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13. ABSTRACT *(Maximum 200 words)*

This annual report of AFOSR contract F49620-88-K-0009 summarizes the work accomplished on studies of mechanical properties of semiconductors and their alloys, and plastic flow and intermetallic compounds. 1) A simple relationship between the elastic constants of semiconductor is found. 2) A systematic study of tight-binding parameters to fit cohesive energy, bulk modulus, and shear coefficients of all diamond and zinc-blende semiconductors has been carried out. 3) An additional, nonequilibrium mechanism is suggested as a possible explanation of ordering in lattice-matched alloys. 4) A KKR-CPA theory is being generalized to study semiconductors. 5) Based on our calculation of surface sublimation energies, a charge transfer mechanism is proposed that affect ordering on semiconductor surfaces. The surfaces of wide gap, ionic compounds are expected to exhibit superlattice arrangements of atoms and vacancies. Consequent effect on epitaxial growth is discussed. 6) Static structural and deformation properties, such as ideal twin-strength and ideal twin-stresses, of metals are studied in a non-self-consistent total energy calculations using the Harris-Foulkes approximation.

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MECHANICAL PROPERTIES OF SEMICONDUCTORS AND THEIR ALLOYS

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I INTRODUCTION

This project began as a study of the mechanical properties of semiconductors and their alloys and then added tasks on plastic flow and stability of intermetallic compounds. The computational methods to accomplish both sets of tasks have common elements, and the symbiosis between them has benefited both. The subjects we have treated this year are:

1) New relation among the c_{11}, c_{12}, c_{44} elastic constants in semiconductors

2) Systematic parameterization studies of tight binding models

3) Calculations of the bulk moduli of ordered semiconductor alloys

4) Development of a full potential KKR band theory

5) Surface sublimation energies and their consequences on
    a) Surface order
    b) MBE growth
    c) Cleavage

6) Harris-Foulks approximation tests
    a) Structural energy-volume relations in first row transition metals
    b) Advances in non-self-consistent total energies
    c) A quantum mechanical calculation of the theoretical strength of metals

7) Twinning and pseudo-twinning in B2 alloys.

These studies have resulted in twenty papers this year; nine have appeared, five have been accepted, four are being refereed, and two are about to be submitted. A complete list of titles is provided in the Appendix. We will identify in this annual report which topics have been written up into journal articles, which are available as reprints or submitted pre-prints (these will be attached herewith), and which have been studied but are not yet in the press. If the results have been published rather than repeating details of the work, we will merely indicate how the completed work fits in with the general objectives of the original proposal. If results have not been published, we will present the details of the work for the first time in the following report.

II SEMICONDUCTORS

A. NEW RELATION AMONG THE ELASTIC CONSTANTS

Previously we had published a paper (van Schilfgaarde and Sher, 1987) identifying a relation between the three independent elastic constants of zincblende-structured semiconductors. The relation was derived from a formalism that allowed hybrid angular distortion and was then simplified to the rigid hybrid case to obtain a simple algebraic expression. In the course of preparing a review article we have reexamined the formalism treating the simple case from the outset. This study identified a numerical error in the original result. The new expression is

$$\frac{9}{c_{44}} = \frac{6}{c_{11} - c_{12}} + \frac{4}{B}$$

where B is the bulk modulus $B = c_{11} + 2c_{12}/3$. This expression fits the experiments of all semiconductors to better than 10 percent, an improvement over the prior result. We will write a paper to present the correct result, which is in the review article.

B. SYSTEMATIC PARAMETERIZATION STUDIES OF TIGHT-BINDING MODELS

This study is also incorporated into the review paper. It provides a means to fit precise values for the bond length, cohesive energy, bulk modulus, and shear coefficients of all diamond and zincblende semiconductors. Then values of c_{44}, the internal displacement parameter, and phonon frequencies are used to test the theory. The predicted values all fit experiment to better than 10 percent. Once the tight-binding parameters are set for bulk compounds, then alloy, impurity, and surface properties can be deduced.

C. CALCULATIONS OF THE COHESIVE ENERGIES AND BULK MODULI OF ORDERED SEMICONDUCTOR ALLOYS

This study has been written for publication in *Physical Review B*. It demonstrates that none of the equilibrium mechanisms proposed to date can account for the observed ordering in a collection of epitaxially grown semiconductors on lattice-matched substrates. A non-equilibrium mechanism that emerges from the work is raised as a possible explanation, but a more detailed investigation is needed to confirm its import. The bulk moduli of ordered ternary semiconductors in CuAuI, CuPt, and chalcopyrite structures are all shown to lie below those of the concentration-weighted average of the constituent compounds.

D. DEVELOPMENT OF A FULL-POTENTIAL KKR BAND THEORY

The KKR theory is a generalization of LMTO in which the linearization is not done. It will allow us to test the sensitivity of LMTO to specific situations where the energy linearization is questionable. Moreover, while an LMTO-CPA formalism has just recently been published (Kudrnovshy et al., 1989) KKR-CPA studies have been pursued for some time. Since much of our attention is directed toward semiconductor alloys this has motivated over KKR effort. A KKR-CPA theory is well developed for metals (Johnson et al., 1990) and its conversion to semiconductors is a goal of ours.

E. SURFACE SUBLIMATION ENERGIES

1. Introduction

In recent years there has been considerable advancement in the field of epitaxial growth of semiconductors, with molecular beam epitaxy (MBE) being one of the most important techniques. Modeling of the MBE growth process involves a description of the incoming and outgoing fluxes of atoms from the surfaces, as well as in-surface migration and reactions among the constituents. An important contribution to the out-flux arises from the sublimation of the constituents from the growth surface. Attempts to determine the activation energy for surface sublimation processes have been made in a variety of experiments on GaAs and CdTe. Because the values obtained depend on the experimental environmental conditions the reported values differ substantially. Moreover, the experiments, in which the evaporation of many layers is permitted, measure quantities related to bulk cohesive energies rather than to the surface-orientation-dependent activation energies that are more relevant to growth modeling. Yet in the modeling of MBE growth, accurate values of the activation energies for the removal of constituent atoms from various sites on a given surface to the vapor are essential. The calculation of these surface sublimation energies (SSE) is essential in understanding and modeling growth.

In addition, properties of semiconductor surfaces during epitaxial growth are sensitively dependent on the nature of the interactions between surface atoms. When the interaction between the atoms is attractive, the surface grows with formation of islands at temperatures below a critical temperature known as roughness transition temperature. However, when the interaction between the atoms is repulsive, the surface undergoes an order-disorder transition. At growth temperatures below the order-disorder transition temperature, surface atoms and vacancies arrange themselves in a superlattice pattern that minimizes the number of atom-atom pairs. Irrespective of the nature of interaction, the sites are occupied uniformly at growth temperatures well above the corresponding critical temperature. The required pair energies can be deduced from the calculated SSEs.

2. Calculational procedure

Several theoretical methods such as cluster methods, slab methods, and Green's function methods have been used in the literature to study semiconductor surfaces. Both the cluster and slab methods approximate the semi-infinite bulk terminated at a particular surface by a finite number of atoms or two-dimensional (2D) atomic layers, respectively. While first-principles electronic structures can be incorporated into these methods, doing so is extremely time consuming, because the size of the matrix involved in these calculations is often large as a result of the range of the surface wave functions.

We use a tight-binding (TB) Green's function (GF) method to calculate the SSE. Although the TB-based approaches are known to yield numerically less accurate results, the trends predicted here are expected to be reliable. The calculation of the SSE proceeds in two steps. First, the GF for the ideal flat surface is calculated in terms of the bulk GF using Dyson's expansion. Second, the GF for the surface with an atom either removed from or added to the ideal surface is calculated in terms of the surface GF. Unlike the cluster or slab methods, in the GF method the size of the matrix equation to be solved is determined by the size of the perturbation Hamiltonian, and thus, exploiting the in-plane periodicity of the unperturbed surface, the resulting matrix is comparatively small. Additionally, the electronic contribution to the total energy can be obtained from the change in the density of states (DOS) which is calculated directly from the unperturbed GF and the perturbation Hamiltonian, thus eliminating problems associated with calculating small energies by taking the differences between two large energies. The DOS is calculated as a continuous function of energy, thus treating bulk- and surface-like states on an equal footing. The details of the calculational procedure have been published (Chen et al., 1989; Berding et al., 1989; Krishnamurthy et al., 1990a, 1990b).

We calculate SSE for two classes of cations and anions for each surface. When the perturbation to the surface GF involves the removal of an atom from an ideal surface, leaving a surface vacancy behind, we refer to the process as the surface sublimation from a *concentrated* surface. The energy required to remove the atom in this limit is denoted E_c. When the perturbation to the surface GF involves the addition of an atom to the ideal surface, thus beginning a new layer of atoms, we refer to the inverse of this addition process as the surface sublimation from a *dilute* surface, and to the energy as E_d. Orientation-dependent E_c and E_d are energies required in modeling MBE growth.

3. Charge transfer and pair energies

The calculated SSEs of anions and cations from various semiconductor surfaces in silicon, GaAs, CdTe, and HgTe are given in Table 1 for (111), $(\overline{111})$ and (100) surfaces. Notice that the (111) surface can terminate either with triply bonded cations or with singly bonded anions. The opposite bonding arrangement is found in the $[\overline{111}]$ direction. We note several features of the SSEs: (1) the SSEs are sensitively dependent on the crystal orientation; (2) in general, they do not vary linearly with the number of bonds being made to the surface; (3) the SSEs for cations and anions differ and are orientation dependent; and (4) they vary considerably between the dilute and concentrated limit, even for the (111) and (100) surfaces where there are no first-neighbor in-plane bonds. The first two points are extremely important to the modeling of MBE growth, where a linear dependence of the surface bonding energies with the number of bonds being made is commonly assumed. Because the SSEs do not exhibit this simple linear variation with the number of bonds being made to the surface, the growth properties based on these energies are expected to differ substantially from those predicted using a linear variation. Although the energy required to remove a cation or anion differs from that deduced from the bulk cohesive energy, we find that average energy per bond for the removal of an anion plus a cation layer equals the bulk cohesive energy, as it should.

TABLE 1. Orientation-dependent SSE and the highest occupied level (measured with respect to the top of the valence band). All energies are in electron-volts. η is the number of bonds with the layer below that are broken.

Orientation	Removed atoms	η	Si			GaAs			CdTe			HgTe		
			E_m	E_d	E_c	E_m	E_d	E_c	E_m	E_d	E_c	E_m	E_d	E_c
(111)	a	1	0.0	2.5	4.6	0.4	2.3	3.8	0.7	3.9	4.2	0.0	1.8	3.8
	c	3	0.0	4.2	6.4	0.55	3.2	3.3	1.6	2.7	0.6	0.0	–0.3	1.1
$(\overline{111})$	a	3	0.0	4.2	6.4	0.0	4.6	5.0	0.0	5.2	2.1	0.0	2.8	2.8
	c	1	0.0	2.5	4.6	1.3	3.3	2.7	1.6	2.2	1.3	0.0	–0.2	0.3
(100)	a	2	0.0	3.7	5.6	0.3	3.4	4.7	0.7	5.0	2.6	0.0	2.4	3.1
	c	2	0.0	3.7	5.6	0.1	2.6	3.6	1.6	2.1	0.1	0.0	-0.2	1.0

Intuitively, one would expect $E_c > E_d$. The removal of an atom from the concentrated limit, in addition to breaking interlayer bonds, requires the breaking of in-plane surface bonds which are first-neighbor bonds for the (110) surface and second-neighbor bonds for the other surfaces. Even in the absence of first-neighbor bonds on the surface, the surface dangling bonds in the concentrated limit interact to form a partially filled band, which lowers energy. When a surface atom is removed, the removal of an electron from these broadened surface states will in general require more energy than if the dangling states were isolated, as in the dilute case. As seen from Table 1, this conventional interpretation explains the trends observed in silicon, HgTe, and most cases in GaAs. However, for other cases, we find that E_c is smaller than E_d. In order to understand the mechanisms that drive some semiconductors to have $E_c < E_d$, we examine the nature of the anion and cation surface states. Notice that $E_c < E_d$ occurs only for polar surfaces in semiconductors with a large band gap.

For an unreconstructed surface, some of the surface states normally lie in the fundamental gap. Compounds have both cation- and anion-derived hybrid surface states, where the cation-derived most often lie higher in energy. The energy separation between the peaks in the DOS in the band-gap region is related to the energy difference between hybrid states, and thus the peak separation is larger in the II-VI than the III-V compounds. Now let us consider the removal of a cation atom from a (111)A surface, in the concentrated limit. The highest occupied surface level is at the cation surface state energy which is very close to the conduction band minimum. When a triply bonded cation is removed from the surface, surface states from the anion previously bonded to the removed cation are created, and a single cation surface state is destroyed. Because this anion surface states lie near the top of the valence band, the electrons from the cation surface states will transfer into this level. This process reduces the energy of the final configuration, and E_c for removal of a cation in this concentrated limit is correspondingly reduced. When the difference in the reduction in energies due to this charge transfer effect outweighs the surface state broadening effect, it results in $E_c < E_d$. Note that these charge transfer processes are reversed for surface sublimation of isolated cations from the anion terminated surface surface, resulting an E_d correspondingly larger.

We conclude that the charge transfer from the cation to anion surface states will increase E_d and decrease E_c, and thus always reduces the difference, $E_c - E_d$. The magnitude of the charge-transfer effect depends on the amount of charge transferred and the separation between the relevant energy levels. Whenever this effect is substantial, E_c can become smaller than E_d. In an elemental semiconductor like silicon, no transfer is expected and E_c is always expected to be larger than E_d, as is observed. In GaAs, although a charge transfer is present, the energy difference between the highest filled level and the newly exposed dangling bond state is very small, resulting in a reduced charge transfer effect. As a consequence, $E_c - E_d$ is reduced and, in general, remains positive. Owing to an increased ionicity in II-VI compounds, the energy separation between the dangling states is large. As illustrated above, the effect of the charge transfer is substantial in CdTe and in most cases causes E_c to be less than E_d. Although HgTe is a II-VI compound, the charge transfer does not occur because it is a semimetal with no forbidden gap, and consequently a charge transfer effect is not present.

In this model, it is clear that the effective atom-atom pair interaction energy, ε_0, between atoms on the surface is simply $(E_c - E_d)\,\eta_0$, where η_0 is the number of near-neighbor surface bonds. A positive (negative) ε_0 implies an attractive (repulsive) interaction between surface atoms.

4. Cleavage energies

We have used the TB-GF method discussed above to calculate the cleavage energies, E_γ, in semiconductors. Because the semiconductors are brittle, it is important to understand failure by cleavage. The elemental semiconductors are known to cleave between (111) planes, which have the lowest planar bond density. The compound semiconductors cleave on the lowest bond density nonpolar plane, the (110) plane. Cleavage energies for the correct cleavage planes were calculated for Si, GaAs, CdTe, and HgTe. We find $E_\gamma(111) = 1360$ ergs/cm^3 for silicon and $E_\gamma(110) = 1000$, 180, and 120 ergs/cm^3 for GaAs, CdTe, and HgTe, respectively. These energies are in good agreement with the available experimental data. Details of the calculations have been published (Berding et al., 1990.)

To explore the cleavage energies in the semiconductor superlattices, we adopted a slab method in place of the Green's function method. In the Green's function method a truly semi-infinite bulk terminating in a surface is created. In the slab method a periodic arrangement of surfaces is constructed via supercells. The limitation of the slab method is the supercell size, which must be large enough to completely decouple the surface states on either side of the slab. In most cases we have found that slabs of only 6 double (anion plus cation) layers are adequate to decouple the surface.

We have done preliminary calculations of the cleavage energies of the CuPt and the CuAu (with 110 ordering parallel to the cleavage surface) superlattice structures of AlGaAs2. We find the cleavage energy of the CuPt structure to be a simple linear average of the cleavage energy of AlAs and GaAs. For the CuAu structure, we find that the surfaces are strongly coupled, even for slabs containing 12 double layers. We are currently investigating the reasons for these surfaces to be strongly coupled in the superlattice, while they are not so for the constituent compounds.

5. Discussion

The relative magnitude of the surface energies can have profound consequences on the growth properties of the semiconductor crystals. When the interaction between the atoms is attractive ($\varepsilon_0 > 0$), the surface will undergo a smooth-to-rough transition as the growth temperature is varied near the critical temperature, T_c. At temperatures below T_c, the growth will take place with the formation of islands, and atomic concentration in those islands will be given by location multiple minima in a free energy as a function of x curve. At temperatures well below T_c, the minima are expected near $x = 0$ and $x = 1$, where x is surface coverage. In these cases, islands formed on the surface are nearly fully occupied and the reminder of the area is nearly empty. As the surface coverage is increased, the islands grow in size with a fixed vacancy concentration until the layer is fully grown.

From Table 2 we conclude that silicon, HgTe, and most GaAs surfaces will exhibit spinodal decomposition between surface atoms and vacancies, while most of the CdTe surfaces and the singly bonded gallium-terminated (111) surface will undergo an order-disorder transition. The actual nature of a surface during growth will be determined by the growth temperature with respect to the critical temperature. We are currently calculating the critical temperature for the various order-disorder transitions.

Table 2

IN-PLANE PAIR INTERACTION ENERGIES AND TRANSITION TEMPERATURES

	Removed	Si		GaAs		CdTe		HgTe	
Orientation	Atoms	ε_0	TcK	ε_0	TcK	ε_0	TcK	ε_0	TcK
(111)	a(1)	0.35	3700	0.25	2600	0.05	500	0.33	3500
	c(3)	0.37	3900	0.02	200	−0.35	1400*	0.23	2400
(111)	a(3)	0.37	3900	0.07	700	−0.52	2100*	0	0
	c(1)	0.35	3700	−0.10	410	−0.15	600*	0.08	900
(100)	a(2)	0.48	3200	0.33	2200	−0.60	4000*	0.18	1200
	c(2)	0.48	3200	0.25	1700	−0.50	3300*	0.30	2200

Because the (100) surface is a square lattice, exact value of 0.57 e_0/k_B given by Onsagar (1944) is used to obtain T_c. k_B is the Boltzmann constant. For the hexagonal lattice, observed in (111) orientation, the exact value of T_c is 0.91 e_0/k_B (Baxter, 1982). The calculated T_c are given in Table 2 for Si, HgTe and most GaAs surfaces. Note that the T_c is much larger than the typical growth temperature for these elements and compounds (except for $(\overline{111})$ Te terminated HgTe surface) ALE growth of these materials is dominated by formation of nearly perfect islands.

When the interaction between surface atoms is repulsive, as in a Ga-terminated $(\overline{111})$ GaAs surface and all CdTe surfaces, the free energy always remains negative with one minimum. However, these surfaces undergo a different kind of phase transition known as order-disorder transition. At temperatures above the critical temperature, T^*_c, the surface is disordered, and sites will be occupied randomly by atoms and vacancies. At temperatures below T^*_c, the atoms and vacancies on the surface will arrange themselves in domains of ordered patterns to minimize the number of atom-atom pairs. The nature of the superlattice arrangements and area of these domains depend on the growth temperature and surface coverage. For example, at temperatures well below T^*_c for a square lattice of 50 percent coverage, the superlattice pattern will look like a checker board, where every near-neighbor site of atom (vacancy) is occupied by vacancies (atoms). This type of arrangement can be envisioned for a mono-layer growth in (100) orientation. T^*_c calculated using Onsagar's result for (100) surfaces and using an exact value of

0.35 e_0/k_B (Schick et al., 1977) for (111) orientations are given in Table 2. We see that the calculated temperatures are well above the typical ALE or MBE growth temperatures for these compounds (except for $(\overline{111})$ Ga terminated GaAs surface). Hence the partially filled growth surface is expected to exhibit superlattice arrangements with atoms and vacancies.

6. Conclusions

We have calculated intralayer and interlayer atom-atom pair interaction energies using a tight-binding Green's function method. These energies are then used in a thermodynamic model to study the nature of growth surfaces. As the growth temperature is varied, attractive interaction between surface atoms leads to smooth-to-rough transition, and Si, HgTe, and most GaAs surfaces are calculated to fall in this category, and the repulsive interactions lead to superlattice ordered-to-disordered transition, and $(\overline{111})$ GaAs and most CdTe surfaces are expected to be into this category. Smooth or rough surface growth is found to be decided by in-plane interactions in an ALE growth and by interplane interactions in double-layer MBE growth. In our calculations of pair energies, we considered only ideal surfaces. The critical temperatures and other conclusions in this paper, can, at best, be expected to represent the trends. Nonidealities such as reconstruction, dimerization, relaxation of adatoms and surface can lower surface energy substantially. Such effects are currently being included.

III FIRST-PRINCIPLES APPROACH TO THE PLASTIC PROPERTIES OF HIGH-TEMPERATURE ALLOYS

A. INTRODUCTION

In brief, the central objective of new aspects of the contract F49620-88-K-0009 was to apply non-self-consistent total energy methods to problems of plastic flow and stability of intermetallic compounds: in particular, those which are promising candidates for high-temperature applications requiring a large strength-to-weight ratio. Under the general headings of development and applications, we have in this initial year of the project, gained a very good understanding of the nature of the non-self-consistent Harris-Foulkes approximation, and made a comprehensive application to static structural and deformation properties of pure metals. This work is outlined in the following three sections, each accompanied by an article either published or submitted. The deformation property we have concentrated on is the ideal twin-strength of the metal—the reason for this is given in Section D. In the final section, we show our most recent results for calculations of ideal twin-stresses in binary alloys.

A significant proportion of our time is spent in program development and testing. We say little of this here, however, concentrating on those results that have advanced our understanding of the topics under research.

B. STRUCTURAL ENERGY-VOLUME RELATIONS IN FIRST-ROW TRANSITION METALS

This is work that was done mostly while the first author (AJP) was in the Max-Planck Institute at Stuttgart. The analysis of the results, and the writing of the paper, however, were done at SRI International. The motivation for this study is explained in the first paragraph of the attached reprint from *Physical Review*. We take the view that for many calculations, especially atomistic simulations, it will be necessary to abandon the accurate first-principles approach and resort to classical or semi-empirical approaches such as a tight-binding approximation. As outlined in our proposal, we will be making some tight-binding calculations, but only after we have convinced ourselves that this is a valid approximation. The paper is therefore important firstly as a guide to users of entirely *ad hoc* classical approaches such as the embedded atom method; and secondly, it is useful to us in that it represents a step toward the validation of the canonical tight-binding model for transition metals beyond the usual assumption of close-packing in the crystal. Furthermore the conclusions of the paper lead to a direct method for deducing the parameters of a transferable tight-binding model. We are still very skeptical of entirely empirical potentials, especially when applied to alloys. However, it is clear that they do and will play an important role in atomistic simulation. Our investigation of the Rose equation of state does not convince us that there is a universal relation that can be used to determine classical potentials. Therefore while our work will be of use in constructing and testing potentials for pure metals, we do not intend to pursue this approach. Any empirical methods we use will be based on the tight-binding approximation. Our work in this direction is encouraged by the results of this paper.

From the point of view of the present work, perhaps the most important conclusion here is the excellence of the Harris-Foulkes approximation in calculating structural properties of transition metals. This gives us confidence that we are pursuing a correct approach. This work is, of course, limited to pure metals. More work will be needed if we are to make a tight-binding model for alloys that we can have confidence in. As far as the validity of the Harris-Foulkes approximation applied to alloys goes, this is the subject of the following section.

C. RECENT ADVANCES IN NON SELF-CONSISTENT TOTAL ENERGY CALCULATIONS IN ALLOYS

This is the title of our presentation to the Spring 1990 MRS symposium *Alloy Phase Stability and Design*. The attached preprint will appear in the published proceedings. These are our first calculations of properties of high-temperature intermetallic alloys, and we concentrate on calculating the very small structural energy differences between the polytypic phases hexagonal DO_{19} and cubic $L1_2$, and the related tetragonal phase DO_{22}. The compositions we have studied are Ni_3Al and Ti_3Al. We also calculate the heats of mixing. While the calculations are directly useful and relevant for the construction of binary alloy phase diagrams, our prime motivation was to gain a better understanding of the non-self-consistent approach that we are adopting (*viz.*, the Harris-Foulkes approximation) and that is also inherent in the tight-binding approximation. We also compare calculations that introduce a shape approximation into the total energy functional, with the full-potential method. A secondary conclusion is that methods which make such an approximation, (e.g., LMTO-ASA or KKR) are likely to be unreliable in phase diagram studies. We also make two important statements in our conclusions.

1. It was not necessary to make our total energy calculations self consistent.
2. The dominating contribution to total energy differences arises from the bandstructure energy. This is precisely the result that would obtained from a tight-binding analysis.

Again, we confirm that we are right in choosing the full-potential but non-self-consistent approach we originally proposed. We also show that we can very accurately calculate structural energy differences in intermetallic alloys and properly reproduce trends in heats of mixing.

D. A QUANTUM MECHANICAL CALCULATION OF THE THEORETICAL STRENGTH OF METALS

The attached preprint with this title is a rewritten version of the paper originally submitted and rejected by *Physical Review Letters*. In the present form, it has been submitted to *Philosophical Magazine Letters*. This work was motivated by the observation by Kohlhoff, Gumbsch and Fischmeister (1990) of the emission of dislocations and twins at crack tips in atomistic simulations. Therefore, it became interesting to know what was the stress needed to nucleate a mechanical twin homogeneously. Following recent work by Yoo and Lee (1990), it has become less clear that our calculated stress indeed represents a nucleation stress, although it must have a bearing on the growth of twins. In fact our work relates most closely to the classical concept of "theoretical strength," and when analyzed in this light our results lead to a confirmation of the very simple Frenkel model. We also show that later modifications of this model—usually attributed to Mackenzie (Cottrell 1953)—are incorrect.

Our other main conclusions from this work are that the theoretical strength of bcc and fcc metals seems to be invariably between 12 and 17 percent of the shear modulus; and that there is a clear separation of the group V and VI transition metals reflected in their plastic behavior. This has been known experimentally, but no theoretical explanation until now has been offered, to our knowledge, in the literature.

E. TWINNING AND PSEUDO-TWINNING IN B2 ALLOYS

We present here, for the first time, results of our most recent work: an extension of the twinning calculations from pure metals to B2 alloys. We have chosen, for a preliminary study of plasticity in intermetallic alloys, to make the most natural extension from the calculations of twinning in bcc metals to twinning in B2 alloys. These are alloys with the CsCl structure, namely a bcc lattice in which each corner atom is occupied by one type and each body-centering position by another type of atom. It has been known for many years (e.g., Christian and Laughlin, 1988) that the usual bcc twinning mode is suppressed by the bcc →B2 ordering reaction. The reason for this is illustrated in Figure 1(a) which shows the effect of operating with a bcc twinning mode on the B2 lattice. It is easily seen that the resulting structure is no longer B2, but a differently ordered structure, illustrated in Figure 2(b). This is an orthorhombic structure we shall denote "o-phase", having space group Cmmm(D_{2h}^{19}). It is not, to our knowledge, the structure of any phase listed in the Structure Reports. Goo et al., (1985) have identified the structure, but incorrectly describe it as tetragonal. It can be seen from Figure 2 that while in the B_2 phase, all atoms have first neighbors of opposite type, in the "o-phase", each atom has equal numbers of like and unlike neighbors. One might imagine, therefore, that the relative stability of the "o-phase" with respect to B2 would relate roughly to the ordering tendency of the bcc phase. To be specific, we have made calculations of the stability of the "o-phase" in CuZn, NiAl and NiTi. These alloys have been chosen because they represent three distinct types of behavior. CuZn is disordered above about 460°C and undergoes a second order bcc →B2 phase transformation below that temperature. NiAl is stable in B2 right up to the congruent melting temperature, 1636°C—the highest melting point in the Al-Ni phase diagram. It is therefore expected to show a much greater stability of B2 with respect to "o-phase" than CuZn. NiTi is also stable in B2 to the congruent melting temperature (lower than the melting temperatures of both Ni and Ti) but in equilibrium undergoes a eutectoidal decomposition at an unknown temperature close to 600°C. NiTi also shows a number of martensitic reactions upon quenching below the eutectoid; these are well known, and exploited in the shape memory phenomenon. Thus while NiTi, like NiAl, shows a pronounced ordering tendency, it is not thermodynamically stable below about 600°C. For these three compositions, we have calculated the two elastic shear constants, $C = c_{44}$ and $C' = \frac{1}{2}(c_{11} - c_{12})$; and the energy differences between B2 and the "o-phase". The results are shown in Table 3.

We immediately see that the ΔE values reflect the stability of the B2 phase deduced above from the phase diagrams. The mechanical stability of these phases is quite curious. In general, the bcc structure is unusual in that a crystal of hard spheres would be unstable in the bcc

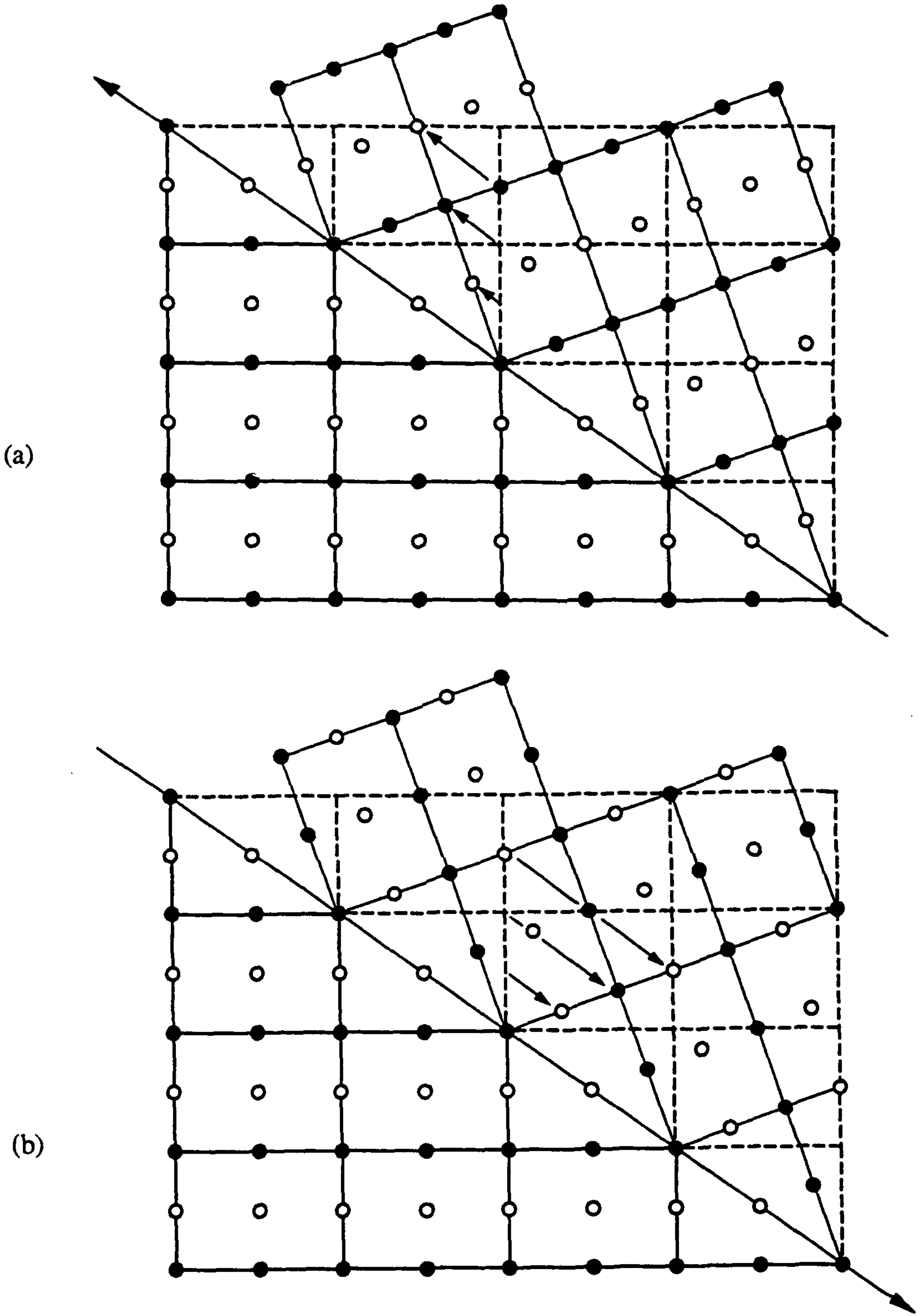

Figure 1. Atomic movements in the twinning of B2 alloys,
(a) Pseudo-twinning, (b) Anti-twinning.

It is seen that, while the usual bcc twinning mode (a) does not correctly restore the B2 structure, the anti-twinning operation does, and it is therefore a true twinning mode of the B2 lattice. (See Christian and Laughlin 1988)

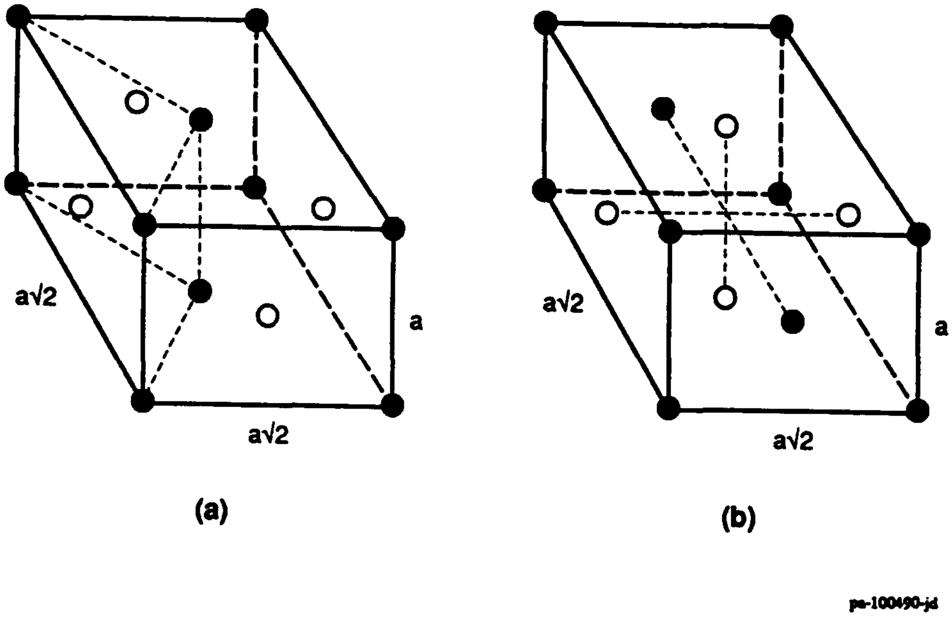

Figure 2. Structure of B2 and the "o-phase". (a) B2 in a setting to show the relationship with (b) the "o-phase".

Table 3

CALCULATED ELASTIC SHEAR CONSTANTS OF THREE B2 ALLOYS AND THE ENERGY DIFFERENCE ΔE BETWEEN THE B2 AND "O-PHASES"

Experimental values of C and C' in parentheses are taken from McManus (1963) and Wasilewski (1966).

	C (GPa)	C' (GPa)	ΔE meV/atom	ΔE kJ/g-atom
CuZn	79	~0	44	4.3
	(83)	(15)		
NiAl	116	36	422	41
	(112)	(35)		
NiTi	230	−37	251	23

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structure with respect to a shear along a $\langle\bar{1}10\rangle$ direction in a $\{110\}$ plane. This instability is manifested in a non positive C' elastic constant. The same is true of a crystal bound together under central forces extending only to first neighbors. The stabilizing influence in the case of a small but non vanishing C' can come from a large entropy gain due to a high density of states of zone-center T_1 phonons associated with the soft elastic constant. This effect is only important at elevated temperatures, while our calculations are implicitly made at 0°K. Therefore, in considering a metal or alloy based on the bcc structure, one must ask the question, "why is it stable in this phase at low temperature?". The answer to this question in the case of the bcc transition metals has been given by Friedel (1968), and is a consequence of the half filling of the d-band. [See Zener (1947) for a discussion of bcc alkali metals.] In alloys, a further stabilizing influence may be the binding due to electrostatic forces, if the atoms have exchanged electrons in bonding. In the light of this, let us discuss the three compounds in turn.

In CuZn, we have correctly calculated C compared with a measurement at 4°K by McManus (1963). Based on earlier measurements of C' Zener (1947) speculated that CuZn showed a temperature anomaly: C' decreasing with decreasing temperature, in accord with the remarks made in the previous paragraph. However, McManus showed that in stoichiometric CuZn C' changes not at all with temperature at low temperatures down to 4°K. On the other hand, we find the B2 CuZn phase to be unstable since $C' \approx 0$. It is actually hard to see why perfectly ordered CuZn *should* be stable at 0°K, since both Cu and Zn are unstable in the bcc phase and there is unlikely to be a large ionic contribution to the bonding. It is very possible that the specimens used by McManus were not perfectly ordered. Certainly C' is known to be very sensitive to stoichiometry. We propose to make further calculations to determine the zero-temperature structure of CuZn.

NiAl is most likely to be stabilized by ionic bonding. We find very good agreement between our calculated and Wasilewski's (1966) measurements at room temperature. This author estimated that the values would increase by no more than 5 percent between room temperature and 0°K. This is to be expected first from the high melting point, and second from the rather flat or anomalous temperature dependence (especially of C') in the B2 alloys. Incidentally, this is a very encouraging result, since until now it has been supposed that only very expensive, self-consistent LAPW calculations (Fu and Yoo, 1989) are sufficiently accurate to calculate elastic constants in alloys. With our non-self-consistent LMTO method, we are able to obtain similar precision using a fraction of the computer time.

It is not surprising that NiTi is unstable in the B2 phase. Crudely, one can imagine the alloy as a virtual d-band transition metal with a bandfilling corresponding to the hexagonal Group VII metals. We find no inclination to develop a magnetic moment: unlike δ-Mn there is no stable antiferromagnetic state in B2 NiTi. The instability of B2 NiTi is clearly seen in the large and negative value of C'. However, there are other reasons for the instability of NiTi, namely nesting of the Fermi surface about two thirds of the way along the Λ direction in the Brillouin zone (Egorushkin and Kulkova 1982). It is this that gives rise to the observed pre-martensitic phenomena, not the inherent instability of the B2 phase discussed above.

We now turn to the question of twinning in the B2 alloys. Strictly, this is now a martensitic transformation since the structure is not restored. It is usual to reserve the name "pseudo-twinning" for twinning that becomes martensitic upon an ordering reaction. It can be seen in

Figure 1(b), that the bcc anti-twinning mode is a true twinning mode also of the B2 structure. (For convenience we refer now to pseudo-twinning and anti-twinning although the latter is simply a different mode having the same composition plane but otherwise different elements.) As in the preprint attached to Section C, we can now compute the one-dimensional energy surfaces for anti-twinning and pseudo-twinning, and determine the critical parameters x_{crit}, the critical strain; and τ, the critical stress. In Figure 3, we show the energy curves. Note that the pseudo-twinning branch is not symmetric about $\frac{1}{2}s_{tw}$ and that $W(s_{tw}) - W^0 = \Delta E$. In Table 4, we show the numerical values of the critical parameters and the shear constant $\mu_t = \frac{1}{3}(C + 2C')$ taken from the calculated values given in Table 3.

Table 4

Calculated critical parameters for pseudo-twinning and anti-twinning in B2 alloys

	μ_t (GPa)	$\frac{x_{crit}}{s_{tw}}$	$\frac{\tau_{tw}}{\mu_t}$	$\frac{\tau_{atw}}{\tau_{tw}}$
CuZn	26	0.23	0.12	2.61
NiAl	63	0.37	0.32	1.15
NiTi	157	0.33	0.06	1.05

Again, we will discuss the three compositions separately.

CuZn conforms to the model propounded by us in relation to the pure metals: namely, the pseudo-twin stress is 12 percent of the shear modulus and the anti-twin stress is some 2-3 times greater. It seems likely that β-brass could deform by psuedo-twinning at very low temperatures just as Cu deforms by twinning close to 0°K. As far as we know, however, there have been no observations of twins in β-brass.

NiAl has a surprisingly large twin stress which is only 15 percent smaller than the anti-twin stress. Figure 3 also indicates that the "o-phase" is unstable since the curve shows no minimum at $x = s_{tw}$. Therefore pseudo-twinning is not expected to occur in NiAl; and considering the high anti-twin stress, neither is anti-twinning. It is known, indeed, that NiAl deforms exclusively by slip.

The NiTi results must be treated cautiously, since we are dealing with a crystal which is inherently mechanically unstable in our 0°K calculations. However, NiTi crystals can be deformed in between the eutectoid and martensite start temperatures, and in doing so Goo et al., (1985) have observed copious deformation twinning to occur. Twins observed on {112} habit planes were speculated by Goo et al., to be pseudo-twins, since they were unable to detect superlattice reflections from the twinned regions. They also were puzzled by the observation that the habit planes observed were not the same as the pseudo-twin composition planes although they were of the same crystallographic type. The pseudo-twinning curve for NiTi in Figure 3 shows a

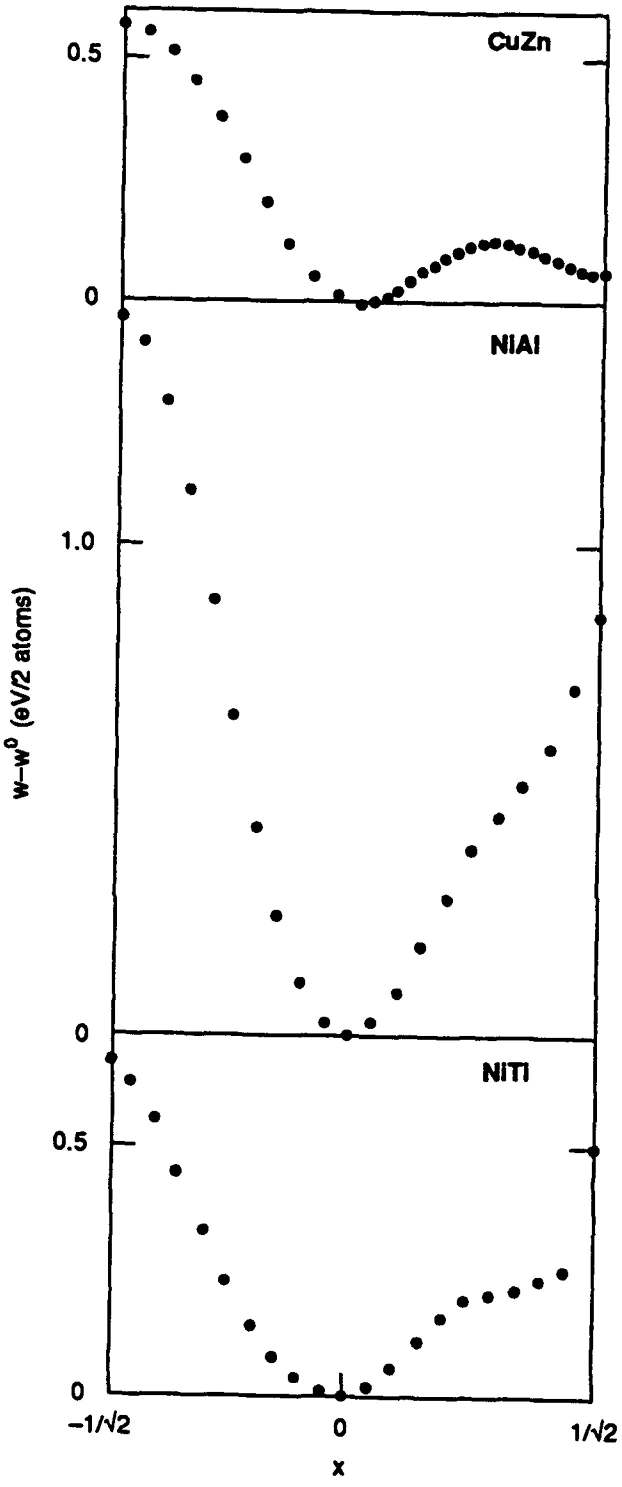

Figure 3. Energy-shear curves for pseudo-twinning and anti-twinning in three B2 alloys.

very rapid energy rise approaching the "o-phase", while the stress to initiate the deformation is rather small—smaller indeed than any of the pure metals. Moreover, the anti-twin stress is only 5 percent larger than this. Our calculations indicate the following conclusions.

1. The possibility of anti-twinning is quite high because of the instability of the "o-phase".
2. Since the "o-phase" is unstable, we reject the possibility that this is the phase observed by Goo et al.
3. Suppose the B2 crystal deformed by pseudo-twinning as far as the saddle-point shown in Figure 3. If the resulting (unstable) structure sheared by internal twinning, say, then the final phase could be a stable structure—B2 even—which would explain the discrepancy between the observed habit plane and the composition plane of the pseudo-twins.

Of course these conclusions are only tentative. Until we have explored more of the energy surface it is only possible to speculate. However, in doing so we can illustrate the value of total energy calculations in helping to interpret available experimental data.

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APPENDIX

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