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LETTER TO THE EDITOR

On the valence band offset controversy in HgTe/CdTe superlattices

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Abstract. Despite a number of experimental and theoretical investigations, the long standing controversy over the value of the valence band offset (Λ) in HgTe/CdTe superlattices remains unresolved. In this paper we present a thorough theoretical study of Λ at the (001) and (110) interfaces. The calculations were performed using a first-principles self-consistent pseudopotential technique, including non-linear core exchange-correlation corrections, and using the local-density approximation for the exchange-correlation potential. Contrary to some previous work, rapid convergence was found with respect to the number of layers of each material included in the unit cell. A value for Λ of 0.30 eV was obtained, independent of the interface orientation, which gives strong support for the larger experimental values of 0.35 eV.

There has been a long standing controversy concerning the valence band offset (Λ) in HgTe/CdTe superlattices. Room-temperature photoemission experiments [1] give 0.35 eV, while low-temperature magneto-optical experiments [2] give a value of only 0.04 eV. Johnson *et al* [3] have apparently resolved this controversy in favour of the larger value of Λ. Using an envelope-function method (EFM), they showed that while the superlattice becomes semimetallic with increasing Λ, it reverts to semiconducting behaviour as Λ is increased still further. Johnson *et al* [3] were able to show that the effective mass and band gap obtained in [2] can be explained by an offset of 0.35 eV. Subsequently Hoffman *et al* [4] have confirmed the existence of the second semiconducting region, using magneto-transport measurements. However, more recently Choi *et al* [5] have carried out far-infrared magneto-optical experiments on superlattices with different thicknesses from those used by Berroir *et al* [2]. They argued that the Johnson *et al* [3] interpretation of the data of [2] is correct for the particular sample used in [2], but in general *only* the smaller value of Λ can provide a successful fit to the magneto-optica data. The problem with the experimental results for Λ is that they are indirect and seem to depend strongly [6] on the approximations involved in the EFM, which is normally used to fit the observed data. Extra complications arise in the present case because of the expected appearance of two semiconducting regions with an intermediate semimetallic one [3].

Theoretical investigations of Λ in HgTe/CdTe superlattices have been carried out by several groups [7–13], using a variety of theoretical techniques. These results generally support the larger value of Λ, giving results in the range from 0.20 to 0.50 eV. Most interestingly, Christensen [13] has found very slow convergence of Λ with respect to the

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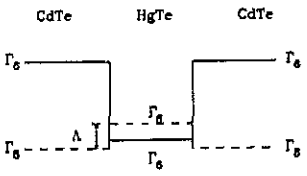

Figure 1. Schematic diagram of the relative energy positions of the bulk HgTe and CdTe band edges in a HgTe/CdTe superlattice.

number of layers of each material in the $(HgTe)_n/(CdTe)_n$ superlattice, n, convergence was not achieved even when $n = 7$—the thickest superlattice considered. Although Λ exhibits oscillatory behaviour with increasing n, its value decreases quite rapidly. This slow convergence has been thought to arise from strong interface effects, which, in turn, would be expected to yield an orientation dependent Λ. However, such orientation dependence has not been found [9, 11, 13] except by Munoz *et al* [10] who used a self-consistent tight-binding method. It should be noted that other recent tight-binding calculations [11] have shown no orientation dependence of Λ in these superlattices. The slow convergence, if correct, not only renders unreliable the values of Λ obtained from self-consistent calculations (using very thin superlattices, 1×1 [8] and 3×3 [9]), and model [7] calculations (which do not take into account the interface effects), but also provides support for the smaller value of Λ (by extrapolating Λ, in [13], to thicker superlattices).

HgTe is a semimetal with a band gap of -0.30 eV, while CdTe is a semiconductor with a band gap of 1.60 eV. A schematic diagram of the relative positions of the bulk Γ_6 and Γ_8 band edges of HgTe and CdTe in a HgTe/CdTe superlattice is shown in figure 1. In thin superlattices the confinement energy of the first electronic state (C1) at the Γ-point in the HgTe well exceeds the HgTe negative band gap, leading to a semiconducting superlattice. With increasing well width, the energy of the C1 state decreases very rapidly relative to the decrease in the confinement energies of the first heavy hole (HH1) and first light hole states. At a certain well width, which depends on the value of Λ, the energies of the C1 and HH1 states cross over and the system exhibits a semiconductor to semimetal transition. Johnson *et al* [3] have shown that by increasing the well width still further, the system may undergo a second transition resulting in a return to semiconducting behaviour. The second transition occurs when the C1 energy band moves below the HH1 state at all points along $K_\perp$, giving a negative band-gap semiconductor with the HH1 band acting as a conduction band. Consequently the behaviour of a HgTe/CdTe superlattice depends crucially on the value of Λ.

In the present work an attempt has been made to obtain an accurate value for Λ in HgTe/CdTe superlattices and study its orientation dependence. For our calculations we have used a first-principles self-consistent pseudopotential technique and the local-density approximation [14] (LDA) for the exchange-correlation (EC) potential. Several (001) and (110) HgTe/CdTe superlattices have been considered. Each superlattice was treated as lattice matched with a lattice parameter of 6.48 Å.

In our calculations the Cd 4d and Hg 5d states are treated as frozen core states, but the non-linearity of the EC interaction with the valence electrons is included correctly [15] (these are referred to as EC corrections). This scheme yields valence band offsets in excellent agreement with all-electron calculations and with experiment for II–IV/IV and II–IV/III–V interfaces [16]. Our previous work [16] has clearly demonstrated that the effects of relaxation of the semi-core d states on the valence band offsets is small. In fact we expect this scheme to work even better for the II–IV/II–IV interfaces considered

here, because of error cancellation between the effects of core relaxation on the two sides of the interface. The pseudopotentials for Hg, Cd, and Te were generated from the scheme of Kerker [17] with the ground state solid configurations (for more details see [16]). Scalar relativistic effects were included, however spin-orbit splitting was not included in the self-consistent calculations but was added *a posteriori*. For the EC potential we used the Ceperley–Alder [18] form of the LDA as parametrized by Perdew and Zunger [19]. In the super-cell calculations, the wavefunctions were expanded in a plane wave basis set including all waves up to 6 Ryd in energy. The effects of basis set truncation were checked; it was found that on increasing the basis set cut-off to 10 Ryd, the value of Λ increased by only 0.02 eV. Extrapolation to an infinite basis set gives a correction of approximately 0.03 eV which was added to the results obtained with the 6 Ryd cut-off. A 24 Ryd cut-off was used for the band structure calculations in the zinc blende geometry for HgTe and CdTe. The Brillouin zone integrations were performed by sampling on regular $4 \times 4 \times 2$ and $4 \times 2 \times 4$ and $4 \times 4 \times 4$ Monkhorst–Pack [20] meshes for the (001), (110) superlattices and zinc blende structures, respectively.

As described in [21], Λ can be calculated from the relation

$$\Lambda = [E_{\mathrm{VBM}}(\mathrm{L}) - E_{\mathrm{VBM}}(\mathrm{R})] + [\bar{V}_{\mathrm{tot}}(\mathrm{L}) - \bar{V}_{\mathrm{tot}}(\mathrm{R})] + \tfrac{1}{3}[\Delta_0(\mathrm{L}) - \Delta_0(\mathrm{R})] \qquad (1)$$

where E_{VBM}, $\bar{V}_{\mathrm{tot}}$ and Δ_0 are the energy of the valence band maximum (VBM) (calculated without including the spin-orbit coupling), the averaged total potential (defined as the sum of the averaged Hartree, exchange-correlation and local part of the ionic potentials), and the spin-orbit splitting (we used values for Δ_0 of 1.05 and 0.93 eV for HgTe and CdTe, respectively). In equation (1) L and R denote the materials on the two sides of the interface. The first term in equation (1) is obtained from self-consistent band structure calculations for two bulk materials with $\bar{V}_{\mathrm{tot}} = 0$; the second term is extracted from similar calculations for supercells containing thick slabs of the two materials, using the macroscopic averaging technique [22]; the third term is added *a posteriori* to account for the spin-orbit splitting [9].

In figure 2 we show V_{tot} and the averaged valence charge density, $\bar{n}$, along the direction normal to the interface for $(\mathrm{HgTe})_n/(\mathrm{CdTe})_n$ (001) superlattices, with $n = 3$ and 6. It is evident from figure 2 that very rapid convergence with respect to n is achieved. This result is in conflict with the very slow convergence found by Christensen [13], who used the LMTO technique. In figure 3 we show $\bar{V}_{\mathrm{tot}}$ and $\bar{n}$ for a $(\mathrm{HgTe})_8/(\mathrm{CdTe})_8$ (110) superlattice. A comparison between figures 2 and 3 shows that Λ is almost independent of orientation: the difference between $\bar{V}_{\mathrm{tot}}(\mathrm{HgTe})$–$\bar{V}_{\mathrm{tot}}(\mathrm{CdTe})$ for the (001) and (110) superlattices is less than 0.01 eV. Both the orientation independence and the rapid convergence are indications that interface effects are small, as is the case for GaAs/AlAs interfaces [22]. The reason for the slow convergence of the Christensen [13] results is unclear to us.

When Λ is a calculated from equation (1) we obtain a value of 0.30 eV for both the (001) and (110) superlattices, in good agreement with the larger experimental value of 0.35 eV. We should mention that in principle there are also 'self-energy' corrections [23] to the energy bands, but unfortunately these have not yet been calculated for II–VI compounds. However, such effects are expected to change Λ by only a small amount and are unlikely to affect our conclusions.

The effects of the semi-core d electrons of Hg and Cd have been taken into account approximately by including the EC corrections (i.e., neglecting the relaxation of these states). Core relaxation was not included explicitly, but these effects are reduced by using *solid-state* configurations for generating the pseudopotentials. The effect of core

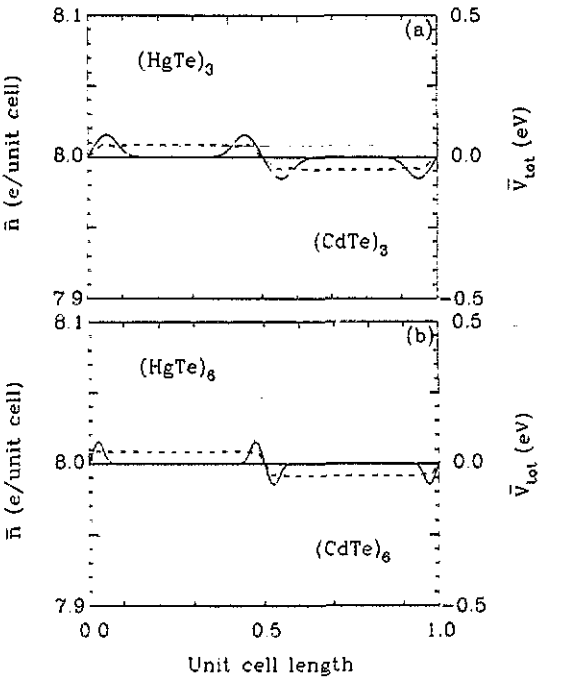

Figure 2. Averaged charge density (full curves), $\bar{n}$, and averaged total potential (broken curves), $\bar{V}_{tot}$, of (*a*) the $(HgTe)_3/(CdTe)_3$ and (*b*) the $(HgTe)_6/(CdTe)_6$ (001) superlattices.

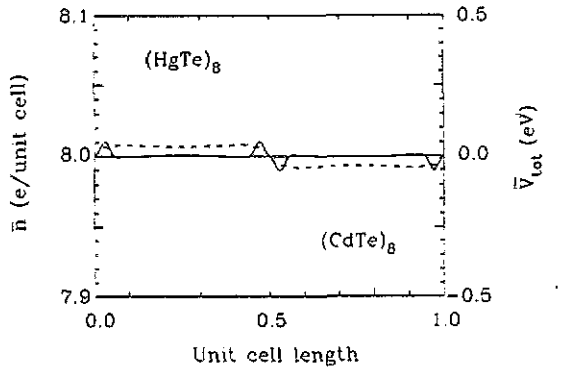

Figure 3. Averaged charge density (full curves), $\bar{n}$, and averaged total potential (broken curves), $\bar{V}_{tot}$, of the $(HgTe)_8/(CdTe)_8$ (110) superlattice.

relaxation is a delicate matter which has not been completely settled yet [16]. However, there are very good reasons to believe that for II–VI compounds the effect on Λ is small [16]. In the present case, because of cancellation between the effects on the two sides of the interface, the effects of core relaxation will be even smaller and it is highly unlikely that our conclusions will be affected. To show the extent of the error cancellation we have performed self-consistent calculations for Λ for a $(HgTe)_3/(CdTe)_3$ superlattice without including the EC corrections, which we think are far more important than the

core relaxation. The value for A so obtained is 0.24 eV, which is only 0.06 eV below the value obtained including the EC corrections. The value of 0.24 eV is in very good agreement with that of Van de Walle and Martin [9] (0.27 eV) who performed a calculation without EC corrections.

In summary, we have performed self-consistent pseudopotential calculations for (001) and (110) oriented HgTe/CdTe superlattices. In contrast to the results of Christensen, we find a rapid convergence with respect to the size of the unit cell. We have obtained a well converged value for the valence band offset of 0.30 eV, which was found to be independent of the interface orientation. This result is in very good agreement with, and gives strong support to, the larger experimental value of 0.35 eV.

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