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Dipole effects and band offsets at semiconductor interfaces

N. E. Christensen
Max-Planck-Institut für Festkörperforschung, Postfach 80 06 65, D-7000 Stuttgart 80, Federal Republic of Germany

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The valence-band offsets in 15 lattice-matched semiconductor heterostructures are calculated from first principles by means of the self-consistent, relativistic linear-muffin-tin-orbital (LMTO) method applied in the supercell geometry. The outermost cation *d*-like states hybridize with the valence-band maximum, and they influence therefore the offset values. Their most important effect, however, is to modify the self-consistent potential as compared to calculations treating these states as atomiclike ("frozen") core states. They must therefore be included as fully relaxed band states. The effects of the size of the supercells are analyzed, and it is found that, although the charge redistributions occur over at least three layers, a $5+5$ cell is usually sufficiently large to give a reliable offset value. CdTe/HgTe represents in this respect an exception, and this system is one case (HgTe/InSb, CdTe/InSb, and InAs/GaSb being other examples) where an "anomalous" charge transfer is found. This anomaly is associated with confinement at the interface. Interface dipole effects are analyzed, and it is demonstrated that they in many cases tend to drive the systems towards a lineup of "charge-neutrality" levels.

I. INTRODUCTION

The electronic structures of semiconductor superlattices have attracted much interest during the last few years due to the great technological importance of such systems. Not only are the properties of structures consisting of ultrathin semiconductor layers of interest, but also the shifts in the bulk electronic structure deeply inside a material L as compared to that in a compound R induced when L and R are joined to form a heterostructure have been the subjects of many experimental as well as theoretical investigations. The difference in energy of the valence-band maxima (VBM) in two semiconductors, with a common interface each of which may be considered as a semi-infinite medium, may in principle seem to be simple to determine from a theoretical point of view, at least as long as the theory can apply idealized models of the interface structure, i.e., assuming that the atoms are not redistributed at the interface, that there are no defects, strain-induced dislocations, etc. Nevertheless, even for such simplified cases, a true first-principles calculation becomes involved since it must incorporate accurately the charge redistributions near the interface, the "interface dipole." The most appealing theoretical method may be one based on a self-consistent Green's-function technique, for example, along the lines suggested by Lambrecht and Andersen,[1] that describes the two sides of the junction as semi-infinite media. A simpler, and frequently used, method consists in performing self-consistent conventional band-structure calculations for an infinite crystal that is considered as made up of "supercells," i.e., cells with a large number of atoms including the interface region are periodically repeated *ad infinitum*. This latter method thus represents a calculation for a "thin-layer" superlattice, and the band offsets can only be deduced if the cells can be chosen so large that the electron distributions in the central parts of the L and R sides of the interface can be considered as "bulklike." This article presents such supercell calculations, and it will in particular address the question of the size of the supercell that is required for obtaining the band offsets. Also the interface dipole and the charge transfer across the interface will be discussed. The majority of the calculations were performed for (110) (nonpolar) interfaces.

Very extensive accounts of supercell calculations aiming at the determination of band offsets were published recently by van de Walle and Martin[2-4] who used the self-consistent, norm-conserving pseudopotential method in conjunction with the local-density approximation (LDA). Their results agree in general fairly well with experiments and other calculations, as do also those based on (partial) alignment of "charge-neutrality levels" as introduced by Tejedor *et al.*[5,6] and by Tersoff.[7,8] There are, however, cases where deviations are noticeable, and when we compared the estimates of band offsets derived from our linear-muffin-tin-orbital (LMTO)[9] calculations for the individual compounds combined with the "dielectric-midgap-energy" (DME) model,[10] we did have difficulties in specific cases. One example is ZnSe/Ge where the supercell calculation of Ref. 4 gives the valence-band offset, $\Delta E_v = 2.17$ eV, in contrast to our value (DME model), 1.46 to 1.57 eV. The experimental results are in the range 1.29 to 1.57 eV, i.e., apparently favoring our results. This might be fortuitous, and we have tried to locate the source of the difference between the two calculated values. The most obvious explanation would of course be to assume that the DME model is not quantitatively accurate enough, and therefore we performed supercell calculations by means of the LMTO method. Using the same cell size as in Ref. 4 (three layers of each compound), this gives $\Delta E_v = 1.39$ eV. One significant difference between the pseudopotential calculations and our scheme is that the LMTO includes the Zn 3d states as self-consistently relaxed band states. We have earlier shown[11] that even in the case of GaAs, where the 3*d* states lie much lower than in ZnSe, they nevertheless do affect the gap by pushing the Γ_8^v state (VBM, E_v) upwards in energy (though in that case only by 0.13 eV). In ZnSe/Ge this effect would then tend to *lower* the offset (when referring to an L/R interface, L is always the compound with the lower VBM). The influence of this hybridization, recently also noted by Wei and Zunger,[12] on the band offset will be discussed in detail below, and it will be shown that the effect is a bit more subtle than we first thought. As yet another explanation of the difficulties with the ZnSe/Ge results, one might note that this is a system where the difference in ionicity between the two compounds is particularly large, and it might therefore be expected that the charge redistributions in the region around the interface would be especially large, and perhaps occur over so many atomic layers that neither of the supercell calculations are converged on cell size. This is one reason for performing the supercell calculations for a series of cell sizes. Another reason is that this allows a systematic study of the evolution of the superlattice electronic structure as the number of atomic layers is gradually increased. Details of such examinations are not included here, apart from the description of the charge rearrangements in the various layers.

The presentation is organized as follows. In the Sec. II the method of calculation is described, Sec. III contains the values obtained for the offsets and includes a discussion of the importance of including the *d* states as relaxed bandlike states as well as the examination of the cell-size effects. Section IV is devoted to the charge distribution in the neighborhood of the interface and the question of anomalous electron transfer due to formation of interface states in some systems. In Section V the extent to which the self-consistent supercell will justify the basic assumption of the DME model,[10] namely, that of interface effects tending to produce a lineup of the "neutrality" (DME) levels of the two compounds, is examined. A brief summary and conclusion follow in Section VI.

II. METHOD OF CALCULATION

The LMTO method in the version that applies spherically symmetrized charge distributions and potentials in atomic spheres, i.e., space filling (and thus slightly overlapping) spheres, the atomic-sphere approximation (ASA),[9] is particularly well suited for the solution of the band-offset problem within the supercell approach. The self-consistent potentials are first calculated for the supercell geometry where the cells are chosen to have an odd number of atomic layers on each side of the interface. The ASA potential consists of individual atomic-sphere potentials, and therefore we can extract the central-layer potentials, which are bulklike if the cell is big enough, and place these on a zinc-blende lattice. In this structure a single bulk-band calculation ("frozen-potential calculation") is made for each of the compounds L and R, and from these band structures the valence-band maxima $E_v(L)$ are found, and the VBM offset is determined as $\Delta E_v \equiv E_v(R) - E_v(L)$.

The self-consistent supercell potentials are generated by including all relativistic effects except the spin-orbit coupling. The final band calculations in the zinc-blende structure, from where the offsets are obtained, are Dirac relativistic.

All calculations are performed within the local approximation to the density-functional theory. The LDA functional constructed by Ceperley and Alder[13] is applied in Perdew and Zunger's parametrized form.[14] The relativistic corrections suggested by MacDonald and Vosko[15] are included.

As usual (e.g., Ref. 11), LMTO calculations for the semiconductors must include so-called "empty spheres" located in the interstitial positions, i.e., atomic spheres without "nuclear" charge. First of all, this changes the diamond-type lattice into a close-packed structure with small overlaps between atomic spheres, and serves to minimize the errors in the LMTO method. Secondly, the empty spheres introduce for the compound semiconductors an important additional variational degree of freedom. Since the "atomic" potentials are made spherically symmetric, they cannot include intra-atomic polarization effects, but allowing for self-consistent charge adjustments in the structure, including the empty spheres is an efficient way to account for these. It has been shown (see, e.g., Ref. 11) that when the potentials are constructed according to the same principles, then the pseudopotential method (including the full nonsphericity of the potential) and the LMTO method leads to the same band structure for compound semiconductors. This assumes that the LMTO includes also the "combined correction term"[9] as is also done in the present work. In view of these observations it is expected that our method also should work well for supercell calculations although dipole-layer effects will occur at the interface.

Most of the calculations reported here are performed for (110) interfaces, i.e., nonpolar interfaces. Cells with up to seven layers on each side are considered: $1+1$, $3+3$, $5+5$, and $7+7$. Each layer contains four "atoms," two real atoms (e.g., Ga and As) and two empty spheres that in general are nonequivalent. Thus, the primitive cell contains in the $7+7$ case 56 atomic positions, and due to the small set of basis functions in the LMTO, it is still possible to treat such a relatively large system as a conventional self-consistent band-structure problem. The basis set includes usually *s*, *p*, and *d* partial waves on all sites. In most cases, two energy panels (see, e.g., Ref. 11) are needed in the construction of the self-consistent potential, and in those the basis set in the lower panel (for example, the energy range of the Ga 3*d* states) is reduced by omission of *d* partial waves on the sites of the anions and the empty spheres.

It is important to note that with the version of the LMTO method which is used here we need to include *d* partial waves in the basis set in order to ensure a sufficient degree of convergence of the angular momentum expansions. Thus, concerning computational efforts it is no complication to include the Ga and Zn 3*d* states, and the Cd and In 4*d* and Hg 5*d* states, as fully relaxed band states. In fact, to treat them as "frozen-core" states would give more practical difficulties because the introduction of empty spheres implies that the atomic-sphere radii are so small that a substantial amount of these *d* electrons would be outside the sphere to which they belong. In the frozen-core procedure a rather large renormalization would then be necessary, and the final result would depend somewhat on which procedure is chosen to perform this renormalization. Thus, in all cases, apart from one test calculation for ZnSe/Ge, the *d* states mentioned above are relaxed in the self-consistent (SCF) calculations. Those of In and Ga are included in the lower-energy panel, whereas those of Zn, Cd, and Hg are lying so high in energy that they are most naturally incorporated in the upper valence-band regime. In order to ensure that the *d*-hybridization effects are properly included in the offset values, the final frozen-potential band calculation on the zinc-blende lattice must be performed with some care. The *d* states must be explicitly included in the band calculation, and in fact not only the corelike *d* states discussed above are important. Also the hybridization to the higher lying conduction *d* states, i.e., the 4*d* states in Ga and Zn, should be taken into account. this effect tends to push the VBM down and acts therefore as a partial compensation of the effects due to the low-lying *d* states. For this reason we always perform two frozen-potential calculations, one with the corelike *d* states, and one with the higher *d* states included. The VBM is then taken as the average of the values obtained from these two calculations.

III. CALCULATED VALENCE-BAND OFFSETS

The values obtained for the VBM offsets by means of the method outlined in the preceding section are given in Table I. This table also contains experimental data, and in the last column we list the results of Van de Walle and Martin's pseudopotential supercell calculations.[4] The LMTO calculations (first four columns of Table I) show that in general the convergence on cell size is good, and in most cases a 5 + 5 cell is sufficiently large to produce a reliable offset value. Even the 1 + 1 cell gives for AlAs/GaAs essentially the same value as obtained with the larger cells. The frozen-potential method as used here tends to average out the charge imbalances in the central layer, and a stable offset value is obtained even with cells that are too small to ensure that the charge distribution in the central layer is strictly bulklike. This is illustrated in the case of AlAs/Ge in Fig. 1 showing the ASA charges on the Ge sites in the 3 + 3, 5 + 5, and 7 + 7 cells. The two Ge atoms should in the central layer have the same charge if this layer were truly bulklike. In

TABLE I. Valence-band offsets in heterostructures (in eV).

	1 + 1[a]	3 + 3	5 + 5	7 + 7	Experiment	3 + 3, VWM[b]
AlP/Si	0.95	0.82	0.93	0.91		1.03
AlP/GaP	0.74	0.62	0.61	0.59		0.36
AlAs/Ge	1.23	1.04	1.06	1.03	0.95[c]	1.05
AlAs/GaAs	0.55	0.58	0.55	0.53	0.55,[d] 0.42[e]	0.37
AlSb/GaSb	0.47	0.47	0.45	0.45	0.4[f]	0.38
GaP/Si	0.33	0.12	0.22	0.27	0.80[g]	0.61
GaAs/Ge	0.66	0.43	0.45	0.46	0.56[h]	0.63
InAs/GaSb	0.29	0.46	0.48	0.46	0.51,[i] 0.57[j]	0.38
ZnSe/Ge	1.85	1.39	1.53	1.58	1.52,[k] 1.29[k]	2.17
ZnSe/GaAs	1.25	0.98	1.07	1.07	1.10[k]	1.59
ZnSe/AlAs	0.89	0.44	0.60	0.60		
CdTe/HgTe	0.52	0.39	0.45	0.22[l]	0.35,[m] 0.12[n]	0.27
CdTe/InSb	1.16	0.92	1.07	0.93	0.87[o]	1.19
HgTe/InSb	0.60	0.32	0.41	0.54		0.91
ZnTe/GaSb	1.11	0.76	0.84	0.83		

[a] Cell size (number of layers on left and right sides). All these calculations are for the (110) interface.

[b] Pseudopotential supercell calculation, Refs. 4, 22, and 23. These data should, with the reservations made in the text, be compared to our calculations in the second column (3 + 3).

[c] M. K. Kelly, D. W. Niles, E. Colavita, G. Margaritondo, and M. Henzler (unpublished), quoted in Ref. 24.

[d] Reference 25.

[e] J. Menendz, A. Pinczuk, D. J. Werder, and J. P. Valladares (unpublished).

[f] Reference 26.

[g] Reference 27.

[h] Reference 28.

[i] Reference 29.

[j] Reference 30. See also Ref. 31.

[k] Reference 32.

[l] Using a 9 + 5 cell we get 0.27 eV for CdTe/HgTe.

[m] Reference 33.

[n] Reference 34. See also Ref. 35.

[o] Reference 36.

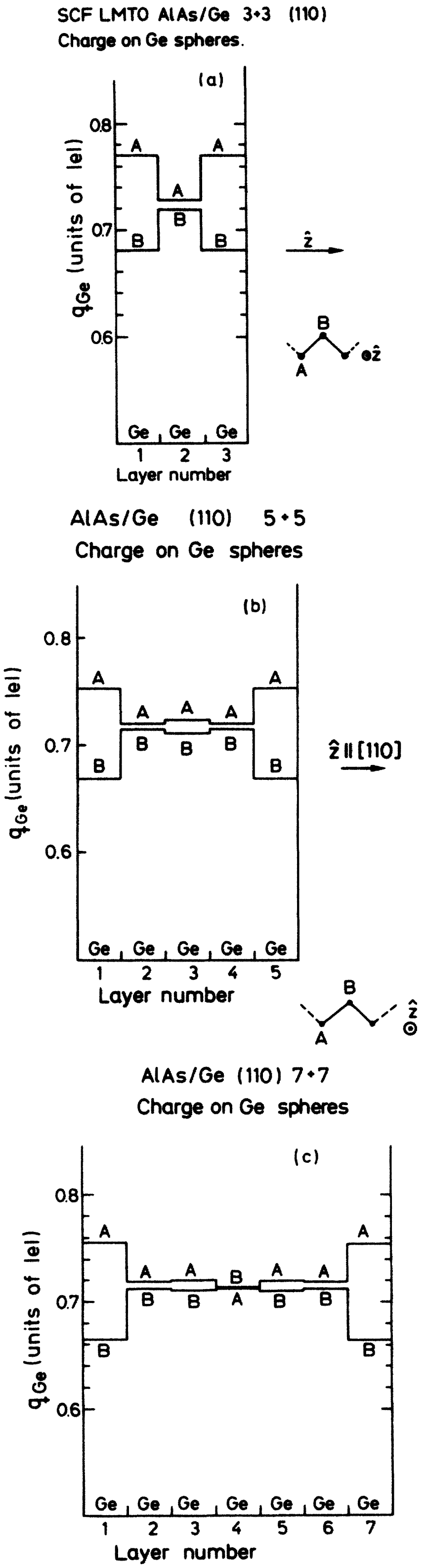

FIG. 1. Charge on the Ge spheres as obtained from self-consistent supercell calculations for AlAs/Ge (110) using (a) a 3 + 3 cell, (b) a 5 + 5 cell, and (c) a 7 + 7 cell. In the bulk the atoms *A* and *B* are equivalent. The *A* atoms are located on the cation sites in the supercell, whereas the Ge atoms labeled *B* here occupy the anion positions. (The Ge spheres are not neutral in the bulk due to the presence of empty spheres; see text.)

particular, in the 3 + 3 and 5 + 5 cells this is not the case. The frozen-potential calculation for the Ge side of the interface is therefore in that case not a usual Ge band structure for the diamond structure, but a $\mathrm{Ge}_A\mathrm{Ge}_B$ sphalerite band structure that takes both Ge potentials and the two (slightly) different empty-sphere potentials into account. This produces effectively an averaging, as mentioned above, and thus explains why the VBM offsets converge relatively rapidly on the cell size. A different procedure was used in the pseudopotential calculations by van de Walle and Martin. They calculated the average potential in the central layers (e.g., Ref. 4), and used then these values to determine the offset of the otherwise unmodified pure bulk potentials of each constituent. It may be expected that the cell-size convergence of the calculated valence-band offsets in that case is even more rapid than with our method. If the potentials in the central layers are not strictly bulklike, then they differ from the bulk potentials not only by an electrostatic offset, but also slightly in shape. Thus, a direct comparison of the sell-size effects on the band-offset values as obtained by the two methods cannot be rigorously made, i.e., the fact that we find that the 3 + 3 cell in most cases is too small to obtain a reliable value does not necessarily imply that this is also the case in van de Walle and Martin's work.

One case, CdTe/HgTe, has not, according to Table I, converged. Here the difference between the 5 + 5 and 7 + 7 results is so large that we do not believe that the offset derived even from the large cell is reliable. This suggests that in that case the charge redistributions are particularly long ranging, and that especially strong interface effects are present. If this is true, then it should also be expected that the offset for CdTe/HgTe should depend on the interface orientation, and this is indeed what Munoz *et al.*[16] find. Also we tried to calculate the offsets for other orientations. For the (100) interface we find, using 3 + 3 cells $\Delta E_v = 0.54$ eV for AlAs/GaAs and 0.43 eV for CdTe/HgTe. Thus (comparing to the second column of Table I) we find for AlAs/GaAs the same as for (110), in agreement with Ref. 16. However, neither for CdTe/HgTe does our calculation indicate any essential orientation effects. This apparent disagreement with the results in Ref. 16 is considered as being obscured by the fact that the 3 + 3 cell for CdTe/HgTe certainly is too small, and we would not take our results as evidence of absence of orientation effects in this system. Thus, from these calculations we do not conclude that interface effects are small in CdTe/HgTe. The discussion in Sec. IV shows that the dipole-induced shifts are indeed significant in CdTe/HgTe. In this context, though, it should be noted that the pseudopotential calculation of Ref. 4 disagrees with Ref. 16 concerning the face dependence of the offset. Further, recent tight-binding calculations[17] suggest that for CdTe/HgTe there should be essentially no face dependence, but for GaAs/AlAs the orientational dependence is large. These latter calculations do use some approximations that make a comparison to *a priori* calculations somewhat difficult, and it appears that this particular question needs some further investigations before the matter can be considered as settled.

TABLE II. Check of the transitivity rule. If this rule would hold perfectly, then the VBM offset [V (AlAs/GaAs), etc.] combinations as indicated should be zero. The values are in eV, and all calculations are for (110) interfaces.

	1 + 1	3 + 3	5 + 5	7 + 7
V(AlAs/GaAs) + V(GaAs/Ge) − V(AlAs/Ge)	−0.02	−0.03	−0.06	−0.04
V(ZnSe/GaAs) + V(GaAs/Ge) − V(ZnSe/Ge)	0.06	0.02	−0.01	−0.05
V(ZnSe/AlAs) + V(AlAs/Ge) − V(ZnSe/Ge)	0.27	0.09	0.13	0.05
V(AlP/GaP) + V(GaP/Si) − V(AlP/Si)	0.12	−0.08	−0.10	−0.05
V(CdTe/HgTe) + V(HgTe/InSb) − V(CdTe/InSb)	−0.04	−0.21	−0.21	−0.26

As mentioned in the Introduction, the influence of the hybridization to the d states on the VBM offsets has been examined. For a given CdTe/HgTe potential (7 + 7 cell) the VBM of CdTe is at −2.321 eV when the frozen-potential calculation includes the Cd 4d states and, using the same potential, we get the value −2.434 eV when the coupling instead is made to the (conduction) 5d states. Similar effects are found for the HgTe side; with Hg 5d states E_v is −2.066 eV, whereas the coupling to the 6d states pushes the VBM down to −2.240 eV. Thus, in this case hybridization to the lower d states would give the offset 0.255 eV, whereas coupling to the higher d states gives 0.194 eV. The average, 0.22 eV, which is the value we prefer, thus differs by less than 0.03 eV from the two extremes above. In ZnSe/Ge, where the d-hybridization effects are only essential on the "left-hand" side, we find that inclusion of the Zn 4d states instead of the 3d states increases the offset by 0.19 eV. Since we in all cases, where relevant, have taken the average between the two kinds of hybridization, we conclude that these effects give rise to very small corrections only, less than 0.1 eV, and we assume that the averaging procedure takes these properly into account. These results refer to one potential, and they therefore represent essentially the hybridization effects as given by perturbation theory. But perturbation theory is not sufficient here. An inclusion of the d states as band states that in the self-consistent calculation are treated as the other valence states is important, and the potential which is obtained by instead forcing them to remain as "frozen," atomiclike (renormalized) states is markedly different, and it is so although d partial waves are still included, and the valence states as usual fulfill the requirement of being orthogonal to all core states. Such a calculation, i.e., one where the Zn 3d states are treated as renormalized core states, was performed for ZnSe/Ge 3 + 3, and the offset derived from that potential is 2.11 eV, a value very close to the one obtained by van de Walle and Matin (2.17 eV, Table I). We take this result as evidence of the importance of including the low-lying d states as fully relaxed band states in the construction of the self-consistent supercell potential. The net effect of including the d states is to push the VBM up in energy, and this then explains why our offset values for AlP/GaP, AlAs/GaAs, and AlSb/GaSb, where this "upshift" occurs only on the R side (Ga), are larger than those obtained in Ref. 4 (last column in our Table I), whereas we for GaAs/Ge (where the lower VBM, GaAs, is pushed upwards) get a smaller offset (0.43 eV) than van de Walle and Martin[4] (0.63 eV). The Cd and Hg d states are higher in energy than the 3d states of Ga, but since the L as well as the R side in CdTe/HgTe are subject to the d-induced upshifts, the net effect is small in CdTe/HgTe. Our result, with the reservation concerning the size convergence, is therefore not very different from that obtained in Ref. 4 in that case. The effect of the relaxed d states is much larger in ZnSe than in GaAs since the Ga 3d states are more localized than the Zn 3d states. Therefore, our VBM offset for ZnSe/GaAs (0.98 for the 3 + 3 cell) is considerably smaller that the pseudopotential value,[4] 1.59 eV.

The fifth column of Table I contains experimental data for the valence-band offsets. Except for GaP/Si and excellent agreement between these data and our theoretical data obtained from the 7 + 7 cells is found. We cannot in our calculations find any reasons for the extraordinary large discrepancy between theory and experiment for GaP/Si. We have examined to what degree the "transitivity rule" holds (see Table II) and the group including GaP/Si does not show any anomalous behavior in that respect. The only case, among those where we have been able to make this test (Table II), where there appears to be a significant deviation from the transitivity rule is found in the group including CdTe/HgTe. This is, however, the case where even the 7 + 7 results are not fully size converged.

IV. INTERFACE DIPOLE

This section describes the charge distributions in the region near the interface as derived from the LMTO supercell calculations. Also, the charge transfer across the interface that follows the formation of the heterostructure is discussed, and so is the variation of the potential and band edges from one atomic layer to the next.

A very simple, approximate method for derivation of the heterostructure band offsets from LMTO bulk-band structures of the individual compound semiconductors was suggested recently[18] (our values are tabulated in Table II of Ref. 4). This model[18] uses the fact that the crystal potential is obtained as a lattice sum of ASA potentials, and that a reference level has been chosen such that the contribution to the potential from a given atomic sphere outside this sphere is proportional to the total charge in that sphere divided by the distance to the sphere center. If the band structures are given on this ASA energy scale, then an estimate of the offsets are simply obtained by subtracting the band-edge energies ob-

TABLE III. Electron transfer (per cell) $\Delta N_e^{L\to R}$, dipole correction ΔE_{dip}, and muffin-tin potential difference, $\Delta V_{\text{MTZ}} = \langle V(S)\rangle_R - \langle V(S)\rangle_L$ as derived from the LMTO supercell 7 + 7 calculations. In addition, the table includes the ionicity values f_i^{*L} and f_i^{*R} for "left" and "right" semiconductors as derived from first principles (Ref. 37).

	f_i^{*L}	f_i^{*R}	$\Delta N_e^{L\to R}$ (10^{-3} electrons)	ΔE_{dip} (eV)	ΔV_{MTZ} (eV)
AlP/Si	0.421	0	−24.9	−0.02	−0.167
AlP/GaP	0.421	0.361	57.9	0.35	0.266
AlAs/Ge	0.367	0	25.0	0.31	0.102
AlAs/GaAs	0.367	0.310	61.0	0.03	0.281
AlSb/GaSb	0.163	0.108	64.7	0.17	0.290
GaP/Si	0.361	0	−88.3	−0.41	−0.526
GaAs/Ge	0.310	0	−40.1	0.24	−0.252
InAs/GaSb	0.553	0.108	−67.4	0.04	−0.480
ZnSe/Ge	0.740	0	−113.1	−0.48	−0.594
ZnSe/GaAs	0.740	0.310	−77.0	−0.77	−0.410
ZnSe/AlAs	0.740	0.367	−130.9	−0.74	−0.626
CdTe/HgTe	0.739	0.683	10.2	−0.22	−0.129
CdTe/InSb	0.739	0.303	−60.4	−0.17	−0.065
HgTe/InSb	0.683	0.303	−88.5	−0.21	−0.310
ZnTe/GaSb	0.560	0.108	−48.8	0.04	−0.211

tained in the two bulk calculations (we note that this scheme is very close in spirit to the model-solid model of Ref. 4; instead of superposing atomic potentials including their overlapping "tails" as in Ref. 4, we use the self-consistent bulk ASA potentials). This scheme[18] does of course not include the effects of charge rearrangements caused by the interface formation, i.e., it neglects the shifts in the energy levels due to change in the interface dipole. In order to estimate the magnitude of these effects, we calculate the quantity ΔE_{dip}, defined as the difference between the VBM offset derived from the supercell (7 + 7 cell) calculation and the value given by the model of Ref. 18. Table III contains these dipole corrections, and it follows that for AlP/Si, AlAs/GaAs, InAs/GaSb, and ZnTe/GaSb these are vanishingly small. The corrections are large in the cases where the ionicity of the L compound is large, ZnSe/Ge, ZnSe/AlAs, and ZnSe/GaAs. The correction for CdTe/HgTe (-0.22 eV) is large as compared to the VBM offset value itself (0.22 eV, with the reservation that this is not fully size converged). Table III further contains the calculated electron transfers from the left-hand side to the right-hand side of the interface, $\Delta N_e^{L\to R}$. Apart from a few exceptions there appears to be a trend indicating that the systems where a large value of this transfer is found are simultaneously those where the correction ΔE_{dip} is large in magnitude.

Assuming that the electrons that are transferred across the interface are essentially coming from the outer parts of the atomic polyhedra, i.e., the electrons that occupy states with a large amplitude in the interstitial region of a muffin-tin (nonoverlapping spheres) model, it is expected that the charge transfer should be proportional to the difference between the muffin-tin potentials on the two sides. We calculate such a potential difference as the potential on the atomic-sphere surfaces averaged over all sites on the right-hand side minus the potentials averaged over the left-hand sites. This is the quantity $\Delta V_{\text{MTZ}} = \langle V(S)\rangle_R - \langle V(S)\rangle_L$ in Table III. In Fig. 2, $\Delta N_e^{L\to R}$ is plotted versus this potential difference, and, disregarding CdTe/HgTe, InAs/GaSb, HgTe/InSb, and CdTe/InSb, it is seen that the expected proportionality is indeed found.

The distribution of (excess) electrons over the layers are shown in Fig. 3. Four examples are chosen, two of which, GaAs/Ge and AlAs/GaAs, according to Fig. 2, behave in a normal fashion and two, CdTe/HgTe and

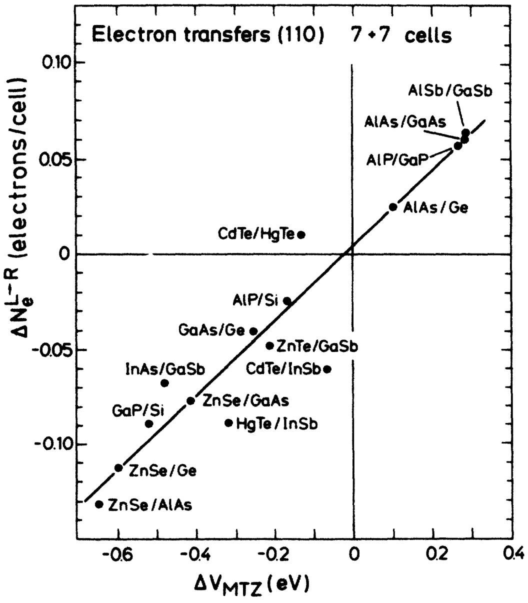

FIG. 2. Electron transfer $\Delta N_e^{L\to R}$ versus the difference ΔV_{MTZ} in what in the text is called the muffin-tin potential floors on the two sides.

CdTe/InSb, where the total electron transfer differs from the proportionality to ΔV_{MTZ}. If we define an interface layer as consisting of only the last layer on the left side and the first on the right-hand side, then this is for the normal cases [Figs. 3(a) and 3(b)] neutral whereas this is not the case for CdTe/HgTe and CdTe/InSb. In CdTe/HgTe an anomalously large amount of electrons are located on the HgTe layer closest to the geometrical interface, indicating a confinement, and we find (not shown in the figure) that these extra electrons tend to be localized on the Hg sites. This we associate with the formation of localized interface states, and this is in close agreement with the conclusions reached by Jaros *et al.*[19] They found that, since Hg acts as a deep-level impurity in CdTe, localized states may occur at the CdTe/HgTe interface. In this way we then understand why $\Delta N_e^{L\rightarrow R}$ for

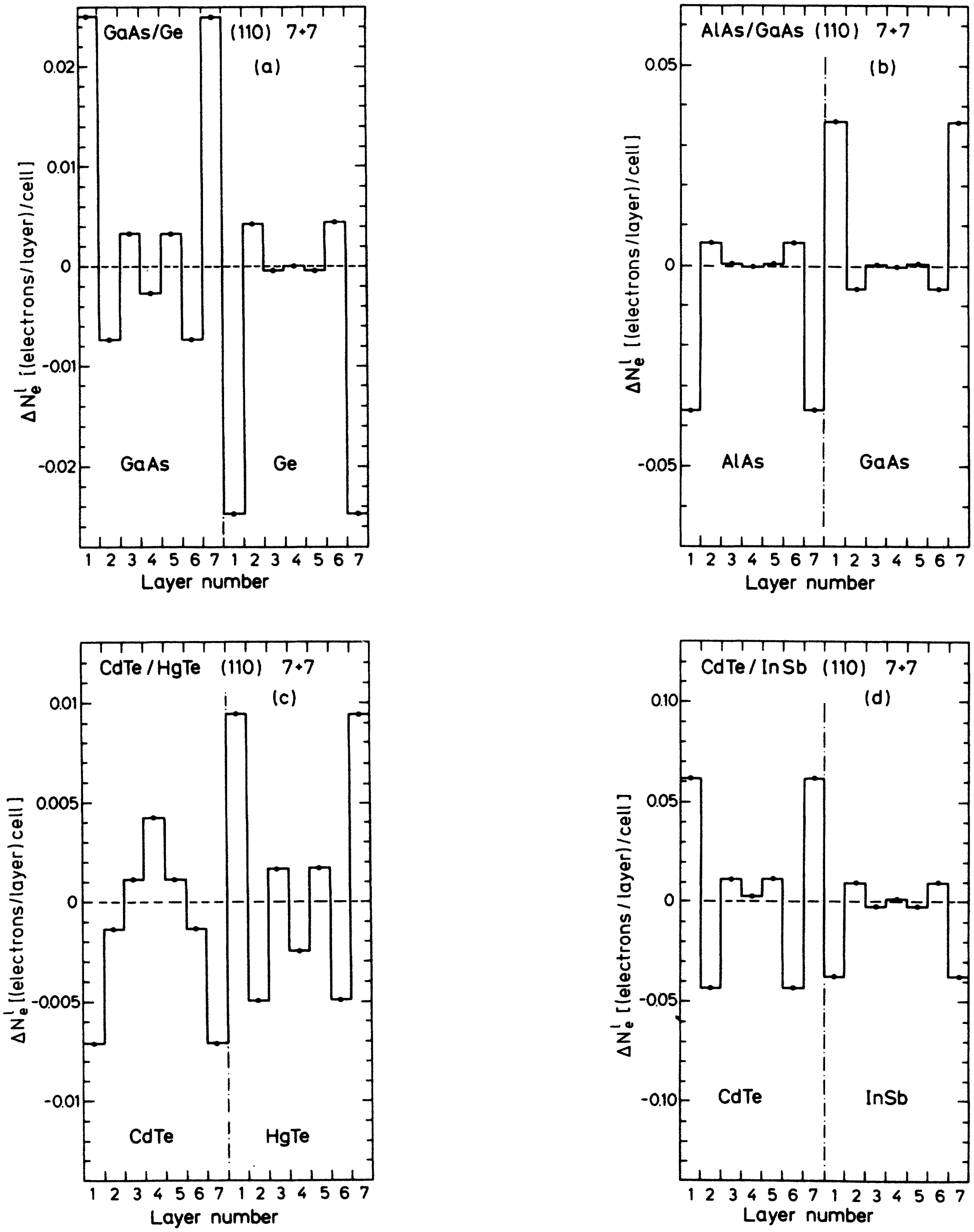

FIG. 3. Excess electron numbers on each atomic layer of the 7 + 7 cells for (a) GaAs/Ge, (b) AlAs/GaAs, (c) CdTe/HgTe, and (d) CdTe/InSb.

CdTe/HgTe is too large as compared to the simple proportionality rule of Fig. 2. The electron distribution in CdTe/InSb [Fig. 3(d)] shows that a similar behavior occurs near that interface, but it is here the CdTe layer that has accumulated too many electrons (in fact, in the Cd spheres). Thus from this it might be suggested that Cd would act as a deep-level impurity in InSb, and we have explained why the charge-transfer value for this system is too low (including its sign) in the sense that the CdTe/InSb point lies far below the straight line in Fig. 2. The other anomalies, InAs/GaSb, HgTe/InSb, are explained in exactly the same way.

Attempts to describe the interface dipole in terms of the spatial variation across the interface of a single kind of potential characteristics must fail. Different electronic states probe different parts of the the full crystal potential. The variation from one layer to the next of one type of potential (e.g., Ga) is not only due to a variation of a Madelung contribution. Also the shape of the potential changes. There is no reason to expect that the part of the Ga potential probed by the Ga 3*d* states, for example, should exhibit the *same* layer-to-layer variation as the part of the crystal potential which the As *p* states predominantly feel on the GaAs side of AlAs/GaAs, and, as illustrated by Fig. 4, it is indeed not so. This figure, Fig. 4, shows for AlAs/GaAs the valence-band edge (Γ_8 state) as calculated by the frozen-potential method applied layer by layer, the centers of the Ga 3*d* states, and the muffin-tin potential within each layer. First, it is seen that the VBM values on each side show virtually no bending. This is consistent with the observation (Sec. III) that for this system we obtain almost the same offset value irrespectively of the cell size. The muffin-tin potential only varies slightly (0.05 eV) in the immediate vicinity of the interface. It is interesting to note that the Ga 3*d* level in fact is the quantity among those which we have considered here that varies most strongly across the cell. This means specifically that the energy difference between these states and the VBM *varies* across the GaAs part of the supercell. The figure even suggests that the Ga 3*d* center in the central layer has not adjusted to its bulk value, i.e., the cell is *not* large enough to ensure size convergence of this parameter. For CdTe/HgTe we examine the spatial profiles, Fig. 5, of the Γ_8^v (VBM), Γ_7^v (split-off state), Γ_6^c (the lowest conduction state at Γ which in HgTe lies *below* Γ_8^v), and the band-center parameters C_{4d}^{Cd} and C_{5d}^{Hg} of the 4*d* and 5*d* states of Cd and Hg, respectively. In all cases strong band bending occurs on the CdTe side, and again it is seen (Fig. 5) that the 7 + 7 cell is not sufficiently large to ensure that the central layer is bulklike. The various states on the two sides of the CdTe/HgTe interface show the same trends with respect to their layer-to-layer variation, but the values of the shifts are clearly state dependent. The difference between the VBM in CdTe in the first and the central layer is 119 meV, whereas the 4*d* center varies by 267 meV. Thus, these two levels, for example, do not follow each other in the band bending regime; they are subject to different surface-induced shifts. The conduction state (Γ_6^c) follows, on the other hand, the Γ_8^v state rather closely on the CdTe as well as on the HgTe side. The gap variation in CdTe is ≈20 meV, and on the HgTe side only ≈10 meV.

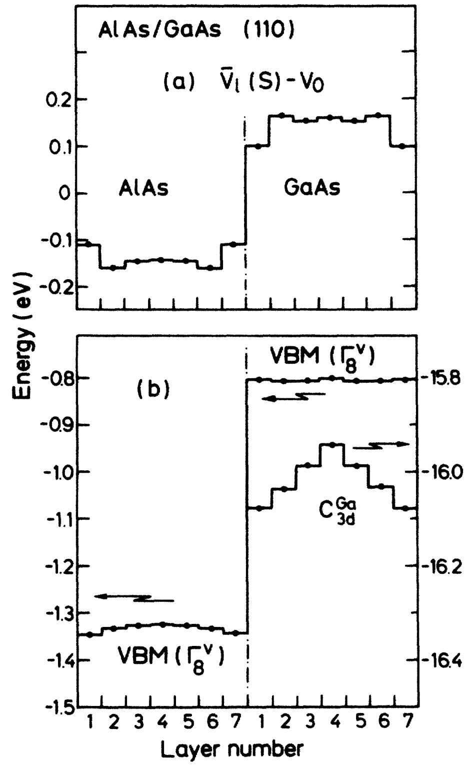

FIG. 4. AlAs/GaAs 7 + 7 (110) supercell calculation. The figure shows (a) the spatial variation of the potential at the atomic-sphere surface, averaged within each layer, $\bar{V}_l(S)-V_0$ (V_0 being the average over the entire cell); (b) the spatial variation of the VBM as calculated by the frozen-potential method, and, on the GaAs side, the variation of the centers (C_{3d}^{Ga}) of the Ga 3*d* bands.

Figure 5 also shows that the characteristic screening length is larger on the CdTe side than in HgTe. Thus, in order to improve the spatial convergence it will be most important to increase the size of the CdTe part of the supercell. A calculation was therefore performed with a 9 + 5 cell, in which case we find a slightly larger offset, 0.27 eV, but the band-edge profiles show (not included here) that neither in this case is size convergence achieved.

V. MODEL THEORIES: DO DME'S TEND TO LINE UP?

This chapter comments briefly on the models based on the assumption of a partial alignment of specific levels in the band structures of the two compounds forming the heterostructure, charge-neutrality levels, or as we[10] called them, dielectric midgap energies (DME, E_D). van de Walle and Martin note[4] in this context that ". . . assuming that a unique neutrality level exists, no convincing evidence has been given so far that the induced dipoles are actually strong enough to drive the system towards the 'neutral' lineup." It is straightforward by means of the present scheme to examine this question. We have

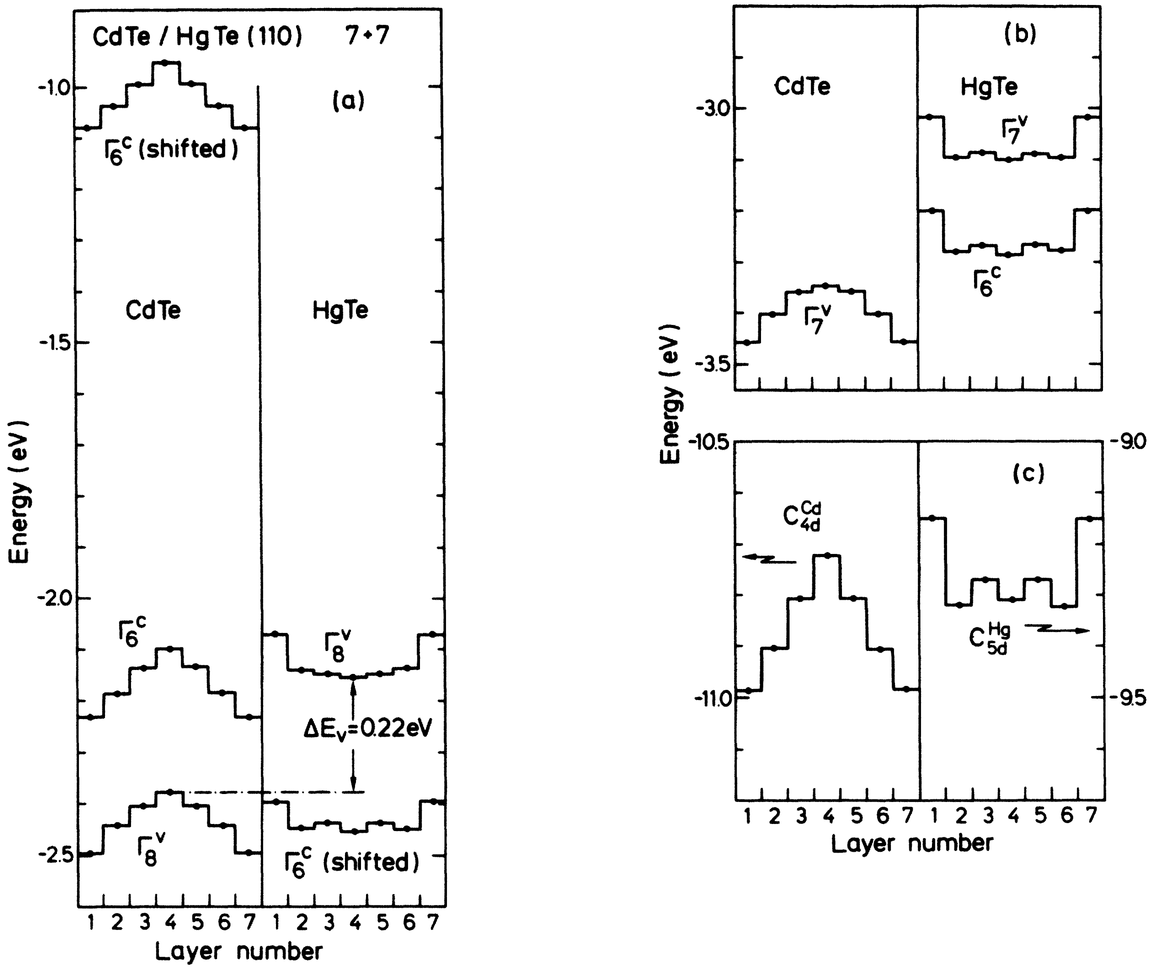

FIG. 5. CdTe/HgTe 7 + 7 (110) supercell calculation. The figure shows the variation from layer to layer of selected states. Since the local-density values of the band gaps are far too small, we also show the Γ_6^c states shifted upwards by the difference between the experimental and calculated gaps in the bulk. Parts (a) and (b) of the figure show the selected valence and conduction states as derived from the frozen-potential calculations, whereas part (c) includes the Cd and Hg d-band-center parameters, C_{4d}^{Cd} and C_{5d}^{Hg} (right-hand energy scale).

the bulk values of the DME levels, E_D, and by using the frozen-potential approach with the self-consistent supercell potentials we can easily derive those corresponding to the potentials in the central layers of the R and L parts of the supercell. We would then, in the spirit of the DME model,[10] expect that ΔE_D as obtained from the bulk calculations should be larger in magnitude than those from the supercell calculation (central layer), and if so, we should also be able to deduce the effective dielectric constant $\bar{\epsilon}$ in Ref. 10. The calculated DME offsets are listed in Table IV, where we also, for comparison, give the VBM offsets as derived from the DME model and the supercell calculations. At a first glance it might be claimed that these results render little support to the hypothesis of the assumed tendency towards lineup of the DME levels, and that they rather justify the scepticism raised in Ref. 4. Nevertheless, the following should be noted. The DME data for interfaces involving Si should not be taken too rigorously since our identification of the Penn gap with the gap at a single Baldereschi point is probably particularly bad for Si for the reasons mentioned in Ref. 10. Further, four other heterostructures, InAs/GaSb, CdTe/HgTe, CdTe/InSb, and HgTe/InSb, should also be excluded from this analysis because these are the cases where we have found an anomalous charge transfer which was associated with the formation of interface states, i.e., there are additional interface effects which the model theory cannot include properly. Considering now the remaining systems, there does indeed seem to be a clear tendency towards the situation where the DME levels would like to line up. In AlAs/GaAs the DME offsets in the bulk and the supercell are both small [a little larger, though, in the self-consistent supercell (SCSC) calculation]. This is consistent with the observation earlier that, as far the upper valence band is concerned, interface effects in this system are vanishingly small. For the three systems with very large interface dipole shifts and large electron transfers (see Table III), ZnSe/Ge, ZnSe/AlAs, and ZnSe/GaAs, it is seen (Table IV) that the large DME offsets are drastically reduced

TABLE IV. Valence-band offsets in heterostructures as derived by means of the dielectric-midgap-energy model (DME), and those obtained from the present supercell calculations (SCSC) (7 + 7 cell), the difference ΔE_D between the DME levels of the R and L compounds as obtained from the bulk band structures and the supercell calculations, respectively. All values are in eV. (Some of the numbers in the first column differ slightly from those given in Ref. 38, because these did not in all cases include the small corrections caused by the coupling to the upper d states; the effects of the core states, of course, were included.)

	ΔE_v (DME)	ΔE_v (SCSC)	ΔE_D (bulk)	ΔE_D (SCSC)
AlP/Si[a]	0.91	0.91	0.03	0.00
AlP/GaP	0.34	0.59	−0.22	0.17
AlAs/Ge	0.84	1.03	−0.18	0.15
AlAs/GaAs	0.39	0.53	0.07	0.12
AlSb/GaSb	0.30	0.45	−0.17	0.08
GaP/Si[a]	0.57	0.27	0.24	−0.16
GaAs/Ge	0.45	0.46	−0.25	−0.01
InAs/GaSb[b]	0.54	0.46	−0.09	−0.18
ZnSe/Ge	1.57	1.58	0.60	0.11
ZnSe/GaAs	1.13	1.07	0.84	0.07
ZnSe/AlAs	0.63	0.60	0.77	0.01
CdTe/HgTe[b]	0.61	0.22	−0.18	−0.39
CdTe/InSb[b]	0.73	0.93	0.37	0.31
HgTe/InSb[b]	0.01	0.45	0.55	0.09
ZnTe/GaSb	0.71	0.83	0.16	0.02

[a] Our DME level for Si is probably not sufficiently well defined.

[b] In these systems anomalous charge transfer is found, and the DME model is expected to be inadequate (see text).

when the heterostructure is formed. For these systems, the basis of the DME model (and charge-neutrality-level theories in general) is especially well founded. It simultaneously follows (Table IV) that the ΔE_v values as derived from the DME model for these interfaces agree extremely well with the supercell results. The simple way used in Ref. 10 for the inclusion of screening in terms of an effective dielectric constant $\bar{\epsilon}$ does not apply satisfactorily in view of the results quoted in Table IV. We can only in few cases deduce values of $\bar{\epsilon}$ that would seem to be reasonable. For ZnSe/Ge, ZnSe/GaAs, ZnSe/AlAs, and ZnTe/GaSb we would get $\bar{\epsilon}=5.5$, 12.0, 77.0, and 8.0, respectively, but the values for AlP/GaP, AlAs/Ge, and AlSb/GaSb would be negative. It remains to be examined whether an improvement of the definition of the DME levels, for example, by using several special points, would lead to more meaningful values of the effective dielectric constant.

VI. SUMMARY AND CONCLUSION

Self-consistent electronic structure calculations for semiconductor compounds in supercell geometries have been used in calculation of heterojunction band offsets, charge redistributions, interface dipole effects and band-edge profiles. The LMTO method in the formulation using ASA type potentials is convenient for extraction of band-structure features and their variation from one atomic layer to the next in the cell, by means of what here is referred to as a frozen-potential method. For all systems, except GaP/Si, where we have experimental values available for the valence-band offsets, an excellent agreement is found with our theoretical results. In the case of CdTe/HgTe it is found that a supercell consisting of seven layers of each compound apparently is not sufficiently large to ensure size convergence of the offset value. The regions of charge redistributions are of large range—in particular, on the CdTe side of the interface.

The inclusion of the outer corelike d states as fully relaxed parts of the valence bands is important in an accurate calculation of the band discontinuities. Inclusion of these effects as a perturbation only is not sufficient. It is essential that these d states are included as band states in the cycle of iterations towards self-consistency, i.e., that their influence on the shape of the crystal potential is fully incorporated. In ZnSe/Ge and ZnSe/GaAs, for example, the inclusion of the Zn (and Ga) $3d$ states reduces the band offsets by ≈ 0.6 eV, whereas perturbation theory, using a given potential, alone would diminish the offset by only ≈ 0.1 eV.

Appreciable interface dipole corrections appear in the junctions where one of the compounds has a large ionicity value. In these systems we also simultaneously find the largest charge transfers across the interface. Anomalous electron transfers are found in CdTe/HgTe, CdTe/InSb, InAs/GaSb, and HgTe/InSb. We believe that these anomalies are associated with the formation of (localized) interface states. We are presently examining this in more detail by studying the full supercell band structures, and by projecting out from those the local density-of-states functions for each layer.[20]

The band-edge profiles, i.e., the variation of specific states from layer to layer in the interface region, depend on which states are considered. In other words, the interface affects, for example, the valence-band edge in a way that differs from the shifts found for core levels. In recent publications Shih and Spicer[21] and Wei and Zunger[12] suggest that intrinsic or natural valence-band offsets, at least in common-anion systems, can be obtained from semiconductor alloys. This leads to an elegant experimental as well as computational method for determination of ΔE_v. The scheme is based on the assumption that corelike levels, e.g., Ga $3d$ in $(\mathrm{GaAs})_{1-x}$ $(\mathrm{AlAs})_x$, stay at a fixed energy on an absolute energy scale when the composition x is varied. If interface-specific shifts were unimportant, the natural VBM should then agree with those observed in the heterostructures. In view of these schemes, and since we find that in GaAs/AlAs there are at most very small interface effects, we would then have thought that the Ga $3d$ levels would all line up at the same energy on the GaAs side in the supercell. This is not the case.

The present calculations further show that the various states shift differently through the supercell; the VBM and d-level profiles in, for example, CdTe/HgTe are different.

The comparison of the offsets of the DME levels in the bulk semiconductors and in the heterostructures demonstrate that the extra dipoles at the interface in several cases are strong enough to produce a tendency toward a neutral lineup. This strengthens somewhat the arguments for the fundamental ideas behind the model theories based on the concept of charge-neutrality points, but on the other hand only experiment or a full calculation can show whether a particular system is normal or anomalous. The model theories do not include the effects caused by localized interface states, and they cannot, of course, describe details such as the state dependence of the interface-induced shifts.

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