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Possibility of heterostructure band offsets as bulk properties: Transitivity rule and orientation effects

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New first-principles calculations of valence-band offsets at ZnTe/InAs, CuBr/Ge, CuBr/AlAs, and ZnSe/CuBr interfaces are reported. These are used, together with earlier theoretical values for other systems, to investigate the range of validity of the transitivity rule. For a wide class of systems this rule is found to hold with good precision, but a few compounds (e.g., CuBr) cause pronounced nontransitivity. For three common-anion systems, GaAs/AlAs, AlP/GaP, and AlSb/GaSb, we examine the dependence of the offset on growth direction. The differences between the (110) and (001) discontinuities for these systems are small, less than 0.07 eV.

I. INTRODUCTION

The so-called "transitivity rule" for heterostructure band offsets states that the offset value for a system A/C may be inferred from the sum (including the proper signs) of the offsets for two heterostructures, A/B and B/C, i.e., considering the valence-band discontinuity ΔE_v:

$$\Delta E_v(A/C) = \Delta E_v(A/B) + \Delta E_v(B/C) . \qquad (1)$$

This relation, has been empirically found to be valid in many cases, and also recent first-principles calculations[1,2] are consistent with this observation. Several *model theories* of band-structure alignment in heterostructures[3–7] have the transitivity rule as a built-in feature. Thus, in order to assert the range of validity of the basic assumptions made in these theories, it is of interest to systematically study the transitivity.[8] A violation of the transitivity rule indicates that interface-specific features play an important role in determining the band offsets. Particular interface states, for example, may form, and when occupied they will cause an "anomalous" charge transfer across the interface. This influences the dipole and, hence, the band offset. Such effects are difficult to examine experimentally. At a real interface the atomic arrangement may be influenced by the growth conditions. Consequently, actual measurements may indicate nontransitivity simply as a result of imperfections introduced in the heterostructures during the sample preparation. Two experimental works by Waldrop and co-workers[9,10] specifically addressed the question of transitivity, and it was found that three series of systems are not transitive. One of these includes CuBr as a constituent. Theoretical, first-principles calculations usually treat perfect, idealized interfaces, and the complications due to unknown atomic positions (interdiffusion) are not included. Thus, in this way it is possible to examine whether nontransitivity occurs as intrinsic effects. It is the purpose of the present work to present the results of such calculations. These are performed by means of self-consistent band-structure calculations treating the interface in a superlattice geometry. We use the linear-muffin-tin-orbital (LMTO) method[11] in conjunction with the local-density approximation (LDA). The LDA functional constructed by Ceperley and Alder[12] is applied in the parametrized form of Perdew and Zunger.[13] The relativistic corrections suggested by MacDonald and Vosko[14] are included.[15] More details of the method are given in Ref. 2. Here we just mention that the outer-core-like cation d states, where necessary, are treated as fully relaxed band states.

II. RESULTS AND DISCUSSION

The majority of the calculations reported here are performed for the (110) (nonpolar) interfaces. The self-consistent potentials are generated for 7+7 supercells, i.e., cells that contain seven layers of each compound. This cell size is sufficient to ensure that the atomic-sphere-approximation (ASA) potentials[11] in the central layers of each side are very close to the bulk values.[2] The valence-band offset is then derived by means of a frozen-potential method.[2]

The calculated valence-band offsets are listed in Table I together with the quantity

$$T(A,B,C) = \Delta E_v(A/B) + \Delta E_v(B/C) - \Delta E_v(A/C) , \qquad (2)$$

which is a measure of the transitivity, $T = 0$ implying that the transitivity rule is fulfilled. Some of the offset values were included in the previous work (Ref. 2), but first-principles calculations of ΔE_v for ZnTe/InAs, and the heterostructures with CuBr as one of the constituents, have not been presented earlier.

In view of the large ionicity of CuBr we found it surprising that the experimental valence-band offset value was reported by Bauer and Margaritondo[16] to be as low as 0.9 eV, and, therefore, we found it interesting to perform the theoretical calculations for that and the related systems listed in Table I. First, the dielectric-midgap model was applied in the same way as in Ref. 7. This gives $\Delta E_v(\mathrm{GuBr/Ge}) = 1.9$ eV, considerably larger than the experimental value[17] quoted above. However, in that case,[7] the midgap energy (DME) was taken to be the average of the highest valence state and lowest conduction state energies at the first Baldereschi point. It is assumed, in this

TABLE I. Check of the transitivity rule. If this rule would hold perfectly, then $T(A,B,C)$ would be zero. The first three columns of numbers give valence-band offsets for the A/B, B/C, and A/C (110) heterostructures. (All values are in eV.)

A/B	B/C	A/C	$\Delta E_v(A/B)$	$\Delta E_v(B/C)$	$\Delta E_v(A/C)$	$T(A,B,C)$
AlAs/GaAs	GaAs/Ge	AlAs/Ge	0.53	0.46	1.03	−0.04
ZnSe/GaAs	GaAs/Ge	ZnSe/Ge	1.07	0.46	1.58	−0.05
ZnSe/AlAs	AlAs/Ge	ZnSe/Ge	0.60	1.03	1.58	0.05
AlP/GaP	GaP/Si	AlP/Si	0.59	0.27	0.91	−0.05
ZnTe/InAs	InAs/GaSb	ZnTe/GaSb	0.31	0.46	0.83	−0.06
CdTe/HgTe	HgTe/InSb	CdTe/InSb	0.27	0.45	0.93	−0.21
CuBr/GaAs	GaAs/AlAs	CuBr/AlAs	0.82	−0.53	0.50	−0.21
CuBr/ZnSe	ZnSe/GaAs	CuBr/GaAs	−0.32	1.07	0.82	−0.08
CuBr/ZnSe	ZnSe/AlAs	CuBr/AlAs	−0.32	0.60	0.50	−0.22
CuBr/ZnSe	ZnSe/Ge	CuBr/Ge	−0.32	1.58	1.10	0.16
CuBr/Ge	Ge/AlAs	CuBr/AlAs	1.10	−1.03	0.50	−0.42
CuBr/Ge	Ge/GaAs	CuBr/GaAs	1.10	−0.46	0.82	−0.18

model theory, that the gap at this point essentially corresponds to the E_2 interband transitions producing the main peak in $\varepsilon_2(\omega)$ of the zinc-blende-type semiconductors. For CuBr this represents a bad approximation. This compound is not as clearly an sp^3 bonded system as the III-V and II-VI compounds, but its valence bands are strongly modified by the high lying Cu-*d* bands, and Cu-*d*-halide-*p* bonding plays an important role in CuBr (the valence-band structure is shown in Fig. 25 of Ref. 18). Therefore, the DME should in fact be defined in a way that takes the upper, hybridized Cu-*d*-Br-*p* bands into account. By doing this it has been found[19] that ΔE_v(CuBr/Ge) is lowered[20] to 1.1 eV. This is also what is obtained from the first-principles supercell calculation (Table I). Consequently, the theoretical calculations do in fact agree with the experimental estimate[16,17] of the very low offset value in that case, and the Cu-*d* states are to a large extent responsible for this low ΔE_v. The fact that the DME model for CuBr/Ge gives exactly the same offset value as the supercell calculation may, in view of Ref. 20, be considered somewhat fortuitous. We have calculated the layer-projected density-of-states functions, and these show that in the regime of the upper valence bands clear interface states form. These are rapidly attenuated on the CuBr side, and somewhat slower decaying on the Ge side of the interface. Such interface specific features are not included in the model theory, and a deviation from the supercell calculation is, therefore, to be expected. Previously (Ref. 2) it was suggested that "anomalous" electron transfer occurred in CdTe/HgTe due to the formation of interface states. Also for that system layer-projected densities of states show the occurrence of occupied interface states. The state producing the most prominent interface state peak has been identified in the superlattice band structure, and Fig. 1 shows its layer projected occupancies. The amplitude peaks at the interface, and decays on both sides. The decay is (in particular on the HgTe side) slow, and the figure illustrates that even the 7+7 cell is not large enough to ensure that the interface states are damped out at the central layers. The dominating orbital nature of this state is Cd-*s*-Hg-*s*. This is interesting as one would in fact anticipate, in a simple effective-mass model, the existence of such an interface state in CdTe/HgTe. A matching of the probability current at the interface requires continuity of $m_{\text{eff}}^{-1}\delta\phi/\delta z$, where m_{eff} is the effective mass, ϕ is the wave function, and $\hat{\mathbf{z}}$ is perpendicular to the interface. The effective mass of the Γ_6 conduction state in CdTe is positive, but Γ_6 lies in HgTe below the valence-band maximum, and its effective mass is negative. Therefore, imposing the above-mentioned matching condition leads to a state that on both sides decays away from the interface.

A unique definition of charge transfer across the interface cannot be given since there is no unique way of specifying a mathematical surface that represents "the interface." Nevertheless, for the (110) interfaces as we study

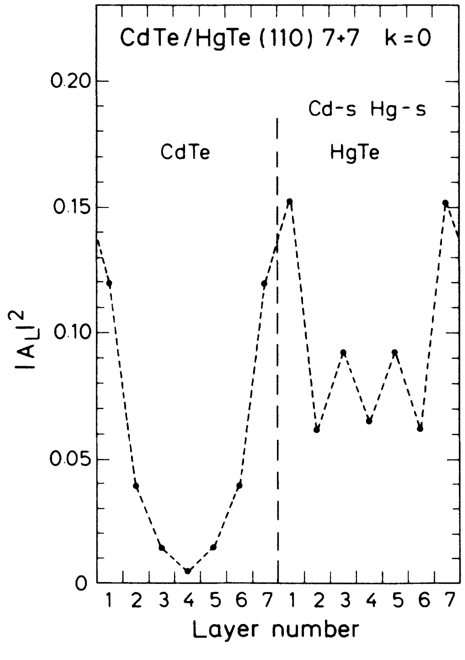

FIG. 1. Layer-projected occupancies of the state (here shown at $k=0$) identified as the occupied Cd-*s*-Hg-*s* interface state in CdTe/Hg/Te.

here, there is a *natural* way of assigning atomic spheres to either the "*A*" or the "*B*" side in the A/B structure. For this orientation this also applies to the "empty" spheres. Thus, in the ASA, where we always choose all spheres to have equal radii, we can study trends in charge transfers. By relating the electron transfers for (110) interfaces to the difference in average potential of the two sides, we previously distinguished between "normal" and "anomalous" electron transfers, depending on whether this potential difference would be proportional or not to the transfer (see Fig. 2 of Ref. 2). For CuBr/GaAs we find, with this interface definition, that 0.145 electrons are transferred from GaAs to CuBr. The relevant potential difference is calculated to be −0.73 eV. In the analysis of Ref. 2 the transfer of 0.145 electrons, if normal, should correspond to a potential difference of −0.1 eV only. Thus, the electron transfer in CuBr/GaAs is strongly anomalous.

Disregarding the series in Table I that includes CdTe/HgTe it follows that all systems, among those examined here, that do not include CuBr are transitive. This conclusion is drawn from Table I if we, somewhat arbitrarily, consider the transitivity rule to be fulfilled if the magnitude of T is smaller than 0.07 eV. In view of inherent numerical inaccuracies this is a reasonable limit. Experimentally, it was found[10] that T(AlAs/GaAs, GaAs/Ge,AlAs/Ge) and T(ZnSe/GaAs,GaAs/Ge,ZnSe/Ge) are −0.18 and 0.20 eV, respectively, and consequently these two systems were classified as nontransitive. Our theoretical values are −0.04 to 0.05 eV, and we therefore consider the transitivity rule in those cases to be fulfilled. Our value of T(CuBr/Ge,Ge/GaAs,CuBr/GaAs) is −0.18 eV, and it has the same sign as the experimental value, −0.70 eV, which however is considerably larger in magnitude. In spite of this we would in agreement with Ref. 10 consider this system as nontransitive. The largest deviation from transitivity in the present study is found for the series CuBr/Ge, Ge/AlAs, CuBr/AlAs, for which T is −0.42 eV.

Interface specific electronic properties affect[2] the charge transfer in CdTe/HgTe, HgTe/InSb, and CdTe/InSb, quantitatively, though, less than in the heterostructures involving CuBr. The offset value for CdTe/HgTe (0.27 eV) is not fully size converged, but nevertheless in good agreement with experiments ranging from 0.12 to 0.35 eV. Therefore, if we tentatively assume that a more satisfactory size convergence would not modify the theoretical value markedly, then we would also characterize the series CdTe/HgTe, HgTe/InSb, CdTe/InSb as nontransitive.

For heterostructures where the band offset is determined entirely by bulk electronic properties, transitivity is a natural consequence. Another characteristic feature of such systems is the independence of the offset on orientation of the interface, i.e., growth direction. The calculations of Ref. 1 demonstrated this for several cases, and the recent work by Bylander and Kleinmann[21] shows that the valence-band discontinuity in GaAs/AlAs is orientation independent. As a further examination of this, we have performed supercell calculations (7+7 cells) comparing the (110) and (001) offsets for a few systems. For AlAs/GaAs, AlP/GaP, and AlSb/GaSb we find the following [the (001)-results being given in parentheses]: 0.53 (0.47), 0.59 (0.52), and 0.45 (0.39) eV, respectively. There seems to be a tendency of the (001) offsets to be slightly lower, but the differences are in all three cases too small, less than 0.07 eV, to be considered significant.[22] It should be noted that the three cases treated here are all behaving as normal heterostructures with respect to charge transfer when studied[2] in the (110) orientation. Thus, no particular interface effects would be expected, and the orientation independence is what would have been anticipated from the discussion of the transitivity. CdTe/HgTe is a common-anion heterostructure where the calculations for the (110) interface showed clear nonbulk features. We have tried to perform, also for this system, calculations in the (001) geometry, but again cell-size convergence problems are encountered. Therefore, we cannot assert from our calculation whether there would be a significant orientation effect for CdTe/HgTe. Other theoretical treatments[1,23,24] tend to disagree with respect to the growth-direction dependence.

In conclusion, the question whether the band offset is a bulk property, i.e., determined entirely by the bulk electronic properties of the individual constituents, cannot be answered in general. There is a wide class of systems for which this is indeed the case, but the present work also shows that there are certain semiconductor compounds (e.g., CuBr) that produce interface specific electronic states that influence the offsets, and this makes an analysis entirely in terms of bulk properties less meaningful. Conclusions drawn from studies of a single or a few heterostructures may be misleading in that respect. For example, the most widely studied heterostructure GaAs/AlAs is probably simultaneously the most "well behaved." The very close similarity between the GaAs and AlAs bonds in length, strength, and polarity, also suggests that the interface electronic structure in that case does not exhibit strong deviations from the bulk. GaAs/AlAs does not therefore, contain the same interface electronic properties as, for example, CuBr/AlAs.

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[15] Since we are calculating valence-band offsets in semiconductor heterostructures we compare the energies of states that have very similar orbital character, namely the anion-*p* states in the two compounds. Therefore, LDA errors are assumed to essentially cancel as also follows from the good agreement between theory and experiment (Ref. 2). This also implies that the actual choice of LDA functional is expected not be be important for the calculation of ΔE_v. CuBr might be expected to represent an exception to this since the upper valence state has a particularly large cation-*d* component. Therefore, we have performed, in this case, a complete calculation with Barth-Hedin exchange correlation. This gives $\Delta E_v = 1.096$ eV, i.e., within the numerical accuracy exactly the same as with the Ceperley-Alder form, 1.098 eV.

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[17] The origin of the experimental offset values listed in the table of Ref. 16, as well as the conditions under which they were obtained are not clear. Therefore, as also stressed in Ref. 16, the numbers listed there should only be taken as a first-order estimate.

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