Monte Carlo study of the liquid CdTe surface

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We study the liquid-vapor interface of CdTe by a Monte Carlo technique. The interatomic interactions are modeled by a combination of two-body and three-body potentials, using the form proposed by Stillinger and Weber, but with the parameters fitted to bulk atomization energies, lattice constants, and melting temperatures. The calculated heat of fusion and elastic constants agree well with experiments. The surface tension is calculated with a direct Monte Carlo evaluation of the free energy required to create the surface. The calculated surface tension is found to be about 220 ergs/cm^2, in good agreement with experimental estimates. The surface region is found to be Cd rich, even though elemental Cd has a higher surface tension than elemental Te.

I. INTRODUCTION

Liquid CdTe is of considerable practical interest because it is the material from which semiconducting crystals of CdTe are grown. If this growth process takes place in a microgravity environment, it will be strongly affected by surface convective processes, which are in turn strongly influenced by the surface tension of CdTe, and by its gradients with respect to temperature and concentration.[1,2]

Liquid CdTe is an extremely difficult material to model from first principles, because it undergoes a semiconductor-to-metal transition, as a function of either temperature or composition. The stoichiometric alloy is semiconducting just above its melting temperature, but becomes a much better conductor at higher temperatures.[3] Similarly, if the stoichiometric alloy is doped with either Cd or Te, its conductivity increases by orders of magnitude.

As a first step in understanding the thermodynamic properties of liquid CdTe, we have modeled the stoichiometric compound by means of empirical two-body and three-body potentials, and calculated the thermodynamic properties of both bulk and surface by Monte Carlo simulation. Both two- and three-body forces are necessary to stabilize the zinc-blende structure of the solid. We fit the parameters of the potentials to the bulk

atomization energies, the lattice constant, and the melting temperature of the alloy. The resulting surface tension is in good agreement with existing experimental estimates. When these results are considered together with the excellent agreement obtained previously for the surface tension of Si,[4] they suggest that this type of modeling is a very fruitful way of investigating the surface properties of semiconducting liquids.

The remainder of this paper is organized as follows. Section II outlines the model used, and the method of calculation. Results are presented in Sec. III; a brief discussion follows in Sec. IV.

II. THE MODEL

We model the potential energy of liquid CdTe as a sum of empirically determined two- and three-body interactions between the atoms. Thus the Hamiltonian of CdTe takes the form

$$H = K + \sum_{\{i<j\}} W_2(\mathbf{R}_i - \mathbf{R}_j) + \sum_{\{i<j<k\}} W_3(\mathbf{R}_i, \mathbf{R}_j, \mathbf{R}_k) ,$$

$$(1)$$

where K is the kinetic energy, W_2 is the two-body potential, and W_3 is the three-body potential.

We take W_2 and W_3 to be of the form proposed by Stillinger and Weber:[5]

$$W_2 = \varepsilon f_2(r_{ij}/\sigma) , \tag{2}$$

$$W_3 = \varepsilon f_3(r_{ij}/\sigma, r_{jk}/\sigma, r_{ki}/\sigma) , \tag{3}$$

$$f_2(r) = \begin{cases} A(Br^{-4}-1)\exp[(r-a)^{-1}], & r<a \\ 0, & r \geq a \end{cases} \tag{4}$$

$$f_3(r_{ij}, r_{jk}, r_{ki}) = h(r_{ij}, r_{ik}, \theta_i) + h(r_{ji}, r_{jk}, \theta_j) + h(r_{ki}, r_{kj}, \theta_k) , \tag{5}$$

$$h(r,s,\theta) = \begin{cases} \lambda \exp[\nu(r-a)^{-1} + \nu(s-a)^{-1}](\cos\theta + \tfrac{1}{3})^2 & \text{for } r<a \text{ and } s<a \\ 0 & \text{otherwise} . \end{cases} \tag{6}$$

There are three distinct two-body potentials in CdTe: Cd-Cd, Cd-Te, and Te-Te. In principle, there are four three-body potentials, but in the interest of minimizing the number of undetermined parameters, we have chosen these all to be identical. The form (5) is chosen so that the three-body potential has its minumum when the three particles are arranged at angles corresponding to the diamond or zinc-blende structure. The constant λ is adjusted so as to give the correct melting temperature of CdTe, as discussed below. In the interest of simplicity, the parameters in the exponentials, namely, a and v, are chosen to have the same values as in Si.[5] The constants ε and σ are chosen to be the same for all three two-body potentials, and are adjusted so as to give the measured atomization energy and to satisfy the requirement that the compound be under zero pressure at the observed zero-temperature lattice constant. (The atomization energy is the energy per atom required to convert a solid into its constituent atoms.) Since the compound solid has only unlike neighbors, these conditions determine only the Cd-Te potentials. The Cd-Cd and Te-Te potentials are determined by considering these elements arranged in a fictitious diamond structure with the same *nearest-neighbor separation* as the actual elements. The constants A and B are then chosen so as to give the correct atomization energy and to satisfy the zero-pressure condition for these fictitious structures at the correct nearest-neighbor separation. This artificial expedient seems necessary to construct Cd-Cd and Te-Te potential appropriate for use in a zinc-blende-structure alloy.

The parameters A and B for the pair potentials are given in Table I. The other parameters entering Eqs. (2)–(6) are chosen as follows: ε = 1.03 eV, σ = 2.51 Å, λ = 25.0, a = 1.80, and v = 1.20. The reasons for these choices are given above. All parameters are dimensionless except ε and σ. The resulting two-body potentials are plotted in Fig. 1. It may be seen that, of the three potentials, the Cd-Cd one is the weakest. The Cd-Te potential is stronger than the average of the Cd-Cd and Te-Te potentials, consistent with the fact that the alloy CdTe is stable relative to its constituent elements.

Given the model Hamiltonian, we have calculated the bulk thermodynamic properties using standard Monte Carlo techniques[6] on a sample typically of 216 = 6×6×6 atoms with periodic boundary conditions. To obtain the surface properties, we used a direct evaluation of the surface tension as proposed by Miyazaki, Barker, and Pound.[7] The method is the same as used earlier by us to evaluate the surface tension of Si,[4] and is described in detail in that reference. Calculations were carried out using the Cray Research, Inc. X-MP/28 computer at the Ohio Supercomputer Center.
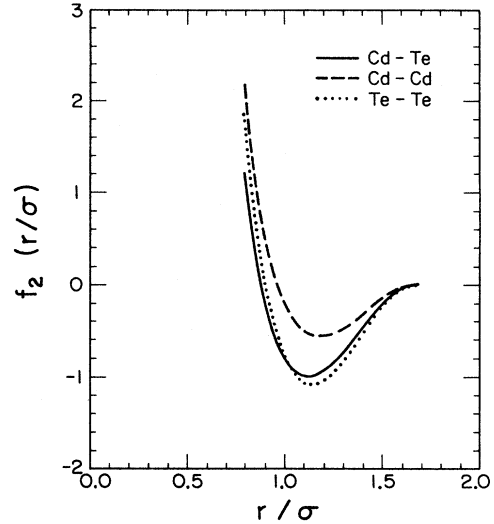

FIG. 1. Pair potentials $f_2(r/\sigma)$ for CdTe: Cd-Cd, Te-Te, and Cd-Te. The potentials are given in units of ε, the particle separations in units of σ.

III. RESULTS

Figure 2 shows the internal energy of CdTe as a function of temperature, as calculated using a value of the three-body parameter λ = 25. Various other values of λ ranging from 21 to 41 were also examined; the present choice gives the best agreement with the measured melting temperature. It is slightly larger than the value λ = 21 appropriate for Si, corresponding to a somewhat stronger three-body potential. This result seems consistent with the fact that stoichiometric CdTe retains some of its zinc-blende structure in the liquid state near

TABLE I. Parameters A and B used in the two-body potentials used to model CdTe.

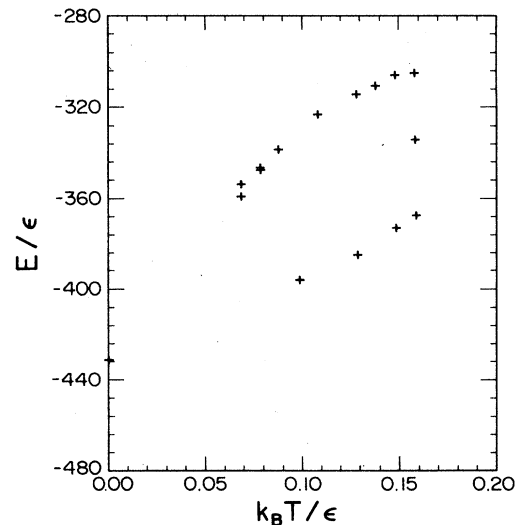|	Cd-Te	Cd-Cd	Te-Te
A	7.0496	5.1726	8.1415
B	0.6022	0.8807	0.6671

FIG. 2. Calculated hysteresis loop for potential energy as a function of temperature for 216-particle, model CdTe system. The energy for the 216-particle system is plotted in units of ε. The lower branch represents the solid phase, the upper branch the liquid. The curves are further described in the text.
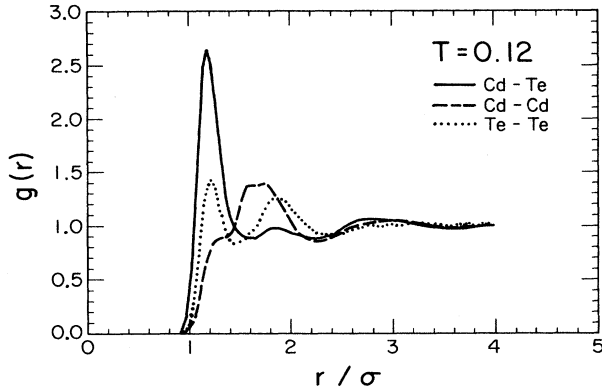
FIG. 3. Partial radial distribution functions $g_{ij}(r)$ for stoichiometric liquid CdTe at a temperature $T = 1430$ K, as calculated via Monte Carlo simulation. The temperature is given in units of ε/k_B.
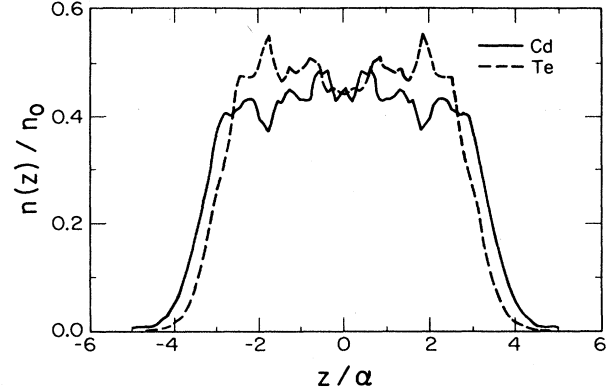

FIG. 4. Partial density profiles for a slab of liquid CdTe with two free surfaces, at a temperature $T = 1430$ K. It is symmetric about the center since the left and right halves of the slab are averaged. n_0 is the liquid atomic number density; $\alpha = n_0^{-1/3}$.

melting, and remains semiconducting, while liquid Si is metallic. To obtain these results, the temperature was first cycled up, starting from $T = 0.10\varepsilon/k_B$, corresponding to a point in the solid region. Some superheating occurred, followed by an apparent melting at around $T = 0.16\varepsilon/k_B$. The melting is indicated by a discontinuity in the energy and an abrupt change of the radial distribution function to a more liquidlike form. When the liquid was cycled back down in temperature, it proved possible to supercool it to about $T = 0.07\varepsilon/k_B$. From these data, the true thermodynamic melting temperature can be estimated as the mean of the apparent melting and apparent freezing temperatures. For the choice $\lambda = 25$, this corresponds to about $T = 1370$ K, very near the actual melting temperature of CdTe, $T = 1365$ K. The average internal energy change near the melting point in our models is 14.5 kcal/mol, which is in good agreement with the experimental heat of fusion, 12.0 kcal/mol.[8] Since the Cd-Cd and Te-Te interactions become important in this quantity (unlike the purely solid-state quantities, which are determined by the Cd-Te interactions only), this agreement is further evidence that our model for these interactions is reasonable.

Figure 3 shows the three radial distribution functions $g_{CdCd}(r)$, $g_{CdTe}(r)$, and $g_{TeTe}(r)$, for the liquid at the melting temperature, $T = 0.12\varepsilon/k_B$. $g_{CdCd}(r)$, for example, represents the probability density for finding a Cd atom at r, given that there is one at the origin. All three functions are normalized to unity at large separations. As can be seen, there is an excess of Cd-Te nearest-neighbor bonds in the liquid state. These represent a residue of the perfect short-range order that exists in the ordered solid; our model predicts that there is still considerable short-range order in the liquid state.

As a further check on our empirical potentials, we have also calculated the linear elastic constants of solid CdTe at the density corresponding to $T = 300$ K, using expressions derived by Cowley[9] (Table II). Agreement with experiment is encouraging, especially since none of the elastic data are used to fit our empirical potential and only one λ is used for all four three-body potentials.

Figure 4 shows the partial density profiles of Cd and Te in the liquid state at $T = 0.12\varepsilon/k_B$. The figure shows a cross section of a slab with two surfaces—the end result of the Monte Carlo simulation described in Ref. 7. The slab is approximately six atomic layers thick. As can be seen, there is some excess of Cd at the surface. This excess is due to the fact that the Cd-Cd potential is the weakest of the three bonds in our model, so that the Cd is somewhat preferentially attracted to the surface. The various oscillations in the bulk are probably due to imperfect statistics, and would probably become much weaker if the run were continued to much longer times.

Table III shows the calculated surface tension of stoichiometric CdTe at three different temperatures, as obtained by a direct evaluation of the free energy required to create the surface at these temperatures. Also shown is the temperature derivative $d\tau/dT$ as calculated by two different methods. The first method involves simply evaluating the difference in surface tensions at different temperatures; this gives $(d\tau/dT)_{dir}$ in Table III. The second method requires calculating the surface energy per unit area, E_s, and hence $(d\tau/dT)_{ent} = -S_s$

TABLE II. Calculated elastic moduli of CdTe at density of room temperature. The unit is 10^{11} dyn/cm. The experimental results are those of McSkimin and Thomas (see Ref. 12).

	C_{11}	C_{12}	C_{44}
This work	4.50	2.00	1.80
Expt.	5.35	3.68	1.99

TABLE III. Calculated surface tension of CdTe. τ is the surface tension, $(d\tau/dT)_{ent}$ is the negative of the surface entropy per unit area, and $(d\tau/dT)_{dir}$ is the temperature derivative of τ, as calculated directly from differences of the surface tension.

	T		
	0.11 (1040 °C)	0.12 (1160 °C)	0.13 (1280 °C)
τ (ergs/cm^2)	234	213	204
$(d\tau/dT)_{ent}$	-0.12	-0.09	-0.03
$(d\tau/dT)_{dir}$	-0.17		-0.08

$=(\tau-E_s)/T$, where S_s is the surface entropy per unit area. In view of the uncertainties involved in calculating small differences between large numbers, the two methods agree well among themselves, and give reasonable values for the derivatives.

We have also calculated both the bulk and the surface specific heat for liquid CdTe at the melting temperature, using the results of the Monte Carlo simulations. $(C_V)_{bulk}$ is found to equal approximately $3.3k_B$/atom. The additional surface specific heat is estimated at $\approx(0.3\pm0.15)k_B$ per surface atom, assuming $2N^2$ surface atoms in a liquid Monte Carlo slab with two free surfaces and N^3 atoms.

IV. DISCUSSION

The calculated surface tension of CdTe agrees well with estimates quoted by Lind et al.,[10] as well as with recent measurements of Wilcox and collaborators.[11] There may also be some experimental evidence of excess Cd surface concentration, as predicted by our calculations, although in view of the uncertainties in our potentials our predictions regarding the surface profile should be viewed with some caution. The Cd excess arises in our calculations from the relatively weak Cd—Cd bonds, which in turn result from our method of fitting the potentials to atomization energies. Nevertheless, it is very encouraging that the present straightforward calculations give such reasonable results.

Because of the expense of the present calculations, we have not attempted to calculate the surface tension as a function of the various parameters which enter the model Hamiltonian. Nevertheless, some information about this dependence is available from our results previously obtained for Si.[4] The Si results were also obtained using empirically determined two- and three-body potentials. Remarkably, the calculated surface tensions can be accurately expressed by the empirical formula

$$\tau(T)=\alpha(k_B T/\varepsilon)\frac{\varepsilon}{\sigma^2} , \qquad (7)$$

where α is a dimensionless number which depends only on the ratio of temperature T to the potential depth parameter ε. The melting temperature T_m is about $0.07\varepsilon/k_B$ for Si and about $0.115\varepsilon/k_B$ for CdTe. Using the calculated surface tension τ and its temperature derivative $d\tau/dT$ for Si, we can linearly extrapolate its

surface tension to $0.115\varepsilon/k_B$ also. When this is done, we find $\alpha(0.115)\approx0.084$ for both Si and CdTe. Thus our results are accurately predicted by the scaling formula (7), even though the surface tensions differ by a factor of 4. We are led to the remarkable conclusion that the surface tension (and by extrapolation, the surface width) depends predominantly on only two of the parameters which determine the empirical potentials. Presumably, one can even use this conclusion to estimate the surface tensions and their temperature derivatives for other tetrahedrally coordinated semiconductors, given values for these two parameters.

The present results suggest that empirical potentials can be used very fruitfully to calculate the surface properties of liquid semiconductors, compound and elemental. Although there is much uncertainty about the potentials, these can be fitted to known bulk properties, and the resulting potentials used to obtain surface properties. The potential can be further improved by considering different λ's of the three-body potential to fit the bulk property, such as the three elastic constants. The potentials are particularly convenient to use in large-scale computer applications, as are now highly feasible with the ready availability of supercomputers.

The calculations presented here can be extended in a number of important ways. The effects of impurities can be investigated, and one can model the variation of the potentials with temperature and composition. The alloy transport properties change dramatically with temperature and composition, suggesting strong variations in electronic screening of the potentials. Another important extension would be to carry out dynamical calculations, to obtain such quantities as viscosity and thermal conductivity. We intend to develop some of these extensions in a subsequent publication.

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