP heterojunctions and obtained $\Delta E_v = 0.16$ eV. It is worth noting that a linear interpolation between the purportedly "strain-free" band offset values measured by Waldrop *et al.* for GaAs/InP[142,143] and AlAs/InP[158] heterojunctions yields an $In_{0.52}Al_{0.48}As$/InP valence-band offset of approximately 0.02 eV, which does not agree well with the direct measurement of the $In_{0.52}Al_{0.48}As$/InP valence-band offset.

The source of the disagreement among these measurements is not entirely clear. However, factors that apparently have not been taken into account in the photoluminescence studies of $In_{0.52}Al_{0.48}As$/InP heterojunctions include the effects of electrostatic band bending and of below-band-gap recombination on the energy of photon emission due to recombination at the interface. It is possible that electrostatic band bending or below-band-gap recombination could reduce the photon energy for emission due to recombination at the $In_{0.52}Al_{0.48}As$/InP interface, increasing the apparent value of the $In_{0.52}Al_{0.48}As$/InP valence-band offset. This effect could provide an explanation for the observed discrepancy between the band offset values obtained by XPS and those obtained by analysis of photoluminescence. For this reason, and also because of the known reliability of band offset values obtained from careful XPS measurements, we believe the valence-band offset obtained in Ref. 158, $\Delta E_v(In_{0.52}Al_{0.48}As/InP) = 0.16$ eV, to be the most trustworthy of the values cited here.

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d. *Transitivity*

A test of the transitivity condition, Eq. (1.1), can provide information regarding the possible influence of interface effects on band offset values in the $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As/InP$ material system. Figure 14 shows experimental band offset data for the $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As$, $In_{0.53}Ga_{0.47}As/InP$, and $In_{0.52}Al_{0.48}As/InP$ heterojunctions; only the selected measurements described in the preceding sections have been included. As shown in the figure, these experimental band offset values clearly obey the transitivity relation; i.e., combining the $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As$ and $In_{0.53}Ga_{0.47}As/InP$ band offset values yields the correct value, to within experimental error, for the $In_{0.52}Al_{0.48}As/InP$ band offset. In addition, Waldrop *et al.*[141] have used XPS to verify directly that band offset transitivity is satisfied for the $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As/InP$ material system. These results provide considerable evidence for the validity of the transitivity rule for heterojunctions with abrupt, high-quality interfaces; the experimental confirmation of transitivity and the close agreement among the selected experimental results also suggest that variation of band offset values with growth conditions is probably not a significant effect in this material system.

Another effect of potential interest in the $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As/$ InP material system is the presence of interface strain at the $In_{0.53}Ga_{0.47}As/$ InP and $In_{0.52}Al_{0.48}As/InP$ heterojunctions. As shown in Fig. 16, the interface in an MAs/InP heterojunction, where $M = In_{0.53}Ga_{0.47}$ or $In_{0.52}Al_{0.48}$, can be either InAs-like (Fig. 16a) or MP-like (Fig. 16b). These two different types of interfaces have been distinguished experimentally in high-resolution x-ray diffraction studies of $In_{0.53}Ga_{0.47}As/InP$ superlattices.[159] In addition, x-ray diffraction measurements performed on InAlAs/InP superlattices have revealed evidence of anion intermixing and the presence of single-monolayer strained layers at the InAlAs/InP interfaces.[160] Hybertsen[161–163] studied the effect of interface strain theoretically in the $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As/$ InP material system and found that, as long as the interfacial strain minimizes the total energy, the exact atomic configuration of the interface has little influence on the band offset values. If the energy was not minimized, however, the band offsets were found to depend quite significantly on the atomic configuration of the interface. Variations in growth conditions and consequently in interfacial quality for the $In_{0.53}Ga_{0.47}As/InP$ and

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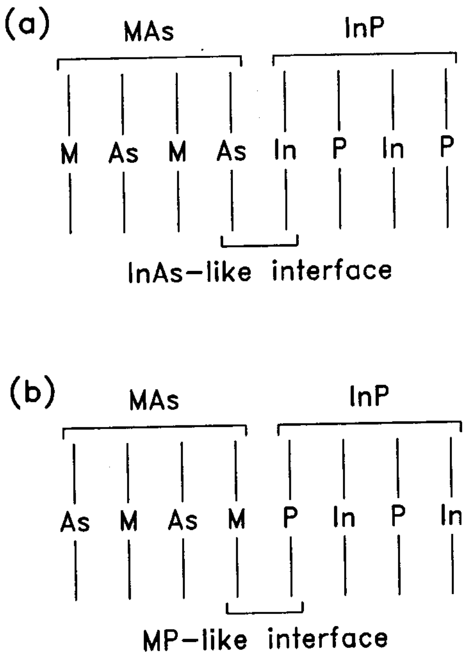

FIG. 16. Schematic diagrams of atomic planes in the MAs/InP heterojunction, where M = $In_{0.53}Ga_{0.47}$ or $In_{0.52}Al_{0.48}$. The InAs-like interface structure is shown in (a), and the MP-like interface is shown in (b).

$In_{0.52}Al_{0.48}As$/InP heterojunctions may therefore be partially responsible for the discrepancies found among the experimental band offset measurements for these material systems. It is perhaps suggestive that very few inconsistencies were found among the experimental band offset measurements for the $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As$ heterojunction, for which interface strain is not a consideration. Further study of this issue will be required to determine conclusively the effect of interface strain and chemical intermixing on band offset values.

e. *Comparison with Theory*

Relatively few theoretical calculations of band offsets are available for the $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As$/InP material system, because most calculations have been performed only for elemental and pure (binary) compound semiconductors. The available theoretical predictions are summarized in Fig. 15 and Table IV. Hybertsen[161–163] has calculated band offsets for this material system using pseudopotentials in a local density functional approach; the alloys are treated in the virtual-crystal approximation. As discussed in the previous section, Hybertsen's calculations indicate that interface strain does not exert a significant influence on band offsets in the $In_{0.53}Ga_{0.47}As/InP$ and $In_{0.52}Al_{0.48}As/InP$ heterojunctions, and he obtains valence-band offsets of 0.41 eV, 0.17 eV, and 0.25 eV for the $In_{0.53}Ga_{0.47}As/InP$, $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As$, and $In_{0.52}Al_{0.48}As/InP$ interfaces, respectively. Lambrecht *et al.*[43] calculated a valence-band offset of 0.22 eV for the $In_{0.5}Ga_{0.5}As/InP$ heterojunction using their self-consistent dipole theory. The interface bond polarity model of Lambrecht and Segall[87] yields a valence-band offset of 0.17 eV for the $In_{0.5}Ga_{0.5}As/InP$ interface. Predictions of other theories for band offset values in alloy heterojunctions can be obtained by interpolation from results for pure binary compounds. An energy level E_i in a ternary alloy $A_xB_{1-x}C$ can be estimated as[164]

$$\begin{aligned} E_i(A_xB_{1-x}C) &= xE_i(AC) + (1-x)E_i(BC) \\ &\quad + 3x(1-x)[-a_i(AC) + a_i(BC)]\left[\frac{a_0(AC) - a_0(BC)}{a_0}\right] \end{aligned} \tag{9.1}$$

where a_i is the deformation potential for E_i and a_0 is the lattice constant. An interpolation from calculations for binary compound semiconductors using the model solid theory of Van de Walle and Martin[84,86] yields valence-band offsets $\Delta E_v(In_{0.53}Ga_{0.47}As/InP) = 0.34$ eV, $\Delta E_v(In_{0.53}Ga_{0.47}As/In_{0.47}Al_{0.48}As) = 0.21$ eV, and $\Delta E_v(In_{0.52}Al_{0.48}As/InP) = 0.13$ eV. A similar procedure for the dielectric midgap energy theory of Cardona and Christensen[39,164] yields valence-band offsets $\Delta E_v(In_{0.53}Ga_{0.47}As/InP) = 0.26$ eV, $\Delta E_v(In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As) = 0.15$ eV, and $\Delta E_v(In_{0.52}Al_{0.48}As/InP) = 0.11$ eV. From these results we see that the best agreement with the accepted experimental values is given by the model solid theory of Van de Walle and Martin, although most of the other theories appear to agree with the experimental results to within the combined experimental and theoretical error bars.

10. INAS/GASB/ALSB

Another nearly lattice-matched material system that has been a subject of considerable study is InAs/GaSb/AlSb. Interest in this material system arises to a considerable degree from the unusual band alignments that are obtainable. In particular, it has been well established through direct measurements

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of the InAs/GaSb band offset,[93,98,116,165] electrical transport studies in InAs/GaSb/AlSb heterostructures,[166–172] and the prediction and observation of a semiconductor–semimetal transition in InAs/GaSb superlattices[170,173–177] that the InAs/GaSb interface is characterized by a type II broken-gap band alignment, as shown in Fig. 2c. This band alignment has been exploited in the development of novel electrical devices[167–172] and narrow-band-gap strained-layer superlattices for detection of infrared radiation,[178–180] and for numerous studies of fundamental physical interest.[170,173–177,181–184] Band alignments given by several experimental measurements are shown in Fig. 17, and the experimental results have been compiled in Table V. Theoretical band offset values for the InAs/GaSb/AlSb material system are summarized in Fig. 18 and Table VI.

a. *Experiment*

Explicit values for the InAs/GaSb band offsets have been obtained by a number of investigators. Sakaki *et al.*[166] measured lattice constants and

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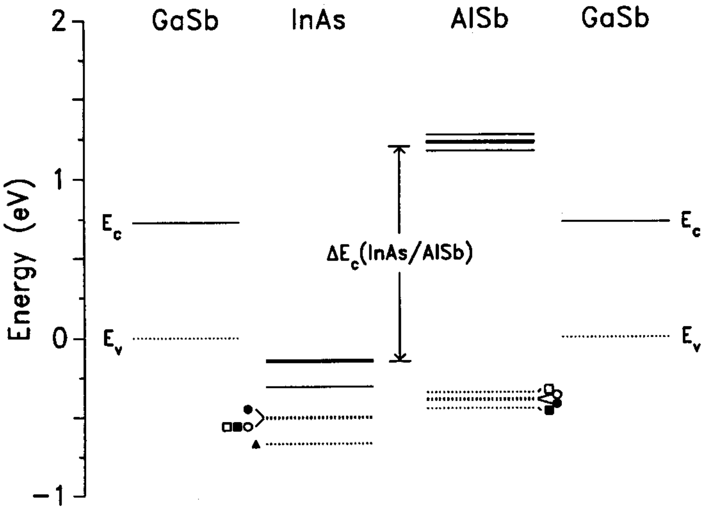

FIG. 17. Summary of experimental band offset data for the InAs/GaSb/AlSb material system. Conduction band edges are represented by solid lines and valence band edges by dotted lines. For the InAs/GaSb heterojunction, data are from Sakaki *et al.*[166] (●); Sai-Halasz *et al.*[165] (○); Claessen *et al.*[93] (■); Gualtieri *et al.*[98] (□); and Srivastava *et al.*[116] (▲). For the GaSb/AlSb heterojunction, data are from Gualtieri *et al.*[99] (●); Yu *et al.*[190] (○); Menéndez *et al.*[72] (■); and Cebulla *et al.*[191] (□). The InAs/AlSb conduction-band offset value is from the measurement of Nakagawa *et al.*[115]

TABLE V. EXPERIMENTAL VALENCE-BAND OFFSETS FOR InAs/GaSb/AlSb

SOURCE	HETEROJUNCTION	ΔE_v (expt.) (eV)	ΔE_c (expt.) (eV)
Sakaki *et al.* (1977)[166]	InAs/GaSb	0.50	—
Sai-Halasz *et al.* (1978)[165]	InAs/GaSb	0.56	—
Claessen *et al.* (1986)[93]	InAs/GaSb	0.56	—
Srivastava *et al.* (1986)[116]	$InAs_{0.95}Sb_{0.05}/GaSb$	0.67 ± 0.04	—
Gualtieri *et al.* (1987)[98]	InAs/GaSb	0.51 ± 0.1	—
Voisin *et al.* (1984)[188]	AlSb/GaSb	0.04 − 0.08	—
Tejedor *et al.* (1985)[189]	AlSb/GaSb	>0.267	—
Gualtieri *et al.* (1986)[99]	AlSb/GaSb	0.40 ± 0.15	—
Menéndez *et al.* (1987)[72]	$Al_xGa_{1-x}Sb/GaSb$	(0.45 ± 0.08)x	—
Cebulla *et al.* (1988)[191]	AlSb/GaSb	0.35	—
Yu *et al.* (1991)[190]	AlSb/GaSb	0.39 ± 0.07	—
Nakagawa *et al.* (1989)[115]	InAs/AlSb	—	1.35 ± 0.05

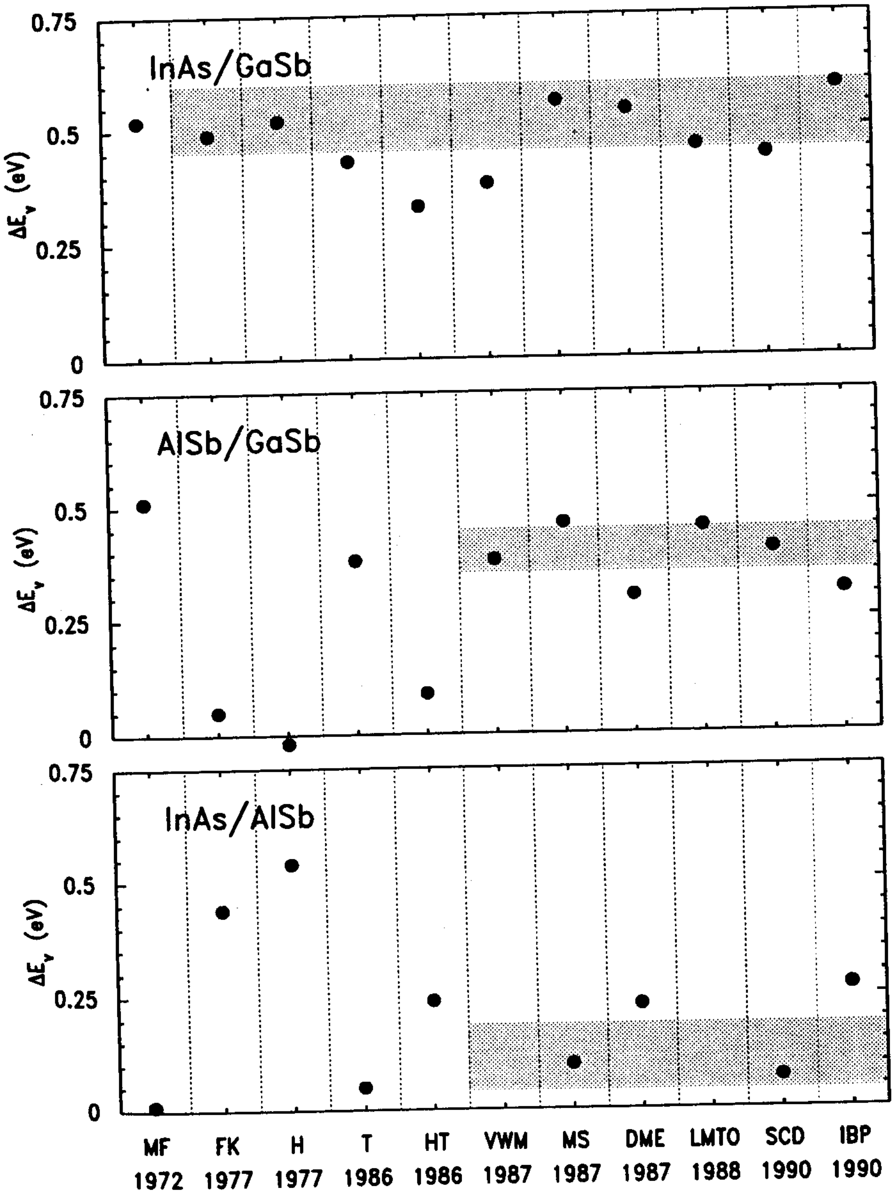

FIG. 18. A comparison of theoretical band offset values for the InAs/GaSb/AlSb material system. Different theories are plotted in approximately chronological order; the approximate range of experimental values throught to have been valid when each theory was developed has been shaded. Theoretical predictions are from the following sources: MF 1972, Ref. 71; FK 1977, Ref. 23; H 1977, Ref. 24; T 1986, Ref. 28; HT 1986, Ref. 29; VWM 1987, Ref. 84; MS 1987, Ref. 84; DME 1987, Ref. 39; LMTO 1988, Ref. 40; SCD 1990, Ref. 43; IBP 1990, Ref. 87.

TABLE VI. THEORETICAL BAND OFFSET VALUES FOR InAs/GaSb/AlSb

SOURCE	ΔE_v (InAs/GaSb) (eV)	ΔE_v (AlSb/GaSb) (eV)	ΔE_v (InAs/AlSb) (eV)
Milnes and Feucht (1972)[71]	0.52	0.51	0.01
McCaldin *et al* (1976)[20]	0.41		
Frensley and Kroemer (1977)[23]	0.49	0.05	0.44
Frensley and Kroemer (1977)[23] (with dipole correction)	0.26	0.73	−0.47
Harrison (1977)[24]	0.52	−0.02	0.54
Freeouf and Woodall (1981)[193]	0.54	0.44	0.10
Katnani and Margaritondo (1983)[21]	0.12		
Tersoff (1986)[28]	0.43	0.38	0.05
Harrison and Tersoff (1986)[29]	0.33	0.09	0.24
Van de Walle and Martin (1987)[84] (self-consistent supercell)	0.38	0.38	
Van de Walle and Martin (1987)[84] (model solid theory)	0.56	0.46	0.10
Cardona and Christensen (1987)[39] (dielectric midgap energy model)	0.54	0.30	0.23
Christensen (1988)[40]	0.46	0.45	
Lambrecht *et al.* (1990)[43] (self-consistent dipole)	0.44	0.40	0.07
Lambrecht and Segall (1990)[87] (interface bond polarity model)	0.59	0.31	0.27

energy band gaps in $In_{1-x}Ga_xAs$ and $GaSb_{1-y}As_y$ alloys and current-voltage characteristics in n-$In_{1-x}Ga_xAs$/p-$GaSb_{1-y}As_y$ heterojunctions; these measurements yielded $\Delta \equiv (E_v^{GaSb} - E_c^{InAs}) = 0.14$ eV, corresponding to a valence-band offset ΔE_v(InAs/GaSb) = 0.50 eV. Sai-Halasz *et al.*[165] measured optical absorption at low temperature in $In_{1-x}Ga_xAs/GaSb_{1-y}As_y$ superlattices, from which they deduced $\Delta = 0.15$ eV, corresponding to a valence-band offset for the InAs/GaSb heterojunction of 0.56 eV. Claessen *et al.*[93] measured the pressure dependence of the InAs/GaSb band offset at 4.2 K, obtaining $\Delta = 0.15$ eV at atmospheric pressure and $d\Delta/dP = -0.0058$ eV/kbar. Gualtieri *et al.*[98] measured the InAs/GaSb valence-band offset by XPS, obtaining ΔE_v(InAs/GaSb) = 0.51 ± 0.1 eV. These results are all in very close agreement. However, Srivastava *et al.*[116] measured capacitance-voltage characteristics for n-$InAs_{0.95}Sb_{0.05}$/n-GaSb heterojunctions and deduced a valence-band offset $\Delta E_v(InAs_{0.95}Sb_{0.05}/GaSb) = 0.67 \pm 0.04$ eV, which differs significantly from the other reported results; the small amount of Sb in the $InAs_{0.95}Sb_{0.05}$ layer should not be sufficient to produce the variation observed here. The source of this discrepancy is not clear, but the wealth of evidence supporting a valence-band offset ΔE_v(InAs/GaSb) $\approx$ 0.51 eV leads us to believe that value to be the most trustworthy.

For the GaSb/AlSb heterojunction, a number of band offset measurements are available. On the basis of common-anion arguments, in early measurements it was often thought, incorrectly, that the valence-band offset should be small. As discussed by McCaldin *et al.*,[20] the presence of Al in the heterojunction precludes the use of the common-anion rule for GaSb/AlSb. Mendez *et al.*[185] measured photoluminescence spectra from GaSb/AlSb superlattices that appeared to be consistent with a small valence-band offset ($\pm$0.05 eV). Griffiths *et al.*[186] obtained photoluminescence data from GaSb/AlSb multiple quantum wells that appeared to be consistent with a small valence-band offset, provided that a nonparabolic model[187] was used for the conduction-band structure. Voisin *et al.*[188] performed optical absorption measurements on GaSb/AlSb superlatices and obtained spectra consistent with valence-band offsets of 0.04 eV and 0.08 eV for the heavy-hole and light-hole valence bands, respectively (the valence bands are actually split because of the slight lattice mismatch between AlSb and GaSb, ~0.6%).

A number of other experiments, however, have provided quite convincing evidence that there is a substantial valence-band offset at the GaSb/AlSb interface. Tejedor *et al.*[189] used resonant Raman scattering to study the electronic structure of GaSb/AlSb superlattices and concluded that ΔE_v(GaSb/AlSb) > 0.267 eV. Gualtieri *et al.*[99] obtained ΔE_v(GaSb/AlSb) = 0.40 $\pm$ 0.15 eV using x-ray photoelectron spectroscopy, and Yu *et al.*[190] used XPS to obtain a valence-band offset ΔE_v(GaSb/AlSb) = 0.39 $\pm$ 0.07 eV. Band offset commutativity was verified in both XPS experiments. Menéndez *et al.*[72] used a light-scattering method to obtain $\Delta E_v = (0.45 \pm 0.08)x$ eV for GaSb/Al_xGa_{1-x}Sb heterojunctions. Measurements of optical absorption and excitation in GaSb/AlSb multiple quantum wells by Cebulla *et al.*[191] yielded a valence-band offset ΔE_v(GaSb/AlSb) = 0.35 eV. Finally, Beresford *et al.*[192]

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[185] E. E. Mendez, C.-A. Chang, H. Takaoka, L. L. Chang, and L. Esaki, *J. Vac. Sci. Technol. B* **1**, 152 (1983).

[186] G. Griffiths, K. Mohammed, S. Subbanna, H. Kroemer, and J. L. Merz, *Appl. Phys. Lett.* **43**, 1059 (1983).

[187] G. Bastard, *Phys. Rev. B* **24**, 5693 (1981).

[188] P. Voisin, C. Delalande, M. Voos, L. L. Chang, A. Segmuller, C.-A. Chang, and L. Esaki, *Phys. Rev. B* **30**, 2276 (1984).

[189] C. Tejedor, J. M. Calleja, F. Meseguer, E. E. Mendez, C.-A. Chang, and L. Esaki, *Phys. Rev. B* **32**, 5303 (1985).

[190] E. T. Yu, M. C. Phillips, D. H. Chow, D. A. Collins, M. W. Wang, J. O. McCaldin, and T. C. McGill. Submitted to *Phys. Rev. B.*

[191] U. Cebulla, G. Tränkle, U. Ziem, A. Forchel, G. Griffiths, H. Kroemer, and S. Subbanna, *Phys. Rev. B* **37**, 6278 (1988).

[192] R Beresford, L. F. Luo, and W. I. Wang, *Appl. Phys. Lett.* **55**, 694 (1989).

observed resonant tunneling of holes in GaSb/AlSb/GaSb/AlSb/GaSb heterostructures, consistent with a substantial valence-band offset, ΔE_v(GaSb/AlSb) ~ 0.4 eV. On the basis of these results, it appears that the GaSb/AlSb heterojunction is indeed characterized by a fairly large valence-band offset, ΔE_v(GaSb/AlSb) ≈ 0.4 eV.

For the last remaining combination, InAs/AlSb, only a single band offset measurement has been reported. Nakagawa *et al.*[115] used capacitance-voltage measurements to obtain a conduction-band offset ΔE_c(InAs/AlSb) = 1.35 ± 0.05 eV, corresponding to a valence-band offset ΔE_v(InAs/AlSb) = 0.09 ± 0.05 eV. Strain effects were not included in this measurement; however, the lattice mismatch of ~1.1% between InAs and AlSb could exert a significant influence on band offsets in coherently strained InAs/AlSb heterojunctions.

The relative positions of the energy bands in the InAs/GaSb/AlSb material system, based on the band offset measurements described in this section, are shown in Fig. 17. Combining the band offset measurements for the InAs/GaSb, GaSb/AlSb, and InAs/AlSb heterojunctions, one can see that the transitivity rule is satisfied to a high degree of accuracy:

$$\begin{aligned}\Delta E_v(\mathrm{InAs/GaSb}) + \Delta E_v(\mathrm{GaSb/AlSb}) + \Delta E_v(\mathrm{AlSb/InAs}) &= 0.51 - 0.40 - 0.09 \\ &= 0.02\ \mathrm{eV}. \qquad (10.1)\end{aligned}$$

From Eq. (10.1) one can argue that deviations from ideal interface structure, if present, exert a relatively small influence on band offsets for this material system. One might have expected such effects to be particularly prominent for the InAs/GaSb interface because of the possibility of forming two distinct types of interface structures (InSb-like or GaAs-like). XPS measurements by Gualtieri *et al.*[98] yielded a valence-band offset of 0.53 eV for InAs deposited on GaSb and a value of 0.48 eV for GaSb deposited on InAs. One might expect that the detailed structure of the interface could be somewhat different for these two growth sequences, and this result therefore suggests that interfacial strain at the InAs/GaSb heterojunction exerts a very limited (< 0.05 eV) influence on band offset values. However, the data of Srivastava *et al.*[116] yielded a valence-band offset $\Delta E_v = 0.67$ eV for the InAs/GaSb heterojunction; interface strain or possibly even a nonabrupt interface in the InAs/GaSb heterojunction may be at least partially responsible for the discrepancy between the results of Srivastava *et al.* and the other measurements that have been reported.[93,98,165,166]

b. *Theory*

Most of the available predictions for band offsets in the InAs/GaSb/AlSb material system are in good agreement with each other and with experimental measurements, the major exceptions being the predictions of early theories for the GaSb/AlSb and InAs/AlSb valence-band offsets. Theoretical band offset values for the InAs/GaSb/AlSb material system are summarized in Fig. 18 and Table VI. The pseudopotential theory of Frensley and Kroemer[23] yields valence-band offsets of 0.49 eV, 0.05 eV, and 0.44 eV for InAs/GaSb, AlSb/GaSb, and InAs/AlSb, respectively. Harrison's LCAO theory[24] predicts ΔE_v(InAs/GaSb) = 0.52 eV, ΔE_v(AlSb/GaSb) = -0.02 eV (valence-band edge of GaSb below that of AlSb), and ΔE_v(InAs/AlSb) = 0.54 eV. Tersoff[28] obtains valence-band offsets of 0.43 eV for InAs/GaSb, 0.38 eV for AlSb/GaSb, and 0.05 eV for InAs/AlSb, whereas Harrison and Tersoff[29] predict ΔE_v(InAs/GaSb) = 0.33 eV, ΔE_v(AlSb/GaSb) = 0.09 eV, and ΔE_v = (InAs/AlSb) = 0.24 eV. The dielectric midgap energy model of Cardona and Christensen[39] yields ΔE_v(InAs/GaSb) = 0.54 eV, ΔE_v(AlSb/GaSb) = 0.30 eV, and ΔE_v(InAs/AlSb) = 0.23 eV, and the model solid theory[86] predicts valence-band offsets of 0.56 eV for InAs/GaSb, 0.46 eV for AlSb/GaSb, and 0.10 eV for InAs/AlSb. The interface bond polarity model of Lambrecht and Segall[87] yields valence-band offsets of 0.59 eV, 0.31 eV, and 0.27 eV for the InAs/GaSb, AlSb/GaSb, and InAs/AlSb heterojunctions, respectively. The electron affinity rule[19] yields ΔE_v(InAs/GaSb) = 0.52 eV, ΔE_v(AlSb/AlSb) = 0.51 eV, and ΔE_v(InAs/AlSb) = 0.01 eV using the electron affinity data of Milnes and Feucht,[71] and ΔE_v(InAs/GaSb) = 0.54 eV, ΔE_v(AlSb/GaSb) = 0.44 eV, and ΔE_v(InAs/AlSb) = 0.10 eV using the compilation of Freeouf and Woodall.[193] The empirical compilation of Katnani and Margaritondo[21] predicts ΔE_v(InAs/GaSb) = 0.12 eV, and the common anion rule[20] yields a valence-band offset of 0.41 eV for the InAs/GaSb heterojunction. Self-consistent calculations of Van de Walle and Martin[84] yield valence-band offsets of 0.38 eV for both the InAs/GaSb and the AlSb/GaSb heterojunctions, and self-consistent LMTO calculations by Christensen[40] predict ΔE_v(InAs/GaSb) = 0.46 eV and ΔE_v(AlSb/GaSb) = 0.45 eV. Self-consistent dipole calculations by Lambrecht *et al.*[43] yield valence-band offsets of 0.44 eV for InAs/GaSb, 0.40 eV for AlSb/GaSb, and 0.07 eV for InAs/AlSb.

V. II–VI Material Systems

There has been considerable interest in II–VI heterojunction systems both for long-wavelength infrared applications and for wide-band-gap visible light-emitting devices. However, with a few exceptions, e.g., HgTe/CdTe, far fewer measurements are available for II–VI heterojunction systems than for III–V interfaces. In this section we review the available data for band offsets in lattice-matched II–VI heterojunction systems.

[193] J. L. Freeouf and J. M. Woodall, *Appl. Phys. Lett.* **39**, 727 (1981).

11. HgTe/CdTe

HgTe/CdTe superlattices have been proposed as a promising material for fabrication of long-wavelength infrared detectors.[194,195] Pure HgTe is a semimetal with an inverted band structure: the conduction band has Γ_8 (light-hole-like) symmetry and is degenerate with the heavy-hole valence band at the Brillouin zone center; the light-hole band has Γ_6 (conduction-band-like) symmetry and is approximately 0.26 eV below the heavy-hole valence-band edge in energy. Figure 19 shows schematic energy band diagrams for HgTe and CdTe. $Hg_{1-x}Cd_xTe$ alloys can have very narrow band gaps and are therefore of interest for long-wavelength infrared applications. Narrow-band-gap HgTe/CdTe superlattices were proposed as an alternative to $Hg_{1-x}Cd_xTe$ alloys. The superlattice band gap is determined primarily by the HgTe layer thickness in the superlattice, whereas the $Hg_{1-x}Cd_xTe$ alloy

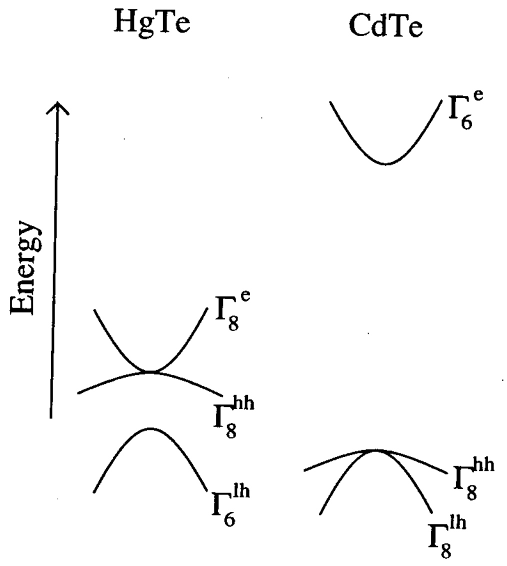

FIG. 19. Schematic energy band diagrams for HgTe and CdTe. CdTe is characterized by a normal band structure, with a Γ_6 conduction band and Γ_8 light-hole and heavy-hole valence bands. HgTe is characterized by an inverted band structure. The Γ_6 *s*-like band is below the Γ_8 valence bands, has negative effective mass, and acts as a filled valence band. The Γ_8 light-hole band has a positive effective mass and acts as the empty conduction band, producing a semiconductor with zero band gap.

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[194] J. N. Schulman and T. C. McGill, *Appl. Phys. Lett.* **34**, 663 (1979).

[195] D. L. Smith, T. C. McGill, and J. N. Schulman, *Appl. Phys. Lett.* **43**, 180 (1983).

band gap is determined by the alloy composition x. The superlattice structure would therefore allow better control over the detector cutoff wavelength, because the superlattice layer thickness can be controlled more easily than the composition of a comparable $Hg_{1-x}Cd_xTe$ alloy.[195] Properties of these superlattices, such as the superlattice band gap, can depend quite sensitively on the value of the HgTe/CdTe band offset,[196] particularly if the valence-band offset deviates significantly from the very small discontinuity originally postulated on the basis of the common-anion rule.[20]

a. *Experiment*

The available experimental data for the HgTe/CdTe valence-band offset are summarized in Fig. 20 and Table VII. Kuech and McCaldin[197] characterized the electrical behavior of HgTe/CdTe lattice-matched heterojunctions grown by a low-temperature metal organic chemical vapor deposition technique. Photoresponse and J–V measurements indicated that the HgTe/CdTe heterojunctions exhibited Schottky-barrier-like behavior, with the barrier height, i.e., the conduction-band offset, ranging from 0.65 to 0.92 eV, depending on the effective donor concentration in the CdTe layer. This

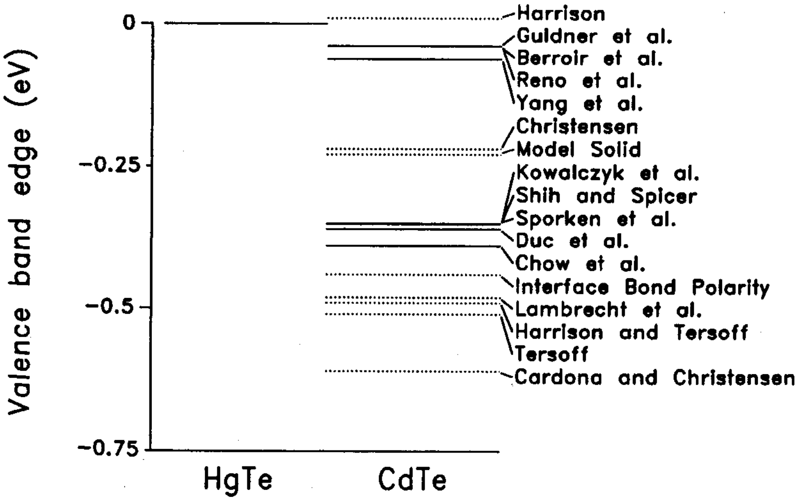

FIG. 20. Summary of experimental and theoretical valence-band offsets for the HgTe/CdTe heterojunction. For the CdTe valence-band edge, experimental measurements and theoretical calculations are indicated by solid and dotted lines, respectively.

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[196] G. Y. Wu and T. C. McGill, *J. Appl. Phys.* **58**, 3914 (1985).

[197] T. F. Kuech and J. O. McCaldin, *J. Appl. Phys.* **53**, 3121 (1982).

TABLE VII. EXPERIMENTAL VALENCE-BAND OFFSET VALUES FOR CdTe/HgTe

SOURCE	TEMPERATURE (K)	ΔE_v (expt.) (eV)
Guldner *et al.* (1983)[198]	1.6	0.04 ± 0.01
Berroir *et al.* (1986)[199]	1.6	0–0.100
Reno *et al.* (1986)[200]	2	0.04
Yang *et al.* (1988)[201]	5	0.063 ± 0.005
Kowalczyk *et al.* (1986)[100]	300	0.35 ± 0.06
Duc *et al* (1987)[101]	300	0.36 ± 0.05
Shih and Spicer (1987)[202]	300	0.35 ± 0.06
Chow *et al.* (1987)[110]	300	0.39 ± 0.075[a]
Sporken *et al.* (1989)[206]	50–300	0.35 ± 0.05

[a]Evidence was observed that the valence-band offset decreases at low temperature.

dependence was taken as evidence for the formation of an inversion layer at the HgTe/CdTe interface, and it was postulated that the actual barrier height was large, corresponding to a small HgTe/CdTe valence-band offset, and that the inversion layer reduced the effective barrier height deduced from the electrical measurements.

Guldner *et al.*[198] performed the first actual measurement of the band offset for HgTe/CdTe, obtaining a very small valence-band offset, $\Delta E_v = 0.04 \pm 0.01$ eV, from an analysis of far-infrared magnetoabsorption measurements on a semimetallic HgTe/CdTe (111) superlattice. Subsequent magnetoabsorption measurements by Berrior *et al.*[199] on an *n*-type semiconducting CdTe (111) superlattice produced results consistent with a valence-band offset $\Delta E_v = 0.04$ eV and yielded lower and upper limits for the valence-band offset of 0 eV and 0.1 eV, respectively. Reno *et al.*[200] studied the room-temperature band gap as a function of HgTe layer thickness in HgTe/CdTe superlattices and obtained results consistent with a small valence-band offset, $\Delta E_v = 0.04$ eV. Yang and Furdyna[201] deduced a valence-band offset $\Delta E_v = 0.063 \pm 0.005$ eV by analyzing far-infrared magnetoabsorption measurements and relating the energy difference between the first heavy-hole subband

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[198] Y. Guldner, G. Bastard, J. P. Vieren, M. Voos, J. P. Faurie, and A. Million, *Phys. Rev. Lett.* **51**, 907 (1983).

[199] J. M. Berroir, Y. Guldner, J. P. Vieren, M. Voos, and J. P. Faurie, *Phys. Rev. B* **34**, 891 (1986).

[200] J. Reno, I. K. Sou, J. P. Faurie, J. M. Berrior, Y. Guldner, and J. P. Vieren, *Appl. Phys. Lett.* **49**, 106 (1986).

[201] Z. Yang and J. K. Furdyna, *Appl. Phys. Lett.* **52**, 498 (1988).

and the first light-hole subband in two HgTe/CdTe (100) superlattices to the valence-band offset.

A number of measurements, however, have yielded substantially larger valence-band offsets for the HgTe/CdTe heterojunction. Kowalczyk *et al.*[100] used XPS to measure the HgTe/CdTe $(\overline{111})$ valence-band offset directly and obtained $\Delta E_v = 0.35 \pm 0.06$ eV. Duc *et al.*[101] also performed XPS measurements for the HgTe/CdTe heterojunction and obtained $\Delta E_v = 0.36 \pm 0.05$ eV. Shih and Spicer[202] used synchrotron photoemission spectroscopy to measure a "natural" valence-band offset, a quantity they claimed to be the change in the energy of the valence-band edge that is intrinsic to the bulk band structure of the heterojunction constituents; their measurements yielded a natural valence-band offset of 0.35 ± 0.06 eV. Current–voltage measurements in $Hg_{0.78}Cd_{0.22}Te/CdTe/Hg_{0.78}Cd_{0.22}Te$ single-barrier heterostructures by Chow *et al.*[110] yielded a valence-band offset of 0.39 ± 0.075 eV for the HgTe/CdTe heterojunction at 300 K. There was some evidence in these experiments that the valence-band offset might decrease at low temperature, possibly accounting for the discrepancy between the room-temperature photoemission data and the low-temperature magnetoabsorption experiments. The observation by Chow *et al.*[203] of negative differential resistance in a HgCdTe/CdTe/HgCdTe single-barrier heterostructure also suggests that at low temperature the HgTe/CdTe valence-band offset is small—less than 0.1 eV. Faurie *et al.*[204] also suggested that a temperature dependence of the valence-band offset might be responsible for the disagreement between the two types of experiments, and Malloy and Van Vechten[205] performed theoretical model calculations that predicted a strong temperature dependence for the HgTe/CdTe valence-band offset. Sporken *et al.*,[206] however, studied the temperature dependence of the HgTe/CdTe valence-band offset using XPS and UPS and found that the valence-band offset changed by only a few milli-electron-volts between 300 K and 50 K; their measurements yielded a valence-band offset of 0.35 ± 0.05 eV.

A possible resolution of the conflicting results obtained in the photoemission and current-voltage measurements at room temperature and the low-temperature magnetoabsorption measurements has been proposed by Johnson, Hui, and Ehrenreich.[207,208] Calculations of superlattice band

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[202] C. K. Shih and W. E. Spicer, *Phys. Rev. Lett.* **58**, 2594 (1987).

[203] D. H. Chow, T. C. McGill, I. K. Sou, J. P. Faurie, and C. W. Nieh, *Appl. Phys. Lett.* **52**, 54 (1988).

[204] J. P. Faurie, C. Hsu, and T. M. Duc, *J. Vac. Sci. Technol. A* **5**, 3074 (1987).

[205] K. J. Malloy and J. A. Van Vechten, *Appl. Phys. Lett.* **54**, 937 (1989).

[206] R. Sporken, S. Sivananthan, J. P. Faurie, D. H. Ehlers, J. Fraxedas, L. Ley, J. J. Pireaux, and R. Caudano, *J. Vac. Sci. Technol. A* **7**, 427 (1989).

[207] N. F. Johnson, P. M. Hui, and H. Ehrenreich, *Phys. Rev. Lett.* **61**, 1993 (1988).

[208] P. M. Hui, H. Ehrenreich, and N. F. Johnson, *J. Vac. Sci. Technol. A* **7**, 424 (1989).

structure using an envelope-function approach[209,210] demonstrated that the magnetoabsorption data of Berrior *et al.*[199] are actually better described by a large valence-band offset ($\sim$0.35 eV) than by the small valence-band offset ($\sim$0.04 eV) that was proposed originally. The calculations of Johnson *et al.* showed that for the superlattice structure used in the experiments of Ref. 199 the superlattice is semiconducting, as observed experimentally, for small valence-band offsets; the superlattice becomes semimetallic as the valence-band offset is increased above 0.23 eV but reverts to semiconducting behavior for valence-band offsets greater than 0.295 eV. The superlattice band gap and electron cyclotron mass calculated for a valence-band offset of 0.35 eV were in good agreement with the experimental values reported by Berroir *et al.*[199]

The results reported to date for the HgTe/CdTe heterojunction indicate quite clearly that that valence-band offset at room temperature is large, ΔE_v(HgTe/CdTe) = 0.35 eV. At low temperature, however, the situation is more ambiguous. The measurements of Sporken *et al.*[206] suggest that the HgTe/CdTe valence-band offset remains nearly constant as the temperature is decreased from room temperature to 50 K. Near 4.2 K, the measurements of Chow *et al.*[110,203] suggest that the valence-band offset is small, but the magnetoabsorption data[199] from HgTe/CdTe superlattices appear to be consistent with both large ($\sim$0.35 eV) and small valence-band offsets.

TABLE VIII. THEORETICAL PREDICTIONS FOR THE CdTe/HgTe VALENCE-BAND OFFSET

SOURCE	ΔE_v (theor.) (eV)
Harrison (1977)[24]	−0.01
Tersoff (1986)[28]	0.51
Harrison and Tersoff (1986)[29]	0.49
Van de Walle and Martin (1987)[84] (model solid theory)	0.23
Cardona and Christensen (1987)[39] (dielectric midgap energy model)	0.61
Christensen (1988)[40]	0.22
Langer and Heinrich (1988)[215]	0.35
Lambrecht *et al.* (1990)[43] (self-consistent dipole)	0.48
Lambrecht and Segall (1990)[87] (interface bond polarity model)	0.44

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[209] N. F. Johnson, H. Ehrenreich, K. C. Hass, and T. C. McGill, *Phys. Rev. Lett.* **59**, 2352 (1987).

[210] N. F. Johnson, H. Ehrenreich, G. Y. Wu, and T. C. McGill, *Phys. Rev. B* **38**, 13095 (1988).

b. *Comparison with Theory*

Theoretical values for the HgTe/CdTe valence-band offset are shown in Fig. 20 and Table VIII. Early treatments of the HgTe/CdTe heterojunction system typically assumed, on the basis of the predictions of the common-anion rule,[20] that the HgTe/CdTe valence-band offset was small. This was done despite the fact that in the original work of McCaldin *et al.*[20] it was not claimed that the common-anion rule would be applicable to compounds containing Hg. The original HgTe/CdTe superlattice proposal[194,211] assumed, on the basis of the electron affinity rule[19] and available electron affinity data for HgTe[212] and CdTe,[212,213] that the HgTe/CdTe valence-band offset was zero. However, the available electron affinity measurements for these materials yield values for the HgTe/CdTe valence-band offset ranging from -0.1 eV (valence band of HgTe below that of CdTe) to 0.3 eV, suggesting that a substantial value for the valence-band offset might be plausible.

Only a few of the early theoretical and empirical treatments of band offsets addressed the HgTe/CdTe heterojunction, and these typically predicted small valence-band offsets for HgTe/CdTe. If the atomic energies given by Harrison[214] are used to calculate valence-band-edge energies for HgTe and CdTe in Harrison's LCAO theory,[24] a valence-band offset of only -0.01 eV is obtained. As we have discussed, the electron affinity rule predicts valence-band offsets ranging from -0.1 eV to 0.3 eV.

Later treatments typically yield substantially larger valence-band offset values. The theory of Tersoff,[28] developed concurrently with but independently of the XPS measurement of Kowalczyk *et al.*,[100] yields a valence-band offset $\Delta E_v(\text{HgTe/CdTe}) = 0.51$ eV. The theory of Harrison and Tersoff[29] yields a very similar result, $\Delta E_v(\text{HgTe/CdTe}) = 0.49$ eV. The transition-metal impurity alignment postulated by Langer and Heinrich[32] predicts a valence-band offset $\Delta E_v(\text{HgTe/CdTe}) = 0.35$ eV, based on an alignment of the Fe impurity level in HgTe and CdTe.[215] The model solid theory of Van de Walle and Martin[86] predicts a valence-band offset for HgTe/CdTe of 0.23 eV. The dielectric midgap energy model of Cardona and Christensen[39] predicts $\Delta E_v(\text{HgTe/CdTe}) = 0.64$ eV, but Christensen[40] has performed self-consistent

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[211] J. N. Schulman and T. C. McGill, *J. Vac. Sci. Technol.* **16**, 1513 (1979).

[212] N. J. Shevchik, J. Tejeda, M. Cardona, and D. W. Langer, *Phys. Status Solidi (B)* **59**, 87 (1973).

[213] R. K. Swank, *Phys. Rev.* **153**, 844 (1967).

[214] W. A. Harrison, "Electronic Structure and the Properties of Solids," pp. 552–553, Dover Publications, New York, 1989.

[215] H. Heinrich, in "New Developments in Semiconductor Physics," Proceedings of the Third Summer School Held at Szeged, Hungary (G. Ferenczi and F. Beleznay, eds), p. 126, Springer-Verlag, New York, 1988.

LMTO calculations of the electronic structure at the HgTe/CdTe heterojunction and found that, because of anomalous charge transfer associated with the formation of interface states, the dielectric midgap energy model should not be expected to be accurate. Christensen's LMTO calculations yield a valence-band offset ΔE_v(HgTe/CdTe) = 0.22 eV. The self-consistent dipole calculations of Lambrecht *et al.*[43] yield a HgTe/CdTe valence-band offset of 0.48 eV, and the interface bond polarity model[87] derived from these calculations predicts a value of 0.44 eV. The scatter among these theoretical values is relatively large, but the qualitative conclusion that a substantial valence-band offset exists in the HgTe/CdTe heterojunction is strongly supported by the more recent theories.

12. CdSe/ZnTe

a. *Experiment*

Although CdSe occurs naturally in the wurtzite crystal structure, a number of investigators have demonstrated that high-quality CdSe in the cubic zincblende structure can be deposited by molecular-beam epitaxy on ZnTe with a lattice mismatch of only ~0.44%.[216–218] In addition, a number of studies of the CdSe/ZnTe heterojunction system were performed several years prior to these demonstrations, but the samples used for these investigations were probably of low quality compared to those that can be grown by current techniques such as molecular-beam epitaxy. The available experimental data on the CdSe/ZnTe valence-band offset are included in Table IX. Gashin and Simashkevich[219,220] fabricated CdSe/ZnTe heterojunctions by evaporating CdSe onto (110) ZnTe, obtaining cubic CdSe with the same crystallographic orientation as the substrate for substrate temperatures ranging from 450 to 700°C. On the basis of electrical measurements and the electron affinity rule for conduction-band offsets,[19] Gashin and Simashkevich proposed a valence-band offset of ~0.13 eV and a conduction-band offset of ~0.4 eV, corresponding to a type I band lineup. However, their

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[216] N. Samarth, H. Luo, J. K. Furdyna, S. B. Qadri, Y. R. Lee, A. K. Ramdas, and N. Otsuka, *Appl. Phys. Lett.* **54**, 2680 (1990).

[217] M. C. Phillips, E. T. Yu, Y. Rajakarunanayake, J. O. McCaldin, D. A. Collins, and T. C. McGill, *J. Cryst. Growth* **111**, 820 (1991).

[218] E. T. Yu, M. C. Phillips, J. O. McCaldin, and T. C. McGill, *J. Vac. Sci. Technol. B* **9**, 2233 (1991).

[219] P. A. Gashin and A. V. Simashkevich, *Phys. Status Solidi (A)* **19**, 379 (1973).

[220] P. A. Gashin and A. V. Simashkevich, *Phys. Status Solidi (A)* **19**, 615 (1973).

[221] F. Buch, A. L. Fahrenbruch, and R. H. Bube, *Appl. Phys. Lett.* **28**, 593 (1976).

[222] F. Buch, A. L. Fahrenbruch, and R. H. Bube, *J. Appl. Phys.* **48**, 1596 (1977).

TABLE IX. EXPERIMENTAL AND THEORETICAL VALENCE-BAND OFFSETS FOR CdSe/ZnTe

SOURCE	ΔE_v (expt.) (eV)	ΔE_v (theor.) (eV)
Buch *et al.* (1976)[221,222]	0.23	
Yu *et al.* (1991)[218]	0.64 ± 0.07	
Milnes and Feucht (1972)[71]		0.89
McCaldin *et al.* (1976)[20]		0.55
Frensley and Kroemer (1977)[23]		0.55
Frensley and Kroemer (1977)[23] (with dipole correction)		0.64
Harrison (1977)[24]		0.85
Freeouf and Woodall (1981)[193]		0.86
Katnani and Margaritondo (1983)[21]		0.35
Harrison and Tersoff (1986)[29]		0.31
Cardona and Christensen (1987)[39]		0.61

estimate of the band offset assumed an electron affinity for CdSe of 3.93 eV, whereas Milnes and Feucht[71] give an electron affinity of 4.95 eV for CdSe. Buch *et al.*[221,222] studied photovoltaic properties of *n*-CdSe/*p*-ZnTe heterojunctions and proposed a CdSe/ZnTe band diagram with a valence-band offset of 0.23 eV and a conduction-band offset of 0.75 eV, corresponding to a type II band alignment.

Several of these early investigations also yielded evidence for interdiffusion of atoms and the resulting formation of an intermediate compound or solid solution at the CdSe/ZnTe interface. However, these studies were performed using material prepared by relatively primitive methods, and the resulting samples were probably of poor quality compared to those grown by modern techniques such as MBE. Fedotov *et al.*[223] observed diffusion of Cd, Zn, and Te atoms in CdSe/ZnTe and CdS/ZnTe heterojunctions and the resulting formation of a region of solid solution, with apparent diffusion lengths of up to several micrometers. Buch *et al.*[221,222] postulated the formation of a $CdSe_{1-x}Te_x$ layer at the CdSe/ZnTe interface on the basis of evidence of absorption near the heterojunction interface at energies as low as 1.45 eV. Photocurrent and cathodoluminescence studies by Simashkevich and Tsiulyanu[224] suggested that a CdSe/ZnTe solid solution was formed at the CdSe/ZnTe heterojunction interface. Finally, Senokosov and Usatyĭ[225]

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[223] Ya. A. Fedotov, S. G. Konnikov, V. A. Supalov, N. M. Kondaurov, A. N. Kovalev, and A. V. Vanyukov, translated from *Izv. Akad. Nauk SSSR Neorg. Mater.* **11**, 2148 (1975).

[224] A. V. Simashkevich and R. L. Tsiulyanu, *J. Cryst. Growth* **35**, 269 (1976).

[225] É. A. Senokosov and A. N. Usatyĭ, *Sov. Phys. Semicond.* **12**, 575 (1978).

postulated, on the basis of electrical and photoresponse measurements, that a high-resistivity layer of CdTe was formed by interdiffusion at an *n*-CdSe/*p*-ZnTe heterojunction.

The advent of crystal growth techniques such as molecular-beam epitaxy has enabled investigators to prepare samples of much higher quality than those used in the aforementioned experiments. Samples can be grown and characterized under carefully controlled conditions, and the resulting measurements are of much greater reliability. Yu *et al.*[218] have used XPS to measure the CdSe/ZnTe valence-band offset for structures grown by molecular-beam epitaxy. Pure ZnTe and cubic zincblende CdSe samples, and heterojunctions consisting of either CdSe deposited on ZnTe or ZnTe deposited on CdSe, were grown by molecular-beam epitaxy; XPS measurements on these samples yielded a valence-band offset $\Delta E_v = 0.64 \pm 0.07$ eV, corresponding to a conduction-band offset $\Delta E_c = 1.22$ eV and a type II band alignment. Commutativity of the band offset was confirmed, although there was also some evidence that the band offset can depend on growth conditions. We consider this measurement to be the most reliable determination of the CdSe/ZnTe valence-band offset.

b. *Theory*

Theoretical predictions for the CdSe/ZnTe valence-band offset extend over a wide range of values. Calculated band offset values for CdSe/ZnTe are included in Table IX. The electron affinity rule[19] predicts $\Delta E_v = 0.89$ eV using the electron affinity data of Milnes and Feucht[71] and $\Delta E_v = 0.86$ eV if the compilation of Freeouf and Woodall[193] is used. Harrison's LCAO theory[24] yields a value of 0.85 eV for the CdSe/ZnTe valence-band offset, and Kraut's adaptation of Harrison's theory[79] using Hartree–Fock neutral atom energies predicts $\Delta E_v = 1.11$ eV. Frensley and Kroemer's pseudopotential theory yields a valence-band offset of 0.55 eV without interfacial dipole corrections and 0.64 eV with dipole corrections included.[23] The theory of Harrison and Tersoff[29] predicts $\Delta E_v = 0.31$ eV. The dielectric midgap energy model of Cardona and Christensen[39] yields a valence-band offset $\Delta E_v = 0.61$ eV.[226] Among the more empirical theories, the common-anion rule[20] predicts $\Delta E_v = 0.55$ eV, and Katnani and Margaritondo[21] obtain $\Delta E_v = 0.35$ eV. The number of theoretical predictions for the CdSe/ZnTe band offset is somewhat limited compared to the number available for other heterojunctions because of the natural wurtzite crystal structure of CdSe; in particular, self-consistent calculations for specific interfaces, such as those of Van de Walle and Martin,[37,38] of Christensen,[40,41] and of Lambrecht *et al.*,[42,43]

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[226] N. E. Christensen, I. Gorczyca, O. B. Christensen, U. Schmid, and M. Cardona, *J. Cryst. Growth* **101**, 318 (1990).

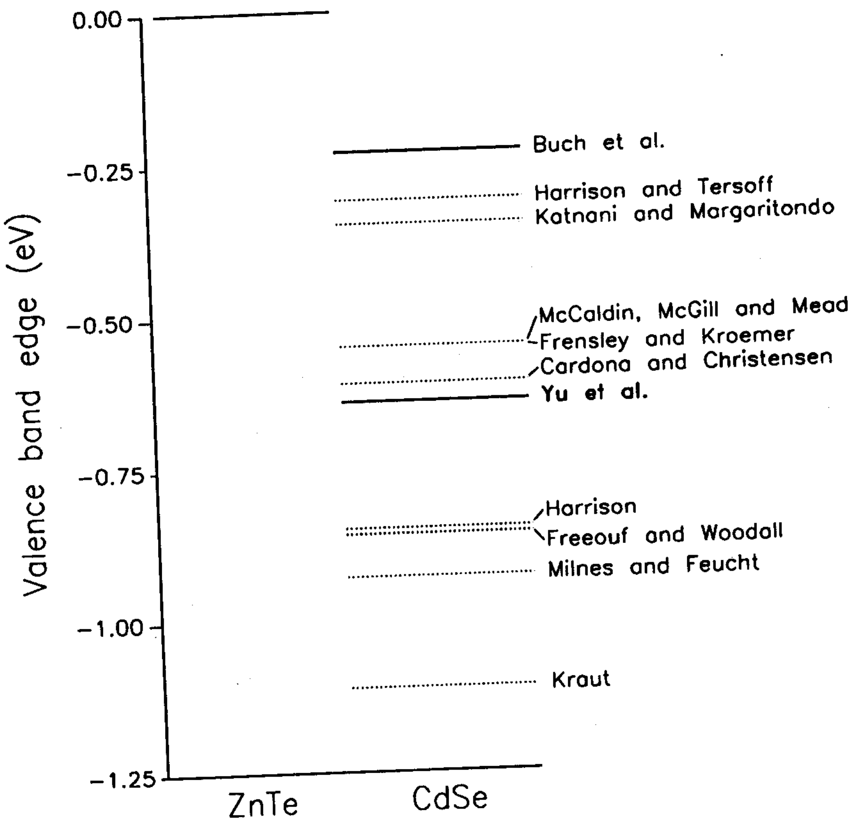

FIG. 21. Valence-band offset values for the CdSe/ZnTe heterojunction predicted by several theories,[19–22,24,29,39,71,79,193] and the valence-band offset values obtained from the measurements of Buch *et al.*[221,222] and of Yu *et al.*[218]

have not been published for the CdSe/ZnTe interface. Figure 21 shows the experimental CdSe/ZnTe valence-band offsets of Yu *et al.*[218] and of Buch *et al.*[221,222] amidst several theoretical predictions for the CdSe/ZnTe valence-band offset; Fig. 22 shows the band alignment corresponding to the measurements of Yu *et al.* for the CdSe/ZnTe heterojunction.

13. OTHER II–VI HETEROJUNCTIONS

a. *Dilute Magnetic Semiconductors*

Materials such as $Cd_{1-x}Mn_xSe$, $Zn_{1-x}Mn_xTe$, $Zn_{1-x}Mn_xSe$, $Hg_{1-x}Mn_xTe$, and $Hg_{1-x}Mn_xSe$ are members of a class of materials known

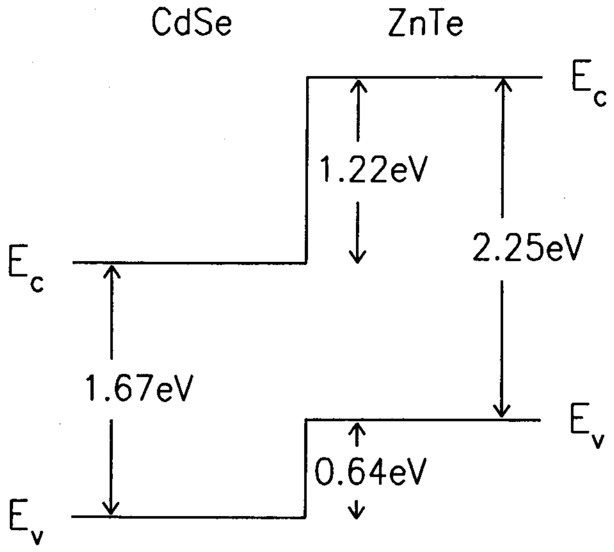

FIG. 22. Conduction- and valence-band alignments determined from the measurements of Yu *et al.*[218] for the CdSe/ZnTe heterojunction. Yu *et al.*obtained $\Delta E_v = 0.64 \pm 0.07$ eV, corresponding to $\Delta E_c = 1.22 \pm 0.07$ eV and yielding a type II, staggered band alignment. Taken from E. T. Yu, M. C. Phillips, J. O. McCaldin, and T. C. McGill, *J. Vac. Sci. Technol. B.* **9**, 2233 (1991).

as semimagnetic (or dilute magnetic) semiconductors. The presence of Mn in these materials gives rise to a number of interesting magnetic and magneto-optic properties. $Cd_{1-x}Mn_xTe$ epilayers,[227,228] $CdTe/Cd_{1-x}Mn_xTe$ superlattices,[229,230] $ZnSe/Zn_{1-x}Mn_xSe$,[231] ZnCdSe/ZnMnSe,[232] and ZnTe/MnTe heterostructures[233] and $Hg_{1-x}Mn_xTe$ epilayers[234] have been grown successfully using molecular-beam epitaxy, and $Cd_{1-x}Mn_xTe/Cd_{1-y}Mn_yTe$

[227] L. A. Kolodziejski, T. Sakamoto, R. L. Gunshor, and S. Datta, *Appl. Phys. Lett.* **44**, 799 (1984).

[228] M. Pessa and O. Jylhä, *Appl. Phys. Lett.* **45**, 646 (1984).

[229] R. N. Bicknell, R. W. Yanka, N. C. Giles-Taylor, D. K. Blanks, E. L. Buckland, and J. F. Schetzina, *Appl. Phys. Lett.* **45**, 92 (1984).

[230] L. A. Kolodziejski, T. C. Bonsett, R. L. Gunshor, S. Datta, R. B. Bylsma, W. M. Becker, and N. Otsuka, *Appl. Phys. Lett.* **45**, 440 (1984).

[231] Y. Hefetz, J. Nakahara, A. V. Nurmikko, L. A. Kolodziejski, R. L. Gunshor, and S. Datta, *Appl. Phys. Lett.* **47**, 989 (1985).

[232] W. J. Walecki, A. V. Nurmikko, N. Samarth, H. Luo, J. K. Furdyna, and N. Otsuka, *Appl. Phys. Lett.* **57**, 466 (1990).

[233] N. Pelekanos, J. Ding, Q. Fu, A. V. Nurmikko, S. M. Durbin, M. Kobayashi, and R. L. Gunshor, *Phys. Rev. B* **43**, 9354 (1991).

[234] J. P. Faurie, J. Reno, S. Sivananthan, I. K. Sou, X. Chu, M. Boukerche, and P. S. Wijewarnasuriya, *J. Vac. Sci. Technol. A* **4**, 2067 (1986).

and $Hg_{1-x}Mn_xTe/Cd_{1-y}Mn_yTe$ superlattices have been proposed as possibilities for magnetically turnable laser and infrared materials, respectively.

A number of studies of $CdTe/Cd_{1-x}Mn_xTe$ multiple quantum wells and superlattices have been reported. The lattice constant a_0 for $Cd_{1-x}Mn_xTe$ decreases linearly with x and is given by $a_0 = (6.487 - 0.149x)$Å. $CdTe/Cd_{1-x}Mn_xTe$ heterojunctions can therefore be grown with little strain for low Mn concentrations, but for large values of x strain effects could be significant. The crystal structure of $Cd_{1-x}Mn_xTe$ is cubic zincblende for $x \lesssim 0.7$–0.75 and hexagonal NiAs for larger values of x. The energy band gap of $Cd_{1-x}Mn_xTe$ increases with composition x; electroreflectance measurements[235] yielded an energy band gap of approximately $1.50 + 1.44x$ eV at room temperature, and studies of piezomodulated and photomodulated reflectivity spectra from $Cd_{1-x}Mn_xTe$ yielded a free exciton energy $1.528 + 1.316x$ eV at 300 K.[236]

Experimental studies of band offsets in the $CdTe/Cd_{1-x}Mn_xTe$ heterojunction have generally yielded fairly small values for the valence-band offset. Pessa and Jylhä[228] studied angle-resolved photoemission from $Cd_{0.6}Mn_{0.4}Te/CdTe$ interfaces and found that the energy of the valence-band maximum did not shift (within ±0.05 eV) upon alloying, suggesting that the $Cd_{0.6}Mn_{0.4}Te/CdTe$ valence-band offset is small. Shih *et al.*[237] used photoemission measurements on $Cd_{1-x}Mn_xTe$ alloys to determine that the "natural" valence-band offset for the CdTe/MnTe heterojunction was zero to within the limits of their experimental uncertainty. Chang *et al.*[238] performed photoluminescence excitation spectroscopy on $CdTe/Cd_{1-x}Mn_xTe$ multiple quantum wells and for $x = 0.24$ deduced a type I band alignment with a heavy-hole valence-band offset $\Delta E_{hh} = 0.025$ eV, corresponding to a conduction-band offset of approximately 0.36 eV. Gregory *et al.*[239] studied photoluminescence spectra from $CdTe/Cd_{1-x}Mn_xTe$ multiple quantum wells in the presence of a magnetic field and for $x = 0.25$ obtained a valence-band offset in the range 0.030–0.055 eV, also with a type I band alignment. Deleporte *et al.*[240] studied photoluminescence and photoluminescence excitation spectra from $CdTe/Cd_{0.93}Mn_{0.07}Te$ superlattices in the presence of a magnetic field and deduced a value for the valence-band offset, once the uniaxial strain

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[235] N. Bottka, J. Stankiewicz, and W. Giriat, *J. Appl. Phys.* **52**, 4189 (1981).

[236] Y. R. Lee, A. K. Ramdas, and R. L. Aggarwal, *Phys. Rev. B* **38**, 10600 (1988).

[237] C. K. Shih, W. E. Spicer, J. K. Furdyna, and A. Sher, *J. Vac. Sci. Technol. A* **5**, 3031 (1987).

[238] S.-K. Chang, A. V. Nurmikko, J.-W. Wu, L. A. Kolodziejski, and R. L. Gunshor, *Phys. Rev. B* **37**, 1191 (1988).

[239] T. J. Gregory, C. P. Hilton, J. E. Nicholls, W. E. Hagston, J. J. Davies, B. Lunn, and D. E. Ashenford, *J. Cryst. Growth* **101**, 594 (1990).

[240] E. Deleporte, J. M. Berroir, G. Bastard, C. Delalande, J. M. Hong, and L. L. Chang, *Superlattices Microstructures* **8**, 171 (1990).

splittings were eliminated, of approximately 15–20% of the total band-gap difference. Finally, Pelekanos *et al.*[241] used optical measurements to obtain band offset values $\Delta E_c = 1.28$ eV, $\Delta E_{hh} = 0.34$ eV, and $\Delta E_{lh} = 0.16$ eV for CdTe/MnTe quantum wells coherently strained to CdTe. In these studies, MnTe was grown in the cubic zincblende form rather than its natural crystal structure, hexagonal NiAs.

Band offsets have also been reported for the ZnSe/$Zn_{1-x}Mn_xSe$,[231] $Zn_{1-y}Cd_ySe/Zn_{1-x}Mn_xSe$,[232] and ZnTe/MnTe[233] heterojunctions. Hefetz *et al.*[231] studied optical spectra from ZnSe/$Zn_{1-x}Mn_xSe$ multiple quantum wells for $x = 0.23$ to $x = 0.51$. Measurements of optical spectra in the presence of a magnetic field suggested that the average valence-band offset $\Delta E_{v,av}$ was small, less than 0.02 eV for $x = 0.23$, at which composition the lattice mismatch between ZnSe and $Zn_{1-x}Mn_xSe$ was estimated to be 1.05%; the band-gap difference for unstrained material at this composition was estimated to be approximately 0.11 eV. Walecki *et al.*[232] used magneto-optical studies of nearly lattice-matched $Zn_{1-y}Cd_ySe/Zn_{1-x}Mn_xSe$ quantum wells to deduce a valence-band offset of 0.030 ± 0.005 eV. Pelekanos *et al.*[233] studied luminescence spectra from a ZnTe/MnTe quantum well and deduced a valence-band offset $\Delta E_v = 0.10$ eV. However, the way in which strain effects were incorporated was not stated; given the lattice mismatch between ZnTe and cubic zincblende MnTe of approximately 4%, the valence-band splittings in the MnTe barrier layers would be expected to be quite large. Nevertheless, the estimate of Pelakanos *et al.* suggests that the valence-band offset is small compared to the total band-gap difference of approximately 0.8 eV between ZnTe and cubic zincblende MnTe.

The band offset theory of Tersoff[28] predicts values for the CdTe/MnTe and ZnTe/MnTe band offsets, although without including effects arising from strain. In these calculations, the cubic zincblende structure was assumed for MnTe and the Mn *d* orbitals were not allowed to mix with the conduction- and valence-band states. For CdTe/MnTe and ZnTe/MnTe, valence-band offsets of 0.75 eV and 0.76 eV, respectively, were obtained. These values appear to be somewhat larger than those obtained experimentally, although it was noted in Tersoff's paper that the approximations made to treat MnTe would probably reduce the accuracy of the MnTe band offset values. The absence of strain effects in these predictions would also affect their expected accuracy; it has been noted by Cardona and Christensen[39] that strain effects, including uniaxial strain components, can strongly influence even the average

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[241] N. Pelekanos, Q. Fu, J. Ding, W. Walecki, A. V. Nurmikko, S. M. Durbin, J. Han, M. Kobayashi, and R. L. Gunshor, *Phys. Rev. B* **41**, 9966 (1990).

valence-band offset predicted by midgap energy theories for lattice-mismatched heterojunctions.

b. *HgTe/ZnTe*

Experimental studies of band offsets for HgTe/ZnTe heterojunctions have been performed, although these studies have not explicitly included the effects of strain arising from the lattice mismatch of approximately 6.5% between ZnTe and HgTe. Duc *et al.*[101] used XPS to measure the HgTe/ZnTe $(\overline{1}\overline{1}\overline{1})$ valence-band offset without accounting for strain effects and obtained a value of 0.25 ± 0.05 eV from their measurements; measurements for samples grown along the (100) orientation yielded a value of 0.36 eV. As discussed in more detail in Section 17, the experimental procedure followed by Duc *et al.* probably yields a rough estimate of the average valence-band offset for the HgTe/ZnTe heterojunction. Shih *et al.*[237,242] performed photoemission measurements on $Hg_{1-x}Zn_xTe$ alloys and obtained a "natural" valence-band offset between HgTe and ZnTe of 0.17 ± 0.06 eV. Marbeuf *et al.*[243] determined a "natural" valence-band offset for HgTe/ZnTe from XPS measurements of core-level energies over the entire compositional range of $Hg_{1-x}Zn_xTe$ alloys and obtained the same value. In each case, the valence-band edge of HgTe was found to be higher in energy than that of ZnTe.

Very few theoretical predictions are available for the HgTe/ZnTe valence-band offset, and the predictions that have been made are probably best considered as band offset values for hypothetical "unstrained" heterojunctions. For most theories, in which energy levels are calculated on an absolute energy scale, this value should correspond approximately to the average valence-band offset; for midgap energy theories such as that of Tersoff,[28] however, strain effects can shift the average valence-band offset in a strained heterojunction away from the hypothetical unstrained value. The electron affinity rule[19] yields a valence-band offset of approximately −0.14 eV (valence-band edge of HgTe below that of ZnTe) using reported electron affinity data for HgTe[212] and ZnTe.[71] Harrison's LCAO theory[24] predicts a valence-band offset of 0.17 eV when the atomic energies given by Harrison[214] are used to calculate the position of the HgTe valence-band edge. Tersoff's theory[28] yields $\Delta E_v = 0.50$ eV. The model solid theory of Van de Walle and Martin[86] predicts an unstrained valence-band offset of 0.34 eV.

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[242] C. K. Shih, A. K. Wahi, I. Lindau, and W. E. Spicer, *J. Vac. Sci. Technol. A* **6**, 2640 (1988).

[243] A. Marbeuf, D. Ballutaud, R. Triboulet, and Y. Marfaing, *J. Cryst. Growth* **101**, 608 (1990).

VI. Strain Effects in Lattice-Mismatched Heterojunctions

Advances in epitaxial growth techniques have stimulated great interest in strained-layer heterostructures realized in lattice-mismatched material systems.[14,18,179,180,244–247] The study of heterostructures in lattice-mismatched material systems involves a number of issues that do not arise for lattice-matched heterojunctions, chief among these being the conditions under which coherently strained epitaxial structures can be grown and the effect of strain on electronic structure in a coherently strained semiconductor heterojunction.

14. INFLUENCE OF STRAIN ON ELECTRONIC STRUCTURE

The effects of strain on band offset values can be understood by examining first the effect of strain on the electronic structure of a bulk semiconductor. We use the Si/Ge material system to illustrate several specific points in this section; however, the ideas presented are applicable to all lattice-mismatched heterojunctions. In **k** · **p** theory, the band structure for a crystal with cubic symmetry near a level that is threefold degenerate (neglecting spin degeneracy) at the Γ point ($\mathbf{k} = 0$) is given by a Hamiltonian of the form[248]

$$H(k_ik_j) = \begin{pmatrix} Lk_x^2 + M(k_y^2 + k_z^2) & Nk_xk_y & Nk_xk_z \\ Nk_xk_y & Lk_y^2 + M(k_x^2 + k_z^2) & Nk_yk_z \\ Nk_xk_z & Nk_yk_z & Lk_z^2 + M(k_x^2 + k_y^2) \end{pmatrix}, \quad (14.1)$$

where the basis elements have been taken to be $\{X, Y, Z\}$, valence-band wave functions that transform as p-like atomic orbitals. Bir and Pikus[249] have shown that, because strain in a cubic crystal can be described by a strain tensor ε_{ij} having the same symmetry as the quadratic tensor k_ik_j in Eq. (14.1), the perturbation Hamiltonian describing strain effects can be written

$$H(\varepsilon_{ij}) = \begin{pmatrix} l\varepsilon_{xx} + m(\varepsilon_{yy} + \varepsilon_{zz}) & n\varepsilon_{xy} & n\varepsilon_{xz} \\ n\varepsilon_{xy} & l\varepsilon_{yy} + m(\varepsilon_{xx} + \varepsilon_{zz}) & n\varepsilon_{yz} \\ n\varepsilon_{xz} & n\varepsilon_{yz} & l\varepsilon_{zz} + m(\varepsilon_{xx} + \varepsilon_{yy}) \end{pmatrix}, \quad (14.2)$$

[244] G. C. Osbourn, R. M. Biefeld, and P. L. Gourley, *Appl. Phys. Lett.* **41**, 172 (1982).

[245] I. J. Fritz, L. R. Dawson, and T. E. Zipperian, *Appl. Phys. Lett.* **43**, 846 (1983).

[246] D. L. Smith, *Solid State Commun.* **57**, 919 (1986).

[247] D. L. Smith and C. Mailhiot, *J. Appl. Phys.* **63**, 2717 (1988).

[248] E. O. Kane, *J. Phys. Chem. Solids* **1**, 82 (1956).

[249] G. L. Bir and G. E. Pikus, "Symmetry and Strain-Induced Effects in Semiconductors," p. 310ff, John Wiley and Sons, New York, 1974.

where l, m, and n are phenomenological deformation potentials. The more familiar deformation potentials[249,250] a, b, and d are given by

$$a = \frac{l + 2m}{3}, \qquad b = \frac{l - m}{3}, \qquad d = \frac{n}{\sqrt{3}}. \tag{14.3}$$

The deformation potential a describes the effect of hydrostatic strain on the average position of the light-hole, heavy-hole, and split-off valence bands, $\delta E_{\mathrm{v,av}} = a(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz})$; b describes valence-band splittings induced by uniaxial strain along the [001] direction, and d describes splittings induced by [111] strain.

To obtain the valence-band splittings with spin–orbit effects included, one must transform from the $\{X, Y, Z\}$ basis to an angular momentum basis $|j, m\rangle$ given, for example, by[251]

$$|\tfrac{3}{2}, \tfrac{3}{2}\rangle = (1/\sqrt{2})(X + iY)\uparrow, \tag{14.4}$$

$$|\tfrac{3}{2}, \tfrac{1}{2}\rangle = (1/\sqrt{6})[2Z\uparrow - (X + iY)\downarrow], \tag{14.5}$$

$$|\tfrac{3}{2}, -\tfrac{1}{2}\rangle = (1/\sqrt{6})[2Z\downarrow - (X - iY)\uparrow], \tag{14.6}$$

$$|\tfrac{3}{2}, -\tfrac{3}{2}\rangle = (1/\sqrt{2})(X - iY)\downarrow, \tag{14.7}$$

$$|\tfrac{1}{2}, \tfrac{1}{2}\rangle = (1/\sqrt{3})[Z\uparrow - (X + iY)\downarrow], \tag{14.8}$$

$$|\tfrac{1}{2}, -\tfrac{1}{2}\rangle = (1/\sqrt{3})[Z\downarrow + (X - iY)\uparrow]. \tag{14.9}$$

Spin–orbit effects split the six bands into a fourfold degenerate $p_{3/2}$ multiplet and a twofold degenerate $p_{1/2}$ multiplet; at the Brillouin zone center, $|\tfrac{3}{2}, \pm\tfrac{3}{2}\rangle$ correspond to the heavy-hole band, $|\tfrac{3}{2}, \pm\tfrac{1}{2}\rangle$ to the light-hole band, and $|\tfrac{1}{2}, \pm\tfrac{1}{2}\rangle$ to the split-off band. In the presence of strain in the [001] direction, the positions of these three valence bands at the Γ point, relative to the average position of the three bands, are[38,250]

$$\Delta E_{hh} = \tfrac{1}{3}\Delta_0 - \tfrac{1}{2}\delta E_{001}, \tag{14.10}$$

$$\Delta E_{lh} = -\tfrac{1}{6}\Delta_0 + \tfrac{1}{4}\delta E_{001} + \tfrac{1}{2}\sqrt{\Delta_0^2 + \Delta_0 \delta E_{001} + \tfrac{9}{4}\delta E_{001}^2}, \tag{14.11}$$

$$\Delta E_{so} = -\tfrac{1}{6}\Delta_0 + \tfrac{1}{4}\delta E_{001} - \tfrac{1}{2}\sqrt{\Delta_0^2 + \Delta_0 \delta E_{001} + \tfrac{9}{4}\delta E_{001}^2}, \tag{14.12}$$

[250] F. H. Pollak and M. Cardona, *Phys. Rev.* **172**, 816 (1968).

[251] C. Kittel, "Quantum Theory of Solids," p. 282, John Wiley and Sons, New York, 1963.

where Δ_0 is the spin-orbit splitting and $\delta E_{001} = 2b(\varepsilon_{zz} - \varepsilon_{xx})$. For strain in the [111] direction, the band edge positions are given by Eqs. (14.10), (14.11), and (14.12) with δE_{001} replaced by $\delta E_{111} = 2\sqrt{3}\ d\varepsilon_{xy}$. Strain-induced splittings for lattice-mismatched heterojunctions can be quite large. For example, experimentally measured values of the deformation potential b in Si[252] and Ge[253] yield linear multiplet splittings δE_{001} that can be as large as a few tenths of an electron volt for highly strained Si and Ge crystals.

To illustrate the effect of strain on electronic band structure, we again consider the Si/Ge material system; effects in other lattice-mismatched heterojunctions are similar. Figure 23 shows the valence-band structure in unstrained and strained Si and Ge. In Si/Ge heterojunctions, Si is typically under (in-plane) tensile strain, and Ge is typically under (in-plane) compressive strain. As shown in the figure, in-plane tensile strain shifts the light-hole band above the heavy-hole band, whereas for in-plane compressive strain the heavy-hole band is above the light-hole band in energy. The band structures in Fig. 23 are calculated for uniaxial strain in the [001] direction and are shown for **k** in the (001) direction in the Brillouin zone.

For the conduction-band valleys, strain effects are described by the deformation potentials Ξ_{d}^{k} and Ξ_{u}^{k}. The shift of a conduction-band valley k is given by[254,255]

$$\Delta E_{\mathrm{c}}^{k} = \Xi_{\mathrm{d}}^{k}\varepsilon_{ii} + \Xi_{\mathrm{u}}^{k} e_i^k e_j^k \varepsilon_{ij}, \tag{14.13}$$

where $\mathbf{e}^k$ is the unit vector parallel to the **k** vector for valley k, and a sum is taken over repeated indices. From Eq. (14.13) it can be seen that the average position of the conduction-band edges for valley k is shifted by an energy $(\Xi_{\mathrm{d}}^{k} + \frac{1}{3}\Xi_{\mathrm{u}}^{k})\varepsilon_{ii}$; the shift in energy of the average valence-band-edge position is $a\varepsilon_{ii}$, yielding a shift in the energy gap between the average positions of the conduction-band edges associated with the conduction-band valley k and of the valence-band edges

$$\Delta E_{\mathrm{g,av}} = (\Xi_{\mathrm{d}}^{k} + \tfrac{1}{3}\Xi_{\mathrm{u}}^{k} - a)\varepsilon_{ii}. \tag{14.14}$$

In addition, degeneracies of indirect conduction-band minima, e.g., the Δ valleys in Si or the L valleys in Ge, can be lifted by strain. Strain-induced conduction-band splittings can be calculated from Eq. (14.13).

These considerations indicate that the effect of strain on the electronic band structure in bulk material is quite large; one would therefore expect

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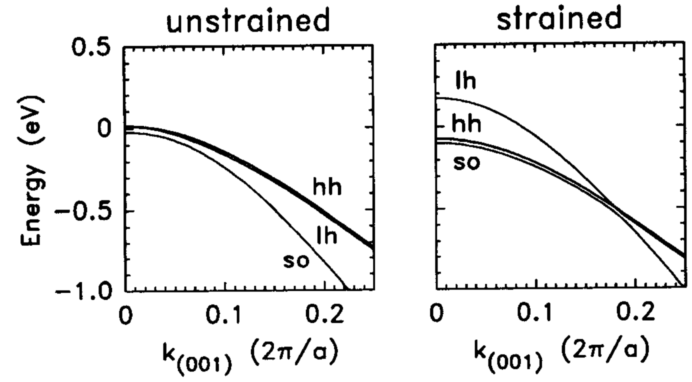
[252] L. D. Laude, F. H. Pollak, and M. Cardona, *Phys. Rev. B* **3**, 2623 (1971).

[253] M. Chandrasekhar and F. H. Pollak, *Phys. Rev. B* **15**, 2127 (1977).

[254] C. Herring and E. Vogt, *Phys. Rev.* **101**, 944 (1956).

[255] I. Balslev, *Phys. Rev.* **143**, 636 (1966).

(a) Si: in-plane tensile strain



(b) Ge: in-plane compressive strain

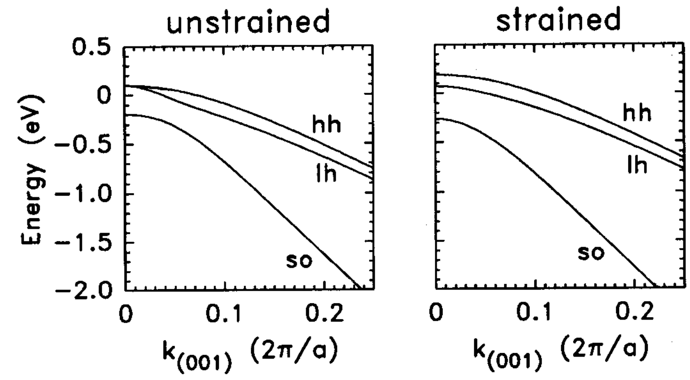


FIG. 23. Effects of strain on bulk band structure in Si and Ge. For Si/Ge heterojunctions, Si is typically under in-plane tensile strain and Ge under in-plane compressive strain. For in-plane tensile strain, the light-hole band is above the heavy-hole band in energy; for compressive strain, the heavy-hole band is higher in energy. Band structures are calculated for uniaxial strain in the [001] direction and are shown for **k** in the (001) direction in the Brillouin zone.

effects of at least comparable magnitude on the electronic structure at a semiconductor heterojunction interface. Calculations by Van de Walle and Martin,[37,38] in which the effect of strain on band offsets is considered explicitly, predicted that strain should exert a strong influence on band offset values in the Si/Ge heterojunction, and experimental results have verified this prediction.[102–104] Experiments on other material systems, such as

$In_xGa_{1-x}As/GaAs$, have also demonstrated the influence of strain on electronic structure in semiconductor heterojunctions. A few theoretical treatments, notably the model solid theory of Van de Walle and Martin,[84–86] provide explicit formalisms for estimating band offsets in coherently strained heterojunction systems.

15. Critical Thickness for Strain Relaxation

An additional issue that arises in studies of lattice-mismatched heterojunctions is the ability to grow actual coherently strained, dislocation-free heterojunctions. Each layer in a coherently strained heterostructure must be kept below the critical thickness for strain relaxation, beyond which strain in the layer will be relieved via the formation of dislocations. Several theoretical models have been developed to predict the critical thickness for strain relaxation,[256–263] and critical thicknesses for a variety of material systems have been measured experimentally.[259,264–268] In this section we present a brief historical overview of the current understanding of critical thickness, from the early thermodynamic equilibrium theories of Van der Merwe through the current nonequilibrium theories in which critical thicknesses depend on conditions such as growth temperature. Experimental data that strongly support the concept of metastable strain states and nonequilibrium critical thicknesses are also discussed.

The early theories of critical thickness, developed primarily by Van der Merwe,[256,257] assumed that the crystal would reach thermodynamic equilibrium and settle into the state of lowest energy. Hence, for film thicknesses

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[256] J. H. Van der Merwe, *J. Appl. Phys.* **34**, 117 (1963).

[257] J. H. Van der Merwe, *J. Appl. Phys.* **34**, 123 (1963).

[258] J. H. Van der Merwe and C. A. B. Ball, in "Epitaxial Growth" (J. W. Matthews, ed.), Part b, Academic Press, New York, 1975.

[259] J. W. Matthews and A. E. Blakeslee, *J. Cryst. Growth* **27**, 118 (1974).

[260] R. People and J. C. Bean, *Appl. Phys. Lett.* **47**, 322 (1985).

[261] B. W. Dodson and J. Y. Tsao, *Appl. Phys. Lett.* **51**, 1325 (1987).

[262] B. W. Dodson and J. Y. Tsao, *Appl. Phys. Lett.* **52**, 852 (1988).

[263] J. Y. Tsao, B. W. Dodson, S. T. Picraux, and D. M. Cornelison, *Phys. Rev. Lett.* **59**, 2455 (1987).

[264] J. C. Bean, L. C. Feldman, A. T. Fiory, S. Nakahara, and I. K. Robinson, *J. Vac. Sci. Technol. A* **2**, 436 (1984).

[265] A. T. Fiory, J. C. Bean, R. Hull, and S. Nakahara, *Phys. Rev. B* **31**, 4063 (1985).

[266] R. H. Miles, T. C. McGill, P. P. Chow, D. C. Johnson, R. J. Hauenstein, C. W. Nieh, and M. D. Strathman, *Appl. Phys. Lett.* **52**, 916 (1988).

[267] J.-P. Reithmaier, H. Cerva, and R. Lösch, *Appl. Phys. Lett.* **54**, 48 (1989).

[268] H.-J. Gossmann, G. P. Schwartz, B. A. Davidson, and G. J. Gualtieri, *J. Vac. Sci. Technol. B* **7**, 764 (1989).

below the critical thickness the film should be coherently strained to match the in-plane lattice parameter of the substrate, and above the critical thickness the mismatch should be accommodated by a network of misfit dislocations. The validity of Van der Merwe's model depends, however, on the crystal being able to reach a state of thermodynamic equilibrium. It may be possible for crystals grown epitaxially at low temperatures to exist in a metastable state. Consider, for example, an interface for which the critical thickness t_c has some finite value. When the thickness of the overlayer is less than t_c, the film will be coherently strained. As the overlayer thickness increases beyond t_c, the film will remain coherently strained until dislocations nucleate to accommodate the misfit. Formation of these dislocations, however, may often require a nonzero activation energy; if the temperature of the crystal is much lower than this activation energy, the crystal may either remain in the metastable, coherently strained state or else form fewer dislocations than needed to minimize the total energy for film thicknesses greater than the critical thickness.

An alternate approach to calculating critical thicknesses was proposed by Matthews and Blakeslee.[259] Rather than minimizing the total energy of strain and dislocations in a crystal, Matthews and Blakeslee considered the forces on dislocation lines in deriving an expression for the critical thickness. The critical thickness in their model depended on the balance between the tension of threading dislocation lines and the lateral force exerted by the misfit strain. For small misfit strain forces, the layers will remain coherently strained; for sufficiently large forces, however, the threading dislocation line will expand by elongating in the plane of an interface, producing a misfit dislocation line along the interface connecting the threading dislocations in each layer. When this occurs, the mismatch is no longer accommodated completely by coherent strain but is accommodated by a combination of misfit dislocations and strain.

Another model for calculating critical thicknesses was proposed by People and Bean.[260] This model is similar to the original theory of Van der Merwe, in that the critical thickness is determined by a minimization of energy in the entire crystal (thermodynamic equilibrium), rather than by requiring that dislocation lines be in mechanical equilibrium. People and Bean considered the energy densities of various types of dislocations and assumed that all misfit dislocations would be of the type with the lowest energy—the screw dislocation. By equating expressions for the energy density in a strained crystal and the energy density in a crystal with misfit dislocations, an expression for the critical thickness was obtained. A phenomenological parameter related to the effective lateral extent of the strain field created by a dislocation was chosen to yield the best agreement with the experimental data of Bean *et al.*[264] Despite the resulting agreement with experimental measurements, the physical basis for this theory and to some extent all thermodynamic equilibrium theories appears to be somewhat incomplete.

Experimental data indicate that factors such as growth temperature and the existence of metastable strain states are of central importance in the relaxation of strained films. Attempts have been made to include the effects of growth temperature and metastability in models of critical thickness. Dodson and Tsao[261,262] have developed a model for strain relaxation in lattice-mismatched heterojunctions via plastic flow; combining this model with the effects of finite instrumental resolution,[269,270] good agreement with the experimental data of Bean *et al.*[264] and of Kasper *et al.*[271] was obtained. Tsao *et al.*[263] also measured the temperature dependence of strain relaxation in Si/Si_xGe_{1-x} heterojunctions, and proposed a model for strain relaxation based on temperature and the difference between stress in the sample arising from misfit strain and that arising from dislocation line tension.

A number of experiments have been performed in which critical thicknesses were measured experimentally. To test their predictions of critical thickness and strain accommodation by dislocations, Matthews and Blakeslee examined $GaAs/GaAs_{0.5}P_{0.5}$ superlattice samples with layer thicknesses ranging from 75 Å to 700 Å using transmission and scanning electron microscopy. They found that the critical thicknesses for generation of misfit dislocations were between 160 Å and 350 Å; this result is in agreement with their theory, which predicts a critical thickness of about 250 Å for their structures. For layer thicknesses above 350 Å, however, the amount of lattice mismatch accommodated by dislocations, as determined by measurements of Burgers vector orientations and average distances between dislocation lines, was found to be much smaller than predicted. This discrepancy suggests that processes inhibiting the formation of stable dislocations, e.g., interactions between dislocations and barriers for nucleation of dislocations, can be of considerable importance. Bean *et al.*[264] performed transmission electron microscopy, x-ray diffraction, and Rutherford backscattering studies of $Si_{1-x}Ge_x$/Si superlattices; the observed critical thicknesses were significantly larger than predicted by the equilibrium model of Van der Merwe. This result, like that of Matthews and Blakeslee, suggests that nonequilibrium effects such as barriers to dislocation formation can play a major role in determining critical thickness values.

There exists considerable other evidence that nonequilibrium effects are indeed of great importance in strain relaxation. Studies by Fiory *et al.*[265] have shown that annealing of $Si_{1-x}Ge_x$ films grown on Si (100) substrates at

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[269] I. J. Fritz, P. L. Gourley, and L. R. Dawson, *Appl. Phys. Lett.* **51**, 1004 (1987).
[270] I. J. Fritz, *Appl. Phys. Lett.* **51**, 1080 (1987).
[271] E. Kasper, H. J. Herzog, and H. Kibbel, *Appl. Phys.* **8**, 199 (1975).

550°C increases the number of strain-relieving dislocations in the film. These experiments strongly suggest that the as-grown $Si_{1-x}Ge_x$ film exists in a metastable state and that annealing at 800–1000°C allows the film to relax gradually toward the minimum-energy equilibrium state. Tsao *et al.*[263] measured the temperature dependence of strain relaxation in Si_xGe_{1-x} layers grown on Ge substrates and found that the onset of strain relaxation depended quite strongly on temperature. Studies by Miles *et al.*[266] of $Si/Ge_{0.5}Si_{0.5}$ superlattices demonstrated a dependence of critical thickness and dislocation density on growth temperature. For superlattices with the same layer thicknesses and same total thickness grown at substrate temperatures ranging between 365°C and 530°C, the dislocation density was shown to increase with growth temperature, indicating that the superlattices, as grown, were in metastable states with fewer dislocations than would have been necessary to minimize the total energy. These studies indicate that a satisfactory theory of critical thicknesses will need to account for the effects of dislocation interactions, barriers to dislocation formation, and other nonequilibrium processes that will, in general, depend on crystal growth parameters and on the growth temperature in particular.

16. SI/GE

The Si/Ge (001) heterojunction has been chosen by a number of investigators as a prototypical material system in which to study the effects of strain on band offset values.[37,38,103,104] The Si/Ge material system is especially appropriate for this type of study, because of the large lattice mismatch (4.18%) between Si and Ge and because conditions under which coherently strained epilayers can be grown are well known.[256,257,266] In addition, theoretical calculations of the Si/Ge (001) valence-band offset have been performed that explicitly incorporate the effects of strain;[37,38] these calculations have been confirmed by several experimental results[102–104] indicating that strain strongly influences the value of the valence-band offset. The Si/Ge interface is also of great technological interest because of the possibility of integrating devices utilizing $Si/Si_{1-x}Ge_x$ heterojunctions directly into existing Si-based structures. The behavior of $Si/Si_{1-x}Ge_x$ heterostructure devices depends critically on the values of the conduction- and valence-band offsets.

a. *Experimental Measurements*

Most of the early Si/Ge band offset measurements were performed on heterojunctions in which the strain configuration was not known. A compilation of these early experimental results is included in Table X. Kuech *et al.*[272]

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[272] T. F. Kuech, M. Mäenpää, and S. S. Lau, *Appl. Phys. Lett.* **39**, 245 (1981).

TABLE X. EARLY EXPERIMENTAL AND THEORETICAL VALENCE-BAND OFFSETS FOR Si/Ge

SOURCE	ΔE_v (expt.) (eV)	ΔE_v (theor.) (eV)
Kuech *et al.* (1981)[272]	0.39 ± 0.04	
Margaritondo *et al.* (1982)[273]	0.2	
Katnani and Margaritondo (1983)[21]	0.17	
Mahowald *et al.* (1985)[274]	0.4 ± 0.1	
Milnes and Feucht (1972)[71]		0.33
Harrison (1977)[24]		0.38
Tersoff (1986)[28]		0.18
Harrison and Tersoff (1986)[29]		0.29

obtained $\Delta E_v = 0.39 \pm 0.04$ eV for Ge deposited on Si (001) from reverse-bias capacitance measurements. Using photoemission spectroscopy, Margaritondo *et al.*[273] measured $\Delta E_v = 0.2$ eV for Ge deposited on Si (111), and Mahowald *et al.*[274] obtained $\Delta E_v = 0.4 \pm 0.1$ eV for Si deposited on Ge (111). Photoemission measurements of Katnani and Margaritondo[21] yielded $\Delta E_v = 0.17$ eV for both Si deposited on Ge and Ge deposited on Si. In all cases, the valence-band edge of Ge was found to be above that of Si. However, strain effects were not accounted for in these measurements, and subsequent experiments have demonstrated that strain exerts a profound influence on band offset values in Si/Ge heterojunctions.

The first Si/Ge band offset measurements in which strain effects were considered were performed by Ni *et al.*[102] In these experiments, XPS was used to measure the Si 2*p* and Ge 3*d* core-level binding energies relative to the conduction- and valence-band edges in heavily doped Si and $Si_{1-x}Ge_x$ samples with varying degrees of strain. *p*-type and *n*-type doping were used to move the Fermi level to the valence- and conduction-band edges, respectively, so that the measured absolute core-level binding energies were automatically referenced to the band edges; one to two monolayers of Sb or In were evaporated on each sample to prevent Fermi-level pinning and the concomitant band bending at the sample surfaces. The Si 2*p* and Ge 3*d* core-level binding energies were then measured in $Si/Si_{1-x}Ge_x$ heterojunctions and combined with the previous measurements to yield values for the conduction- and valence-band offsets. This technique also allowed band gaps in strained Si and $Si_{1-x}Ge_x$ samples to be determined. The strain-dependent band gaps

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[273] G. Margaritondo, A. D. Katnani, N. G. Stoffel, R. R. Daniels, and T.-X. Zhao, *Solid State Commun.* **43**, 163 (1982).

[274] P. H. Mahowald, R. S. List, W. E. Spicer, J. Woicik, and P. Pianetta, *J. Vac. Sci. Technol. B* **3**, 1252 (1985).

measured by Ni *et al.* were in good agreement with photocurrent measurements performed by Lang *et al.*,[275] and the conduction-and valence-band offsets measured for Si/$Si_{0.74}Ge_{0.26}$ on Si, Si/$Si_{0.52}Ge_{0.48}$ on Si, and Si/$Si_{0.52}Ge_{0.48}$ on $Si_{0.75}Ge_{0.25}$ were in good agreement with band offset values obtained theoretically by interpolation[38,276] from the pure Si/Ge heterojunction calculations of Van de Walle and Martin.[37,38] For the case of Si/$Si_{0.74}Ge_{0.26}$ on Si, band offset values $\Delta E_c = 0.00 \pm 0.06$ and $\Delta E_v = 0.18 \pm 0.06$ eV were measured; for Si/$Si_{0.52}Ge_{0.48}$ on Si, $\Delta E_c = 0.03 \pm 0.06$ eV and $\Delta E_v = 0.36 \pm 0.06$ eV were obtained; and for Si/$Si_{0.52}Ge_{0.48}$ on $Si_{0.75}Ge_{0.25}$, $\Delta E_c = 0.13 \pm 0.06$ and $\Delta E_v = 0.24 \pm 0.06$ eV were measured.

The strain dependence of the valence-band offset in pure Si/Ge heterojunctions has also been studied using XPS. In these experiments it was necessary to account explicitly for the strain dependence of the core-level and valence-band-edge binding energies.[277] Schwartz *et al.*[103] used XPS to measure Si 2*p* to Ge 3*d* core-level binding energy separations in heterojunctions consisting of either six monolayers of Ge coherently strained to Si (001) or six monolayers of Si coherently strained to Ge (001). Because the samples needed to be transferred through atmosphere to the XPS chamber, each sample was capped with 12 monolayers of the unstrained material to prevent possible alterations in strain in the coherently strained layer arising from oxidation. Strain in these samples was determined from Raman scattering measurements; the results were not inconsistent with the heterostructures being coherently strained. Core-level to valence-band-edge binding energies for unstrained Si and Ge were obtained from previously published results, and the strain dependence of the core-level to valence-band-edge binding energies in bulk material was then calculated using a linear muffin-tin orbital method. The resulting strain-dependent core-level to valence-band-edge binding energies were then combined with the heterojunction measurements to obtain strain-dependent valence-band offsets for the Si/Ge (001) heterojunction. For Ge coherently strained to Si (001) and Si coherently strained to Ge (001), Schwartz *et al.* obtained valence-band offsets of 0.74 ± 0.13 eV and 0.17 ± 0.13 eV, respectively.

Yu *et al.*[104,105] also applied the XPS technique to measure the strain dependence of the Si/Ge (001) valence-band offset. In these experiments, Yu *et al.* determined experimentally the strain dependence of the Si 2*p* and Ge 3*d* core-level to valence-band-edge binding energies in Si and Ge, respectively, by measuring core-level to valence-band-edge binding energies in strained films of pure Si and pure Ge. Strain in these films was varied by growing layers of Si and Ge coherently strained to $Si_{1-x}Ge_x$ alloy layers of varying

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[275] D. V. Lang, R. People, J. C. Bean, and M. Sergent, *Appl. Phys. Lett.* **47**, 1333 (1985).

[276] R. People and J. C Bean, *Appl. Phys. Lett.* **48**, 538 (1986).

[277] J. Tersoff and C. G. Van de Walle, *Phys. Rev. Lett.* **59**, 946 (1987).

composition, allowing the Si 2*p* and Ge 3*d* core-level to valence-band-edge binding energies to be measured directly as functions of strain. The Si 2*p* to Ge 3*d* core-level binding energy separation was then measured as a function of strain in Si/Ge superlattices; by varying the Si and Ge layer thicknesses in the superlattices, heterojunctions with different levels of strain were obtained, allowing the strain dependence of the heterojunction core-level energy separation to be measured. Strain configurations for all samples were measured using x-ray diffraction. The XPS measurements were then combined to yield strain-dependent values for the Si/Ge (001) valence-band offset. For Ge coherently strained to Si (001) and Si coherently strained to Ge (001), the measured valence-band offsets were 0.83 ± 0.11 eV and 0.22 ± 0.13 eV, respectively.

The Si/Ge heterojunction measurements of Schwartz *et al.*[103] and of Yu *et al.*[104] can be compared to the $Si/Si_{1-x}Ge_x$ measurements of Ni *et al.*[102] and to modulation doping results reported by People *et al.*[278] and by Abstreiter *et al.*[279] using an interpolation scheme adapted from the method proposed by Van de Walle and Martin.[38] Table XI shows band offsets measured for various $Si/Si_{1-x}Ge_x$ heterojunctions; for the alloy heterojunctions, band offsets interpolated from the Si/Ge measurements of Refs. 103 and 104 are listed. Figures 24 and 25 show conduction- and valence-band offsets for $Si_{1-x}Ge_x/Si_{1-y}Ge_y$ heterojunctions coherently strained to either Si (001) or Ge (001), obtained by interpolation from the measurements of Yu *et al.*[104]

Semiquantitative information about band offsets at $Si/Si_{1-x}Ge_x$ heterojunctions has been deduced from modulation doping measurements in $Si/Si_{1-x}Ge_x$ heterostructures. People *et al.*[278] observed modulation doping effects for holes in $Si/Si_{0.8}Ge_{0.2}$ heterojunctions coherently strained to Si (001) substrates; this result, combined with their failure to observe modulation doping effects for *n*-type samples, indicated that $\Delta E_v \gg \Delta E_c$ for $Si/Si_{0.8}Ge_{0.2}$ heterojunctions coherently strained to Si (001). Interpolation from the Si/Ge (001) valence-band offsets measured by Yu *et al.*[104] yields $\Delta E_v = 0.16$ eV and $\Delta E_c = -0.02$ eV for this heterojunction; these values are consistent with People's results. The band alignment corresponding to the measured values of Yu *et al.* and the observed modulation doping behavior are shown schematically in Fig. 26a.

In another experiment, Abstreiter *et al.*[279] observed enhanced electron mobilities in $Si/Si_{0.5}Ge_{0.5}$ superlattices coherently strained to a $Si_{0.75}Ge_{0.25}$

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[278] R. People, J. C. Bean, D. V. Lang, A. M. Sergent, H. L. Störmer, K. W. Wecht, R. T. Lynch, and K. Baldwin, *Appl. Phys. Lett.* **45**, 1231 (1984).

[279] G. Abstreiter, H. Brugger, T. Wolf, H. Jorke, and H. J. Herzog, *Phys. Rev. Lett.* **54**, 2441 (1985).

TABLE XI. EXPERIMENTAL BAND OFFSET MEASUREMENTS FOR VARIOUS Si/$Si_{1-x}Ge_x$ HETEROJUNCTIONS

HETEROJUNCTION	ΔE_v (eV)			ΔE_c (eV)		
	Ref. 102	Ref. 103[a]	Ref. 104[a]	Ref. 102	Ref. 103[a]	Ref. 104[a]
Si/Ge on Si	—	0.74 ± 0.13	0.83 ± 0.11	—	—	—
Si/Ge on Ge	—	0.17 ± 0.13	0.22 ± 0.13	—	—	—
Si/$Si_{0.74}Ge_{0.26}$ on Si	0.18 ± 0.06	0.18	0.21	0.00 ± 0.06	-0.05	-0.03
Si/$Si_{0.52}Ge_{0.48}$ on Si	0.36 ± 0.06	0.35	0.39	0.03 ± 0.06	-0.05	-0.01
Si/$Si_{0.52}Ge_{0.48}$ on $Si_{0.75}Ge_{0.25}$	0.24 ± 0.06	0.23	0.26	0.13 ± 0.06	0.10	0.14

[a] For alloy heterojunctions, the band offsets shown were obtained by interpolation from measured results for pure Si/Ge heterojunctions.

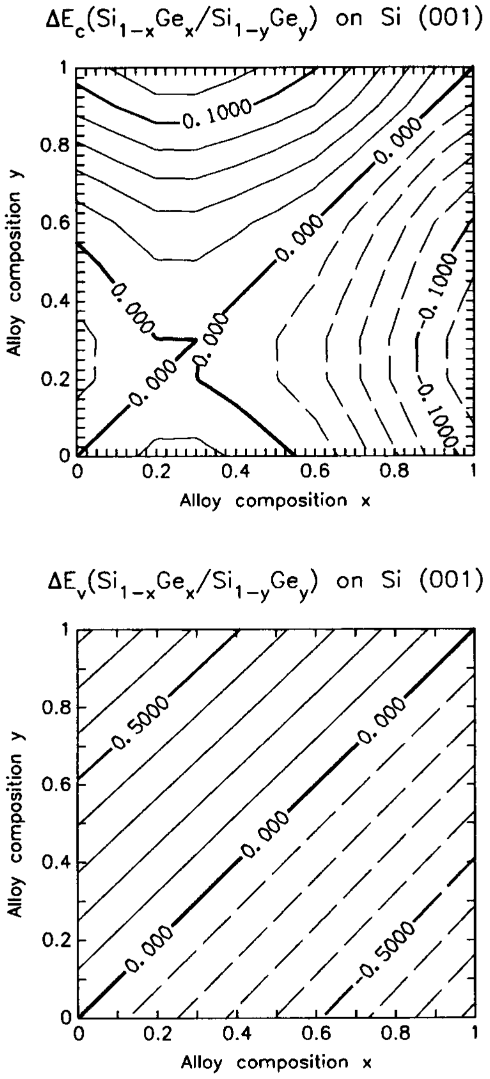
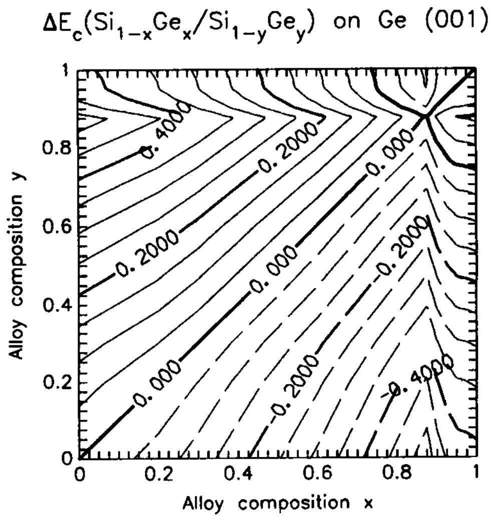


FIG. 24. Contour plots of conduction-band (upper) and valence-band (lower) offsets for $Si_{1-x}Ge_x/Si_{1-y}Ge_y$ (001) alloy heterojunctions coherently strained to a Si (001) substrate, calculated using Si/Ge (001) valence-band offsets measured by Yu *et al.*[104] and an interpolation scheme adapted from that of Van de Walle and Martin.[38] The signs of the band offsets are such that the valence- and conduction-band offsets are positive if the band edge in the $Si_{1-y}Ge_y$ layer is higher than in the $Si_{1-x}Ge_x$ layer. In the contour plots, positive band offset values are indicated by the solid contour lines and negative values by the dashed lines.



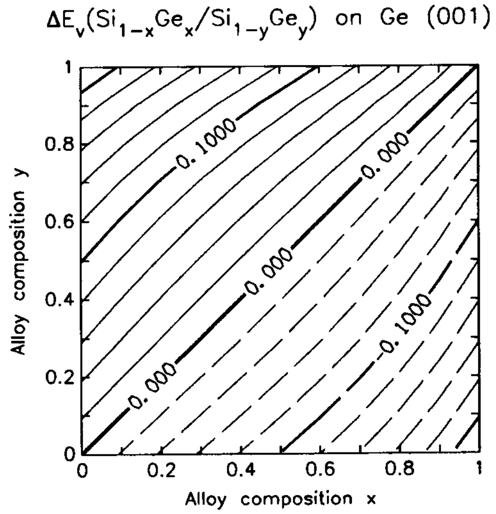


FIG. 25. Contour plots of conduction-band (upper) and valence-band (lower) offsets for $Si_{1-x}Ge_x/Si_{1-y}Ge_y$ (001) alloy heterojunctions coherently strained to a Ge (001) substrate, calculated using Si/Ge (001) valence-band offsets measured by Yu *et al.*[104] and an interpolation scheme adapted from that of Van de Welle and Martin.[38] The signs of the band offsets are such that the valence- and conduction-band offsets are positive if the band edge in the $Si_{1-y}Ge_y$ layer is higher than in the $Si_{1-x}Ge_x$ layer. In the contour plots, positive band offset values are indicated by the solid contour lines and negative values by the dashed lines.

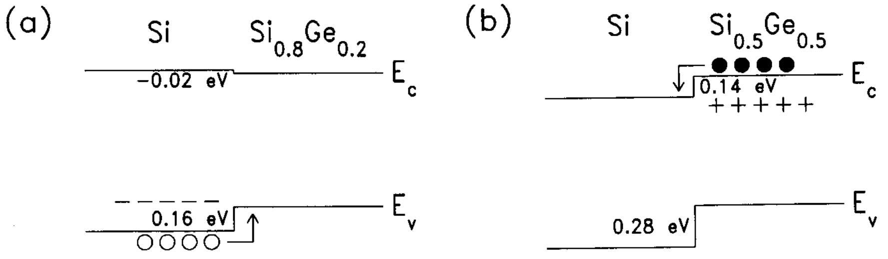


FIG. 26. Schematic diagrams of modulation doping effects reported in the literature, and the band alignments obtained by interpolation from Si/Ge valence-band offsets measured by Yu *et al.*[104] For the heterojunction shown in (a), People *et al.*[278] observed modulation doping effects when the Si layer was doped *p*-type but not when the doping was *n*-type, indicating that $\Delta E_v \gg \Delta E_c$. The band alignment shown in the figure is consistent with People's results. For the heterojunction shown in (b), which is coherently strained to a $Si_{0.75}Ge_{0.25}$ (001) buffer layer, Abstreiter *et al.*[279] observed enhanced electron mobilities when the $Si_{0.5}Ge_{0.5}$ layer was doped *n*-type. As seen in the figure, the band offsets obtained by interpolation are consistent with this observation.

(001) buffer layer when the $Si_{0.5}Ge_{0.5}$ superlattice layers were doped *n*-type. For this heterojunction system, interpolation from the measurements of Yu *et al.*[104] yields a valence-band offset of 0.28 eV and a conduction-band offset of 0.14 eV, consistent with Abstreiter's results. The band alignment corresponding to the measured values of Yu *et al.* and the modulation doping behavior observed by Abstreiter *et al.* are shown schematically in Fig. 26b.

b. *Theoretical Calculations*

Early theoretical predictions for the Si/Ge band offset, shown in Table X, typically did not account for the effects of strain. The electron affinity rule,[19] applied using the electron affinity data of Milnes and Feucht,[71] yielded $\Delta E_c = 0.12$ eV and $\Delta E_v = 0.33$ eV for an unstrained Si/Ge heterojunction. Harrison's LCAO theory[24] yielded $\Delta E_v = 0.38$ eV, and Harrison and Tersoff's theory[29] yielded $\Delta E_v = 0.29$ eV. Tersoff's theory[27,28] yielded $\Delta E_v = 0.18$ eV.

The first theoretical treatment to consider explicitly the effects of strain on band offsets was that of Van de Walle and Martin,[37,38] who performed self-consistent local-density-functional calculations, using *ab initio* pseudopotentials, of the electronic structure of Si/Ge interfaces. Their results indicated that, in coherently strained heterojunctions, strain should exert a strong influence on band offset values; however, the discontinuity in the average position of the light-hole, heavy-hole, and split-off valence bands at the interface should be approximately independent of strain. For a Si/Ge heterojunction coherently strained to Si (001), a valence-band offset of 0.84 eV was calculated; for a Si/Ge heterojunction coherently strained to Ge (001), a value of 0.31 eV was obtained. The discontinuity at the Si/Ge interface in the average position of the light-hole, heavy-hole, and split-off valence bands was calculated to be approximately 0.53 eV, and this quantity was found to be nearly independent of strain and substrate orientation. These predictions were subsequently confirmed by the experimental measurements described in the previous section.

Figure 27 shows the conduction- and valence-band alignments predicted by Van de Walle and Martin for $Si/Si_{1-x}Ge_x$ heterojunctions coherently strained to Si (001) (Fig. 27a) and to Ge (001) (Fig. 27b). Band alignments for pure Si/Ge heterojunctions were calculated explicitly, and results for $Si_{1-x}Ge_x$ alloys were obtained by interpolation. The interpolation scheme was based on the observation that, in their calculations, the discontinuity across the Si/Ge interface in the average position of the light-hole, heavy-hole, and split-off valence bands, $\Delta E_{v,av}$, was nearly independent of strain and substrate orientation. $\Delta E_{v,av}$ was taken to be a linear function of alloy composition, as shown in Fig. 27; this assumption was based on the validity of the model solid theory,[84–86] which yields valence-band offsets that are rigorously linear in alloy composition. The apparent linear dependence of the $GaAs/Al_xGa_{1-x}As$ valence-band offset on alloy composition, discussed in Section 8, also lends support to this assumption. The valence-band splittings were calculated using Eqs. (14.10)–(14.12), with values for δE_{001} and Δ_0 for $Si_{1-x}Ge_x$ alloys obtained by linear interpolation from the values for pure Si and Ge. To obtain conduction-band offsets, the average position of the Δ conduction bands was determined in each layer from experimentally measured[280] band gaps, adjusted to account for hydrostatic strain via the deformation potential given by Eq. (14.14). The conduction-band splittings were calculated via Eq. (14.13), yielding the actual positions of the strain-split conduction-band edges.

Conduction- and valence-band offsets can be read directly from Fig. 27. For heterojunctions coherently strained to Si (001), one can see that the conduction-band offsets are always quite small because of the splitting of the Δ conduction-band valleys, but that the valence-band offsets are enhanced by strain-induced valence-band splitting. For heterojunctions coherently strained to Ge (001), the conduction-band offsets are often somewhat larger than the valence-band offsets; in this case, the strain-induced splittings tend to reduce the valence-band offsets while increasing the conduction-band offsets.

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[280] R. Braunstein, A. R. Moore, and F. Herman, *Phys. Rev.* **109**, 695 (1958).

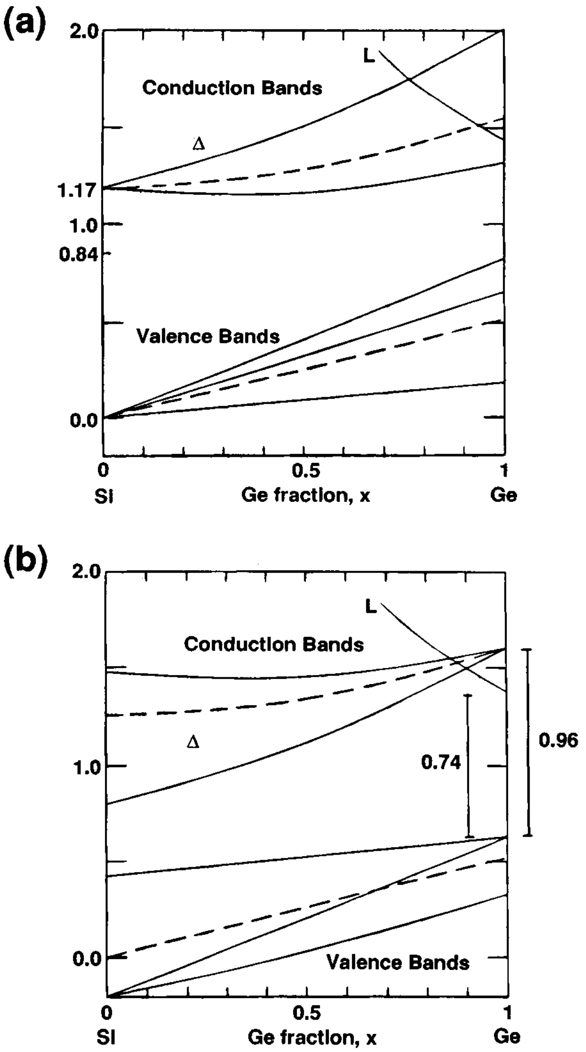

FIG. 27. Conduction- and valence-band alignments for $Si_{1-x}Ge_x$ alloy layers coherently strained to (a) Si (001) and (b) Ge (001). Solid lines represent actual conduction- and valence-band edges, and dashed lines represent weighted averages of the light-hole, heavy-hole, and split-off valence-band edges or of the Δ conduction-band edges. Taken from C. G. Van de Walle and R. M. Martin, *Phys. Rev. B* **34**, 5621 (1986).

Another interpolation scheme, based on early calculations of Van de Walle and Martin[37] that did not include spin-orbit splitting, was proposed by People and Bean.[276] In this approach, a bilinear interpolation, i.e., linear in heterojunction alloy composition and in substrate alloy composition, was used to obtain the valence-band offset at a Si/$Si_{1-x}Ge_x$ heterojunction coherently strained to a $Si_{1-y}Ge_y$ (001) substrate. Indirect band gaps for $Si_{1-x}Ge_x$ layers with various levels of strain were determined using a phenomenological deformation potential theory,[281] and these were used to obtain conduction-band offsets. This interpolation scheme and the method of Van de Walle and Martin both yield very similar results for alloy heterojunction band offsets.

The interpolation scheme of People and Bean[281] predicts the following band offset values: $\Delta E_v = 0.15$ eV and $\Delta E_c = -0.02$ eV for Si/$Si_{0.8}Ge_{0.2}$ coherently strained to Si (001); $\Delta E_v = 0.37$ eV and $\Delta E_c = -0.02$ eV for Si/$Si_{0.5}Ge_{0.5}$ coherently to Si (001); and $\Delta E_v = 0.30$ eV and $\Delta E_c = 0.15$ eV for Si/$Si_{0.5}Ge_{0.5}$ coherently strained to $Si_{0.75}Ge_{0.25}$. Van de Walle and Martin[38] predicted the following band offsets for various Si/$Si_{1-x}Ge_x$ heterojunctions: $\Delta E_v = 0.17$ eV and $\Delta E_c = 0.00$ eV for Si/$Si_{0.8}Ge_{0.2}$ coherently strained to Si (001); $\Delta E_v = 0.38$ eV and $\Delta E_c = -0.02$ eV for Si/$Si_{0.5}Ge_{0.5}$ coherently strained to Si (001); and $\Delta E_v = 0.28$ eV and $\Delta E_c = 0.13$ eV for Si/$Si_{0.5}Ge_{0.5}$ coherently strained to $Si_{0.75}Ge_{0.25}$. A comparison with the results in Table XI shows that these theoretical values are very clearly confirmed by experimental measurements.

The model solid theory of Van de Walle and Martin[84–86] can also be used to calculate band offsets for the Si/Ge heterojunction system. In the model solid theory, band-edge positions are calculated on an absolute energy scale, as described in Section 3; this model also allows absolute deformation potentials for hydrostatic shifts and uniaxial splittings to be calculated. For a strained crystal, the average valence-band-edge energy $E_{v,av}$ is given by

$$E_{v,av} = E^0_{v,av} + a_v \operatorname{Tr} \varepsilon, \tag{16.1}$$

where $E^0_{v,av}$ is the average valence-band-edge energy in the absence of strain, $\operatorname{Tr} \varepsilon = (\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz})$, and a_v is the hydrostatic deformation potential for the average valence-band-edge energy. The valence-band splittings given by Eqs. (14.10)–(14.12) then yield the energies of the actual valence-band edges. Conduction-band offsets can be obtained using experimental values for energy band gaps and calculated hydrostatic and uniaxial deformation potentials for the conduction bands. The model solid theory yields $\Delta E_v = 0.88$ eV and $\Delta E_v = 0.31$ eV for Ge coherently strained to Si (001) and Si

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[281] R. People and J. C. Bean, *Appl. Phys. Lett.* **48**, 538 (1986).

coherently strained to Ge (001), respectively; these calculations are in good agreement with the full self-consistent interface calculations from which the model solid theory was derived.

17. INGAAS/GAAS

The lattice-mismatched $In_xGa_{1-x}As/GaAs$ heterojunction has also been subject of considerable study; much of the interest in the $In_xGa_{1-x}As/GaAs$ material system is due to potential high-speed electronic and optoelectronic device applications. A number of studies of $In_xGa_{1-x}As/GaAs$ heterojunctions have also been directed toward achieving a basic physical understanding of strained-layer quantum-well and superlattice structures.

a. *Experiment*

Experimental measurements of the $In_xGa_{1-x}As/GaAs$ band offset are summarized in Table XII. The earliest experimental measurement of band offsets in a $GaAs/In_xGa_{1-x}As$ heterojunction was that of Kowalczyk *et al.*,[96] who measured the valence-band offset in the InAs/GaAs heterojunction, for which the lattice mismatch is approximately 7%, using XPS. In these experiments, the In 4*d* and Ga 3*d* core-level to valence-band-edge binding energies were measured in unstrained InAs and GaAs, respectively, and the In 4*d* to Ga 3*d* heterojunction core-level energy separation was measured in heterojunctions assumed to consist of InAs coherently strained to GaAs. Their measurements yielded an InAs/GaAs valence-band offset $\Delta E_v = 0.17 \pm 0.07$ eV, with the valence-band edge of InAs above that of GaAs. Although these experiments did not account for the effects of strain, one might hope that the valence-band offset measured in this way would still provide some information about band offsets in strained heterojunctions. This could be true because experiments on strained heterojunctions have indicated that hydrostatic shifts in core-level binding energies are relatively small compared to strain-induced splittings of the valence-band-edge positions.[104,282,283] Combining core-level energy separations measured in strained heterojunctions with core-level to valence-band-edge binding energies measured in bulk material should therefore yield an approximate determination of the average valence-band offset $\Delta E_{v,av}$, once a correction for spin–orbit splitting has been included. Thus, it is possible that the valence-band offset determined by Kowalczyk *et al.* could be used to provide a

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[282] W.-X. Ni and G. V. Hansson, *Phys. Rev. B* **42**, 3030 (1990).

[283] R. W. Grant, J. R. Waldrop, E. A. Kraut, and W. A. Harrison, *J. Vac. Sci. Technol. B* **8**, 736 (1990).

TABLE XII. EXPERIMENTAL BAND OFFSET VALUES FOR $In_xGa_{1-x}As/GaAs$

SOURCE	HETEROJUNCTION	RESULT
Kowalczyk *et al.* (1982)[96]	InAs/GaAs	$\Delta E_v = 0.17 \pm 0.07$ eV
Marzin *et al.* (1985)[284]	$In_{0.15}Ga_{0.85}As/GaAs$	$\left.\begin{array}{r}\Delta E_{hh} = 0.052\ \text{eV}\\ \Delta E_{lh} = -0.018\ \text{eV}\\ \Delta E_c = 0.110\ \text{eV}\end{array}\right\} \Delta E_c = 0.68\Delta E_g$
	$In_{0.17}Ga_{0.83}As/GaAs$	$\left.\begin{array}{r}\Delta E_{hh} = 0.060\ \text{eV}\\ \Delta E_{lh} = -0.019\ \text{eV}\\ \Delta E_c = 0.126\ \text{eV}\end{array}\right\} \Delta E_c = 0.68\Delta E_g$
Ji *et al* (1987)[285]	$In_xGa_{1-x}As/GaAs$ $x = 0.13\text{–}0.193$	$\Delta E_c = 0.70\Delta E_g$
Ramberg *et al.* (1987)[293]	$In_xGa_{1-x}As/GaAs$ $x < 0.08$	$\Delta E_v = 0.97x$ eV $\approx 0.8\text{–}0.9\Delta E_g$
Menéndez *et al.* (1987)[294]	$In_{0.05}Ga_{0.95}As/GaAs$	$\Delta E_v = 0.035\text{-}0.041$ eV $= (0.60 \pm 0.04)\Delta E_g$ $\Delta E_{v,av} = (0.49 \pm 0.1)x$ eV
Joyce *et al.* (1988)[295]	$In_{0.04}Ga_{0.96}As/GaAs$	$\Delta E_c = (0.36 \pm 0.12)\Delta E_g$
	$In_{0.12}Ga_{0.88}As/GaAs$	$\Delta E_c = (0.62 \pm 0.08)\Delta E_g$
Andersson *et al.* (1988)[286]	$In_xGa_{1-x}As/GaAs$ $x = 0.073\text{–}0.36$	$\Delta E_c = (0.83 \pm 0.06)\Delta E_g$
Pan *et al.* (1988)[287]	$In_{0.12}Ga_{0.88}As/GaAs$	$\Delta E_v = (0.30 \pm 0.05)\Delta E_g$
Yu *et al.* (1989)[296]	$In_{0.093}Ga_{0.907}As/GaAs$	$\Delta E_v = 0.6\Delta E_g$
	$In_{0.138}Ga_{0.862}As/GaAs$	$\Delta E_v = 0.3\Delta E_g$
Niki *et al.* (1989)[288]	$In_xGa_{1-x}As/GaAs$	$E_g(In_xGa_{1-x}As) = 1.424 - 1.15x$ eV $\Delta E_c = 0.65\Delta E_g$
Huang *et al.* (1989)[289]	$In_xGa_{1-x}As/GaAs$ $x = 0.09\text{–}0.20$	$\Delta E_c = 0.70\Delta E_g$
Reithmaier *et al.* (1990)[290]	$In_xGa_{1-x}As/GaAs$ $x = 0.18\text{–}0.25$	$\Delta E_c = 0.6\Delta E_g$
Zou *et al.* (1991)[291]	$In_xGa_{1-x}As/GaAs$ $x = 0.09\text{–}0.28$	$\Delta E_c = 0.60\Delta E_g$
Letartre *et al.* (1991)[292]	$In_{0.25}Ga_{0.75}As/GaAs$	$\Delta E_c = 0.141 \pm 0.06$ eV $\approx 0.5\Delta E_g$

meaningful estimate of a quantity such as $\Delta E_{v,av}$ for the InAs/GaAs heterojunction.

Most measurements of band offsets in strained $In_xGa_{1-x}As/GaAs$ heterojunctions have been performed for heterostructures coherently strained to a GaAs (001) substrate; in this situation, the GaAs layer in the heterojunction is relaxed, and the $In_xGa_{1-x}As$ layer experiences biaxial compression. Such a scheme facilitates the growth of $In_xGa_{1-x}As/GaAs$ superlattice samples with varying quantum-well thicknesses but equal levels of strain, an important consideration in certain optical band offset measurement techniques. For samples in which only the $In_xGa_{1-x}As$ layer is strained, the heavy-hole and light-hole valence bands are degenerate at the zone center in the GaAs layers

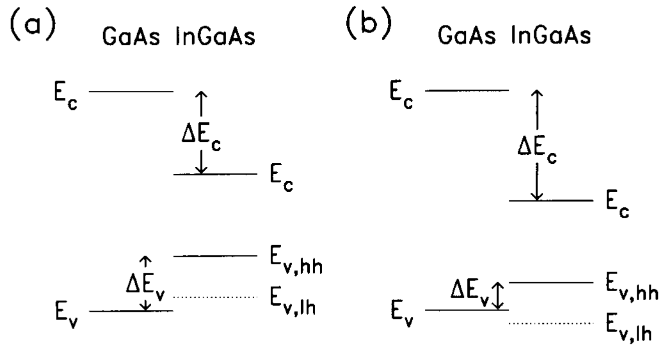

FIG. 28. Two types of band alignments that have been postulated for the $In_xGa_{1-x}As/GaAs$ heterojunction strained to GaAs. In each case, uniaxial strain splits the $In_xGa_{1-x}As$ heavy-hole ($E_{v,hh}$) and light-hole ($E_{v,lh}$) valence bands; the valence-band offset ΔE_v is defined to be the separation between the valence-band edge in GaAs and the heavy-hole valence-band edge in $In_xGa_{1-x}As$.

and are split in the $In_xGa_{1-x}As$ layers. The conduction and valence bands can be aligned at the heterojunction in a number of ways. Figure 28 shows the two types of alignments that have been postulated on the basis of experimental measurements.

Marzin *et al.*[284] measured optical absorption spectra in $In_xGa_{1-x}As/GaAs$ superlattices with $x \approx 0.15$ coherently strained to GaAs. The positions of excitonic absorption peaks were fitted using the ratio of the conduction-band offset to the band-gap difference, $\Delta E_c/\Delta E_g$, as the only adjustable parameter; the Bastard envelope function model,[187] with strain effects added, was used to calculate the superlattice electronic structure, and an exciton binding energy of 8 meV was assumed. For $x = 0.17$, Marzin *et al.* obtained $\Delta E_c = 0.126$ eV, $\Delta E_{hh} = 0.06$ eV, and $\Delta E_{lh} = -0.019$ eV; for $x = 0.15$, the measured band offsets were $\Delta E_c = 0.110$ eV, $\Delta E_{hh} = 0.052$ eV, and $\Delta E_{lh} = -0.018$ eV. These measurements correspond to $\Delta E_c/\Delta E_g = 0.68$. Ji *et al.*[285] measured low-temperature optical transmission spectra for $In_xGa_{1-x}As/GaAs$ multiple quantum wells strained to GaAs substrates. Transmission spectra were measured for samples with varying $In_xGa_{1-x}As$ composition and quantum-well width, and the energies of the observed features were compared to transition energies calculated theoretically with the ratio of the valence-band offset to the total band-gap difference, $\Delta E_v/\Delta E_g$, as an adjust-

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[284] J.-Y. Marzin, M. N. Charasse, and B. Sermage, *Phys. Rev. B* **31**, 8298 (1985).

[285] G. Ji, D. Huang, U. K. Reddy, T. S. Henderson, R. Houdré, and H. Morkoç, *J. Appl. Phys.* **62**, 3366 (1987).

able parameter. For $x = 0.13$–0.193, Ji *et al.* obtained $\Delta E_v/\Delta E_g = 0.30$, independent of composition. Andersson *et al.*[286] measured photoluminescence and photoconductivity spectra from $In_xGa_{1-x}As/GaAs$ quantum wells coherently strained to GaAs (001) with compositions $x = 0.073$–0.36 and obtained $\Delta E_c/\Delta E_g = 0.83 \pm 0.06$, independent of x. Pan *et al.*[287] measured photoreflectance spectra for $In_xGa_{1-x}As/GaAs$ multiple quantum wells coherently strained to GaAs (001); these measurements yielded $\Delta E_v/\Delta E_g = 0.30 \pm 0.05$ for $x = 0.11$ and 0.12. Niki *et al.*[288] measured band gaps of strained $In_xGa_{1-x}As$ layers in $In_xGa_{1-x}As/GaAs$ multiple quantum wells coherently strained to GaAs and, for $x = 0.12$ to 0.25, obtained a linear relation between the composition and band gap, $E_g(In_xGa_{1-x}As) = 1.424 - 1.15x$ eV. In these experiments, the energy of the excitonic absorption feature was taken to be the band-gap energy; corrections for quantum confinement effects were estimated to be less than 3% of the total band gap. Combining these results with previously published measurements of the $In_xGa_{1-x}As/GaAs$ conduction-band offset, Niki *et al.* deduced $\Delta E_c = 0.75x$ eV, or $\Delta E_c/\Delta E_g = 0.65$, independent of x. Photoluminescence measurements by Huang *et al.*[289] in $In_xGa_{1-x}As/GaAs$ quantum wells analyzed as a function of $In_xGa_{1-x}As$ composition and quantum-well width yielded a conduction-band offset $\Delta E_c/\Delta E_g = 0.70$ for $x = 0.09$–0.20. Reithmaier *et al.*[290] used optical absorption, photoluminescence, and electronic Raman scattering to determine band offsets in $In_xGa_{1-x}As/GaAs$ quantum wells with x ranging from 0.18 to 0.25, obtaining $\Delta E_c/\Delta E_g = 0.6$ independent of x. Photoluminescence measurements by Zou *et al.*[291] yielded $\Delta E_c/\Delta E_g = 0.60$ for $In_xGa_{1-x}As/GaAs$ quantum wells coherently strained to GaAs with $x = 0.09$–0.28. Letartre *et al.*[292] used deep-level transient spectroscopy (DLTS) and C–V profiling to determine the conduction-band offset in a $GaAs/In_{0.25}Ga_{0.75}As/GaAs$ quantum well, obtaining $\Delta E_c = 0.141 \pm 0.006$ eV $\approx 0.5\,\Delta E_g$. These measurements generally seem to indicate that, with the effects of strain included, the conduction-band offset is comparable to or somewhat larger than the valence-band offset for $In_xGa_{1-x}As/GaAs$ heterojunctions.

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[286] T. G. Andersson, Z. G. Chen, V. D. Kulakovskii, A. Uddin, and J. T. Vallin, *Phys. Rev. B* **37**, 4032 (1988).

[287] S. H. Pan, H. Shen, Z. Hang, F. H. Pollak, W. Zhuang, Q. Xu, A. P. Roth, R. A. Masut, C. Lacelle, and D. Morris, *Phys. Rev. B* **38**, 3375 (1988)

[288] S. Niki, C. L. Lin, W. S. C. Chang, and H. H. Wieder, *Appl. Phys. Lett.* **55**, 1339 (1989).

[289] K. F. Huang, K. Tai, S. N. G. Chu, and A. Y. Cho, *Appl. Phys. Lett.* **54**, 2026 (1989).

[290] J.-P. Reithmaier, R. Höger, H. Riechert, A. Heberle, G. Abstreiter, and G. Weimann, *Appl. Phys. Lett.* **56**, 536 (1990).

[291] Y. Zou, P. Grodzinski, E. P. Menu, W. G. Jeong, P. D. Dapkus, J. J. Alwan, and J. J. Coleman, *Appl. Phys. Lett.* **58**, 601 (1991).

[292] X. Letartre, D. Stievenard, and E. Barbier, *Appl. Phys. Lett.* **58**, 1047 (1991).

A number of measurements have been reported, however, that appear to contradict this conclusion. Ramberg *et al.*[293] measured current gain in *npn* GaAs/$In_xGa_{1-x}As$/GaAs heterojunction bipolar transistor structures and deduced a valence-band offset $\Delta E_v = 0.97x$ eV for $x = 0$–0.08; this measurement corresponds to $\Delta E_v = \approx 0.8$–$0.9\,\Delta E_g$, using the dependence of the $In_xGa_{1-x}As$ energy gap on x measured by Niki *et al.*[288] However, evidence was observed in these structures of some strain relaxation in the $In_xGa_{1-x}As$ layers, which would affect the values of the band offsets in these heterojunctions. Menéndez *et al.*[294] used a light-scattering method to measure band offsets in $In_xGa_{1-x}As$/GaAs quantum wells strained to GaAs for $x = 0.05$. By fitting the energies of the intersubband transitions by electrons in the $In_xGa_{1-x}As$ conduction band to a theoretical model with the ratio of the conduction-band offset to the total band-gap difference, $\Delta E_c/\Delta E_g$, as an adjustable parameter, Menéndez *et al.* obtained $\Delta E_c/\Delta E_g = 0.40 \pm 0.04$; their results corresponded to a valence-band offset $\Delta E_v = 0.035$–0.041 eV. These measurements, both for very low In concentrations in the alloy, suggest that the valence-band offset in $In_xGa_{1-x}As$/GaAs heterojunctions is larger than the conduction-band offset. Menéndez *et al.* also used their measurements to extrapolate a value for the average valence-band offset, $\Delta E_{v,av} = (0.49 \pm 0.1)x$ eV.

A possible reconciliation of these results has been proposed[295] based on measurements that demonstrate a concentration dependence of the $In_xGa_{1-x}As$/GaAs band offset. Joyce *et al.*[295] analyzed photoluminescence measurements for $In_xGa_{1-x}As$/GaAs quantum wells and obtained conduction-band offsets $\Delta E_c/\Delta E_g = 0.62 \pm 0.08$ for $x = 0.12 \pm 0.002$ and $\Delta E_c/\Delta E_g = 0.36 \pm 0.12$ for $x = 0.04 \pm 0.01$. Photocurrent measurements by Yu *et al.*[296] yielded $\Delta E_v/\Delta E_g = 0.6$ for $x = 0.093$ and $\Delta E_v/\Delta E_g = 0.3$ for $x = 0.138$. These two measurements suggest that the $In_xGa_{1-x}As$/GaAs band offset might be concentration-dependent, and the concentration dependence measured by Joyce *et al.*[295] and Yu *et al.*[296] is consistent with other experimental measurements performed for more restricted compositional ranges.[284–290,292–294] The compositional dependence of $\Delta E_v/\Delta E_g$ observed by Joyce *et al.*[295] and by Yu *et al.*[296] also casts doubt on the validity of extrapolating the average valence-band offset obtained by Menéndez *et al.*[294] for $In_{0.05}Ga_{0.95}As$/GaAs to the case of InAs/GaAs. If $\Delta E_v/\Delta E_g$ is indeed

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[293] L. P. Ramberg, P. M. Enquist, Y.-K. Chen, F. E. Najjar, L. F. Eastman, E. A. Fitzgerald, and K. L. Kavanagh, *J. Appl. Phys.* **61**, 1234 (1987).

[294] J. Menéndez, A. Pinczuk, D. J. Werder, S. K. Sputz, R. C. Miller, D. L. Sivco, and A. Y. Cho, *Phys. Rev. B* **36**, 8165 (1987).

[295] M. J. Joyce, M. J. Johnson, M. Gal, and B. F. Usher, *Phys. Rev. B* **38**, 10978 (1988).

[296] P. W. Yu, G. D. Sanders, K. R. Evans, D. C. Reynolds, K. K. Bajaj, C. E. Stutz, and R. L. Jones, *Appl. Phys. Lett.* **54**, 2230 (1989).

dependent on composition, the extrapolated average valence-band offset $\Delta E_{v,av}$(InAs/GaAs) = 0.49 ± 0.1 eV obtained by Menéndez *et al.* would be substantially larger than the actual value.

b. *Theory*

Priester *et al.*[297] calculated band offsets for GaAs/$In_xGa_{1-x}As$ heterojunctions using a self-consistent tight-binding method. These calculations yielded $\Delta E_v = 0.020$ eV for $x = 0.05$, which differs somewhat from the value $\Delta E_v = 0.035$-0.041 eV measured by Menéndez *et al.*;[294] for $x = 0.15$, Priester *et al.* obtained $\Delta E_{hh} = 0.056$ eV and $\Delta E_{lh} = -0.015$ eV, in good agreement with a number of experimental measurements.[284,285,287,289–291] For the pure GaAs/InAs heterojunction, Priester *et al.* obtained an average valence-band offset $\Delta E_{v,av}$ that depends slightly on strain. For InAs coherently strained to GaAs $\Delta E_{v,av} = 0.090$ eV, whereas $\Delta E_{v,av} = 0.185$ eV for GaAs coherently strained to InAs. These values are in reasonable agreement with the measurements of Kowalczyk *et al.*[96] for InAs/GaAs heterojunctions, which would have yielded an average valence-band offset of approximately 0.16 eV, but disagree with the average valence-band offset obtained by extrapolation from the measurements of Menéndez *et al.*,[294] $\Delta E_{v,av}$(InAs/GaAs) = 0.49 ± 0.1 eV. In light of the possible compositional dependence of $\Delta E_v/\Delta E_g$ proposed by Joyce *et al.*[295] and Yu *et al.*,[296] however, the extrapolation performed by Menéndez *et al.* of $\Delta E_{v,av}$ for InAs/GaAs from measurements on $In_{0.05}Ga_{0.95}As$/GaAs may be somewhat dangerous. On the basis of their calculations, Priester *et al.* also predicted that the band alignment for a GaAs/$In_xGa_{1-x}As$ heterojunction strained to GaAs would be type I for both light and heavy holes when $x = 1$, as shown in Fig. 28a, but would be type I for heavy holes and type II for light holes when $x = 0.15$, as shown in Fig. 28b.

The model solid theory of Van de Walle and Martin[86] also yields predictions for the GaAs/$In_xGa_{1-x}As$ band offset. The model solid theory yields $\Delta E_{hh} = 0.023$ eV and $\Delta E_{lh} = -0.001$ eV for $x = 0.05$; for $x = 0.15$, the predicted band offsets are $\Delta E_{hh} = 0.068$ eV and $\Delta E_{lh} = 0.002$ eV. These predictions indicate that approximately 40% of the band-gap discontinuity appears as the valence-band offset and that the ratio $\Delta E_c/\Delta E_v$ depends only very weakly on x. These calculations are in reasonable agreement with the measurements of a number of investigators[284,285,287–292] for GaAs/$In_xGa_{1-x}As$ heterojunctions with x ranging approximately from 0.09 to 0.28. The measurements of Andersson *et al.*[286] yielded a conduction-band offset somewhat larger than that predicted by the model solid theory, whereas

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[297] C. Priester, G. Allan, and M. Lannoo, *Phys. Rev. B* **38**, 9870 (1988).

Ramberg *et al.*[293] and Menéndez *et al.*[294] obtained conduction-band offsets considerably smaller than the values given by the model solid theory. The average valence-band offset $\Delta E_{v,av}$ predicted by the model solid theory for the pure GaAs/InAs heterojunction depends only slightly on strain. For InAs coherently strained to GaAs, $\Delta E_{v,av} = 0.18$ eV; for GaAs coherently strained to InAs, $\Delta E_{v,av} = 0.16$ eV. These compare quite favorably with the average valence-band offset $\Delta E_{v,av} = 0.16$ eV one would obtain from the measurements of Kowalczyk *et al.*[96] on pure InAs/GaAs heterojunctions but are in disagreement with the value of Menéndez *et al.*,[294] $\Delta E_{v,av} = 0.49 \pm 0.1$ eV. Again, however, one should recall the caveat regarding the extrapolation of the measurements of Menéndez *et al.* from $In_{0.05}Ga_{0.95}As$/GaAs to InAs/GaAs.

Cardona and Christensen[39] have also calculated values for the InAs/GaAs valence-band offset using their model based on dielectric midgap energies. For the InAs/GaAs heterojunction, their calculations yield an average valence-band offset $\Delta E_{v,av} = 0.18$ eV. This value is in good agreement with the value estimated from the measurements of Kowalczyk *et al.*,[96] $\Delta E_{v,av} = 0.16$ eV. In making this comparison, it is necessary to note that the quantity measured by Kowalczyk *et al.* is probably representative more of the average valence-band offset $\Delta E_{v,av}$ than the actual valence-band offset ΔE_v as had been assumed by Cardona and Christensen in comparing their calculations to experimental measurements.

18. OTHER LATTICE-MISMATCHED HETEROJUNCTIONS

a. *CdTe/ZnTe*

CdTe and ZnTe have cubic lattice constants of 6.48 Å and 6.10 Å, respectively, yielding a lattice mismatch of approximately 6%. A number of studies have been performed of band offsets in CdTe/ZnTe heterojunctions, the general conclusion being that the average valence-band offset between CdTe and ZnTe is quite small. Menéndez *et al.*[298] studied resonance Raman spectra from CdTe/ZnTe strained-layer superlattices grown on $Cd_{0.1}Zn_{0.9}Te$ buffer layers. Their experiments indicated that the heavy-hole wave functions were not well localized in the CdTe layers, suggesting that the CdTe/ZnTe valence-band offset was small. Duc *et al.*[101] used XPS to measure the CdTe/ZnTe valence-band offset, not accounting for effects of strain, for the $(\bar{1}\bar{1}\bar{1})$ orientation and obtained a value of 0.10 ± 0.06 eV. A difference in the Cd $4d_{5/2}$ to Zn $3d_{5/2}$ core-level energy separation of 0.047 eV was observed

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[298] J. Menéndez, A. Pinczuk, J. P. Valladares, R. D. Feldman, and R. F. Austin, *Appl. Phys. Lett.* **50**, 1101 (1987).

between the cases of CdTe grown on ZnTe and ZnTe grown on CdTe, suggesting that the core-level binding energies were not strongly affected by strain. For the (100) orientation, Hsu and Faurie[299] used the same technique to obtain a CdTe/ZnTe valence-band offset of 0.07 eV, with a difference in core-level energy separations for the two heterojunction growth sequences of 0.17 eV. As discussed in Section 17, the quantities measured by Duc *et al.* and by Hsu and Faurie might provide a rough estimate of the average valence-band offset $\Delta E_{v,av}$ for the CdTe/ZnTe heterojunction. For both orientations, this average valence-band offset appears to be considerably smaller than the total band-gap difference between unstrained CdTe and ZnTe of 0.75 eV. Mathieu *et al.*[300,301] performed theoretical calculations of the subband structure for CdTe/ZnTe strained-layer superlattices, accounting for the effects of strain, and used their calculations to analyze photoluminescence spectra from a number of CdTe/ZnTe superlattices. Their analysis yielded zero-strain valence-band offsets (i.e., values obtained after band-edge shifts arising from both uniaxial and hydrostatic strain have been removed) of 0.060 ± 0.020 eV[300] and 0.055 ± 0.040 eV,[301] depending on the parameters used to calculate the subband structure in the superlattices. Studies of optical spectra from CdTe/$Cd_{1-x}Zn_xTe$ quantum wells and superlattices with $x =$ 0.08–0.15 grown on $Cd_{0.96}Zn_{0.04}Te$ buffer layers indicated that the average valence-band offset was small and that the superlattice band structure was actually type I for the heavy-hole valence band and type II for the light-hole valence band.[302,303] These measurements all suggest that the valence-band offset for CdTe/ZnTe is quite small compared to the total band-gap difference between CdTe and ZnTe.

Most band offset theories are in qualitative agreement with this conclusion. It is probably most appropriate to compare the early theories of band offsets, in which strain effects were not considered, to the average valence-band offsets deduced from experimental measurements. The electron affinity rule[19] predicts valence-band offsets of 0.04 eV using the electron affinity data of Milnes and Feucht[71] and 0.07 eV using the data compiled by Freeouf and Woodall.[193] The common-anion rule[20] predicts that the CdTe/ZnTe valence-band offset should be zero. The theory of Frensley and Kroemer[23] yields a valence-band offset of −0.16 eV (type II band alignment), and Harrison's LCAO theory[24] predicts 0.18 eV. Tersoff's interface dipole

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[299] C. Hsu and J. P. Faurie, *J. Vac. Sci. Technol. B* 6, 773 (1988).

[300] H. Mathieu, J. Allegre, A. Chatt, P. Lefebvre, and J. P. Faurie, *Phys. Rev. B* **38**, 7740 (1988).

[301] H. Mathieu, A. Chatt, J. Allegre, and J. P. Faurie, *Phys. Rev. B* **41**, 6082 (1990).

[302] H. Tuffigo, A. Wasiela, N. Magnea, H. Mariette, and Y. Merle d'Aubigné, *Superlattices Microstructures* **8**, 283 (1990).

[303] Y. Merle d'Aubigné, H. Mariette, N. Magnea, H. Tuffigo, R. T. Cox, G. Lentz, L. S. Dang, J.-L. Pautrat, and A. Wasiela, *J. Cryst. Growth* **101**, 650 (1990).

theory[28] predicts a valence-band offset of -0.01 eV, while the theory of Harrison and Tersoff[29] yields -0.03 eV. The empirical results of Katnani and Margaritondo[21] yield a CdTe/ZnTe valence-band offset of 0.10 eV. Among the more recent band offset theories, the model solid theory of Van de Walle and Martin yields[86] average valence-band offsets of 0.05–0.08 eV and with strain splittings included predicts a type I band alignment for the heavy-hole valence bands and a type II alignment for the light-hole bands, consistent with the experimental observations of Tuffigo *et al.*[302]

The available experimental and theoretical data on the CdTe/ZnTe band offset indicate that the average valence-band offset is quite small, in agreement with the general trend predicted for heterojunction systems with a common anion by early theories such as the common-anion rule and the LCAO theory of Harrison. Strain-induced splittings in the valence bands, however, could still produce substantial offsets for the individual valence bands in coherently strained CdTe/ZnTe heterojunctions. Because of the small average valence-band offset, the conduction-band offset should be quite large for all levels of strain; the model solid theory, for example, predicts CdTe/ZnTe conduction-band offsets ranging approximately from 0.36 eV to 0.54 eV, depending on the strain configuration of the heterojunction.

b. *ZnSe/ZnTe*

A few studies have also been performed of band offsets in the ZnSe/ZnTe material system; the lattice mismatch between ZnSe and ZnTe is approximately 7%. Experimental values for the average or in some cases "unstrained" valence-band offset for ZnSe/ZnTe are shown in Table XIII and Fig. 29. Fujiyasu *et al.*[304] studied photoluminescence from ZnTe/ZnSe superlattices grown on GaAs (100) substrates and deduced from the variation in photoluminescence energy with the ZnSe and ZnTe layer thicknesses that the band alignment was type II. Rajakarunanayake *et al.*[305,306] used theoretical calculations of band structure in ZnSe/ZnTe strained-layer superlattices to analyze photoluminescence data obtained by Kobayashi *et al.*[307] Depending on whether the superlattice photoluminescence was attributed to Te_1 isoelectronic traps in ZnSe or to band-to-band transitions, valence-band offsets of

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[304] H. Fujiyasu, K. Mochizuki, Y. Yamazaki, M. Aoki, A. Sasaki, H. Kuwabara, Y. Nakanishi, and G. Shimaoka, *Surf. Sci.* **174**, 543 (1986).

[305] Y. Rajakarunanayake, R. H. Miles, G. Y. Wu, and T. C. McGill, *Phys. Rev. B* **37**, 10212 (1988).

[306] Y. Rajakarunanayake, R. H. Miles, G. Y. Wu, and T. C. McGill, *J. Vac. Sci. Technol. B* **6**, 1354 (1988).

[307] M. Kobayashi, N. Mino, H. Katagiri, R. Kimura, M. Konagai, and K. Takahashi, *Appl. Phys. Lett.* **48**, 296 (1986).

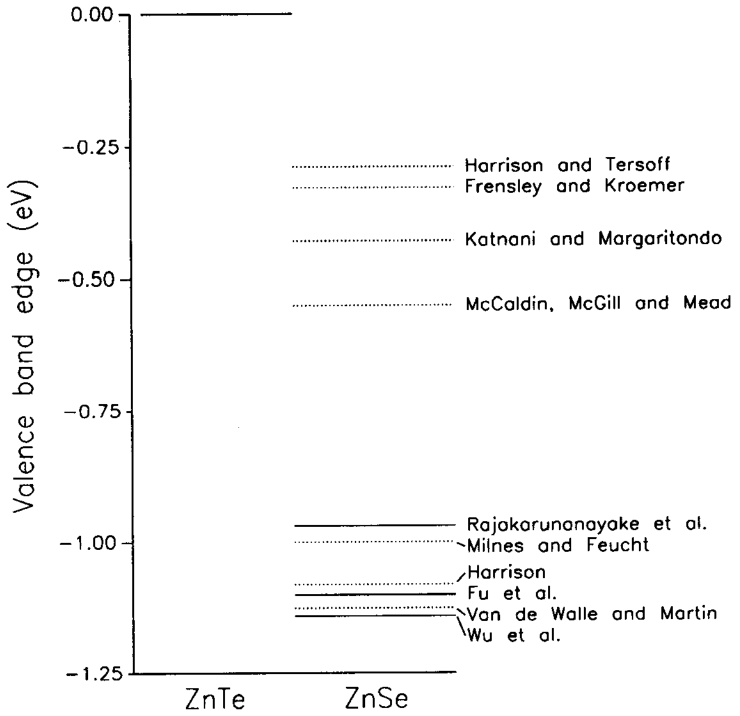

FIG. 29. Summary of experimental and theoretical values for either the average or the "unstrained" valence-band offset in the ZnSe/ZnTe heterojunction.

TABLE XIII. EXPERIMENTAL AND THEORETICAL VALUES FOR EITHER AVERAGE OR "UNSTRAINED" VALENCE-BAND OFFSETS FOR ZnSe/ZnTe

SOURCE	ΔE_v (expt.) (eV)	ΔE_v (theor.) (eV)
Rajakarunanayake *et al.* (1988)[305,306]	0.97 ± 0.1	
Wu *et al.* (1990)[308]	1.14 ± 0.1	
Fu *et al.* (1990)[310]	~1.1	
Milnes and Feucht (1972)[71]		1.0
McCaldin *et al.* (1976)[20]		0.55
Frensley and Kroemer (1977)[23]		0.33
Harrison (1977)[24]		1.08
Katnani and Margaritondo (1983)[21]		0.43
Harrison and Tersoff (1986)[29]		0.29
Van de Walle and Martin (1987)[86]		1.36 ("unstrained")
(model solid theory)		1.10–1.15 (average)

0.97 ± 0.10 eV or 1.20 ± 0.13 eV, respectively, were deduced. The valence-band offsets quoted by Rajakarunanayake *et al.* are for the average position of the heavy-hole and light-hole band edges in each material, a quantity that was assumed to be independent of strain; the actual discontinuities in the valence bands will depend on the strain-induced splittings in each layer. A similar analysis by Wu *et al.*[308] yielded an unstrained valence-band offset of 1.136 ± 0.1 eV, using photoluminescence data of Konagai *et al.*;[309] their analysis assumed that the observed photoluminescence was attributable to excitonic recombination in the superlattice. Photoluminescence studies by Fu *et al.*[310] also suggested that the band alignment for the ZnSe/ZnTe heterojunction was type II; their measurements were consistent with the average valence-band offset predicted by Van de Walle and Martin[86] of approximately 1.1 eV. These measurements suggest that, before strain-induced valence-band splittings are included, the ZnSe valence-band edge is approximately 1 eV lower in energy than the ZnTe valence-band edge. However, uncertainties regarding the nature of luminescence from ZnSe/ZnTe superlattices, and in particular the role of Te isoelectronic traps in ZnSe,[311,312] could affect the band offset values extracted from these experiments.

Theoretical predictions for the unstrained ZnSe/ZnTe valence-band offset extend over a wide range of values. Frensley and Kroemer[23] predict a valence-band offset of 0.33 eV without interfacial dipole corrections. Harrison's LCAO theory[24] yields $\Delta E_v = 1.08$ eV. Tersoff's theory[28] yields an unstrained valence-band offset of 0.86 eV, while Harrison and Tersoff[29] obtain a value of 0.29 eV. The "unstrained" value from Tersoff's theory should be viewed with caution, however, because strain can shift the average valence-band offset to a value several tenths of an electron volt away from the simple unstrained band offset. The model solid theory of Van de Walle and Martin[86] yields an unstrained valence-band offset of 1.36 eV. For actual strained ZnSe/ZnTe heterojunctions, the model solid theory yields average valence-band offsets of approximately 1.10–1.15 eV. The electron affinity rule[71] predicts a valence-band offset of approximately 1 eV, and the common-anion rule[20] yields $\Delta E_v = 0.55$ eV. Finally, the empirical compilation of Katnani and Margaritondo[21] predicts a valence-band offset of 0.43 eV.

It is apparent that many of the theoretical predictions for the ZnSe/ZnTe

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[308] Y. Wu, S. Fujita, and S. Fujita, *J. Appl. Phys.* **67**, 908 (1990).

[309] M. Konagai, M. Kobayashi, R. Kimura, and K. Takahashi, *J. Cryst. Growth* **86**, 290 (1988).

[310] Q. Fu, N. Pelekanos, W. Walecki, A. V. Nurmikko, S. Durbin, J. Han, M. Kobayashi, and R. L. Gunshor, Proceedings of the International Conference on Semiconductor Physics, Greece, p. 1353, 1990.

[311] D. Lee, A. Mysyrowicz, A. V. Nurmikko, and B. J. Fitzpatrick, *Phys. Rev. Lett.* **58**, 1475 (1987).

[312] T. Yao, M. Kato, H. Tanio, and J. J. Davis, *J. Cryst. Growth* **86**, 552 (1988).

valence-band offset are in relatively poor agreement with each other and with the available experimental data. The theoretical models of Harrison,[24] Tersoff,[28] and Van de Walle and Martin[84–86] appear to yield values that are in good agreement with experiment, but the others deviate significantly from the experimental results. Again, however, it should be noted that most of the predicted band offsets do not incorporate the effects of strain. As discussed by Cardona and Christensen,[39] strain can strongly influence the value of even the average valence-band offset in certain models for predicting band alignments, such as their own dielectric midgap energy model[39] and the model of Tersoff.[28]

VII. Heterovalent Material Systems

Studies of heterovalent material systems, e.g., III–V/II–VI or compound/elemental semiconductor heterojunctions, are often complicated by chemical or structural imperfections at the heterojunction interface. Early theoretical studies by Harrison *et al.*[313] demonstrated that intermixing is required in polar heterovalent interfaces, such as GaAs/Ge (001), to prevent large charge accumulations at the heterojunction interface. Experimental studies, particularly of III–V/II–VI interfaces, suggest that interfacial reactivity may be endemic in heterovalent material systems. In this section we review the experimental data available on band offsets at heterovalent interfaces and discuss effects such as interfacial reactivity and antiphase disorder that can affect structural quality and band offset values in these material systems.

19. GAAS/GE

a. *Experiment*

The most widely studied of the heterovalent material systems has been GaAs/Ge. In one of the initial applications of the XPS technique for measuring band offsets, Grant *et al.*[94] estimated a valence-band offset of 0.3 ± 0.3 eV for Ge deposited on (110) GaAs. These experiments also revealed that the valence-band offset varied by as much as ±0.1 eV for Ge deposited on GaAs layers with different crystal orientations or surface reconstructions. A later, more refined measurement of bulk core-level binding energies for GaAs and Ge[53] yielded a valence-band offset of 0.55 ± 0.03 eV for GaAs/Ge (110) and valence-band offsets ranging from 0.48 eV to 0.66 eV for other GaAs substrate orientations and surface reconstructions.[69] Bauer and McMenamin[314] used synchrotron radiation photoemission spectro-

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[313] W. A. Harrison, E. A. Kraut, J. R. Waldrop, and R. W. Grant, *Phys. Rev. B* **18**, 4402 (1978).
[314] R. S. Bauer and J. C. McMenamin, *J. Vac. Sci. Technol.* **15**, 1444 (1978).

scopy to measure valence-band offsets for Ge deposited on GaAs (110). For heterojunctions formed at substrate temperatures of ~430°C and above, in which significant interdiffusion occurs, a valence-band offset of 0.2 ± 0.1 eV was obtained; for abrupt interfaces obtained at a growth temperature of 350°C, however, a valence-band offset of approximately 0.7 eV was measured. At an intermediate growth temperature of 420°C, Perfetti *et al.*[315] used angle-resolved ultraviolet photoemission spectroscopy to measure $\Delta E_v = 0.25$ eV for Ge deposited on GaAs (110). These measurements demonstrate that the structural quality of the Ge overlayer and the detailed chemical nature of the interface can exert a substantial influence on band offset values. Other studies, however, suggest that the valence-band offset may be less sensitive to the conditions under which the interface is prepared than would be indicated by the aforementioned results. Katnani *et al.*[316–319] used photoemission to obtain a valence-band offset of 0.47 ± 0.05 eV for the GaAs/Ge heterojunction and performed a number of experiments indicating that the surface reconstruction on which the interface is grown, changes in interface orientation, and even the introduction of Al interlayers at the GaAs/Ge interface all shifted the value of the valence-band offset by not more than ±0.05 eV. Results of selected experimental band offset measurements for GaAs/Ge are shown in Fig. 30. Measured band offsets for purportedly abrupt GaAs/Ge heterojunctions are also compiled in Table XIV.

Growth sequence can also influence the structural quality of a GaAs/Ge heterojunction and consequently the band offset value. Photoemission measurements by Zurcher and Bauer[320] yielded a valence-band offset of 0.23–0.26 eV for GaAs deposited on Ge (110), significantly lower than the values measured for abrupt interfaces formed by depositing Ge on GaAs (110). Structural studies of GaAs/Ge heterostructures[321] demonstrated that for growth of GaAs on (100) or (111) Ge, antiphase boundaries form in the GaAs layers and the GaAs surface becomes rough on an atomic scale; for growth of GaAs on (110) Ge, however, the GaAs surface was seen to remain fairly smooth, suggesting that if antiphase boundaries are formed, their effect on surface morphology is less significant than for the (100) and (111)

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[315] P. Perfetti, D. Denley, K. A. Mills, and D. A. Shirley, *Appl. Phys. Lett.* **33**, 667 (1978).

[316] A. D. Katnani, P. Chiaradia, H. W. Sang, Jr., and R. S. Bauer, *J. Vac. Sci. Technol. B* **2**, 471 (1984).

[317] A. D. Katnani, H. W. Sang, Jr., P. Chiaradia, and R. S. Bauer, *J. Vac. Sci. Technol. B* **3**, 608 (1985).

[318] A. D. Katnani, P. Chiaradia, H. W. Sang, Jr., P. Zurcher, and R. S. Bauer, *Phys. Rev. B* **31**, 2146 (1985).

[319] A. D. Katnani and R. S. Bauer, *J. Vac. Sci. Technol. B* **3**, 1239 (1985).

[320] P. Zurcher and R. S. Bauer, *J. Vac. Sci. Technol. A* **1**, 695 (1983).

[321] C.-A. Chang and T.-S. Kuan, *J. Vac. Sci. Technol. B* **1**, 315 (1983).

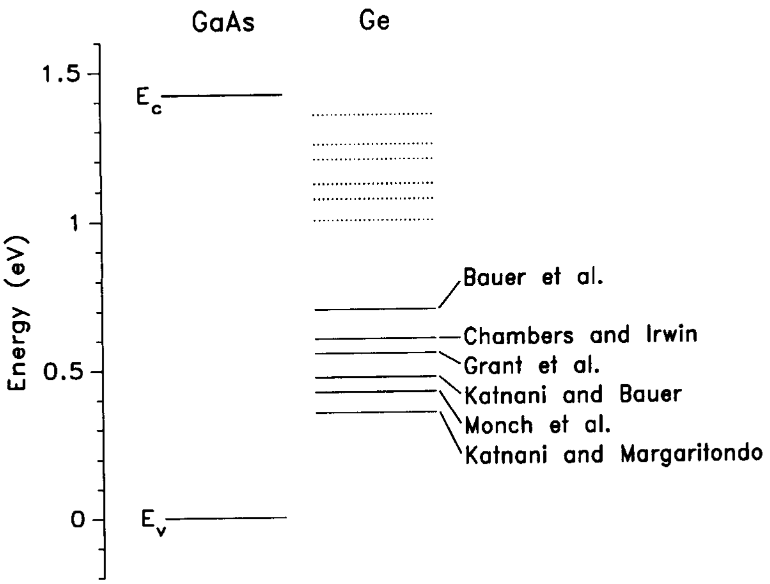

FIG. 30. Band alignments obtained from experimental measurements on purportedly abrupt GaAs/Ge heterojunctions. Ge valence- and conduction-band edge energies are indicated by solid and dotted lines, respectively.

TABLE XIV. EXPERIMENTAL BAND OFFSETS FOR PURPORTEDLY ABRUPT GaAs/Ge HETEROJUNCTIONS

SOURCE	HETEROJUNCTION	ΔE_v (expt.) (eV)
Grant *et al.* (1978, 1980)[94,53]	GaAs/Ge (110)	0.55 ± 0.03
Bauer *et al.* (1978)[314]	GaAs/Ge (110)	0.7
Mönch *et al.* (1982)[323]	GaAs/Ge (110)	0.42 ± 0.1
Katnani and Margaritondo (1983)[21]	GaAs/Ge (110)	0.35
Katnani *et al.* (1984)[316–319]	GaAs/Ge (100), (110), (111), (211)	0.47 ± 0.05
Chambers and Irwin (1988)[324]	GaAs/Ge (001)	0.60 ± 0.05

orientations. Because the (100) and (111) surfaces of GaAs consist of alternating planes of pure Ga and As, the initial layer of GaAs on (100) or (111) Ge will have regions of pure Ga and of pure As; further growth of GaAs then leads to the formation of antiphase boundaries between these regions. For the (110) orientation, Kroemer[322] has discussed a similar mechanism for

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[322] H. Kroemer, *Surf. Sci.* **132**, 543 (1983).

the formation of antiphase domains. When Ge is deposited on GaAs, formation of antiphase domains is not a consideration and epilayers of high structural quality can be grown.

A number of other measurements of the GaAs/Ge band offset have been reported. Mönch *et al.*[323] used photoemission to measure valence-band offsets in GaAs/Ge (110) heterojunctions. For epitaxial Ge deposited on GaAs at 300°C, a valence-band offset of 0.42 ± 0.1 eV was obtained; for amorphous Ge deposited at 20°C, the measured valence-band offset was 0.65 ± 0.1 eV. Katnani and Margaritondo[21] used photoemission spectroscopy to measure the valence-band offset for Ge deposited on a cleaved GaAs substrate and obtained $\Delta E_v = 0.35$ eV. Chambers and Irwin[324] used XPS to study GaAs/Ge (001) heterojunctions and obtained a valence-band offset of 0.60 ± 0.05 eV. The GaAs/Ge band offset has also been determined from electrical measurements. Ballingall *et al.* studied J-V characteristics for *n*-Ge/*n*-GaAs heterojunctions and deduced conduction-band offsets of 0.08 ± 0.01 eV[325] and 0.05 ± 0.03 eV,[326] corresponding to a valence-band offset of approximately 0.70 eV; however, some grading at the Ge/GaAs interface was thought to be present in those samples.

Combining the measurements just described, it would appear that the experiments performed using heterojunctions thought to be abrupt and of high quality yield valence-band offsets ranging approximately from 0.35 eV to 0.7 eV, with the band alignment being type I. Figure 30 summarizes the GaAs/Ge energy band alignments measured by various investigators. It is quite clear from the wide range of band offset values reported for heterojunctions prepared under different conditions that the detailed atomic structure of the GaAs/Ge interface can have a substantial effect on band offset values. The dependence of the GaAs/Ge valence-band offset on growth conditions may be partially responsible for the rather wide range of experimental valence-band offsets reported even for supposedly abrupt GaAs/Ge heterojunctions.

b. *Theory*

Theoretical predictions for the GaAs/Ge valence-band offset will not, of course, account for the nonideal aspects of interfacial structure discussed earlier and are therefore best compared to the experimental measurements performed using abrupt, high-quality heterojunctions. For all of the predictions in the following discussion, the valence-band edge of Ge is higher in

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[323] W. Mönch, R. S. Bauer, H. Gant, and R. Murschall, *J. Vac. Sci. Technol.* **21**, 498 (1982).

[324] S. A. Chambers and T. J. Irwin, *Phys. Rev. B* **38**, 7484 (1988).

[325] J. M. Ballingall, R. A. Stall, C. E. C. Wood, and L. F. Eastman, *J. Appl. Phys.* **52**, 4098 (1981).

[326] J. M. Ballingall, C. E. C. Wood, and L. F. Eastman, *J. Vac. Sci. Technol. B* **1**, 675 (1983).

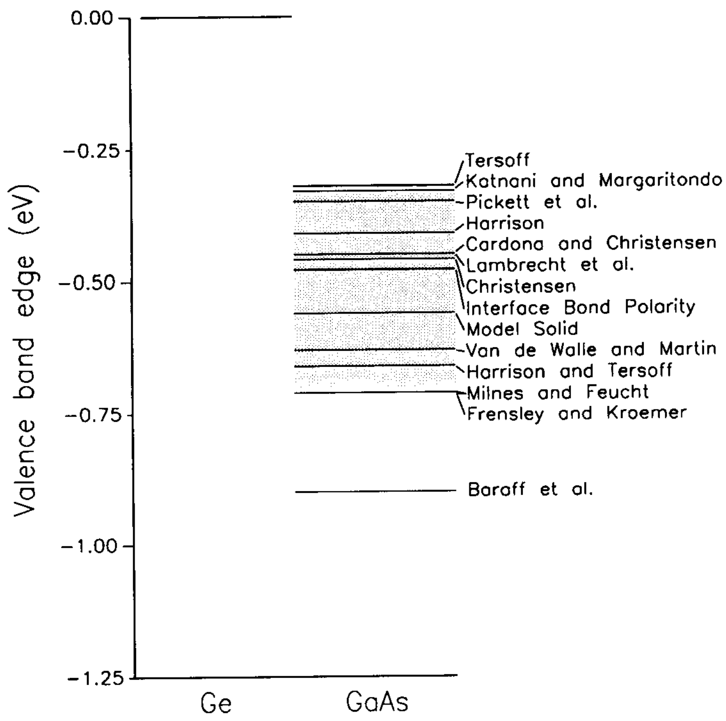

FIG. 31. Theoretical values for the GaAs/Ge valence-band offset. The shaded region indicates the approximate range of experimental values reported for the valence-band offset in abrupt GaAs/Ge heterojunctions.

energy than that of GaAs. Theoretical values for the GaAs/Ge valence-band offset are shown in Fig. 31 and Table XV. Frensley and Kroemer's pseudopotential theory[23] predicts $\Delta E_v = 0.71$ eV, and Harrison's LCAO theory[24] yields $\Delta E_v = 0.41$ eV. Tersoff's interface dipole theory[28] predicts a valence-band offset of 0.32 eV, and Harrison and Tersoff[29] obtain a value of 0.66 eV. The dielectric midgap energy model of Cardona and Christensen[39] predicts a valence-band offset of 0.45 eV, and the model solid theory of Van de Walle and Martin[86] yields a value of 0.56 eV. The interface-bond-polarity model of Lambrecht and Segall[87] predicts a valence-band offset of 0.48 eV. Among the empirically derived models, the electron affinity rule[19] yields a valence-band offset of 0.71 eV using the electron affinity data of Milnes and Feucht,[71] and the empirical compilation of Katnani and Margaritondo[21] predicts a valence-band offset of 0.33 eV. In addition, a number of self-consistent interface and supercell calculations have been performed for the GaAs/Ge interface. Among the earliest of these calculations were those reported by Baraff

TABLE XV. THEORETICAL PREDICTIONS FOR THE GaAs/Ge VALENCE-BAND OFFSET

SOURCE	ΔE_v (theor.) (eV)
Milnes and Feucht (1972)[71]	0.71
Baraff *et al.* (1977)[33,34]	~ 0.9
Pickett *et al.* (1977)[35]	0.35
Frensley and Kroemer (1977)[23]	0.71
Harrison (1977)[24]	0.41
Katnani and Margaritondo (1983)[21]	0.33
Tersoff (1986)[28]	0.32
Harrison and Tersoff (1986)[29]	0.66
Van de Walle and Martin (1987)[84] (self-consistent supercell)	0.63
Van de Walle and Martin (1987)[86] (model solid theory)	0.56
Cardona and Christensen (1987)[39] (dielectric midgap energy model)	0.45
Christensen (1988)[40]	0.46
Lambrecht *et al.* (1990)[43] (self-consistent dipole)	0.45
Lambrecht and Segall (1990)[87] (interface bond polarity model)	0.48

et al.[33,34] and by Pickett *et al.*[35] Baraff *et al.*[33,34] performed calculations for the GaAs/Ge (100) interface and obtained a valence-band offset of ~0.9 eV, and Pickett *et al.*[35] obtained $\Delta E_v = 0.35$ eV for the GaAs/Ge (110) interface. Self-consistent interface calculations by Van de Walle and Martin [84] yielded $\Delta E_v = 0.63$ eV. Self-consistent calculations performed by Christensen[40] using LMTO methods applied in a supercell geometry yielded $\Delta E_v = 0.46$ eV, and the self-consistent dipole theory of Lambrecht *et al.*[42,43] predicted a valence-band offset of 0.45 eV.

The valence-band offsets predicted by most theories appear to be within the range of reported experimental values, although the experimental range is uncomfortably wide. Most of the available theories, despite their widely disparate physical justifications, predict values ranging approximately from 0.3 eV to 0.7 eV. This is in contrast to the situation for many other heterojunction systems, in which the predicted band offset values extend over a range of several tenths of an electon volt. However, the wide range of experimental values reported makes difficult any judgement regarding the relative accuracy of different band offset theories for the GaAs/Ge heterojunction.

An added complication is that, as pointed out by Harrison *et al.*,[313] atomic intermixing must occur to prevent large charge accumulations at the GaAs/Ge interface. None of the theoretical treatments currently available account for this intermixing. In some sense, therefore, the heterojunctions treated theoretically may be quite different from those realized experimentally. Studies of other material systems such as AlSb/GaSb/ZnTe[105,190] have demonstrated that interfacial reactivity can have a substantial effect on band offsets, but a quantitative understanding of these effects has yet to be attained.

20. GaAs/ZnSe

a. *Experiment*

The GaAs/ZnSe material system has been the most extensively studied of the lattice-matched III–V/II–VI heterojunctions. Interest in III–V/II–VI material systems arises from both the desire to use III–V substrate materials for epitaxial growth of II–VI semiconductors and the possibility of developing novel electronic and optoelectronic devices utilizing III–V/II–VI heterojunctions. Several investigators have reported studies of the structural, chemical, and electronic properties of III–V/II–VI interfaces, with the most effort having been devoted to the GaAs/ZnSe material system.

Tu and Kahn[124] studied interfaces between GaAs and ZnSe or Se in the (100) and (110) orientations and observed evidence that a compound containing Ga and Se was formed at the GaAs/ZnSe interface. For ZnSe deposited on GaAs, Auger electon spectroscopy (AES) data indicated that, for both the (110) and (100) orientations, a Se-rich region of approximately 5 Å thickness was formed at the interface. For the (110) orientation, annealing at 460°C transformed a 30 Å ZnSe epilayer into Ga_2Se_3 in the hexagonal wurtzite structure, as determined from low-energy electron diffraction (LEED) patterns. AES and LEED data for Se deposited on GaAs helped confirm that the intermediate compound was formed via Se–As interchange. Kobayashi[327] found that a Se treatment of Ga-terminated GaAs (001) surfaces at a substrate temperature of 500°C strongly suppressed Ga diffusion into ZnSe epilayers deposited on GaAs; AES analysis indicated that this suppression was due to the formation of several monolayers of GaAsSe on the GaAs surface upon exposure to Se. Li *et al.*[328] studied GaAs/ZnSe (100) interfaces using transmission electron microscopy and observed evidence of the presence of a Ga_2Se_3 layer at the heterojunction interface, and Krost

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[327] N. Kobayashi, *Jpn. J. Appl. Phys.* **27**, L1597 (1988).

[328] D. Li, J. M. Gonsalves, N. Otsuka, J. Qiu, M. Kobayashi, and R. L. Gunshor, *Appl. Phys. Lett.* **57**, 449 (1990).

et al.[329] observed evidence of the formation of Ga_2Se_3 at the GaAs/ZnSe interface using Raman spectroscopy. In studies of GaAs/ZnSe electrical device structures, Qian *et al.*[330,331] were able to produce GaAs/ZnSe interfaces with interface state densities comparable to those found in GaAs/Al_xGa_{1-x}As heterojunctions, and Qiu *et al.*[332] demonstrated that the interface state density was strongly dependent on the stoichiometry of the GaAs surface on which ZnSe was deposited.

Early measurements of the GaAs/ZnSe valence-band offset suggested that the detailed structure of the heterojunction interface could have a substantial effect on the band offset value. Experimental measurements of the GaAs/ZnSe band offsets are summarized in Fig. 32 and Table XVI. Kowalczyk

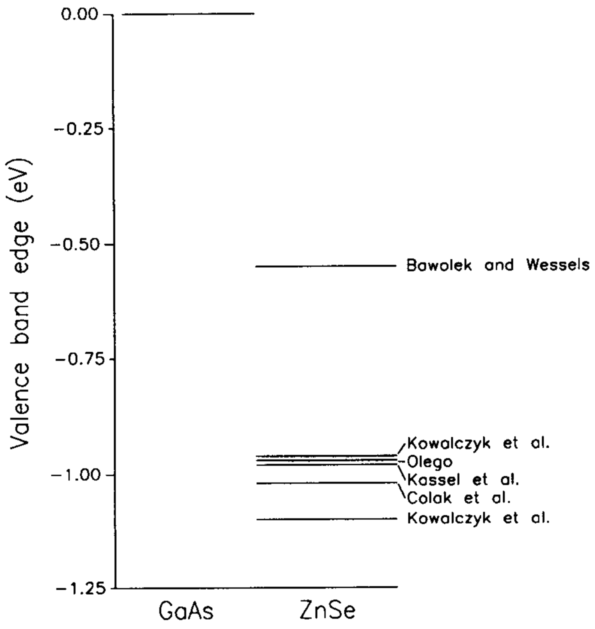

FIG. 32. Reported experimental values for the GaAs/ZnSe valence-band offset. In all cases the band alignment at the GaAs/ZnSe heterojunction is type I.

[329] A. Krost, W. Richter, D. R. T. Zahn, K. Hingerl, and H. Sitter, *Appl. Phys. Lett.* **57**, 1981 (1990).

[330] Q.-D. Qian, J. Qiu, M. R. Melloch, J. A. Cooper, Jr., L. A. Kolodziejski, M. Kobayashi, and R. L. Gunshor, *Appl. Phys. Lett.* **54**, 1359 (1989).

[331] Q. D. Qian, J. Qiu, M. Kobayashi, R. L. Gunshor, M. R. Melloch, and J. A. Cooper, Jr., *J. Vac. Sci. Technol. B* **7**, 793 (1989).

[332] J. Qiu, Q.-D. Qian, R. L. Gunshor, M. Kobayashi, D. R. Menke, D. Li, and N. Otsuka, *Appl. Phys. Lett.* **56**, 1272 (1990).

TABLE XVI. EXPERIMENTAL BAND OFFSET VALUES FOR GaAs/ZnSe

SOURCE	ΔE_v (expt.) (eV)	ΔE_c (expt.) (eV)
Kowalczyk *et al.* (1982)[65]	0.96–1.10	—
Bawolek and Wessels (1985)[334]	—	0.69
Colak *et al.* (1989)[333]	—	0.2–0.3
Olego (1989)[335,336]	—	0.31 ± 0.05
Kassel *et al.* (1990)[337]	—	0.30 ± 0.05

et al.[65] measured the GaAs/ZnSe (110) valence-band offset using XPS and found that the value depended on the method used to prepare the heterojunction. For ZnSe grown on GaAs at ~300°C a valence-band offset of 0.96 eV was obtained, whereas for ZnSe deposited on GaAs at room temperature and crystallized at 300°C the measured valence-band offset was 1.10 eV. Electrical measurements performed by Colak *et al.*[333] for metal/n-ZnSe/n^+-GaAs heterostructures yielded a conduction-band offset of approximately 0.2–0.3 eV, corresponding to a valence-band offset of approximately 1 eV. J-V measurements on n-n ZnSe/GaAs heterojunctions by Bawolek and Wessels[334] yielded a conduction-band offset of 0.69 eV, corresponding to a valence-band offset of 0.55 eV. Olego[335,336] measured a conduction-band offset of approximately 0.31 ± 0.05 eV, corresponding to $\Delta E_v = 0.97$ eV, for the GaAs/ZnSe (100) heterojunction using a Raman scattering technique. Finally, optical studies of ZnSe/GaAs heterojunctions performed by Kassel *et al.*[337] yielded a conduction-band offset $\Delta E_c = 0.30 \pm 0.05$ eV, corresponding to $\Delta E_v = 0.98$ eV. In all of these measurements the band alignment was type I, and most of the experimental band offset measurements yielded results very close to $\Delta E_v = 0.97$ eV. One explanation proposed by Bawolek and Wessels[334] for the discrepancy between their measurements and those of other investigators was the possible presence of a high interface state density in their heterojunctions.

b. *Theory*

A large number of theoretical predictions are available for the GaAs/ZnSe valence-band offset. In all cases, the GaAs valence-band edge is predicted to

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[333] S. Colak, T. Marshall, and D. Cammack, *Solid-State Electron.* **32**, 647 (1989).

[334] E. J. Bawolek and B. W. Wessels, *Thin Solid Films* **131**, 173 (1985).

[335] D. J. Olego, *Phys. Rev. B* **39**, 12743 (1989).

[336] D. J. Olego and D. Cammack, *J. Cryst. Growth* **101**, 546 (1990).

[337] L. Kassel, H. Abad, J. W. Garland, P. M. Raccah, J. E. Potts, M. A. Haase, and H. Cheng, *Appl. Phys. Lett.* **56**, 42 (1990).

be higher in energy than that of ZnSe, with most of the theories yielding a type I band alignment. Theoretical values for the GaAs/ZnSe valence-band offset are summarized in Fig. 33 and Table XVII. The pseudopotential theory of Frensley and Kroemer[23] predicts a valence-band offset of 1.11 eV without interfacial dipole corrections and 1.21 eV if dipole corrections are included, both corresponding to a type I band alignment. Harrison's LCAO theory[24] predicts $\Delta E_v = 1.05$ eV, yielding a type I band alignment. Tersoff's interface dipole theory[28] predicts $\Delta E_v = 1.20$ eV and a type I alignment, and Harrison and Tersoff's theory[29] yields a valence-band offset of 1.35 eV, corresponding to a type II staggered band alignment. Cardona and Christensen's dielectric

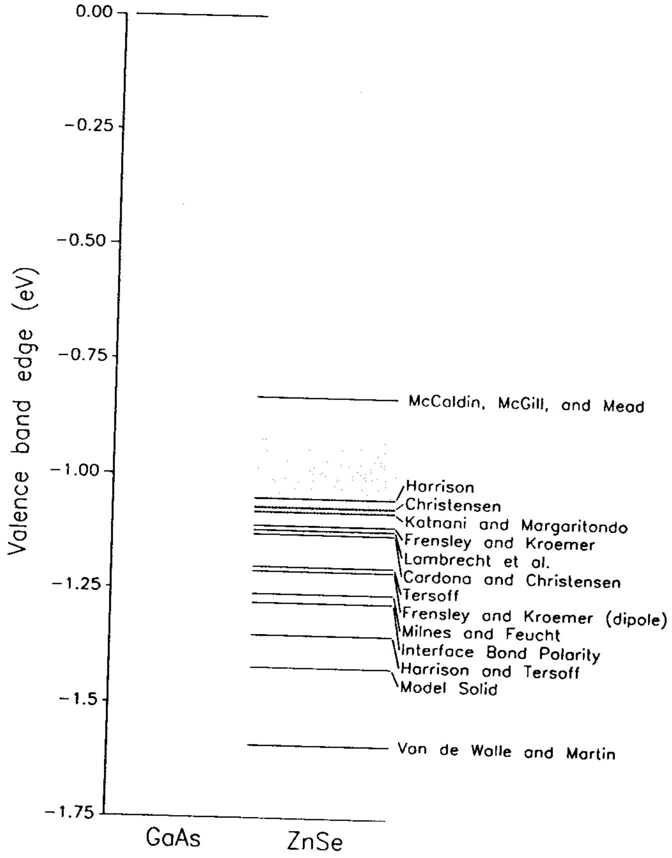

FIG. 33. Theoretical values for the GaAs/ZnSe valence-band offset. The shaded region indicates the approximate range of experimental values reported for the GaAs/ZnSe valence-band offset.

TABLE XVII. THEORETICAL PREDICTIONS FOR THE GaAs/ZnSe BAND OFFSET

SOURCE	ΔE_v (theor.) (eV)	ΔE_c^a (theor.) (eV)
Electron affinity rule (1972)[71]	1.26	−0.02
McCaldin *et al.* (1976)[20]	0.83	0.41
Frensley and Kroemer (1977)[23]	1.11	0.13
Frensley and Kroemer (1977)[23] (with dipole correction)	1.21	0.03
Harrison (1977)[24]	1.05	0.19
Katnani and Margaritondo (1983)[21]	1.08	0.16
Tersoff (1986)[28]	1.20	0.04
Harrison and Tersoff (1986)[29]	1.35	−0.11
Van de Walle and Martin (1987)[84] (self-consistent supercell)	1.59	−0.35
Van de Walle and Martin (1987)[86] (model solid theory)	1.42	−0.18
Cardona and Christensen (1987)[39] (dielectric midgap energy model)	1.13	0.11
Christensen (1988)[40]	1.07	0.17
Lambrecht *et al.* (1990)[43] (self-consistent dipole)	1.12	0.12
Lambrecht and Segall (1990)[87] (interface bond polarity model)	1.28	−0.04

[a] Conduction-band offsets are obtained assuming room-temperature band gaps of 1.43 eV and 2.67 eV for GaAs and ZnSe, respectively. A positive value of ΔE_c corresponds to a type I alignment, a negative value to a type II staggered alignment.

midgap energy theory[39] predicts a valence-band offset of 1.13 eV, a type I band alignment, and the model solid theory of Van de Walle and Martin[86] yields $\Delta E_v = 1.42$ eV, corresponding to a type II alignment. The interface bond polarity model of Lambrecht and Segall[87] yields $\Delta E_v = 1.28$ eV and a type II band alignment. Among the more empirical treatments, the electron affinity rule[19,71] yields a valence-band offset of 1.26 eV and a type II alignment. The common-anion rule[20] predicts $\Delta E_v = 0.83$ eV and the empirical treatment of Katnani and Margaritondo[21] yields a valence-band offset of 1.08 eV, both producing type I alignments. The more recent self-consistent interface and supercell calculations have also been applied to the GaAs/ZnSe heterojunction, typically for the (110) orientation. Self-consistent interface calculations by Van de Walle and Martin[84] yielded $\Delta E_v = 1.59$ eV, corresponding to a type II alignment. Self-consistent calculations of Christensen[40] using LMTO methods yielded a valence-band offset of 1.07 eV, and Lambrecht *et al.*[43] obtained $\Delta E_v = 1.12$ eV from their self-consistent dipole calculations; these predictions both yield a type I band alignment.

As seen in Fig. 33, the theoretically predicted valence-band offsets span a wide range of values, and relatively few values are in good agreement with the experimental band offset values. Most theories appear to predict valence-band offsets that are substantially larger than the experimental values; the calculations of Van de Walle and Martin[84,86] are especially prominent in this respect. Given that interfacial reactions are known to occur in the GaAs/ZnSe heterojunction, the tendency of theories to predict valence-band offsets consistently larger than the experimental values may be suggestive. As discussed in Section 19, theoretical treatments of band offsets typically consider abrupt interfaces, which in the case of the GaAs/ZnSe heterojunction fail to describe the actual interface that is produced experimentally. Experiments described in Sections 21 and 22 suggest that interfacial reactivity is fairly common in III–V/II–VI heterojunctions. An understanding of this tendency and its effect on band offset values may help to provide insight into the fundamental physics of band offsets.

21. AlSb/GaSb/ZnTe

a. *Experiment*

Much of the interest in the AlSb/GaSb/ZnTe material system has been due to the desire to obtain visible light emission from wide-gap II–VI semiconductors such as ZnTe. The inability to dope ZnTe *n*-type led to the proposal of visible light-emitting diode (LED) structures based on heterojunction injection of minority carriers into wide-gap II–VI materials, rather than recombination in simple *p*–*n* homojunction structures. The AlSb/ZnTe heterojunction was proposed as a particularly promising material system for this application.[338] In addition, the nearly lattice-matched AlSb/GaSb/ZnTe material system has proved to be a convenient system for studying the physics and chemistry of heterovalent interfaces.

Wilke and Horn[106] used photoemission to study GaSb/ZnTe (110) heterojunctions and observed evidence of the formation of a reacted layer containing Ga and Te at the GaSb/ZnTe interface; in addition, Sb from the GaSb substrate was observed on top of the ZnTe overlayer. The interface reaction appeared to occur as the first layers of ZnTe were deposited on the GaSb surface. These measurements also yielded a value for the GaSb/ZnTe (110) valence-band offset, $\Delta E_v = 0.34 \pm 0.05$ eV, with the band alignment

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[338] J. O. McCaldin and T. C. McGill, *J. Vac. Sci. Technol. B* **6**, 1360 (1988).

being type I. Schwartz *et al.*[339] measured the AlSb/ZnTe (100) valence-band offset using XPS and obtained a value of 0.35 ± 0.11 eV. Yu *et al.*[105,190] used XPS to investigate band offsets and interfacial reactions in the AlSb/GaSb/ZnTe (100) material system. For the AlSb/ZnTe and GaSb/ZnTe interfaces, Yu *et al.* observed evidence for the formation of an interfacial layer containing Te reacted with the Group III(Al or Ga) atoms from the III-V substrate. The observation of analogous behavior at the GaAs/ZnSe interface suggests that the compounds most likely to have been formed at the AlSb/ZnTe and GaSb/ZnTe interfaces are Al_2Te_3 and Ga_2Te_3, respectively. Yu *et al.* obtained the following values for valence-band offsets in the AlSb/GaSb/ZnTe material system: $\Delta E_v(\text{AlSb/ZnTe}) = 0.42 \pm 0.07$ eV, $\Delta E_v(\text{GaSb/ZnTe}) = 0.60 \pm 0.07$ eV, and $\Delta E_v(\text{GaSb/AlSb}) = 0.39 \pm 0.07$ eV. In each case the band alignment was found to be type I. These measured band offsets can be combined to determine whether the transitivity condition, Eq. (1.1), is obeyed for the AlSb/GaSb/ZnTe material system. Theoretical[41,43,84] and experimental[128,141] evidence indicates that for abrupt, high-quality heterojunctions in most lattice-matched material systems, the transitivity condition should be obeyed; a deviation from transitivity would therefore imply that structural or chemical anomalies at specific interfaces were affecting band offset values. Combining the band offset values measured by Yu *et al.*,[105,190] one can see that the transitivity condition is violated for the AlSb/GaSb/ZnTe material system by 0.21 ± 0.05 eV. The violation of transitivity is shown explicitly in Fig. 34. This discrepancy is far larger than the experimen-

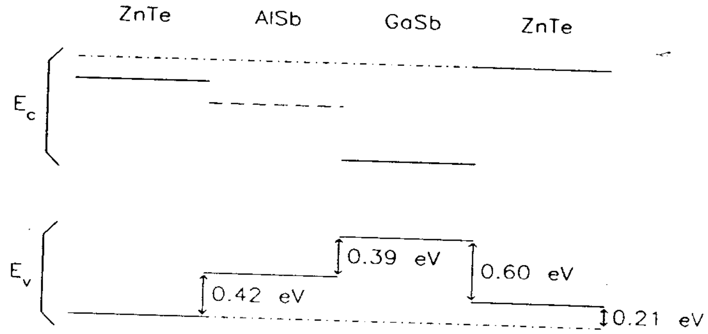

FIG. 34. Nontransitivity in the AlSb/GaSb/ZnTe material system. The valence-band offsets labeled in the figure were measured by Yu *et al.*[105,190] Combining these measurements demonstrates that transitivity is violated by 0.21 ± 0.05 eV.

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[339] G. P. Schwartz, G. J. Gualtieri, R. D. Feldman, R. F. Austin, and R. G. Nuzzo, *J. Vac. Sci. Technol. B* 8, 747 (1990).

tal uncertainty of the measurements. From Eq. (6.1) one can see that the transitivity rule can be verified simply from the measured core-level energy separations in the AlSb/ZnTe, GaSb/ZnTe, and AlSb/GaSb heterojunctions; if transitivity were valid for the AlSb/GaSb/ZnTe material system, one would expect Eq. (1.1) to be obeyed to within ±0.05 eV or better. The measurements of Yu *et al.* therefore demonstrate a clear violation of the transitivity rule, suggesting that reacted layers at the AlSb/ZnTe and GaSb/ZnTe interfaces can exert a significant influence on band offset values.

Comparing the results of band offset measurements for the AlSb/GaSb/ZnTe material system, we see that the values measured for the AlSb/ZnTe valence-band offset by Schwartz *et al.*[339] and by Yu *et al.*,[105,190] 0.35 ± 0.11 eV and 0.42 ± 0.07 eV, respectively, are in good agreement. However, the GaSb/ZnTe valence-band offset measured by Wilke and Horn,[106] 0.34 ± 0.05 eV, and the value of 0.60 ± 0.07 eV obtained by Yu *et al.*[190] are in relatively poor agreement. The origin of this discrepancy is not known, but a number of possibilities exist. Wilke *et al.* and Yu *et al.* both observed evidence of a GaSb/ZnTe interfacial reaction, which could have affected the values of the band offsets differently for the two measurements. In addition, the difference in crystal orientation—(100) for Yu *et al.* and (110) for Wilke *et al.*—would have affected the detailed structure of the interfaces and could therefore have influenced the measured band offset values.

b. *Theory*

Theoretical predictions for the AlSb/GaSb heterojunction were discussed in Section 10. For the AlSb/ZnTe and GaSb/ZnTe heterojunctions, a large number of predictions are available. These predictions are summarized in Table XVIII. For AlSb/ZnTe, Frensley and Kroemer's pseudopotential theory[23] yields a valence-band offset of 0.80 eV without interfacial dipole corrections and 0.13 eV if the dipole correction is included. Harrison's LCAO theory[24] predicts $\Delta E_v = 0.83$ eV. Tersoff's theory[28] yields a valence-band offset of 0.39 eV, and the treatment of Harrison and Tersoff[29] predicts a value of 1.17 eV. Cardona and Christensen's dielectric midgap energy model[39] predicts a valence-band offset of approximately 0.41 eV, and the model solid theory[86] yields $\Delta E_v = 0.43$ eV. The interface-bond-polarity model of Lambrecht *et al.*[87] predicts a valence-band offset of 0.66 eV. Among the empirical rules for determining band offset values, the electron affinity rule[19] yields a valence-band offset of 0.51 eV using the electron affinity values of Milnes and Feucht[71] and a value of 0.59 eV using the compilation of Freeouf and Woodall.[193] Among those who have made self-consistent calculations of band offsets for specific interfaces, only Lambrecht *et al.*[43] have treated the AlSb/ZnTe interface, obtaining $\Delta E_v = 0.60$ eV. If one assumes transitivity

TABLE XVIII. THEORETICAL VALENCE-BAND OFFSETS FOR ZnTe/AlSb AND ZnTe/GaSb

SOURCE	ΔE_v(ZnTe/AlSb) (theor.) (eV)	ΔE_v(ZnTe/GaSb) (theor.) (eV)
Milnes and Feucht (1972)[71]	0.51	1.02
McCaldin *et al.* (1976)[20]		0.69
Frensley and Kroemer (1977)[23]	0.80	0.85
Frensley and Kroemer (1977)[23] (with dipole correction)	0.13	0.86
Harrison (1977)[24]	0.83	0.81
Freeouf and Woodall (1981)[193]	0.59	1.03
Katnani and Margaritondo (1983)[21]		0.77
Tersoff (1986)[28]	0.39	0.77
Harrison and Tersoff (1986)[29]	1.17	1.26
Van de Walle and Martin (1987)[86] (model solid theory)	0.43	0.89
Cardona and Christensen (1987)[39] (dielectric midgap energy model)	0.41	0.71
Christensen (1988)[40]	0.38	0.83
Lambrecht *et al.* (1990)[43] (self-consistent dipole)	0.60	0.96
Lambrecht and Segall (1990)[87] (interface bond polarity model)	0.66	1.01

and combines calculated band offsets for the GaSb/AlSb and GaSb/ZnTe interfaces, one obtains a valence-band offset of 0.38 eV from the calculations of Christensen.[40] In all cases the valence-band edge of AlSb is predicted to be higher in energy than that of ZnTe.

Figure 35 shows the band alignments measured by Yu *et al.*[105,190] and by Schwartz *et al.*[339] among values predicted by several theories. In general, the theoretically predicted valence-band offsets are larger than the experimentally measured values. For some of the early theories, notably those of Harrison[24] and of Frensley and Kroemer,[23] this discrepancy appears to arise largely from the early belief that the common anion rule[20] should be valid for compounds containing Al. If the valence-band offsets predicted by those theories for the GaSb/ZnTe interface are combined with the experimentally measured AlSb/GaSb band offset,[72,99,190,191] considerably better agreement with experiment is obtained. Most of the other theoretical predictions for the AlSb/ZnTe valence-band offset are within approximately 0.3 eV of the experimental values, although the theoretical values still tend to be larger than the measured band offsets. The source of this trend is not known at the present time, but it could be related to the interfacial reactions known to occur at AlSb/ZnTe heterojunctions.

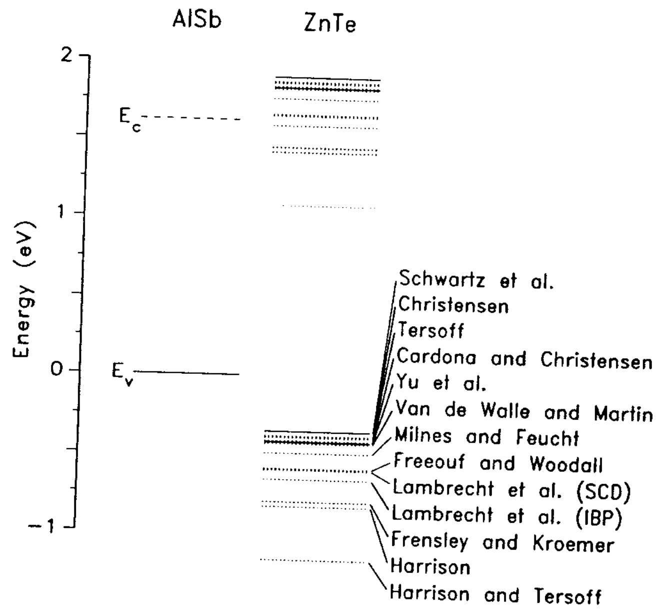

FIG. 35. Band alignments measured experimentally by Schwartz *et al.*[339] and by Yu *et al.*,[105,190] and alignments predicted theoretically.[23,24,28,29,39,40,43,71,84–87,193] For the ZnTe conduction- and valence-band edges, experimentally determined band alignments are indicated by solid lines and theoretical values by dotted lines. The indirect conduction-band edge of AlSb is indicated by the dashed line.

For the GaSb/ZnTe interface, Frensley and Kroemer[23] obtain valence-band offsets of 0.85 eV and 0.86 eV with interface dipole corrections neglected and included, respectively, and Harrison's LCAO theory[24] predicts ΔE_v = 0.81 eV. Tersoff's theory[28] yields a valence-band offset of 0.77 eV, and Harrison and Tersoff obtained 1.26 eV. The dielectric midgap energy model[39] yields a valence-band offset of 0.71 eV, and the model solid theory[86] predicts ΔE_v = 0.89 eV. The interface-bond-polarity model[87] yields ΔE_v = 1.01 eV. The electron affinity rule[19] yields a valence-band offset of approximately 1.02 eV, and the common-anion rule[20] predicts a value of 0.69 eV. The empirical compilation of Katnani and Margaritondo [21] yields a valence-band offset of 0.77 eV. The self-consistent supercell calculations of Christensen[40] yield a valence-band offset of 0.83 eV, and the self-consistent dipole theory of Lambrecht *et al.*[43] predicts ΔE_v = 0.96 eV. In all cases the valence-band edge of GaSb is predicted to be higher in energy than that of ZnTe.

Figure 36 shows the band alignments measured by Wilke and Horn[106] and by Yu *et al.*[190] among values predicted by various theories. As with the AlSb/ZnTe interface, the theoretical predictions for the GaSb/ZnTe valence-

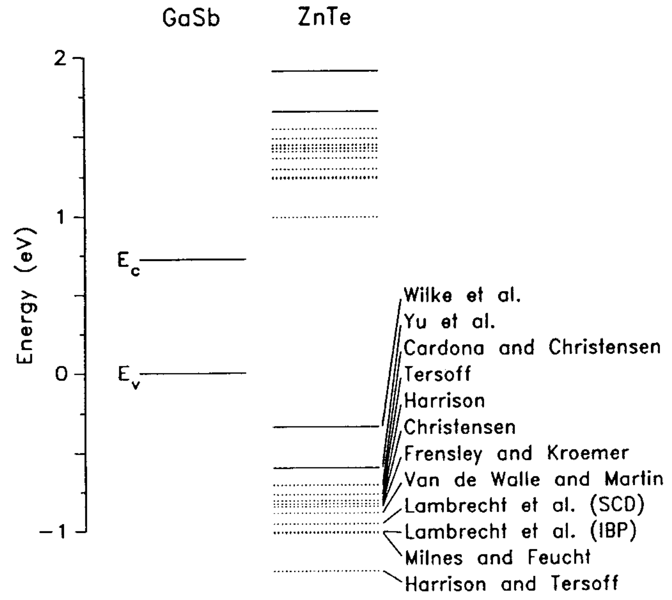

FIG. 36. Band alignments measured experimentally by Wilke *et al.*[106] and by Yu *et al.*,[190] and alignments predicted theoretically.[23,24,28,29,39,40,43,71,84–87] For the ZnTe conduction- and valence-band edges, experimentally determined band alignments are indicated by solid lines, and theoretical values by dotted lines.

band offset are consistently larger than the experimental values. The origin of this trend is unclear, but its presence for both AlSb/ZnTe and GaSb/ZnTe suggests that interfacial reactivity in these heterojunctions may be a contributing factor.

22. OTHER HETEROVALENT INTERFACES

a. *ZnSe/Ge*

Figure 37 shows theoretical and experimental values for the ZnSe/Ge valence-band offset, and theoretical predictions are compiled in Table XIX. Kowalczyk *et al.*[65] used XPS to measure the valence-band offset in ZnSe/Ge (110) heterojunctions formed by deposition at room temperature and subsequent crystallization at ~300°C. For ZnSe deposited on Ge, a valence-band offset of 1.29 eV was obtained, whereas for Ge deposited on ZnSe the measured valence-band offset was 1.52 eV. Katnani and Margaritondo[21] measured a valence-band offset of 1.40 eV for Ge deposited on ZnSe using

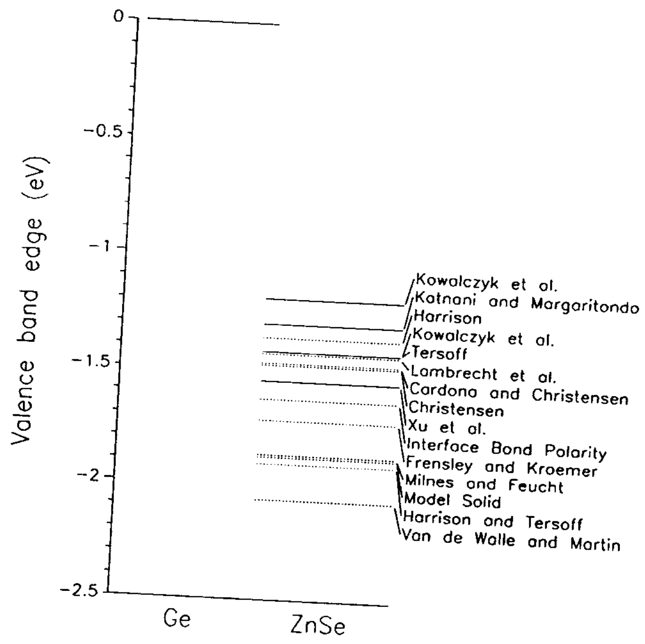

FIG. 37. Experimental and theoretical values for the ZnSe/Ge valence-band offset. Experimental results are indicated by solid lines, theoretical predictions by dotted lines.

synchrotron photoemission spectroscopy, and Xu *et al.*[97] used photoemission spectroscopy to deduce a valence-band offset of 1.65 ± 0.1 eV for Ge deposited on ZnSe (100). In all cases the valence-band edge of Ge was found to be above that of ZnSe.

As seen in Fig. 37, the various band offset theories generally predict very large values for the ZnSe/Ge valence-band offset. The electron affinity rule[71] yields a value of 1.97 eV. Frensley and Kroemer[23] predict a valence-band offset of 1.82 eV, and Harrison's LCAO theory[24] yields $\Delta E_v = 1.46$ eV. Tersoff[28] obtains a valence-band offset of 1.52 eV, and Harrison and Tersoff[29] predict a value of 2.01 eV. The dielectric midgap energy model of Cardona and Christensen[39] yields $\Delta E_v = 1.57$ eV, and the model solid theory[86] predicts a valence-band offset of 1.98 eV. The interface bond polarity model of Lambrecht and Segall[87] yields $\Delta E_v = 1.73$ eV. Early self-consistent calculations by Pickett and Cohen[340] predicted a valence-band offset of 2.0 ± 0.3 eV. Self-consistent interface calculations of Van de Walle and Martin[84] yield a valence-band offset of 2.17 eV, and self-consistent

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[340] W. E. Pickett and M. L. Cohen, *Phys. Rev. B* **18**, 939 (1978).

TABLE XIX. THEORETICAL PREDICTIONS FOR THE ZnSe/Ge VALENCE-BAND OFFSET

SOURCE	ΔE_v (theor.) (eV)
Electron affinity rule (1972)[71]	1.97
Frensley and Kroemer (1977)[23]	1.82
Harrison (1977)[24]	1.46
Pickett and Cohen (1978)[340]	2.0
Tersoff (1986)[28]	1.52
Harrison and Tersoff (1986)[29]	2.01
Van de Walle and Martin (1987)[84] (self-consistent supercell)	2.17
Van de Walle and Martin (1987)[86] (model solid theory)	1.98
Cardona and Christensen (1987)[39] (dielectric midgap energy model)	1.57
Christensen (1988)[40]	1.58
Lambrecht *et al.* (1990)[43] (self-consistent dipole)	1.53
Lambrecht and Segall (1990)[87] (interface bond polarity model)	1.73

supercell calculations by Christensen[40] predict a value of 1.58 eV. Finally, the self-consistent dipole calculations of Lambrecht *et al.*[43] yield $\Delta E_v = 1.53$ eV. From Fig. 37 it is apparent that the theoretical valence-band offsets are quite consistently larger than the experimental values. This trend is similar to that observed in the III-V/II-VI heterojunctions discussed in Sections 20 and 21.

b. *GaP/Si*

The GaP/Si band offset was measured by Katnani and Margaritondo[21] using synchrotron photoemission spectroscopy; a valence-band offset of 0.95 eV was obtained for Si deposited on GaP. Perfetti *et al.*[341,342] used synchrotron photoemission to measure both ΔE_v and ΔE_c for Si deposited on GaP (110) and obtained $\Delta E_v = 0.8 \pm 0.1$ eV. In both cases the valence-band edge of GaP was found to be lower in energy than that of Si. Theoretical predictions for the GaP/Si valence-band offset encompass a wide range of

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[341] P. Perfetti, F. Patella, F. Sette, C. Quaresima, C. Capasso, A. Savoia, and G. Margaritondo, *Phys. Rev. B* **29**, 5941 (1984).

[342] P. Perfetti, F. Patella, F. Sette, C. Quaresima, C. Capasso, A. Savoia, and G. Margaritondo, *Phys. Rev. B* **30**, 4533 (1984).

values. Milnes and Feucht[71] predict $\Delta E_v = 1.43$ eV. The pseudopotential theory of Frensley and Kroemer[23] yields a valence-band offset of 0.96 eV, and Harrison's LCAO theory[24] predicts a value of 0.50 eV. Tersoff's theory[28] predicts a valence-band offset of 0.45 eV, and Harrison and Tersoff[29] obtain a value of 0.69 eV. The dielectric midgap energy model of Cardona and Christensen[39] yields a valence-band offset of approximately 0.57 eV, and the model solid theory of Van de Walle and Martin[86] predicts $\Delta E_v = 0.36$ eV. The interface bond polarity model[87] yields a valence-band offset of 0.33 eV. Self-consistent interface calculations by Van de Walle and Martin [84] yielded a valence-band offset of 0.61 eV. Christensen[40] performed self-consistent supercell calculations using LMTO methods and obtained $\Delta E_v = 0.27$ eV, and self-consistent dipole calculations by Lambrecht *et al.*[43] yielded a valence-band offset of 0.31 eV. Experimental and theoretical values for the GaP/Si valence-band offset are shown in Fig. 38, and theoretical values are also compiled in Table XX.

c. *CdS/InP*

The CdS/InP heterojunction system has been studied as a possible candidate for the fabrication of photovoltaic detectors and solar cells. Experimental and theoretical values for the CdS/InP valence-band offset are shown in Fig. 39 and Table XXI. Shay *et al.*[117,118] used *C–V* measurements on *n*-CdS/*p*-InP heterojunctions to deduce a conduction-band offset of 0.56 eV, corresponding to a valence-band offset of 1.63 eV and a type II, staggered band alignment. *C–V* measurements by Yoshikawa and Sakai[343] yielded a conduction-band offset of 0.112 eV, corresponding to a valence-band offset of 1.19 eV. Wilke *et al.*[107] used photoemission to measure a valence-band offset of 0.77 eV for the CdS/InP (110) heterojunction, corresponding to $\Delta E_c = 0.30$ eV and a type I band alignment. In the measurements of Shay *et al.* and of Yoshikawa *et al.*, the CdS layers appeared to have been grown in their equilibrium wurtzite crystal structure; the measurements of Wilke *et al.* were performed using samples in which CdS in the metastable zincblende crystal structure was deposited on InP. In all of these measurements, the valence-band edge of InP was found to be higher in energy than that of CdS. However, the measured values for the CdS/InP valence-band offset are in relatively poor agreement. Theoretically, the situation is similar. Frensley and Kroemer[23] predict valence-band offsets of 0.84 eV without their dipole correction and 1.13 eV with the correction, while Harrison's LCAO theory[24] predicts $\Delta E_v = 1.48$ eV. Harrison and Tersoff[29] obtain a valence-band offset of 1.37 eV. The electron affinity rule[19] yields a valence-band offset

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[343] A. Yoshikawa and Y. Sakai, *Solid-State Electron.* **20**, 133 (1977).

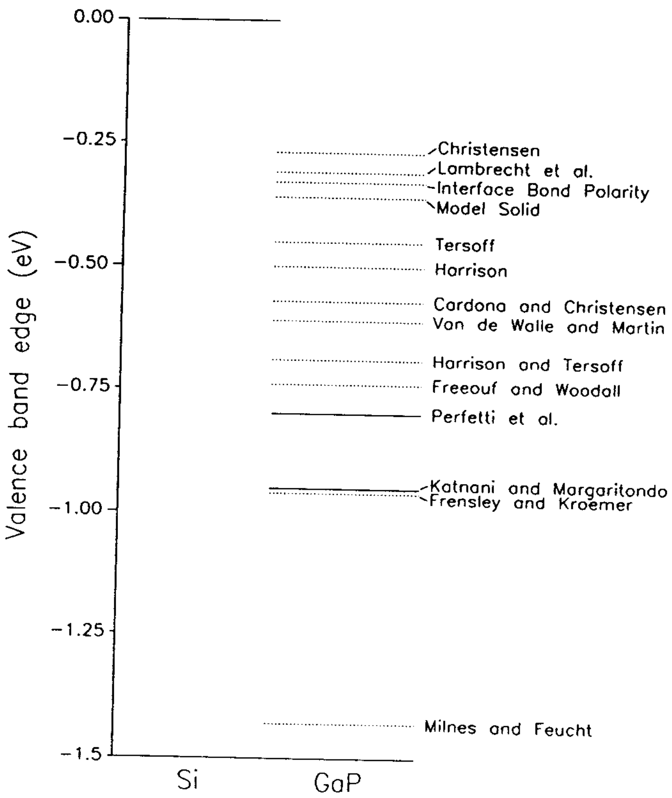

FIG. 38. Summary of experimental and theoretical valence-band offsets for the GaP/Si heterojunction. Experimental and theoretical values are indicated by solid and dotted lines, respectively.

of 1.46 eV using the data compiled by Freeouf and Woodall,[193] and the common-anion rule[20] predicts $\Delta E_v = 0.91$ eV. Finally, the empirical compilation of Katnani and Margaritondo[21] yields a valence-band offset of 1.04 eV. Most other theoretical treatments have not considered the CdS/InP heterojunction system because the equilibrium crystal structure of CdS is wurtzite rather than cubic zincblende.

d. *InSb/CdTe/α-Sn*

A number of studies have been devoted to band alignments in the nearly lattice-matched InSb/CdTe/α-Sn material system. InSb and CdTe are conventional semiconductors with energy band gaps of approximately 0.18 eV and 1.50 eV, respectively, at room temperature; α-Sn is a semimetal with a

TABLE XX. THEORETICAL PREDICTIONS FOR THE GaP/Si VALENCE-BAND OFFSET

SOURCE	ΔE_v (theor.) (eV)
Milnes and Feucht (1972)[71]	1.43
Frensley and Kroemer (1977)[23]	0.96
Harrison (1977)[24]	0.50
Freeouf and Woodall (1981)[193]	0.74
Tersoff (1986)[28]	0.45
Harrison and Tersoff (1986)[29]	0.69
Van de Walle and Martin (1987)[84] (self-consistent supercell)	0.61
Van de Walle and Martin (1987)[86] (model solid theory)	0.36
Cardona and Christensen (1987)[39] (dielectric midgap energy model)	0.57
Christensen (1988)[40]	0.27
Lambrecht *et al.* (1990)[43] (self-consistent dipole)	0.31
Lambrecht and Segall (1990)[87] (interface bond polarity model)	0.33

TABLE XXI. EXPERIMENTAL AND THEORETICAL VALENCE-BAND OFFSETS FOR CdS/InP

SOURCE	ΔE_v (expt.) (eV)	ΔE_v (theor.) (eV)
Shay *et al.* (1976)[117,118]	1.63	
Yoshikawa and Sakai (1977)[343]	1.19	
Wilke *et al.* (1989)[107]	0.77	
Freeouf and Woodall (1981)[193]		1.46
McCaldin *et al.* (1976)[20]		0.91
Frensley and Kroemer (1977)[23]		0.84
Frensley and Kroemer (1977)[23] (with dipole correction)		1.13
Harrison (1977)[24]		1.48
Katnani and Margaritondo (1983)[21]		1.04
Harrison and Tersoff (1986)[29]		1.37

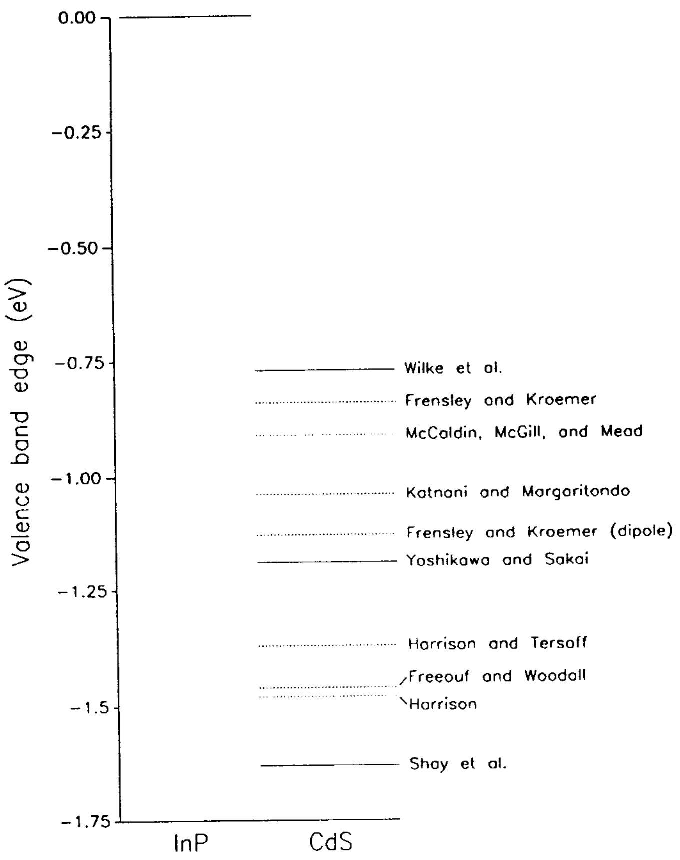

FIG. 39. Summary of experimental and theoretical valence-band offsets for the CdS/InP heterojunction. Experimental and theoretical values are indicated by solid and dotted lines, respectively.

negative energy band gap, $E_g(\Gamma_7^- - \Gamma_8^+) = -0.41$ eV. Experimental and theoretical band offset values for the InSb/CdTe/α-Sn material system are shown in Fig. 40 and Table XXII. Mackey *et al.*[108] used photoemission to measure a valence-band offset of 0.87 ± 0.10 eV for the CdTe/InSb heterojunction, with the valence-band edge of InSb above that of CdTe; their measurements also revealed evidence that an interfacial compound containing In and Te was formed at the CdTe/InSb interface. Förster *et al.*[344] used ultraviolet photoemission spectroscopy (UPS) to study the Sn/InSb (110)

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[344] A. Förster, A. Tulke, and H. Lüth, *J. Vac. Sci. Technol. B* 5, 1054 (1987).

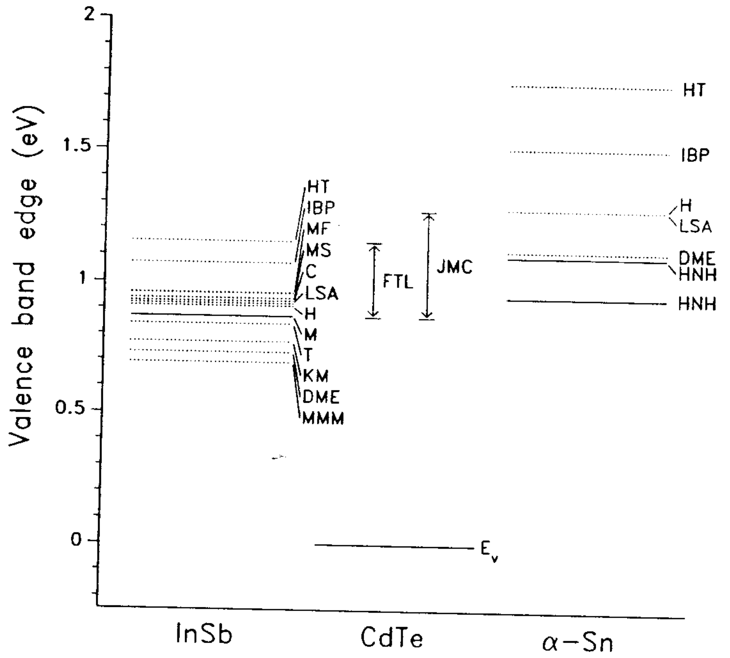

FIG. 40. Experimental and theoretical values for valence-band offsets in the InSb/CdTe/α-Sn material system. Experimental values for the CdTe/InSb and α-Sn/CdTe valence-band offsets are indicated by solid lines, theoretical values by dotted lines. The arrows show measured values for the InSb/α-Sn valence-band offset. The theories shown obey transitivity to better than ±0.05 eV. For the three interfaces, the values shown are from the following sources: HT, Ref. 29; IBP, Ref. 87; MF, Ref. 71; MS, Ref. 86; C, Ref. 40; LSA, Ref. 43; H, Ref. 24; M, Ref. 108; T, Ref. 28; KM, Ref. 21; DME, Ref. 39; MMM, Ref. 20; HNH, Ref. 346; FTL, Ref. 344; JMC, Ref. 345.

interface and obtained a valence-band offset of approximately 0.28 eV for amorphous or polycrystalline α-Sn deposited on (110) InSb. John *et al.*[345] used synchrotron photoemission to measure the valence-band offset for α-Sn/InSb (100) and obtained $\Delta E_v = 0.40 \pm 0.06$ eV for Sn deposited on both the Sb-stabilized $c(4 \times 4)$ and the In-stabilized $c(8 \times 2)$ surfaces of InSb (100). Höchst *et al.*[346] used photoemission to study the α-Sn/CdTe (110) heterojunction and measured a valence-band offset of 1.1 eV assuming zero band gap for the α-Sn film, or approximately 0.95 eV using indirect evidence of the development of a nonzero band gap in thin α-Sn films.

Most of the available theoretical band offset values are in reasonably good agreement with these experimental results. For the CdTe/InSb heterojunc-

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[345] P. John, T. Miller, and T.-C. Chiang, *Phys. Rev. B* 39, 3223 (1989).
[346] H. Höchst, D. W. Niles, and I. Hernández-Calderón, *J. Vac. Sci. Technol. B* 6, 1219 (1988).

TABLE XXII. EXPERIMENTAL AND THEORETICAL VALENCE-BAND OFFSET VALUES FOR InSb/CdTe/α-Sn

SOURCE	HETEROJUNCTION	ΔE_v (expt.) (eV)	ΔE_v (theor.) (eV)
Mackey *et al.* (1986)[108]	CdTe/InSb	0.87 ± 0.1	
Förster *et al.* (1987)[344]	InSb/α-Sn (110)	0.28	
John *et al.* (1989)[345]	InSb/α-Sn (100)	0.40 ± 0.06	
Höchst *et al.* (1988)[346]	CdTe/α-Sn (110)	0.95-1.10	
Milnes and Feucht (1972)[71]	CdTe/InSb		0.96
McCaldin *et al.* (1976)[20]	CdTe/InSb		0.69
Harrison(1977)[24]	CdTe/InSb		0.91
Katnani and Margaritondo (1983)[21]	CdTe/InSb		0.77
Tersoff (1986)[28]	CdTe/InSb		0.84
Harrison and Tersoff (1986)[29]	CdTe/InSb		1.15
Cardona and Christensen (1987)[39]	CdTe/InSb		0.73
Christensen (1988)[40]	CdTe/InSb		0.93
Van de Walle and Martin (1986)[86] (model solid theory)	CdTe/InSb		0.94
Lambrecht *et al.* (1990)[43]	CdTe/InSb		0.92
Lambrecht and Segall (1990)[87]	CdTe/InSb		1.07
Harrison (1977)[24]	InSb/α-Sn		0.37
Harrison and Tersoff (1986)[29]	InSb/α-Sn		0.61
Cardona and Christensen (1987)[39]	InSb/α-Sn		0.39
Lambrecht *et al.* (1990)[43] (self-consistent dipole)	InSb/α-Sn		0.39
Lambrecht and Segall (1990)[87] (interface bond polarity model)	InSb/α-Sn		0.48
Harrison (1977)[24]	CdTe/α-Sn		1.28
Harrison and Tersoff (1986)[29]	CdTe/α-Sn		1.76
Cardona and Christensen (1987)[39]	CdTe/α-Sn		1.12
Lambrecht *et al.* (1990)[43] (self-consistent dipole)	CdTe/α-Sn		1.28
Lambrecht and Segall (1990)[87] (interface bond polarity model)	CdTe/α-Sn		1.51

tion, Harrison[24] predicts a valence-band offset of 0.91 eV. Tersoff's theory[28] yields $\Delta E_v = 0.84$ eV, and Harrison and Tersoff[29] obtain a valence-band offset of 1.15 eV. Cardona and Christensen predict a value of 0.73 eV for the CdTe/InSb valence-band offset, and the model solid theory of Van de Walle and Martin[86] yields $\Delta E_v = 0.94$ eV. The interface bond polarity model of Lambrecht and Segall[87] predicts a valence-band offset of 1.07 eV. Among the empirical models for band offset values, the electron affinity rule[71] yields a valence-band offset of 0.96 eV, and the empirical compilation of Katnani and

Margaritondo[21] predicts $\Delta E_v = 0.77$ eV. The common-anion rule[20] yields a valence-band offset of 0.69 eV. Finally, Christensen's self-consistent supercell calculations using LMTO methods[40] yielded a valence-band offset of 0.93 eV, and the self-consistent dipole calculations of Lambrecht *et al.*[43] predicted $\Delta E_v = 0.92$ eV. As shown in Fig. 40, these values are all in reasonably good agreement with the reported experimental values. Considering the complex nature of the CdTe/InSb interface,[108] however, it is interesting that theoretical treatments that do not account for interfacial reactivity still yield values in good agreement with experiment.

Fewer theoretical predictions are available for the α-Sn/InSb and α-Sn/CdTe interfaces. For the α-Sn/InSb interface, Harrison[24] predicts a valence-band offset of 0.37 eV, while the theory of Harrison and Tersoff[29] yields a value of 0.61 eV. The interface bond polarity model of Lambrecht *et al.*[87] predicts a valence-band offset of 0.48 eV. The dielectric midgap energy model of Cardona and Christensen[39] predicts $\Delta E_v = 0.39$ eV, and self-consistent dipole calculations of Lambrecht *et al.*[43] yield a valence-band offset of 0.39 eV. The predicted values of Harrison, of Cardona and Christensen, and of Lambrecht *et al.* are in reasonable agreement with the experimental results, while the value proposed by Harrison and Tersoff is somewhat larger than the measured values. For the α-Sn/CdTe interface, Harrison[24] obtains a valence-band offset of 1.28 eV, and Harrison and Tersoff[29] predict $\Delta E_v =$ 1.76 eV. The interface bond polarity model of Lambrecht *et al.*[87] yields a valence-band offset of 1.51 eV. Cardona and Christensen[39] obtain 1.12 eV for the α-Sn/CdTe valence-band offset, and the self-consistent dipole calculations of Lambrecht *et al.*[43] yield $\Delta E_v = 1.28$ eV. The results of Harrison, of Cardona and Christensen, and of the self-consistent dipole calculations by Lambrecht *et al.* are in reasonable agreement with the measured band offset values; the valence-band offset predictions of Harrison and Tersoff and of the interface bond polarity model are considerably larger than the measured value. One should recall, however, that the structural and chemical complexity of heterovalent interfaces is ignored in current theoretical treatments. It may not be prudent to attach great meaning to detailed quantitative correlations between experimental measurements and theoretical predictions for band offsets in heterovalent material systems.

e. *CuBr/GaAs/Ge*

Waldrop *et al.*[347,348] have studied band offsets in the nearly lattice-matched CuBr/GaAs/Ge heterojunction system using XPS. Initial studies[347]

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[347] J. R. Waldrop and R. W. Grant, *Phys. Rev. Lett.* **43**, 1686 (1979).

[348] J. R. Waldrop, R. W. Grant, S. P. Kowalczyk, and E. A. Kraut, *J. Vac. Sci. Technol. A* **3**, 835 (1985).

demonstrated that valence-band offsets for the Ge/CuBr, CuBr/GaAs, and GaAs/Ge heterojunctions were highly nontransitive. Although it is possible that this nontransitivity arises from nonideal structure at specific interfaces, Christensen[41] has performed theoretical calculations indicating that CuBr can produce interface-specific electronic states that influence band offset values and yield an intrinsic deviation from transitivity even for abrupt, ideal interfaces. The later measurements of Waldrop *et al.*[348] yielded valence-band offsets of 0.85 eV and 0.7 eV for the CuBr/GaAs and CuBr/Ge interfaces, respectively. The CuBr valence-band edge was found to be lower in energy than both the GaAs and the Ge valence-band edges. Combining these results with their value of 0.56 ± 0.04 eV for the GaAs/Ge valence-band offset,[348] one sees that transitivity is violated by approximately 0.7 eV. Only a few theoretical predictions are available for heterojunctions containing CuBr. Harrison [24] predicts valence-band offsets of 2.78 eV and 2.37 eV for CuBr/Ge and CuBr/GaAs, respectively. The interface bond polarity model of Lambrecht and Segall[87] yields ΔE_v(CuBr/Ge) = 1.48 eV and ΔE_v(CuBr/GaAs) = 1.04 eV. Self-consistent supercell calculations by Christensen[41] yield valence-band offsets of 1.10 eV for CuBr/Ge and 0.82 eV for CuBr/GaAs, and self-consistent dipole calculations by Lambrecht *et al.*[43] predict ΔE_v(CuBr/Ge) = 1.16 eV and ΔE_v(CuBr/GaAs) = 0.74 eV. Except for the CuBr/GaAs valence-band offsets predicted by Christensen[41] and by Lambrecht *et al.*,[43,87] these theoretical values are in relatively poor agreement with the reported experimental results. Experimental and theoretical values for band offsets in the CuBr/GaAs/Ge material system are summarized in Table XXIII.

TABLE XXIII. EXPERIMENTAL AND THEORETICAL BAND OFFSET VALUES FOR CuBr/GaAs/Ge

SOURCE	ΔE_v (CuBr/GaAs) (eV)	ΔE_v (GaAs/Ge) (eV)	ΔE_v (Ge/CuBr) (eV)
Waldrop *et al.* (1985)[a,348]	0.85	0.56	0.7
Harrison (1977)[24]	2.37	0.41	2.78
Christensen (1988)[41]	0.82	0.46	1.10
Lambrecht *et al.* (1990)[43] (self-consistent dipole)	0.74	0.45	1.16
Lambrecht and Segall (1990)[87] (interface bond polarity model)	1.04	0.48	1.48

[a] The values of Waldrop *et al.*[348] are experimental; all others are theoretical calculations.

VIII. Discussion

If there is any trend that becomes obvious upon examining the wealth of experimental and theoretical work devoted to band offsets, it is that the subject remains one of considerable uncertainty. The inherent complexity of the subject has led us to adopt an approach to the band offset problem that may best be described as "enlightened empiricism." By examining a wide variety of theoretical and experimental approaches to the band offset problem, as we have done in this review, we have sought to develop a balanced perspective that might allow us to gain new insights that have not previously been made evident in the literature.

As our review of the available literature has revealed, both triumphs and failures have been experienced in the experimental study of band offsets. The successes have been achieved in spite of, and the failures in many cases have occurred because of, the notoriously difficult nature of many band offset measurement techniques. For material systems such as GaAs/$Al_xGa_{1-x}As$, GaSb/AlSb, and HgTe/CdTe, there have been relatively sudden shifts in the experimentally accepted band offset values. These shifts can certainly be attributed in part to difficulties in interpreting and analyzing experimental data, but it is also possible that some early experimental results were colored by early theoretical predictions of band offset values that later were found to be incorrect. Despite some early lapses, however, experimental techniques such as photoelectron spectroscopy, J-V and C-V measurements, and even optical spectroscopy have been developed to a level such that, with care, reliable measurements of band offsets can be obtained quite routinely.

Although enormous progress has been achieved in the theoretical study of band offsets, a consistently reliable predictive theory has yet to be developed. In a few cases such as HgTe/CdTe, a theoretical treatment[28] has succeeded in predicting a reasonably accurate band offset value independently of an accurate experimental determination and in fact in conflict with earlier experimental and theoretical values. More often, however, theories have been successful primarily in reproducing band offset values after reliable experimental measurements have been performed. This tendency can be seen quite clearly in Figs. 11 and 18. Although the ability to reproduce a set of reliable experimental band offset values is a laudable and important achievement, predictive—rather than "postdictive"—ability is a much more stringent test of the power and validity of a given band offset theory.

Another curious issue is that a number of current theories, such as those of Van de Walle and Martin[84–86] and of Cardona and Christensen,[39] appear to yield band offset values in reasonable agreement with experiment, even though the physical ideas upon which these theories are based vary considerably. Theories and empirical rules have been proposed based on surface properties such as electron affinity,[19,71] interface properties such as Schottky barrier heights,[20] calculations of bulk band structure on an absolute energy scale,[22–24,84] effective "midgap" or charge neutrality energy points,[25,26,28,39] or other interfacial dipole effects.[87] As will be shown in this section, however, there is no single theory that yields band offset values that are substantially more accurate than those predicted by any other theory.

Throughout this discussion one must keep in mind that the concept of a band offset is in reality an idealization of an extremely complex situation at a semiconductor interface. The concept of a perfectly abrupt discontinuity in the band edges is inconsistent with the uncertainty principle; the abrupt discontinuity actually represents an energy shift that occurs over a small number of unit cells near the interface. Furthermore, structural and chemical changes occur in the region very near the interface that can substantially affect the detailed electronic structure at the interface. Despite these caveats, the concept of a well-defined band offset has proved to be an enormously useful tool in predicting the viability and expected performance of a given device structure. It has been the inherent complexity of the subject that has frustrated attempts to attain a detailed quantitative understanding of band offsets.

In the following sections we have attempted to arrange band offset values in several heterojunction systems into an organized structure and to identify trends that might act as guides in evaluating the literature and perhaps improve our ability to predict band offset values for unstudied heterojunction systems. A further motivation was the thought that the success of a particular theory for a large number of heterojunctions might serve to validate the approach and suggest that the physical concepts underlying that theory might be the dominant ones. We have tried to look objectively at the accuracy of several theories in predicting band offsets in a set of lattice-matched heterojunctions for which reasonably well-defined experimental values are available, and thereby to extract some insights into the factors that exert an especially strong influence over band offset values.

23. THEORY VERSUS EXPERIMENT IN LATTICE-MATCHED HETEROJUNCTIONS

In Figs. 41 through 55 we have plotted, for a number of the more widely quoted band offset theories, the difference between theoretical and experimental valence-band offset values, $\Delta \equiv \Delta E_v^{th} - \Delta E_v^{expt}$, for several lattice-matched heterojunction systems. The figures have been placed in approximately chronological order. Because of the complications that are known to arise in coherently strained heterojunctions, we have chosen to make this

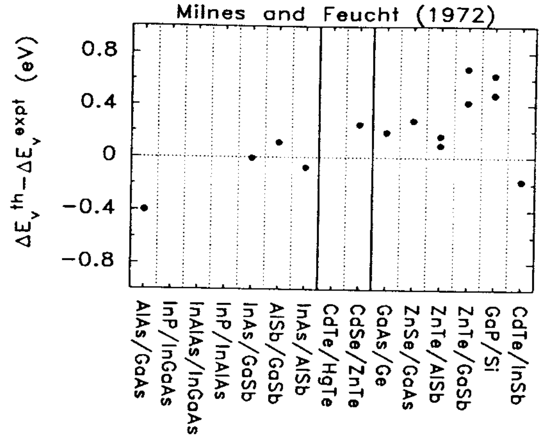

FIG. 41. Comparison of experimental and theoretical valence-band offsets for predictions of Milnes and Feucht.[71]

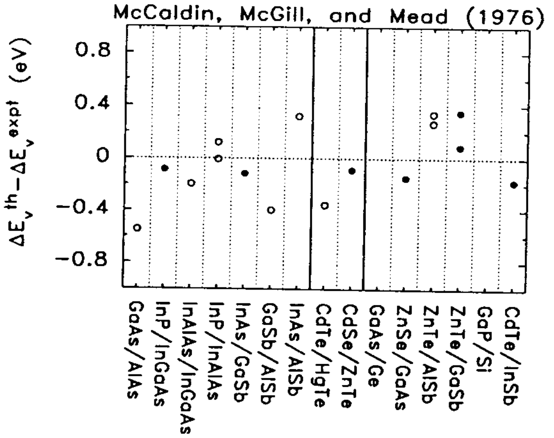

FIG. 42. Comparison of experimental and theoretical valence-band offsets for predictions of McCaldin *et al.*[20] Filled and open circles represent predictions for compounds that are, respectively, within and outside the scope of the original predictions as made by McCaldin *et al.*

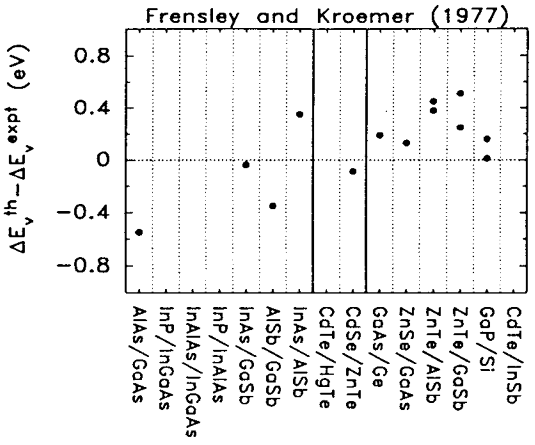

FIG. 43. Comparison of experimental and theoretical valence-band offsets for predictions of Frensley and Kroemer.[23]

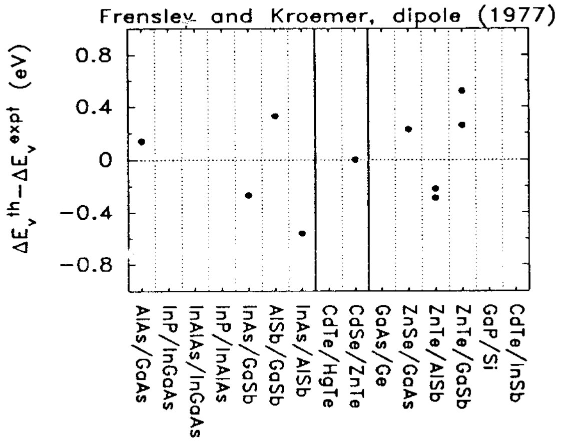

FIG. 44. Comparison of experimental and theoretical valence-band offsets for dipole-corrected predictions of Frensley and Kroemer.[23]

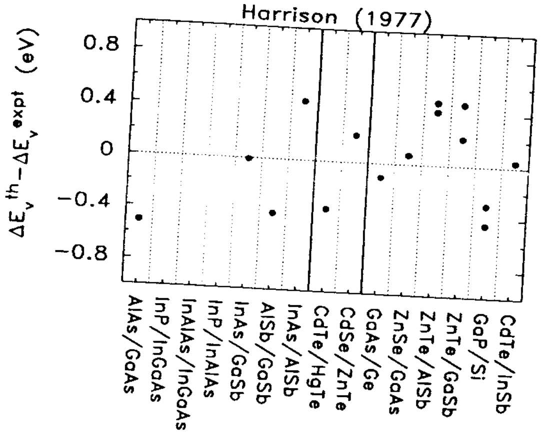

FIG. 45. Comparison of experimental and theoretical valence-band offsets for predictions of Harrison.[24]

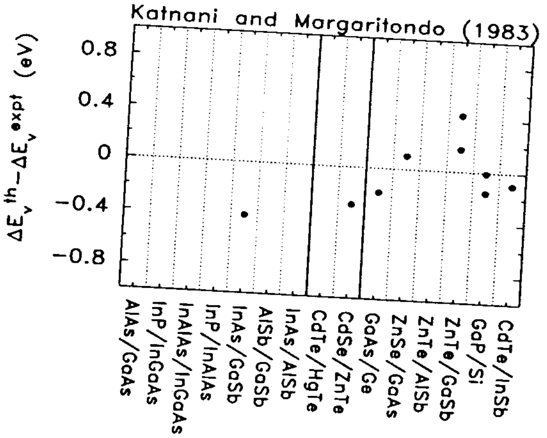

FIG. 46. Comparison of experimental and theoretical valence-band offsets for predictions of Katnani and Margaritondo.[21]

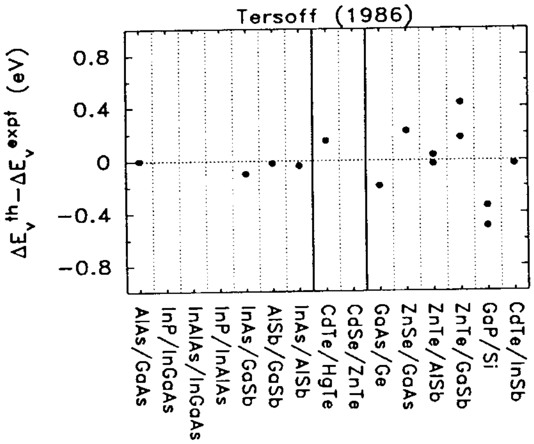

FIG. 47. Comparison of experimental and theoretical valence-band offsets for predictions of Tersoff.[28]

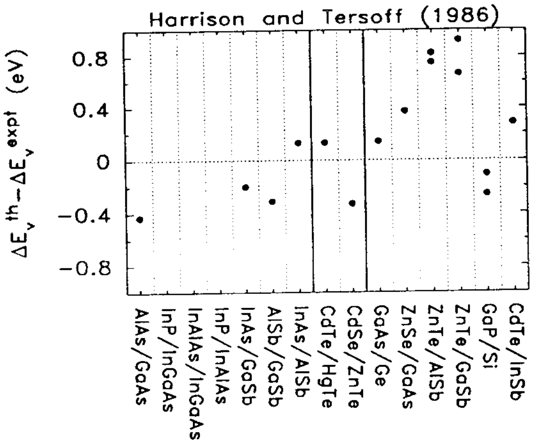

FIG. 48. Comparison of experimental and theoretical valence-band offsets for predictions of Harrison and Tersoff.[29]

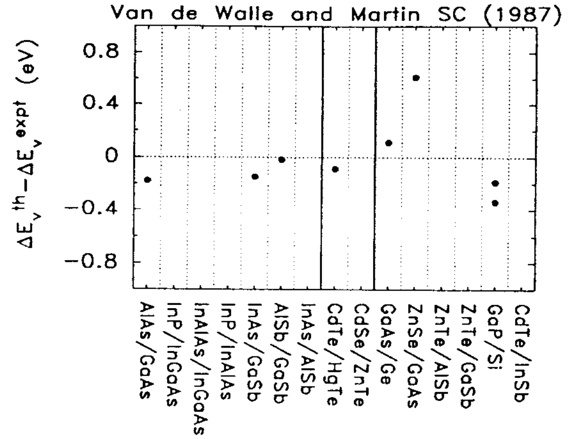

FIG. 49. Comparison of experimental and theoretical valence-band offsets for predictions corresponding to self-consistent calculations of Van de Walle and Martin.[84]

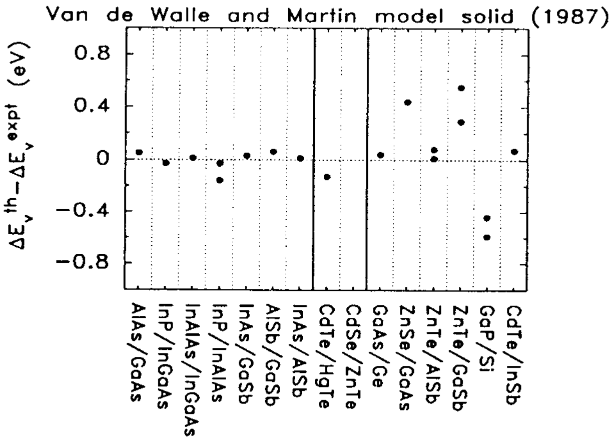

FIG. 50. Comparison of experimental and theoretical valence-band offsets for predictions of the model solid theory of Van de Walle and Martin.[84]

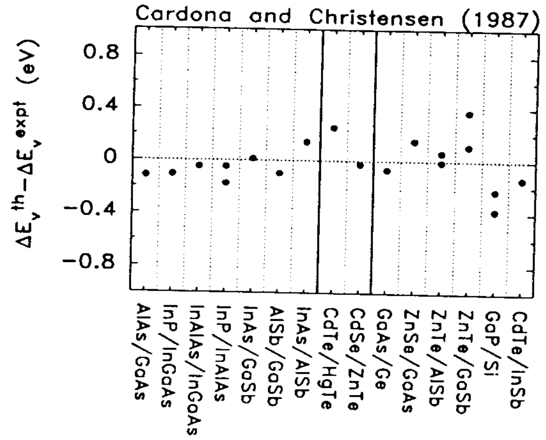

FIG. 51. Comparison of experimental and theoretical valence-band offsets for predictions of the dielectric midgap energy model of Cardona and Christensen.[39]

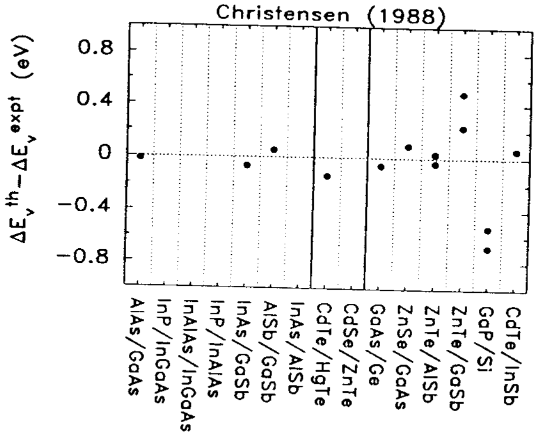

FIG. 52. Comparison of experimental and theoretical valence-band offsets for predictions of Christensen.[40]

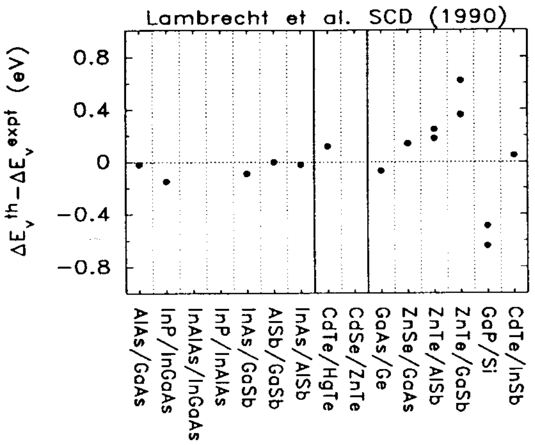

FIG. 53. Comparison of experimental and theoretical valence-band offsets for predictions of the self-consistent dipole calculations of Lambrecht *et al.*[43]

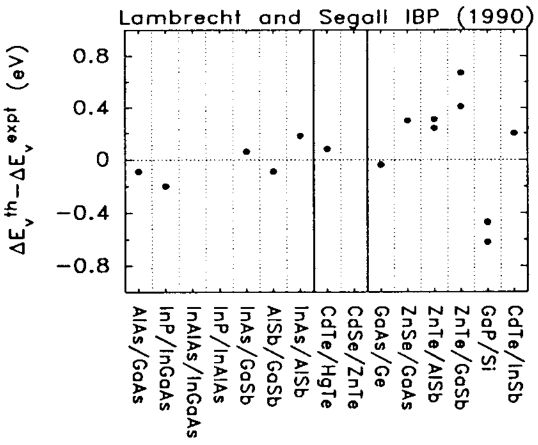

FIG. 54. Comparison of experimental and theoretical valence-band offsets for predictions of the interface bond polarity model of Lambrecht and Segall.[87]

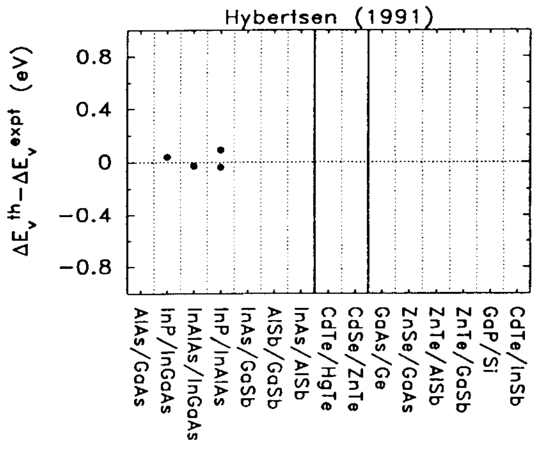

FIG. 55. Comparison of experimental and theoretical valence-band offsets for predictions of Hybertsen.[161,162]

comparison only for lattice-matched heterojunctions; in addition, we have included only systems for which the experimental band offset value is reasonably well known. The experimental values we have chosen are compiled in Table XXIV. For values obtained from a single reference, the error bars in the table are quoted directly from that reference; for values obtained by averaging the results of several experiments, the error bars represent the standard deviation of the collection of experimental values.

The heterojunctions included in Figs. 41 through 55 have been divided into three categories: III-V/III-V systems (AlAs/GaAs, InP/InGaAs, InAlAs/InGaAs, InP/InAlAs, InAs/GaSb, AlSb/GaSb, InAs/AlSb), II-VI/II-VI systems (CdTe/HgTe, CdSe/ZnTe), and heterovalent systems (GaAs/Ge, ZnSe/GaAs, ZnTe/AlSb, ZnTe/GaSb, GaP/Si, CdTe/InSb). Multiple points for a single heterojunction represent different experimental band offset values, as listed in Table XXIV. If a theory did not predict a band offset value for a given heterojunction system, no value is shown.

For the III-V/III-V heterojunction systems, the clearest trend is chronological. The early theories (Figs. 41 through 46) show considerable disagreement with the experimental band offset values that are now accepted; the later theories, beginning with that of Tersoff[28] (Figs. 47 through 55), generally agree much better with the currently available experimental values. The early theories were particularly bad for heterojunctions containing Al; however, most of the early treatments (with the exception of the dipole-corrected theory of Frensley and Kroemer[23] and the empirical compilation of

TABLE XXIV. SELECTED EXPERIMENTAL BAND OFFSET VALUES FOR LATTICE-MATCHED HETEROJUNCTIONS

HETEROJUNCTION	ΔE_v (eV)
AlAs/GaAs	0.55[a]
InP/InGaAs	0.37 ± 0.03[b]
InAlAs/InGaAs	0.20 ± 0.03[c]
InP/InAlAs	0.16[d], 0.29[e]
InAs/GaSb	0.53 ± 0.03[f]
AlSb/GaSb	0.40 ± 0.04[g]
InAs/AlSb	0.09 ± 0.05[h]
CdTe/HgTe	0.36 ± 0.02[i]
CdSe/ZnTe	0.64 ± 0.07[j]
GaAs/Ge	0.52 ± 0.13[k]
ZnSe/GaAs	0.98 ± 0.07[l]
ZnTe/AlSb	0.35 ± 0.11[m], 0.42 ± 0.07[n]
ZnTe/GaSb	0.34 ± 0.05[o], 0.60 ± 0.07[p]
GaP/Si	0.8 ± 0.1[q], 0.95[r]
CdTe/InSb	0.87 ± 0.10[s]

[a] Refs. 48 and 49.

[b] Statistical average of values from Refs. 88, 111, 112, 136, 137, 138, 139, 140, and 141.

[c] Statistical average of values from Refs. 90, 114, 141, 149, 150, 151, 152, and 153.

[d] Ref. 158.

[e] Ref. 157.

[f] Statistical average of values from Refs. 93, 98, 165, and 166.

[g] Statistical average of values from Refs. 72, 99, 188, 190, and 191.

[h] Ref. 115.

[i] Statistical average of values from Refs. 100, 101, 110, 202, and 206.

[j] Ref. 218.

[k] Statistical average of values from Refs. 21, 53, 94, 314, 316, 317, 318, 319, 323, and 324.

[l] Statistical average of values from Refs. 65, 333, 335, 336 and 337.

[m] Ref. 339.

[n] Ref. 105.

[o] Ref. 106.

[p] Ref. 190.

[q] Refs. 341 and 342.

[r] Ref. 21.

[s] Ref. 108.

Katnani and Margaritondo[21]) were quite accurate in predicting the InAs/GaSb valence-band offset.

For II-VI/II-VI heterojunctions, the number of lattice-matched systems for which experimental data are available is very small. For the HgTe/CdTe heterojunction, no theory is in extremely close agreement with the experimental value, but the more recent theories, beginning with that of Tersoff,[28] are in general agreement with the qualitative conclusion that the valence-band offset is not small; the early LCAO theory of Harrison[24] had predicted a very small valence-band offset for HgTe/CdTe. It is also useful to examine the CdSe/ZnTe heterojunction, because a reliable experimental band offset value was not available until quite recently.[218] Surprisingly, the early theories of McCaldin *et al.*[20] (Fig. 42) and of Frensley and Kroemer[23] (Fig. 43) are in good agreement with the experimental value. Because the equilibrium crystal structure of CdSe is wurtzite rather than cubic zincblende, few of the more recent theories treat the CdSe/ZnTe heterojunction; however, the dielectric midgap energy model of Cardona and Christensen[39] is in good agreement with experiment. These theoretical values were all obtained prior to the experimental measurement of Yu *et al.*[218]

Predictions for the heterovalent material systems are generally in poorer agreement with experimental values than predictions for pure III–V/III–V or II–VI/II–VI heterojunctions. In fairness to the theorists, this tendency may be due in part to greater uncertainties in the experimental band offset values. For heterojunctions for which a large number of experiments have been performed, such as GaAs/Ge, the range of experimental values is quite large—approximately 0.35 eV, as shown in Table XIV—and even the statistically reduced error bar is ±0.13 eV. In addition, the experimental band offsets for heterovalent material systems shown in Table XXIV and Figs. 41 through 54 are often based on only one or two experimental measurements.

The greater ambiguity of the experimental situation for heterovalent material systems compared to that for isovalent heterojunctions may be due only in part to a lack of extensive experimental data for each heterojunction. As discussed in Section VII, many, if not all, heterovalent material systems are characterized by some degree of chemical reactivity at the interface. Experiments by Kowalczyk *et al.*[65] demonstrated that the GaAs/ZnSe valence-band offset can depend on the conditions under which the interface was prepared, and work of Yu *et al.*[190] indicated that interfacial reactions affected band offset values in the AlSb/GaSb/ZnTe material system.

An examination of theoretical and experimental valence-band offset values for III–V/II–VI heterojunctions reveals that, in every case except CdTe/InSb, the theoretical values tend to be quite consistently larger than the experimental values. For the calculations of Van de Walle and Martin,[84] shown in Figs. 49 and 50, the theoretical values for ZnSe/GaAs are much larger than the experimental value. This general trend among theoretical predictions can be seen quite clearly in Figs. 33 (ZnSe/GaAs), 35 (ZnTe/AlSb), and 36 (ZnTe/GaSb). The same tendency is also observed for the ZnSe/Ge heterojunction, as can be seen in Fig. 37. For the one exception to this trend, CdTe/InSb, the experimental value is based on a single measurement.[108] Given the expected complexity of the CdTe/InSb interface, it is quite possible that the measured band offset could depend significantly on the detailed structure of the interface.

This systematic trend between the predicted and observed values of valence-band offsets in III–V/II–VI heterojunctions suggests that the chemical reactions and atomic intermixing that are known to occur may tend to reduce the value of the valence-band offset. Harrison *et al.*[313] realized very early that, for polar orientations such as (100), some atomic intermixing was required in heterovalent interfaces to prevent large charge accumulations at the heterojunction. Thus, one of the driving forces for interfacial chemical reactions may be the minimization of interfacial charge. This minimization may be partially responsible for the somewhat curious fact that for many heterovalent systems, theoretical treatments that do not include any effects of interfacial reactivity predict valence-band offsets in fairly close agreement with experimental values. Because the effect of heterovalent interface reactions may in fact be to minimize interfacial charge, idealized "model" theories, which is what current theories are, may be able to provide a qualitatively and perhaps even semiquantitatively accurate description of band offsets in heterovalent material systems. The final atomic arrangement that results may yield a valence-band offset that is close to, but consistently smaller than, what would be expected on the basis of a simplified, idealized description of bulk energy levels or minimization of interfacial dipoles.

Regarding the successes and failures of specific theories for the entire range of heterojunction systems considered here, there is little that can be said. Most of the recent theories yield band offset values in good agreement with experiment for III–V/III–V heterojunctions; the dielectric midgap energy model of Cardona and Christensen,[39] shown in Fig. 51, was also able to predict the value of the CdSe/ZnTe valence-band offset quite accurately. This suggests that, for isovalent heterojunctions, the more modern theories may have a limited degree of actual predictive power. Among the early theories and empirical rules, the predictions of the common-anion rule of McCaldin *et al.*,[20] shown in Fig. 42, may yet be of some interest. The actual predictions of the common-anion rule, based on measured Schottky barrier heights, are shown as solid circles in Fig. 42 and were quite good at the time the predictions were made. Predictions for heterojunctions not claimed by McCaldin *et al.* to be within the scope of the rule, i.e., for compounds containing Al or Hg, are shown as open circles in the figure. With these additions the accuracy of the common-anion rule predictions is comparable to that of its contemporaries—the electron affinity rule[71] (Fig. 41), Frensley and Kroemer[23] (Figs. 43 and 44), and Harrison[24] (Fig. 45). Thus, within its known limitations the common-anion rule, as seen in Fig. 42, may still serve as a useful qualitative guide to band offset values in lattice-matched heterojunctions.

The final point to note in comparing the currently available theories is that no single theory yields band offset values in good agreement with experimental measurements for all or even most of our selected set of heterojunctions. In addition, even the more recent theories are based on widely disparate underlying physical concepts, e.g., calculated band structures referred to atomic potentials, various charge neutrality or effective midgap energy levels, or screened interfacial dipoles. However, these theories all appear to predict band offset values with approximately the same degree of accuracy. On the basis of these observations it would seem that none of the current theories includes all of the relevant physics governing band offsets to the accuracy required to yield reliable values for all heterojunctions. Nevertheless, the success of both model theories and *ab initio* calculations for III–V/III–V heterojunctions, which are well understood experimentally and in which interfacial reactions are not an important factor, suggests that current theories can provide predictive guidance for a limited range of heterojunction systems.

24. STRAIN

As described in Section VI, strain effects have an extremely strong influence on band offset values in lattice-mismatched heterojunction systems. Theoretical and experimental studies of band offsets in the Si/Ge material system indicate that the dominant effect of strain is the splitting of the heavy-hole, light-hole, and split-off valence-band edges induced by uniaxial strain, rather than shifts in the average valence-band-edge positions arising from hydrostatic strain. Thus, the discontinuity in the average position of the light-hole, heavy-hole, and split-off valence-band edges in a coherently strained Si/Ge heterojunction depends only weakly on strain, and the actual band-edge positions are determined primarily by the uniaxial splitting of the valence-band edges. Calculations of absolute deformation potentials using the model solid theory of Van de Walle and Martin[86] suggest that the weak dependence of the average valence-band offset on strain should be characteristic of other lattice-mismatched heterojunctions as well. The success of the calculations of Van de Walle and Martin[37,38] for the Si/Ge heterojunction suggests that the effects of strain on band offsets are well understood theoretically and also adds to the evidence that current theoretical treatments can, in limited circumstances, exhibit considerable predictive power.

Detailed investigations of strain effects may also provide some insight into the respective roles of absolute energy scales and effective midgap or charge neutrality energy levels in determining band offset values. As pointed out by Cardona and Christensen,[39] strain in lattice-mismatched heterojunctions can strongly influence the calculated average valence-band offset in theories based on effective midgap energy levels. Detailed investigations of quantities such as the pressure dependence of band offsets or, if possible, "unstrained" band offsets for lattice-mismatched heterojunctions might provide one way to distinguish between theories based on absolute energy scales and those based on effective midgap or charge neutrality levels.

25. Unresolved Issues

At this point it must surely be evident to the reader that many issues remain unresolved in the study of band offsets. One issue of interest is the extent to which band offsets can be controlled by altering the atomic composition and structure of the heterojunction interface. Investigations of interfacial reactivity in heterovalent material systems have demonstrated that interfacial reactions can exert a substantial influence on band offset values. Studies described in Section VII of material systems such as GaAs/Ge, ZnSe/GaAs, and AlSb/GaSb/ZnTe suggest that band offsets can shift by up to a few tenths of an electron volt by this mechanism. Another possibility is to alter the effective barrier height for carriers in a heterostructure device by δ-doping near a heterojunction interface.[349,350] However, it will also be necessary to determine the degree to which such adjustments can be made without inducing severe deterioration in other aspects of device performance.

Another issue that deserves investigation is the degree to which fluctuations in interfacial structure can affect band offsets. Ballistic electron emission microscopy (BEEM) has been used to study Au–GaAs (100) interfaces with nanometer spatial resolution, and the electronic structure of the interface was found to be highly heterogeneous.[351,352] Similar effects might be observed in semiconductor heterojunctions, particularly in heterovalent material systems in which chemical reactions are known to occur at the heterojunction interface. Such inhomogeneities could have significant implications for nanometer-scale device structures such as quantum wires and quantum dots.

Perhaps the most important issue that remains unresolved is the question of what actually determines band offset values. A number of current theories appear to yield band offset values that are, for a limited set of heterojunctions, in reasonable agreement with experiment. However, the physical ideas on which these theories are based vary considerably, ranging, for example, from careful calculations of band structure on energy scales referenced to atomic energies to alignment of effective midgap or charge neutrality energy levels.

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Studies such as those described in Section 24 might provide some information. There also remain several relatively unstudied material systems that may eventually become technologically relevant and at the very least could add to the available data used to develop and test new theories of band offsets. Relatively unexplored III–V materials include most nitride compounds. A wide range of II–VI compounds remain uncharted territory; these include compounds containing Be, Mg, and Ca, as well as oxygen compounds and, to a lesser extent, sulfides.

It is possible, however, that the prediction of band offset values to a high degree of accuracy (e.g., ±0.1 eV or better) may remain an intractable problem for some time to come. Given the known variability of band offsets with the detailed structure of a heterojunction interface, it will probably be difficult to account for all the factors that can influence band offsets at the 0.1 eV energy scale and below. However, it would be desirable and certainly of considerable importance to be able to develop a quantitative understanding of correlations between certain deviations from ideal interface structure and corresponding shifts in band offset values. Such an understanding would probably provide a great deal of insight into the fundamental physics governing band offsets.

IX. Conclusions

In this article we have reviewed the available experimental and theoretical studies of band offsets in semiconductor heterojunctions. Our approach has been to attempt to blend experimental observations and theoretical insights and develop a perspective that might best be referred to as enlightened empiricism. Experimentally, reliable band offset values are now known for a fairly large set of semiconductor heterojunctions, and experimental techniques have been sufficiently well developed that, with care, reliable band offset measurements can be performed quite consistently. The current level of theoretical understanding is such that a number of model theories, as well as some *ab initio* calculations, are able to provide band offset values in fairly good agreement with experimental values, and even with a limited amount of predictive power, for a restricted set of heterojunctions—primarily isovalent (III–V/III–V, II–VI/II–VI, or IV/IV) heterojunctions rather than heterovalent material systems. The inherent chemical complexity of heterovalent interfaces and the limited amount of experimental data available have hindered attempts to develop an accurate quantitative description of band offsets in these material systems.

At the current stage of the subject's development, it will probably be difficult to develop a detailed, comprehensive, and quantitatively accurate (to within ±0.1 eV or better) theory of band offsets, simply because the underlying physics governing band offsets is not understood in detail. The reactive nature of heterovalent interfaces will make even an accurate structural description of these heterojunctions quite difficult. However, it will be important to develop or enhance our understanding of a number of issues: the role of chemical reactions and detailed interfacial atomic structure in determining band offset values; how, in detail, strain and lattice mismatch affect band offsets; band offset values in previously unstudied heterojunctions; and possible inhomogeneities in electronic structure on nanometer spatial scales arising from details of atomic structure at interfaces. These and other issues are likely to continue to provide substantial challenges to both experimentalists and theorists in the years to come.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge our many valuable discussions with the students and faculty members associated with the McGill research group at Caltech. We would also like to thank Professor Henry Ehrenreich for his support and encouragement during the writing of this article, and for his critical reading of the manuscript.

Part of this work was supported by the Defense Advance Research Projects Agency, monitored by the Office of Naval Research, under grant N00014-90-J-1742.