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Heterojunctions of Model CdTe/CdSe Mixtures.

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1 Abstract

We report on the strain behavior of compound mixtures of model group II-VI semiconductors. We use the Stillinger-Weber Hamiltonian that we recently introduced, specifically developed to model binary mixtures of group II-VI compounds such as CdTe and CdSe. We employ molecular dynamics simulations to examine the behavior of thin sheets of material, bilayers of CdTe and CdSe. The lattice mismatch between the two compounds leads to a strong bending of the entire sheet, with about a 0.5 to 1 degree deflection between neighboring planes. To analyze bilayer bending, we introduce a simple one-dimensional (1D) model and use energy minimization to find the angle of deflection. The analysis is equivalent to a least-squares straight line fit. We consider the effects of bilayers which are asymmetric with respect to the thickness of the CdTe and CdSe parts. Form this we learn that the bending can be subdivided into four kinds depending on the compressive/tensile nature of each outer plane of the sheet. We use this approach to directly compare our findings with experimental results on the bending of CdTe/CdSe rods. To reduce the effects of the lattice mismatch we explore diffuse interfaces, where we mix (i.e., alloy) Te and Se, and determine the strain response.

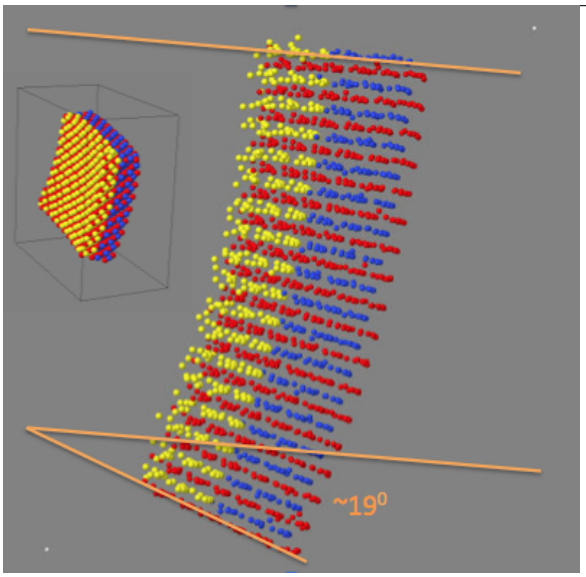

Figure 1: Curved minimum energy configuration of a bilayer sheet of CdSe (left layer) and CdTe (right layer). The dimensions of the sheet are approximately $56.5\mathring{A} \times 56.5\mathring{A} \times 18.8\mathring{A}$. Cd, Se and Te, are denoted by red, yellow and blue respectively. The dots are not drawn to scale, to highlight the layers. The image presents a side-on view of a three-dimensional bilayer zincblende structure (see the inset), highlighting the alternating stacking between layers of Cd and layers of Se and Te. Each layer contains 54 atoms. The orange construction lines help to determine the degree of bending (here expressed as an angle) for a sheet of 36 layers. The deflection angle between two layers is $\sim 0.54°$.

2 Introduction

Semi-conductor compounds, such as CdTe, CdSe, and mixtures thereof (or $CdTe_{1-x}Se_x$ for short) [5], are often used in configurations that produce interfaces (or heterojunctions) between the two phases. A familiar example is that of core/shell quantum dots (QDs) where the core may consist of CdTe and the surrounding shell of CdSe. Other examples include rod shaped particles [2] and layered materials. Even though the crystal forms of the two phases may be the same (e.g., zincblende or the hexagonal form: wurtzite), the lattice mismatch between the two pure phases, i.e., the difference in lattice parameter, makes for an interface that displays strain and stress. The existence of the strain and/or stress is believed to affect the performance of the semi-conductor materials, for instance through the radiationless recombination of electrons and holes.

It has been proposed that alloying of the interfacial region may help to relieve some of the stress and or strain. Experimentally, it is difficult to measure the stress and strain behavior at the nanoscale. Microscopy techniques such as TEM and SEM (tunneling and scanning microscopy) can image individual atoms but it is still hard to determine the full 3D structure and the identity of each atom. Stress measurements would appear to be even more challenging. At the same time, these are situations where simulations can be usefully employed to explore the behavior of heterojunctions, and provide a fundamental understanding of the phenomena.

In this paper we report on molecular dynamics (MD) simulations of a thin finite-sized bilayer sheet with a heterojunction where CDTe meets CdSe (or, in some cases, CdS). The bilayer sheet responds

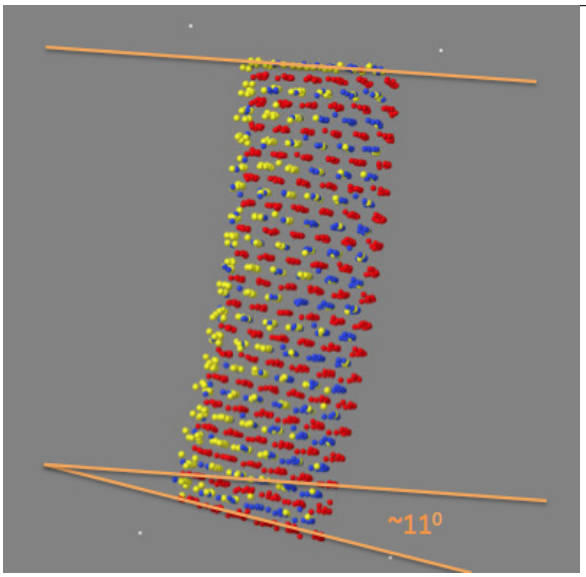

Figure 2: Curved minimum energy configuration of a bilayer sheet of CdSe (left layer) and CdTe (right layer), see also caption of figure 1. This image shows the result of performing 800 swaps between Se and Te atoms, thereby alloying the heterojunction. This results in a reduction of the sheet's curvature. The deflection angle between two layers is $\sim 0.31°$.

to the lattice mismatch with a pronounced curvature that corresponds to neighboring crystal planes to adapt a wedge shape with a 0.5 to 1 degree angle between them. Shim and Mcdaniel [5] have observed bending of the heterojunction of CdTe and CdSe by HAADF-STEM [7] imaging. Their high-resolution images show that the bending is the result of an actual deflection of the crystal planes. The authors call the extent of the deflection surprising. Specifically, the angle of deflection was found to be larger than what was expected if the lattice spacing simply varied from the bulk CdSe value on one side of the bilayer to the bulk CdTe value on the opposing side. Instead, the crystal plane spacing on the outer edge of the CdSe layer was *smaller* than that in a bulk CdSe phase, while on the opposing side it was *equal* than bulk CdTe.

We introduce a simple 1D model to help explain the nature of the observed curvature, and apply it to predict the angle of deflection. This simple model helps in providing an explanation as to why the crystal bending for symmetric bilayers is larger than expected based on the bulk lattice parameters. In addition, the 1D model can be used to generalize to the richer class of asymmetric bilayers as well as predict bending responses to alloying of the bilayer.

3 Results

To model group II-group IV materials we use the three-body potenial we recently developed [1, 3], which is based on the well-known Stillinger-Weber potential [4]. We performed molecular dynamics (MD) simulations of N=1944 particles, arranged in a zincblende structure of 9 by 9 unit cells in a sheet of 3 unit cells. Each cubic unit cell contains 8 atoms. Half the group IV atoms were Te while the other half was Se (and in some runs S). The sheets consist of 12 atomic (100) planes parallel

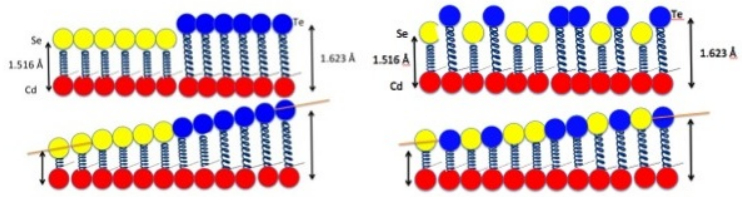

Figure 3: Sketch of the one-dimensional model used to analyze the crystal plane deflections observed in the curved bilayer sheets shown in figures 1 and 2. We show the Cd atoms in red, Se in yellow, and Te in blue. Each Se and Te is connected to a Cd atom. We approximate the interaction potential by a harmonic potential, illustrated by a spring. On the left (top) is an unconstrained fully segregated bilayer configuration, whereby each atomic pair is at an equilibrium distance of $a_{latt}/4$, which leads to a larger distance for CdTe. The bottom left diagram illustrates the effect of constraining the Se and Te to a crystal plane (as observed in figures 1 and 2), and minimizing the total energy. The result is a deflection of the crystal plane. On the top right we show an alloyed bilayer configuration that has two Te atoms swapped for two Se atoms (in a symmetric fashion). The panel on the bottom right shows the constrained, energy minimized configuration for the alloyed bilayer, at a reduced slope.

to the heterojunction. Initially, the entire starting sample generated consisted of CdTe. All the Te atoms on one side of the sheet were then replaced by Se. MD simulations were performed at room temperature, i.e. $T = 300K$, which is far below the melting point and hence the sample remains in the crystalline state. For some of the samples we use steepest descent to obtain energy-minimized structures to facilitate quantifying the degree of bending.

Given that the lattice parameters are significantly different (i.e. 6.46Å for CdTe, 6.06Å for CdSe and 5.84Å for CdS) the sheet initially exhibits considerable stress, which is then released by pronounced deformation of the sheet. The final appearance of the sheet is a strongly bent bilayer with the CdTe side a convex surface (positive radius of curvature) while the CdSe side is concave (a negative radius of curvature), see the inset to figure 1. In figure 1 we show a typical example of a bent bilayer sheet. The entire sheet is still locally in a zincblende structure, but a highly distorted one. In the zincblende structure there are alternating (100) planes of Cd and planes of Se/Te atoms. In the picture, the sheet is angled in such a way as to highlight the relative position of the planes. We note that all the atoms are still organized in planes, but that neighboring planes exhibit a deflection from the parallel configuration into a wedge-like structure. We quantified the bending by simply measuring the angle of the two outer planes, as indicated in the figure. The angle is found to be $\sim 19^\circ$ which corresponds to a deflection angle of $\sim 0.54^\circ$ for each neighboring pair of planes.

In figure 2 we present the MD results for a slightly alloyed sample, where some Se atoms appear to the right of the heterojunction and the same number of Te atoms have moved to the left. This was accomplished by performing 800 pair swaps or interchanges, where a pair swap is executed by randomly selecting one Se atom and one nearby Te atom, and then swapping their positions. Alloying reduces the curvature. The measured angle of the entire sheet is $\sim 11^\circ$ which corresponds to a deflection angle of $\sim 0.31^\circ$ for each neighboring pair of planes. By symmetry, a fully randomly mixed bilayer has zero bending, of course.

Shim and McDaniel [5] reported on a very similar experimental system involving CdTe and CdSe, when a rod of CdSe was grown onto a spherical CdTe nanoparticle. The authors used a HAADF-STEM image to illustrate [6] the nonparallel nature of the crystal planes, and measured the angles

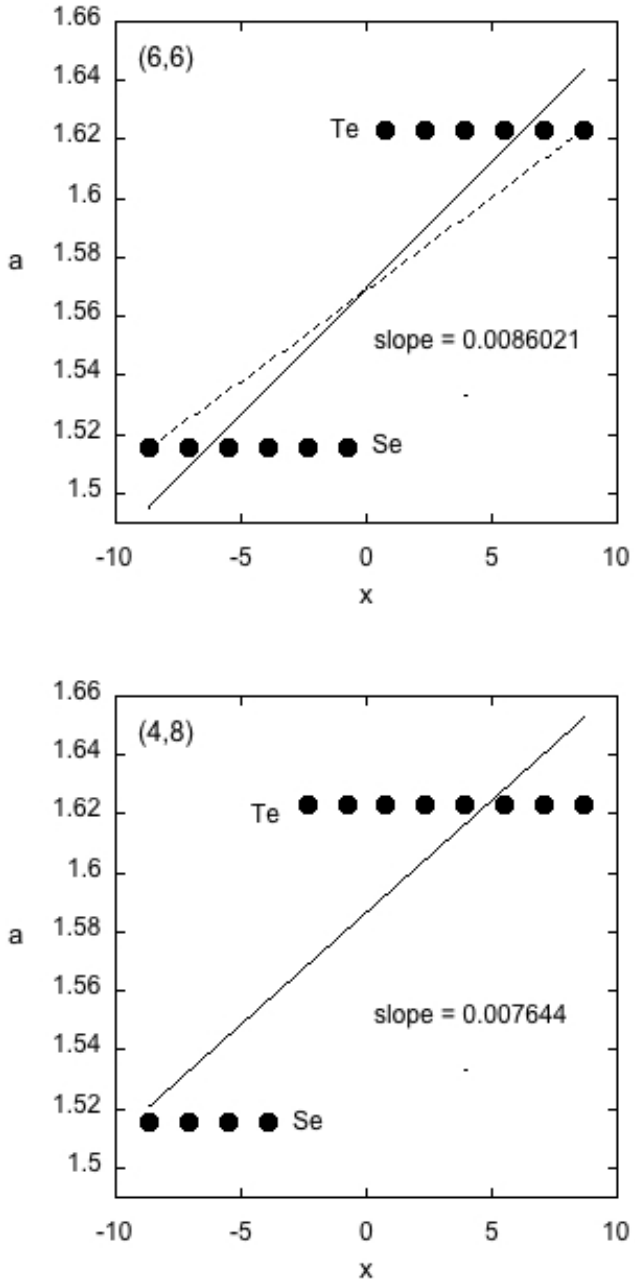

Figure 4: One-dimensional model of the layer deflection for a bilayer sheet. In the top panel the bilayer is symmetric, 6 planes each (labeled (6,6)), while in the bottom panel we show an asymmetric bilayer (i.e., (4,8)). We plot the distance, a (in Å), between atoms in neighboring crystal planes. One plane (not shown) consists of 12 Cd atoms, the other layer has m Se atoms (on the left) and n Te atoms (on the right). The solid line shows the result of a energy minimization which is equivalent to a least-squares fit of a straight line. The slopes correspond to 0.49° (top panel) and 0.44° . For the (6,6) bilayer the left hand side is in compression, while the other end is in tension. In contrast, for the (4,8) bilayer both sides are in tension.

of deflection between two neighboring crystal planes. As suggested by the lattice parameters, the layers were closer together on the CdSe side of the rod, and wider on the CdTe side. The authors noted, however, that the narrowest part of the interlayer distance was noticeably smaller than that in pure CdSe. However, the widest part was about the same as in pure CdTe. In their figure (i.e., figure 7 of [5]) the label the CdSe side as "in compression" and the CdTe side as "in tension". The authors further reported that there was variation in the results among the different rods, some had larger deviations from the bulk spacings.

We will now show that a quantitative explanation for the crystal plane deflection and the size of the observed angle can be obtained from a simple model. In addition this approach can be readily used the explore the behavior of asymmetric bilayers as well as the effects of alloying. A diagram of our model is depicted in figure 3. We consider one Cd crystal plane interacting with one crystal plane made up of equal amounts of Se and Te (we will consider unequal amounts later in this paper). The left panels show a completed segregated bilayer structure that has all the Se atoms on the left hand side and all the Te on the right. Each Se or Te atom interacts with a Cd atom in the layer below. We approximate the interaction by a simple harmonic potential, and in the figure we illustrate its equilibrium position by the extent of the spring. The Se-Cd equilibrium distance is equal to one quarter of the lattice parameter of pure CdSe at $T = 300$K, i.e, $a_1 \equiv a_{latt}/4 = 1.51579$ Å. Similarly, the Te-Cd equilibrium distance is denoted $a_2 \equiv a_{latt}/4 = 1.62298$ Å. For the horizontal spacing we choose a constant distance equal to the average of a_1 and a_2, so that the thickness of the bilayer sheet is equal to that of the simulated structure.

The total energy of the model structure is the defined sum of the harmonic pair energies, i.e.,

$$U = \frac{1}{2}\sum_{i=1}^{2N} \epsilon_i (y_i - a_i)^2 \tag{1}$$

where index i denotes the pairs, N is the number of Se atoms (equal to the number of Te atoms), and $a_i = a_1$ for a Se-Cd pair and a_2 for a Te-Cd pair. The separation of pair i is denoted by y_i, the horizontal position of the pair is x_i. The strength of the interaction of pair i is ϵ_i. For simplicity we set $\epsilon_1 = \epsilon_2 = 1$.

To represent the structures observed in figures 1 and 2, we demand that the positions of all the Se and all the Te atoms fall onto one plane. In our one-dimensional model that requirement is equivalent to stating the all the positions y_i fall onto a straight line. The application of this constraint is illustrated in the bottom panels of figure 3.

The equilibrium configuration of our model is defined as the straight-line configuration that minimizes the total energy U, see equation 1. Writing $y_i = b + mx_i$, the problem then is to determine the slope m and intercept b that minimizes U. This is in fact a very familiar problem, as it is identical to performing a least-squares fit of a straight line to $2N$ measured data points $\{x_i, y_i\}$. For the latter problem one minimizes the chi-square merit function

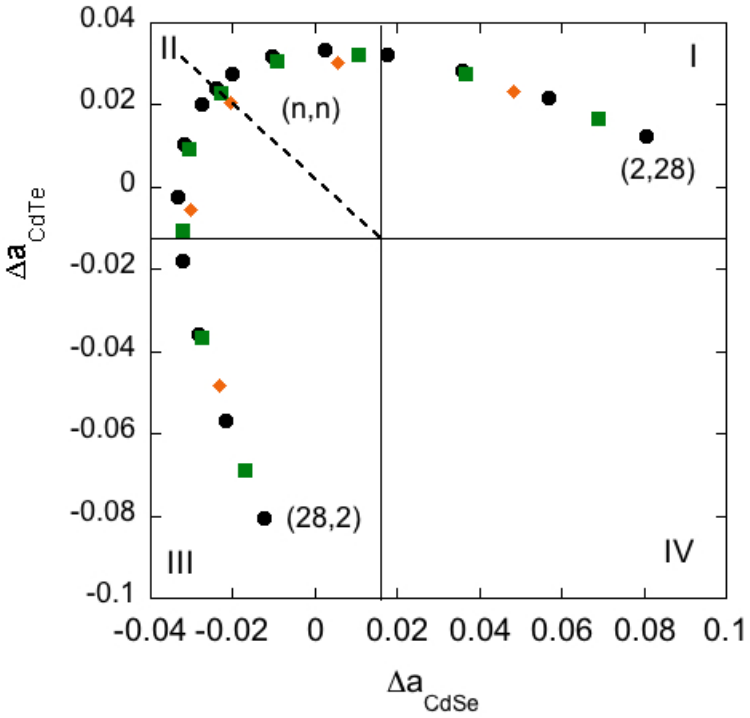

Figure 5: The effects of asymmetry in a CdSe/CdTe bilayer. We use the simple 1D model to explore the distortion response of segregated (n, m) bilayers, consisting of m planes of CdSe next to n planes of CdTe. We have plotted the distortion $\Delta a = a_i - a_2$ at the outer edge of the CdTe layer versus the $a_i - a_1$ at the outer edge of the CdSe layer. The circles, squares and diamonds refer to bilayers composed of a total of 30, 20 and 12 planes respectively. The dashed line indicates the thickness trend of *symmetric* films for which $m = n$. The data fall into three of four quadrants. In quadrant I both deviations are positive indicating that both outer edges of the bilayer are in tension, while in III both are in compression. Quandrant II signifies compression of the CdSe side combined with tension on the CdTe side (see figure 4). No segregated bilayers can end up in quadrant IV. However, alloyed bilayers can.

$$\chi^2(m,b) \;=\; \sum_{i=1}^{2N}\left(\frac{a_i - b - mx_i}{\sigma_i}\right)^2 \tag{2}$$

where σ_i is the uncertainty associated with measurement $y_i = b + mx_i$. Thus, setting $\sigma_i = \epsilon_i = 1$, $U = 1/2\chi^2$.

In figure 4, top panel, we illustrate the results of the energy minimization of a perfectly segregated *symmetric* bilayer of CdSe and CdTe. This (n,m) bilayer has $n = 6$ crystal planes parallel to the heterojunction containing Se, and $m = 6$ planes containing Te. The slope of the plane that minimizes U is 0.008602 and, as pointed out, it can be most easily obtained by performing a least-square straight-line fit to the data points shown.

Also indicated in figure 4 is the result of a linear interpolation between a_1 and a_2, indicated by the dashed line. The slope of this line is a measure of the crystal plane deflection if one naively assumed that the plane spacing across the bilayer varied from that of bulk CdSe phase (on the outer left of the bilayer) to that of bulk CdTe phase (on the outer right of the bilayer). That assumption always leads to an underestimation the angle of deflection between two neighboring planes. Instead, the outer part of the CdSe is found to be in compression, while the outer side of the CdTe part of the bilayer is in tension, as the solid line ends below the Se atoms on the left and above the Te atoms on the right.

Our simple model demonstrates why this has to be the case mathematically. In physical terms, given the imposed constraint that the Se and Te atoms must be co-planar, typically none of the individual pairs i (Se-Cd or Cd-Te) can adopt their equilibrium distance a_i (a_1 or a_2). Instead, for symmetric bilayers the total energy of the distortion is minimized by over-compressing the outer Se-Cd pairs and over-stretching the outer Te-Cd pairs, such that the inner Se-Cd and Cd-Te pairs can adopt a separation that is closer to the equilibrium distance of the isolated pair.

The results of our simple model are quantitatively correct as well. From the slope found in figure 4, $0.008602 \equiv tan(\theta)$, we identify the angle of deflection (or a CdSe/CdTe bilayer of 3 unit cells thick) as $\theta = 0.49^\circ$, in good agreement with the the MD value of $\sim 0.54^\circ$. Similarly, for a bilayer of CdS/CdTe the MD result is $\theta \sim 0.83^\circ$, while our simple model predicts $\theta = 0.76^\circ$.

By restricting ourselves to symmetric bilayers, we have not presented a complete story of the bending phenomenon. To explore the richness of bilayer response to lattice mismatch we must turn to consider asymmetric bilayers, i.e., $n \neq m$. The bottom panel of figure 4 shows the results of a (4,8) bilayer. Here the energy minimization leads to a situation where *both* outer layers are in tension. Conversely, a (8,4) bilayer has both outer layers in compression. For a given number of planes (i.e. bilayer thickness) there are various combinations m and n to be considered. In figure 5 we have collected results for $n+m = 12, 20$ and 30. The last set corresponds to the rod diameter in the work of Shim and McDaniel [5] while the first set is similar to our MD simulations (see figures 1 and 2). To avoid clutter we generally only plot the data for even values of n and m.

We plot the deviations from the bulk crystal plane spacing on the CdTe side versus the corresponding deviation on the CdSe side. We will start with the results of a symmetric (n, n) bilayer. These

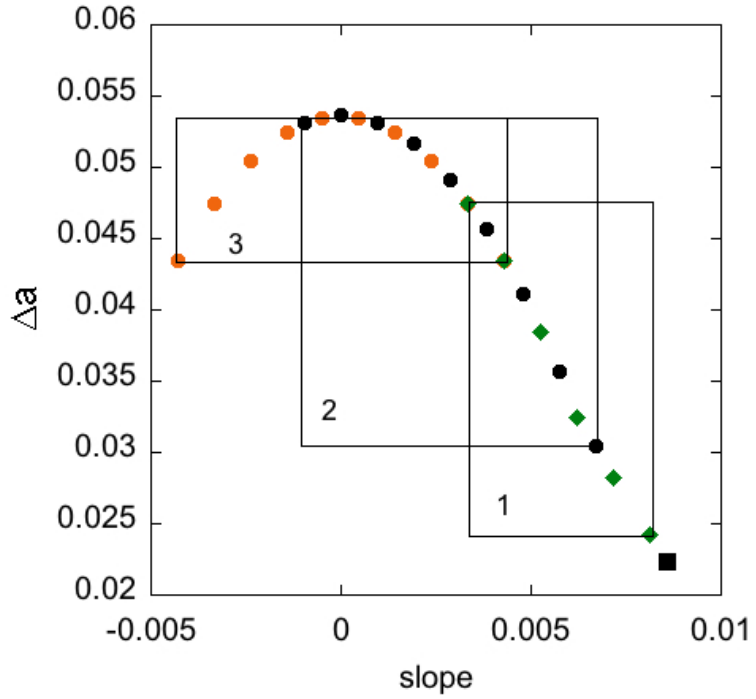

Figure 6: The displacement per particle as a function of the slope for all possible symmetric permutations of 1, 2, and 3 particles swaps. $\Delta a \equiv (2N)^{-1} \sum |y_i - a_i|$. The black solid square indicates the perfectly segregated configuration. The green diamonds denote one-particle swaps, the solid black circles denote two-particle swaps, while the orange circles are the three-particle swaps. The boxes drawn indicate the range of slope-displacements relationship outcomes, and highlight that there is considerable overlap between 2 and 3 particle swaps, say. There are more permutations than symbols visible in the plot. This is a reflection of degeneracy, the occurrence of which increases with the number of swaps. The loci of the points shown form a quartic, i.e., $y = 0.053785 + 0.13197x - 624.17x^2 - 11634x^3 + 3.8058 \times 10^6 x^4$

bilayers all fall onto a straight (dashed) line through the origin, with a negative deviation for the CdSe layer (compression) and a positive deviation for the CdTe layer(tension), c.f., figure 4. The angle of deflection of the symmetric bilayers decreases with n, varying as n^{-1}. As we have seen, if we deviate from the symmetric layer and consider a (4,8) layer then we obtain *positive* deviations for both the CdSe and CdTe layers. Hence this state lies in the first quadrant of figure 5. Larger deviations from the symmetric case produce states placed farther from the origin in quadrant I. All states in quadrant I exhibit tension on both sides of the bilayer.

A (8,4) bilayer produces a state in the third quadrant, which corresponds to compression on both sides of the bilayer. By varying the values n and m for constant $n + m$ we trace out an envelope of points that populate three of the four quadrants. The data are symmetric around $y = -x$, due to the symmetrical nature of the 1D model. The absence of data in quadrant IV implies that the bilayer can not combine expansion of CdSe side (which has the smaller lattice parameter) with compression of CdTe side. We will see later that points in quandrant IV can only result from alloying the bilayers.

We now return to the experimental results of Shim and McDaniel who report $\Delta a_{\mathrm{CdSe}} = 0.09$Å and $\Delta a_{\mathrm{CdTe}} = 0$. This places their state point on the border of quadrant II and III. Note that

Shim and McDaniel report on the spacings between (111) planes, while we have considered (100) planes. Now, the ratio of these two sets of plane spacings is equal to $4/(\sqrt{(}3)/3) = 2.31$. Thus, the corresponding Shim-McDaniel estimate for the (100) spacing would be 0.04Å, which lies very close to the envelope of points in the phase diagram of figure 5. From the estimated thickness, $n + m$ =30, and we identify the state point which most closely matches $\Delta a_{\mathrm{CdSe}} = 0.04$Å and $\Delta a_{\mathrm{CdTe}} = 0$ as $n = 22, m = 8$. This is certainly consistent with the information provided in figure 7 of [5], but Shim and McDaniel do not report on the specific values for n and m.

Although they observe $\Delta a_{\mathrm{CdTe}} = 0$, Shim and McDaniel label the CdTe as in tension, whereas we consider this side to be in a neutral, unstrained state. It could be that the authors simply assumed that if the CdSe side was clearly in compression that the other side had to be in tension. Although this may appear as a natural assumption, our discussion here clearly demonstrates that bent bilayers can, in fact, exhibit three combinations of tension and compression, as indicated by the three quadrants in figure 5. Thus, observing the state of one side of a bent bilayer does not uniquely determine state of the opposite side.

Finally, we use the simple one-dimensional model to study the effect of alloying, limiting ourselves to symmetric bilayers. An example of alloying is shown in figure 3, which illustrates the effect of swapping two Se atoms with two Te atoms. For simplicity we will restrict ourselves to the 'symmetric' swaps shown in the panels on the right hand side of figure 3, where we swapped Se positions 2 and 4 with Te positions $2N - 2$ and $2N - 4$. For $N = 6$ one only needs to consider swapping 1, 2, or 3 atoms, as swapping more atoms merely results in reversing the identities of the left and right hand side of the bilayer. In figure 4 we have collected the results of alloying. We plot the average displacement per particle, $\Delta a \equiv (2N)^{-1} \sum |y_i - a_i|$, versus the slope. We note that all the data fall onto a quartic curve. Alloying reduces the bending of the bilayer (i.e., smaller slope of deflection), while increasing the value of Δa. Entirely eliminating the bending (i.e., zero slope), can be accomplished with certain two- or three-particle swaps, but not with one-particle swaps.

4 Conclusions

The MD simulations of thin bilayers of group II - IV compounds, i.e., CdTe/CdSe structures, that we have presented show that the lattice mismatch produces pronounced bending of the bilayer sheet. The angle of deflection between two neighboring (100) planes is of the order of one degree. Alloying the bilayers produces less bending and smaller angles of deflection. We presented a simple 1D model to help explore the details of this phenomenon. The energy minimization of the 1D model structure is mathematically identical to a simple straight-line least squares fit, and hence easy to interpret. It gives an accurate prediction of the MD simulation result, and we have used it to explore more details of the bent bilayer structures. For symmetric (n, n), fully segregated, bilayers the angle of deflection scales as n^{-1}. More general, asymmetric bilayers, show a variety of outcomes. These are characterized by the distortion on either end of the sheet. Three types of outcomes are found: plane separation reductions on both sides produce a bilayer that is in compression on both sides. Similarly, plane separation increases lead to bilayers that are in tension on both sides. The last type of outcome consists of compression on the CdSe side and tension of the CdTe. The reverse of this latter state is not possible. Finally, all symmetric bilayers lie in quadrant II.

We compared our predictions for the deflection angle, and the compression/tension state of the bilayer to experimental findings for bilayer CdSe/CdTe rods, as reported by Shim and Mcdaniel [5] and find good agreement with their high resolution TEM results. Our simple model predicts that the parts of the rods used in these measurements had 27% of the diameter consist of CdTe. Our model also enables a simple assessment of the results of alloying around the heterojunction with an eye on reducing the strain (i.e., the angle of deflection). The model calculations indicate that at a given mole fraction, guest atoms (i.e, Se in CdTe or vice versa, Te atoms in a CdSe) are most effective in reducing the angle of plane deflection if they are located far from the location of the heterojunction.

5 Acknowledgements

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