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The temperature dependence of band offsets for semiconductor heterojunctions in general and for the particular cases of AlAs–GaAs and HgTe–CdTe

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Abstract. We devise a simple theory for the temperature dependence of the valence and conduction band offsets in semiconductor heterojunctions using the thermodynamic point of view. The temperature dependencies of the offsets originate from the separate contributions of holes in the valence bands and of electrons in the conduction bands of the two semiconductors to the temperature dependence of their respective band gaps. We use the earlier determination of these contributions by Heine and Henry from isotope shifts of luminescent lines due to impurities. By considering this temperature dependence of the band offset we suggest an explanation for the discrepancy between the determinations of AlAs–GaAs valence band offset by Wolford *et al* and by Batey and Wright. Whereas for most pairs of semiconductors the bands move in the same direction with varying temperature, for the particular case of HgTe–CdTe they move in opposite directions. From this we predict a much greater than usual temperature dependence for the band offsets for HgTe–CdTe junctions and reconcile the major discrepancy between valence band offsets determined by Kowalczyk *et al* and by Chow *et al*.

1. Introduction

With the dramatic advance of semiconductor heterojunction technology [1–10] has come a concomitant increase of interest in the origin [11–18] of the valence and conduction band offsets, or discontinuities, ΔE_v and ΔE_c, respectively. In spite of the implied simiplicity in the concept of band offsets, no single theoretical description has been acknowledged as correct. To add an additional factor to this uncertainty, we wish to explore the temperature dependence of the band offsets, an issue ignored until raised by recent experiments [19, 20].

Approaches to the problem of the band offsets divide into two categories: thermodynamic, and electronic structure calculations. In addition to differences in the method of calculation between the two approaches, there is a difference in the way they view the small, but detectable, effect of depolarising fields set up around the boundaries of the samples as a result of dipole layers that are concomitant with those boundaries. The distinction is particularly clear and acute for the case of the band offset to vacuum, i.e. for the questions of the 'work functions' or 'ionisation potentials' of metals or of

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semiconductors. For the purposes of the present paper, which is concerned with the temperature dependence of the band offsets, the point to keep in mind is that the effect of depolarising fields on junctions between two semiconductors is small at all temperatures and, owing to its origin, should be expected to have very little temperature dependence in the range $0 < T < 310$ K in which the data we discuss were taken. However, there seems to be such a semantic disagreement, and some confusion, between the two camps over this issue that some space must be taken to discuss it. ([11] and [13] contain previous attempts to resolve these semantic arguments and confusion.)

Those who use thermodynamic approaches are usually concerned with differences in free energy, chemical potential etc. between bulk phases. For such a consideration, any junction between two phases is irrelevant; there need not be any junction so long as they can somehow exchange the energy, particles etc. relevant to the problem. Thus, with the thermodynamic approach to the band offset (and work function) problems [11–13, 15], one ascribes absolute values (usually relative to an idealised 'vacuum level' [11]) to the enthalpies, entropies, and standard free energies of the valence and conduction band edge density of states distributions in the equipotential bulk region of each semiconductor [21, 22], when no bias field is applied externally. (Recall that the standard free energies are the total free energies minus all explicitly concentration dependent entropy terms; in particular, the entropy terms resulting from the statistical distribution of the free carriers among the band states are absent from these standard free energies. Thurmond has given a particularly clear and authoritative account [21] of this point. Any good text book contains a general discussion, usually when treating the law of mass action.) Those who use this thermodynamic approach then define the band offset as simply the difference between these absolute standard free energies:

$$\Delta E_{\mathrm{v}}(\mathrm{A/B}) = E_{\mathrm{v}}(\mathrm{A}) - E_{\mathrm{v}}(\mathrm{B}) \tag{1}$$

$$\Delta E_{\mathrm{c}}(\mathrm{A/B}) = E_{\mathrm{c}}(\mathrm{A}) - E_{\mathrm{c}}(\mathrm{B}). \tag{2}$$

The result is, by this definition, independent of crystallographic orientation and transitive from one material to another; that is, for example,

$$\Delta E_{\mathrm{c}}(\mathrm{AlAs/GaAs(110)}) = \Delta E_{\mathrm{c}}(\mathrm{AlAs/GaAs(100)}) \tag{3}$$

$$\Delta E_{\mathrm{v}}(\mathrm{AlAs/GaP}) = \Delta E_{\mathrm{v}}(\mathrm{AlAs/GaAs}) + \Delta E_{\mathrm{v}}(\mathrm{GaAs/GaP}). \tag{4}$$

Furthermore, for any pair of semiconductors A and B,

$$\Delta E_{\mathrm{v}}(\mathrm{A/B}) - \Delta E_{\mathrm{c}}(\mathrm{A/B}) = \Delta E_{\mathrm{cv}}(\mathrm{B}) - \Delta E_{\mathrm{cv}}(\mathrm{A}) \tag{5}$$

where

$$\Delta E_{\mathrm{cv}} = E_{\mathrm{c}} - E_{\mathrm{v}} \tag{6}$$

denotes the band gap, E_{v} is the absolute standard free energy of the valence band edge distribution, and E_{c} is the absolute standard free energy of the conduction band edge distribution.

The fact that, by the thermodynamic approach definition, band offsets must be independent of orientation and transitive can readily be appreciated by considering, as in figure 1, the addition of a third material, C, to form junctions to the first two, A and B. The change in energy, enthalpy, total free energy or standard free energy upon transferring one carrier from the bulk of A to the bulk of B must be independent of the path utilised. Thus, the transit may be directly through the A/B junction or through the A/C junction followed by a path through sample C and through the C/B junction.

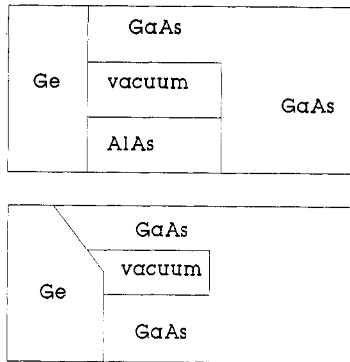


Figure 1. The change in energy etc when an electron goes from a particular state at a particular point in the bulk of Ge to a particular state at a particular point in the bulk of GaAs cannot depend upon the path taken. Thus, the bulk-to-bulk band offset, the definition used by those who use the thermodynamic approach, cannot depend on the orientation of the junction and must be a transitive property.

Because this is true regardless of the orientation of either junction or of the material C, which might be vacuum, it is plain that these bulk-to-bulk band offsets must be transitive and independent of orientation.

Now, it is well known [11] that when one measures the quantity generally known as the 'work function' of a metallic or semiconducting crystal (e.g. by photoemission), the result depends upon crystal orientation to a small degree; it depends very sensitively on the presence of any foreign atoms, e.g. Cs or O, on the surface. It is also well known [11] that the reason for this is that such experiments do not measure the chemical potential difference etc between the bulk of the crystal and the vacuum level, but instead they measure an effective potential energy barrier between a region in the sample near the surface and a region close above the sample, and because the termination of the sample at surfaces of various orientation, chemistry and condition produces electrostatic dipoles that depend upon that orientation, chemistry and condition. These dipoles produce depolarising fields that extend around the exterior of the sample, and, to a much smaller degree, extend also within the sample near the surfaces (or junctions). These fields would be irrelevant to the experiment if the electron were making a transition from the bulk to the idealised point at infinite separation from the sample and from all other charges, but practical experiments do not work that way.

Those who use the thermodynamic approach realise, and readily admit, that practical experiments that measure the 'work function' do find a quantity that is neither transitive nor orientation independent. They distinguish [11–13] the 'work function' from the thermodynamic parameter that they would call the 'band offset between the sample material and vacuum'. Some attempt [13] to avoid confusion on this point is made by calling the thermodynamic 'band offset to vacuum' the 'ionisation potential'. It is quite a tractable problem to extract [11] the 'ionisation potential' from an adequate set of data on the 'work function'.

Unless the sample is heated so much that its surface chemistry changes or the surface atoms diffuse enough to change their local surface array, the dipole layer fields that produce this distinction between 'work function' and 'ionisation potential' will not change. If the surface dipoles do not change with T, then the magnitude of the distinction

will not change with T. Thus, the dipole fields will then make no contribution to any measured dependence on T of either the 'work function' or the 'ionisation potential'.

In general, practical junctions between crystalline samples also produce electrostatic dipoles that also produce fringing, or depolarisation fields. For semiconducting samples these fields are much weaker than those in vacuum because of the conductivity of the two solids. However, they do have a finite effect upon the effective barrier a carrier encounters transiting the junction in a practical experiment. Just as the chemistry of the surface has much more effect on the 'work function' that does the crystal orientation, the effective barrier at a semiconductor junction is expected to be much more sensitive to the local chemistry of the interface than to its orientation. (Indeed, the Freeouf–Woodall and Spicer defect models for Schottky barrier heights attribute a dramatic effect to a local chemistry at the interface different from that of the bulk sample.) Again, those with a thermodynamic point of view regard these junction field effects as a minor nuisance that should be extracted from the raw data in order to determine the true, bulk-to-bulk band offset, which must be transitive and orientation independent.

With the electronic structure approach [14, 16–18], one solves a Schrödinger equation for the particular chemistry and orientation of the junction as exactly and as rigorously as possible. With such an approach one has to deal explicitly with the junction dipole in detail. Those who use this approach regard these dipoles and their depolarisation fields with more respect than do those who use the thermodynamic approach. They generally include their effect when they seek to relate the results of their Schrödinger equation calculations, which are eigenvalues and not free energies, on the two sides to ΔE_v and ΔE_c. (The problem of relating eigenvalues to the enthalpies and free energies of the band density of states distributions is discussed on pages 8 to 18 of [22].)

Thus, with the electronic structure approach, one includes the small effect of the depolarising field in one's definition of the 'band offset' which is then an effective barrier height for transit of the carrier. Fortunately, the two approaches are now beginning to concur [18] with one another in cases like AlAs/GaAs where the close matching of the lattice constants makes for very simple junctions.

The effective barrier definition of the 'band offset' depends on the sample geometry and the distance of the two reference points from the interface. In general, it can be non-transitive and orientation dependent. It may be claimed to be more directly related to the result of practical experiments, but, in our view, it is not nearly so well nor clearly defined a concept and it is not nearly so easily applied to the question of the temperature dependence of the band offsets. Again, the reader should keep in mind that, because these junction dipole fields should not depend on T in the range of the relevant experiments, this distinction between the definitions of 'band offset' will have no significance for any discussion of the *temperature dependence* of the band offset.

The purpose of the present work is to address the problem of the temperature dependence of the band offsets. Although it seems not to have been done before, we will see that this is a very simple problem if one uses the thermodynamic approach. (It would appear to be rather difficult from the electronic structure approach.) We see from equations (1) to (6) that all that is required is a determination of the variation of E_v and E_c with T for the two semiconductors that form the junction. Most of what is required to establish $E_v(T)$ and $E_c(T)$ has already been developed and published with reference to the closely related problem of $\Delta E_{cv}(T)$, for which empirical values are established for most semiconductors [21].

Also for the problem of $\mathrm{d}\Delta E_{cv}/\mathrm{d}T$ there is a simple thermodynamic approach [22, 23] which avoids the difficulties of electronic structure calculations. One notes that the

explicit effect of T on the electronic eigenvalues is a very small part of the total $\mathrm{d}\Delta E_{cv}/\mathrm{d}T$ (as can be determined from the coefficient of thermal expansion and the pressure dependence of ΔE_{cv}) and the vast majority of the effect comes from the electron–phonon interaction. The electron–phonon interaction can be evaluated by considering the small perturbative effect upon the phonons of the thermally excited electrons, the e_c, and holes, the h_v, which are never more [21] than 1 part in 10^4 of the bonding electron density, using a simple bond-charge theory [24, 25] of phonon energies. This approach has been shown to give quantitative agreement with experiment for the phonon frequencies [26], as well as for $\Delta E_{cv}(T)$, up to the melting points of Si and Ge. (Of course, there is also an electronic structure approach [27] which considers the massive perturbation of (vibronic) electronic levels by phonons, which are several times more numerous than are host atoms. These two approaches now concur rather well.)

2. Temperature dependence of band offset

With the thermodynamic approach [21, 22] one readily sees that for most semiconductors ΔE_{cv} decreases with increasing T because the thermal excitation of both the e_c and h_v softens transverse acoustic phonon modes by (respectively) putting charge into antibonding states in the conduction band and taking it away from bonding states in the valence band. This results in a large positive (standard) entropy, ΔS_{cv}, for the reaction [21, 22] that thermally excites the e_c and h_v,

$$0 \leftrightarrow e_c + h_v \qquad \Delta E_{cv}. \tag{7}$$

As ΔE_{cv} is the (standard) chemical potential for $e_c + h_v$ pairs, it is equal to a free energy and follows the universal relation [21] of Gibbs

$$\Delta E_{cv}(T) = \Delta H_{cv}(T) - T\,\Delta S_{cv}(T) \tag{8}$$

where ΔH_{cv} is the corresponding (standard) enthalpy of the reaction. $\Delta E_{cv}(T)$, $\Delta H_{cv}(T)$, and $\Delta S_{cv}(T)$, as determined by Thurmond in [21] for the case of GaAs are plotted in figure 2. Note that basic considerations of thermodynamics require that $\Delta S_{cv}(T = 0\ \mathrm{K}) = 0$, and if $\Delta S_{cv} > 0$ for $T > 0$, then $\mathrm{d}\,\Delta E_{cv}(T)/\mathrm{d}T < 0$ and $\mathrm{d}\,\Delta H_{cv}(T)/\mathrm{d}T > 0$.

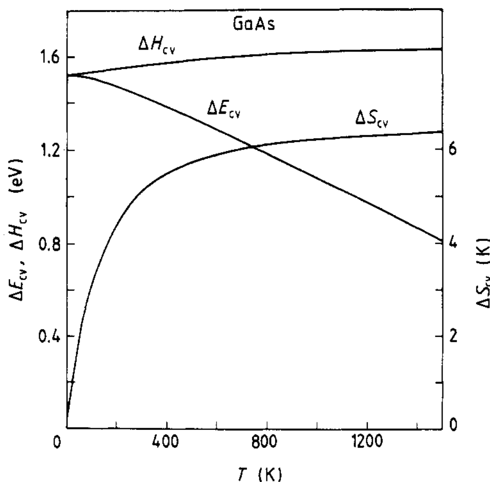


Figure 2. The empirical variation with temperature, as determined by Thurmond [21], of the free energy, the enthalpy, and the entropy of the band gap, i.e. of the creation of a pair of free carriers, in GaAs.

Where ΔS_{cv} denotes the combined effect of one e_c and one h_v, it is sometimes possible to separate the two effects by observing the isotope shifts of zero-phonon optical transitions due to impurities [28, 29]. One may deduce from the isotope shift the local softening effect on the phonon modes about the impurity when one electron or one hole localises into a state about the impurity. Heine and Henry studied this problem [28] for several semiconductors, particularly GaP and ZnO. They concluded that, at least for these cases, a hole is almost four times as effective in softening phonons as is an electron. That is

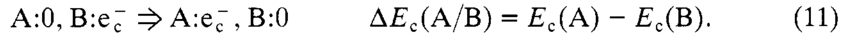
$$S_h = (3.6 \pm 1) S_e \tag{9}$$

with

$$\Delta S_{cv} = S_e + S_h. \tag{10}$$

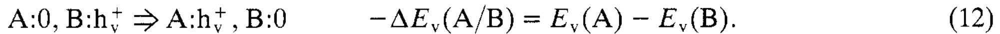
As suggested by Heine and Henry, we assume that this distribution of the weight of the two contributions is essentially the same for all tetrahedrally bonded semiconductors.

Let us now define the band offset problem in thermodynamic terms. (Care is required not to make a sign error.) We have the two semiconductors, A and B, and consider the reaction that transfers an e_c from B to A at the cost of free energy $\Delta E_c(\mathrm{A/B})$,



$$\mathrm{A{:}0,\ B{:}e_c^- \Rightarrow A{:}e_c^-,\ B{:}0} \qquad \Delta E_c(\mathrm{A/B}) = E_c(\mathrm{A}) - E_c(\mathrm{B}). \tag{11}$$

We also have the reaction that transfers a h_v from B to A at the cost of free energy $-\Delta E_v(\mathrm{A/B})$ (note the effect of the difference in the sign of the charge of the h_v and the e_v),



$$\mathrm{A{:}0,\ B{:}h_v^+ \Rightarrow A{:}h_v^+,\ B{:}0} \qquad -\Delta E_v(\mathrm{A/B}) = E_v(\mathrm{A}) - E_v(\mathrm{B}). \tag{12}$$

The vacuum level, or any other reference state, R, may be introduced by breaking these reactions into two parts, i.e.

$$\mathrm{B{:}e_c^-,\ R{:}0 \Rightarrow B{:}0,\ R{:}e^-} \tag{13}$$

followed by

$$\mathrm{R{:}e^-,\ A{:}0 \Rightarrow R{:}0,\ A{:}e_c^-} \tag{14}$$

and correspondingly for the hole reaction. Adding reactions (11) and (12), we have

$$\mathrm{A{:}0,\ B{:}e_c^- + h_v^+ \Rightarrow A{:}e_c^- + h_v^+,\ B{:}0} \qquad \Delta E_c(\mathrm{A/B}) - \Delta E_v(\mathrm{A/B}) \tag{15}$$

which immediately implies

$$\Delta E_{cv}(\mathrm{A}) - \Delta E_{cv}(\mathrm{B}) = \Delta E_c(\mathrm{A/B}) - \Delta E_v(\mathrm{A/B}) \tag{16}$$

as claimed above at equation (5). When we differentiate equation (16) with respect to T, we have

$$\mathrm{d}\,\Delta E_{cv}(\mathrm{A})/\mathrm{d}T - \mathrm{d}\,\Delta E_{cv}(\mathrm{B})/\mathrm{d}T = \mathrm{d}\,\Delta E_c(\mathrm{A/B})/\mathrm{d}T - \mathrm{d}\,\Delta E_v(\mathrm{A/B})/\mathrm{d}T. \tag{17}$$

Now we recall the basic thermodynamic identity that the entropy is the negative of the derivative of the corresponding free energy (or chemical potential) with respect to T, so

$$S_c(\mathrm{A}) = -\mathrm{d}E_c(\mathrm{A})/\mathrm{d}T \qquad S_v(\mathrm{A}) = -\mathrm{d}E_v(\mathrm{A})/\mathrm{d}T \tag{18}$$

and, of course, the same for B while for the band gaps themselves

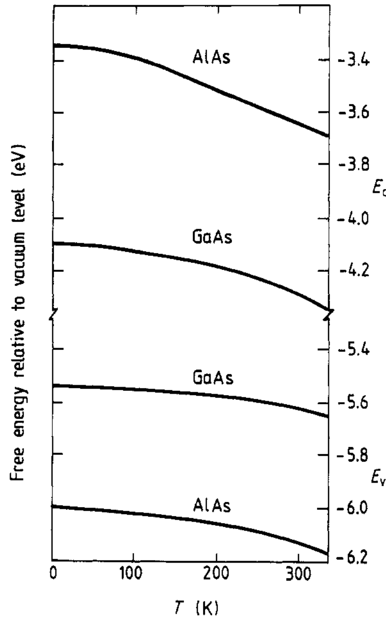


Figure 3. Variation with T of the valence and conduction band edge free energies, E_v and E_c, for GaAs and AlAs.

$$\Delta S_{cv}(A) = -dE_{cv}(A)/dT. \tag{19}$$

Finally, when we compare equation (10) with (18), we have the interesting result that

$$S_e + S_h = S_c - S_v \tag{20}$$

or

$$S_c = \Delta S_{cv} + S_h. \tag{21}$$

This merely states the fact that, in order for the band gap to decrease with rising T, the absolute free energy E_c must fall faster than the absolute free energy E_v by ΔS_{cv}. This is illustrated in figure 3 for the cases of GaAs and AlAs.

We now introduce the physical assumption of equation (9), that the fraction of ΔS_{cv} due to h_v is a constant 77% (± 5) for all tetrahedrally bonded semiconductors, and we equate this with S_v:

$$S_v = S_h \tag{22}$$

so we have

$$d\,\Delta E_v(A/B)/dT = 0.77\,(\pm\,0.05)(d\,\Delta E_{cv}(A)/dT - d\,\Delta E_{cv}(B)/dT). \tag{23}$$

While equation (22) is attractive on intuitive physical grounds, it is not clear whether it is rigorously exact. The biggest problem is that it assumes that the effect on the lattice modes of a localised hole or electron, as observed in the isotope shift experiments [28], is the same as that of a delocalised h_v or e_c in the band edge density of state distribution. Van Vechten and Thurmond have argued that this should be so to a good approximation [22, 29] and correlated it to the proposition that for any tetrahedral semiconductor the temperature dependence of the various direct band gaps in the optical spectrum (the fundamental gap and all higher gaps) should be the same. (This implies that a delocalised

state at any point in the Brillouin zone has the same effect on the lattice, so the effect of a localised state, having components from many points in the zone, would also be the same.) What experiments have been done to test this hypothesis [30] (on Si) support it. Aside from this problem of a possible distinction between localised and delocalised carriers, one can question the consequences of the possible alternative assumptions that $S_v < S_h$ or $S_v > S_h$. If $S_v < S_h$, one would have to conclude that the addition of antibonding charge, i.e. the e_c, someshow stiffens the lattice relative to the degree indicated by the isotope shift experiments—so the entropy of the valence band edge distribution could be reduced. This seems most unlikely. If $S_v > S_h$, then there must be some contribution to the entropy of both the valence and conduction band density of states beyond that due to the lattice modes. (Recall the quantitative description of the variation of the mode frequencies [26] to the melting points of Si and Ge.) No source of such a contribution is apparent.

Let us now note the consequence of equations (21), (22) and (23) for ΔE_c:

$$\mathrm{d}\,\Delta E_c(\mathrm{A/B})/\mathrm{d}T = 1.77\,(\pm\,0.05)(\mathrm{d}\,\Delta E_{cv}(\mathrm{A})/\mathrm{d}T - \mathrm{d}\,\Delta E_{cv}(\mathrm{B})/\mathrm{d}T). \tag{24}$$

Furthermore, because ΔH_V and ΔH_c are connencted by thermodynamic identities [21] to ΔS and ΔE_c and ΔE_v:

$$\mathrm{d}\,\Delta H_v(\mathrm{A/B})/\mathrm{d}T = 0.77\,(\pm\,0.05)(\mathrm{d}\,\Delta H_{cv}(\mathrm{A})/\mathrm{d}T - \mathrm{d}\,\Delta H_{cv}(\mathrm{B})/\mathrm{d}T) \tag{25}$$

and

$$\mathrm{d}\,\Delta H_c(\mathrm{A/B})/\mathrm{d}T = 1.77\,(\pm\,0.05)(\mathrm{d}\,\Delta H_{cv}(\mathrm{A})/\mathrm{d}T - \mathrm{d}\,\Delta H_{cv}(\mathrm{B})/\mathrm{d}T). \tag{26}$$

To carry this discussion any further, we must consider specific cases. We find data adquate for a discussion available for two cases—those of GaAs–AlAs junctions and of HgTe–CdTe functions, and that these generally support the foregoing simple theory.

3. The case of AlAs–GaAs

In the AlAs–GaAs heterojunction, E_v for GaAs is higher [31] than for AlAs at $T = 0$. It was found in [32] that $\mathrm{d}\,\Delta E_{cv}/\mathrm{d}T$ is a linear function of the mole fraction of Al in the $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ alloy system for $x < 0.50$. We use their extrapolation to AlAs, which concluded that $\mathrm{d}\,\Delta E_{cv}/\mathrm{d}T$ for AlAs is 1.6 ± 0.2 times that for GaAs. Consequently, E_v(GaAs) will decrease with rising T more slowly than will E_v(AlAs), and ΔE_v(GaAs/AlAs) will become larger. (See figure 3.) However, ΔH_v(GaAs/AlAs), which equals ΔE_v(GaAs/AlAs) at $T = 0$ K, will decrease with rising T because H_v(GaAs) will increase more slowly than H_v(AlAs).

Consider now what empirical information relevant to the simple theory of equations (23) and (24) is available. The theory implies that for most cases $\mathrm{d}E_V(\mathrm{A/B})/\mathrm{d}T$ and $\mathrm{d}E_c(\mathrm{A/B})/\mathrm{d}T$ are both small because the $\mathrm{d}\Delta E_{cv}(\mathrm{A})/\mathrm{d}T \simeq \mathrm{d}\,\Delta E_{cv}(\mathrm{B})/\mathrm{d}T$ for most pairs of semiconductors A and B. Furthermore, the total variation of ΔE_{cv}(A) over the range of accurate experiments, generally from $T = 0$ K to 300 K, is not much larger than the experimental uncertainty in ΔE_v(A/B) or ΔE_c(A/B). (For GaAs, $\Delta E_{cv}(T = 0\ \mathrm{K}) - \Delta E_{cv}(T = 295\ \mathrm{K}) = 94$ meV, while $\Delta H_{cv}(T = 295\ \mathrm{K}) - \Delta H_{cv}(T = 0\ \mathrm{K}) = 39$ meV.)This is certainly consistent with the fact that the authors have not been able to find any explicit discussion of the temperature dependence of band offsets in the previous

literature. However, one can look at discrepancies in determinations made at different values of T.

The case of AlAs–GaAs heterojunctions has probably been studied more carefully and with better prepared samples than any other. For the cases $Al_xGa_{1-x}As$ alloys on GaAs, Wolford *et al* determined [31] that $\Delta E_v(T = 8\ K) = 110 \pm 8$ meV for GaAs–$Al_{0.28}Ga_{0.72}As$ and $\Delta E_v(T = 8\ K) = 320 \pm 10$ meV for GaAs–$Al_{0.70}Ga_{0.30}As$. They used optical methods; it is shown in [22] that such optical experiments do in fact measure chemical potentials and thus, as Wolford *et al* imply, do determine ΔE_vs or ΔE_{cv}s rather than ΔH_vs or ΔH_{cv}s. Another careful determination of similarly well prepared samples was made [33] for higher T by Batey and Wright. They studied the thermionic emission of h_vs across the junction in p-type material as a function of alloy composition and of T for the interval 79.6 K to 294.4K. They concluded that

$$\Delta E_v(\mathrm{GaAs/Al}_x\mathrm{Ga}_{1-x}\mathrm{As}) = 0.55x\ \mathrm{eV}\ (\pm\ 20 - 40\ \mathrm{meV}) \tag{27}$$

where x is the mole fraction of Al in the alloy. This implies that $\Delta E_v = 154 \pm 30$ meV for GaAs–$Al_{0.28}Ga_{0.72}As$ in contrast to Wolford and co-workers' 110 ± 8 meV, and 385 ± 30 meV for GaAs–$Al_{0.70}Ga_{0.30}As$ in contrast to 320 ± 10 meV.

Batey and Wright obtained equation (27) by fitting their data for the thermionic emission current, J_s, with a Richardson equation

$$J_s = A^* T^2 \exp(-\phi/kT) \tag{28}$$

where A^* is the Richardson constant and s the activation barrier for holes. The limit of ϕ as bias voltage goes to zero can be simply related to ΔE_v, if, as Batey and Wright did, one takes account of the temperature variation of the Fermi level. However, in their analysis of Arrhenius plots of ϕ versus $1/T$, ΔE_v was treated as if it were independent of T. A reanalysis of the raw data including the expected variation of ΔE_v (and thus of ϕ) with T is required.

Although the issue may now be unresolvable, we can discuss the implications of the temperature dependence of ΔE_v regarding a reconciliation of these two experiments. First let us note that, since ϕ is a free energy barrier, as is ΔE_v, Batey and Wright should have measured a larger value than Wolford *et al* simply because, as noted above, the facts that $d\Delta E_{cv}/dT$ is greater for AlAs than for GaAs and that $E_v(\mathrm{GaAs}) > E_v(\mathrm{AlAs})$ imply that $\Delta E_v(\mathrm{GaAs/AlAs})$ increases with T. For the case of the 70% AlAs alloy, we have

$$\Delta E_{cv}(T = 0\ \mathrm{K}) - \Delta E_{cv}(T = 295\ \mathrm{K}) = 94(1 + 0.7\ (0.6 \pm 0.2))\ \mathrm{meV} = 134 \pm 13\ \mathrm{meV}. \tag{29}$$

Thus, ΔE_{cv} decreases by 40 ± 13 meV more in the alloy than in pure GaAs and, by our argument, $77 \pm 5\%$ of this difference occurs at the valence band edge. Thus, we predict that ΔE_v should be as much as 31 ± 10 meV greater at 295 K that at 0 K. Depending on the details of Batey and Wright's analysis of their data, then one sees that the expected variation of ΔE_v with T accounts for 31 ± 10 meV of the 65 ± 40 meV discrepancy between that determination and the optical experiment [31] at a constant $T = 8$ K.

A final resolution of this descrepancy will require a reanalysis of the raw data of the thermionic emission study, which is not available to the present authors. However, it would appear that the consequences of the variation of ΔE_v with t have the approximate magnitude and arguably the correct sign to reconcile these two fine experiments [31, 33].

4. The case of HgTe–CdTe

Let us turn to a case where the effect of T should be expected to be larger and to be more clearly recognised. Such a case, where the offsets have also received much experimental attention, is the HgTe–CdTe heterojunction [19, 20, 34, 35]. There is a large literature on this heterojunction due to the effort to develop infra-red devices based upon it.

The reader should note that, because HgTe is a semimetal, the antibonding-s Γ_6 level lies below the bonding-p Γ_8 level. However, by convention, one continues to label Γ_6 as 'E_c' and Γ_8 as 'E_v'.

Kowalczyk *et al* concluded from a room temperature optical experiment [34] that $\Delta E_v(\text{HgTe/CdTe}) = 0.35 \pm 0.06$ eV, i.e. that the HgTe valence band edge is higher than that of CdTe by this amount. This conclusion has been controversial because while others have repeated Kowalczyk and co-workers' experiment [36], several other determinations of the band offset have implied values an order of magnitude lower (see the discussion in [19]).

First we note that the experiments giving the smaller values for ΔE_v were all done at low temperatures (around 4 K). Some of these estimated ΔE_v from the optical properties of superlattice structures. The methods used for those inferences are somewhat controversial. We choose to avoid that controversy by instead basing our discussion on estimates of ΔE_v derived entirely from electronic transport measurements [37]. Chow *et al* deduced [35] $\Delta E_v(\text{HgTe/CdTe}) < 0.10$ eV at $T = 4$ K using the same structure that demonstrated [20] $\Delta E_v(\text{HgTe/CdTe}) = 0.35 \pm 0.06$ eV at $T = 300$ K, consistent with [34]. In particular, they demonstrated negative differential resistance in $Hg_{0.78}Cd_{0.22}Te$/CdTe junction device [35] at $T = 4$ K and argued forcefully that this observation requires $\Delta E_v(\text{HgTe/CdTe}) < 0.10$ eV.

We now consider whether the discrepancy in $\Delta E_v(\text{HgTe/CdTe})$ can be ascribed to the expected temperature variation of the two E_vs. We first note that HgTe has the property $d\,\Delta E_{cv}/dT > 0$ in sharp contrast to the $d\,\Delta E_{cv}/dT < 0$ behaviour of CdTe, GaAs, AlAs, Si, and most other semiconductors. As shown by Heine and Van Vechten, this is because [23] the top of the valence band in HgTe consists of states with antibonding-s character, rather than bonding-p character as with the other semiconductors; the states at the bottom of the conduction band have bonding-p character. Thus, the effect of thermally excited e_cs and h_vs is to stiffen, rather than to soften, the phonon modes as $\Delta S_{cv} < 0$. This means that for HgTe, and its alloys, E_v rises with increasing T while for CdTe, E_v falls. (See figure 4.) It then follows from equation (23) that if $E_v(\text{HgTe}) > E_v(\text{CdTe})$ at $T = 0$, then $\Delta E_v(\text{HgTe/CdTe})$ will increase rapidly with T for $T > 0$. (If $E_v(\text{HgTe}) < E_v(\text{CdTe})$ at $T = 0$, then with increasing T they would cross and $E_v(\text{HgTe})$ will rapidly rise above $E_v(\text{CdTe})$.) The variation is particularly rapid because both terms in equation (23) are positive; there is no cancellation between them. Indeed, we expect

$$\begin{aligned}\Delta E_v(\text{HgTe/CdTe}, T = 300\ \text{K}) &- \Delta E_v(\text{HgTe/CdTe}, T = 0\ \text{K}) \\ &= 0.77[(\Delta E_{cv}(\text{HgTe}, T = 300\ \text{K}) \\ &- \Delta E_{cv}(\text{HgTe}, T = 0\ \text{K})) + (\Delta E_{cv}(\text{CdTe}, T = 0\text{K}) \\ &- \Delta E_{cv}(\text{CdTe}, T = 300\ \text{K}))]. \end{aligned} \tag{30}$$

To be quantitative, $\Delta E_{cv}(\text{HgTe})$ increases [38] by about 0.160 eV between 0 and 300 K

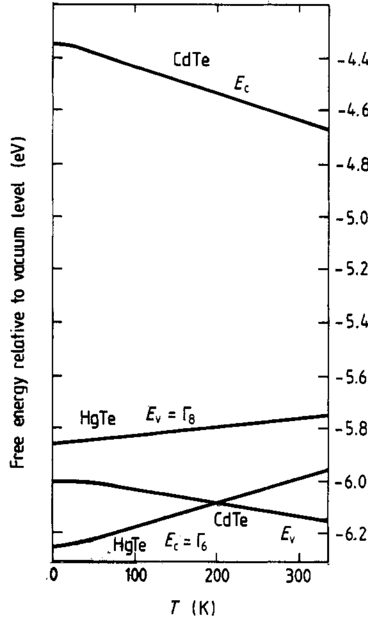


Figure 4. Variation with T of the valence and conduction band edge free energies for HgTe–CdTe. In this figure we have assumed ΔE_v(HgTe/CdTe) = 50 meV at $T = 0$ K and the variation with T of ΔE_{cv} for both HgTe and CdTe to be as reported in [38]. The HgTe bands are labelled according to the prevailing 'negative band gap' convention also used in [34–39]. Thus, the antibonding-s Γ_6 level, which corresponds to the bottom of the conduction band in CdTe (and in GaAs), is labelled 'E_c' even though it lies below the bonding-p Γ_8 level, which corresponds to the top of the valence band in CdTe (and in GaAs, AlAs etc), and which is labelled 'E_v'. The ΔE_v values quoted are indeed the differences of the Γ_8 levels across the junction.

while ΔE_{cv}(CdTe) decreases [38] about 0.161 eV. Thus, the expected variation of ΔE_v is

$$\Delta E_v(\text{HgTe/CdTe}, T = 300\text{ K}) - \Delta E_v(\text{HgTe/CdTe}, T = 0\text{ K}) = 0.247\text{ eV}. \tag{31}$$

To this can be added the effect of the alloy variation of E_v; Chow *et al* set their lower limit E_v on the basis of a 78% Hg alloy rather than for pure HgTe. Approximating the variation of the E_v as linear, we estimate that if $\Delta E_v(T = 0) = 0.10$ eV for the 78% alloy, as Chow *et al* allow, then it is 0.13 eV for pure HgTe. (This should be a small overestimate due to the alloy disorder induced bowing of the band edges [22, 38].) We would then calculate

$$\Delta E_v(\text{HgTe/CdTe}, T = 300\text{ K}) = 0.13 + 0.25 = 0.38\text{ eV} \tag{32}$$

which is even larger than estimated by Kowalczyk *et al* but within their error limit, $\Delta E_v(\text{HgTe/CdTe}, T = 300\text{ K}) = 0.35 \pm 0.06$ eV. Obviously, the value calculated at equation (32) can be reduced by allowing for the alloy bowing (an effect estimated to be roughly 0.01 eV) and by assuming $\Delta E_v(T = 0)$ to be less than the maximum allowed by Chow *et al.* In addition, the variation of ΔE_{cv}(CdTe) may be less than reported in [38] and assumed here. Zanio reported [39] the variation to be only 0.10 eV from 0 to 300 K, which would reduce the estimate of equation (32) to 0.33 eV.

5. Summary

We conclude that this variation with T is the likely explanation for the discrepancy between the experimental determinations of ΔE_v(HgTe/CdTe) by Chow *et al* and by Kowalczyk *et al*; both results can be quite correct. Furthermore, the very simple theory proposed here is consistent with all data available to us.

We have presented the thermodynamic perspective on the temperature dependence of the band offsets in heterojunctions. We have argued that the magnitude of the variation is directly proportional to the difference in the band gap temperature variation. The HgTe–CdTe and AlAs–GaAs systems were specifically discussed, but extensions to other materials combinations and to the effect of pressure on the band offsets follow in similar fashion.

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