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Theoretical study of titanium surfaces and defects with a new many-body potential

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ABSTRACT

It is shown that any force model using short-range pair-functional interactions can only have three independent h.c.p. elastic constants. Empirical data show that these elastic properties are nearly realized in a number of materials. A new parametrization of a Finnis-Sinclair-type many-body potential for titanium is presented using these relations. Particular care is taken to describe the anisotropy of the shear constants and the deviation of the c/a lattice parameter ratio from ideal, while maintaining smooth monotonic functions. Energies, stresses and reconstruction modes of various low-index surfaces are calculated and general rules for surface stability are proposed. Various stacking faults on the basal and pyramidal plane are investigated.

§1. INTRODUCTION

The success of many-body empirical potentials, in their many variants, in describing surface structures and reconstructions has been the most significant factor in the renewed interest in these methods (Daw and Baskes 1984, Finnis and Sinclair 1984, Ercolessi, Tossati and Parrinello 1986, 1988, Stott and Zaremba 1980, Norskov and Lang 1981, Chen, Voter and Srolovitz 1986). The underlying physics of these methods lie in their ability to include the energetic consequences of the band theory without explicitly calculating the details of the band shape (Ackland, Finnis and Vitek 1988). Consequently they are particularly useful for describing situations in which there are large changes in atomic coordination, but less good for predicting phase transformations. Moreover, they permit anisotropic elastic effects unconstrained by the Cauchy relations which bedevil pair potentials.

Application of many-body potentials to h.c.p. metals appears to be an obvious step to take. The metallurgical interest of basal as opposed to prism plane slip and the nature of the associated dislocations should be accessible to a model capable of correctly describing the five independent elastic constants and the non-ideal c/a lattice parameter ratio. Moreover, there has been renewed interest in reconstructions of the prismatic plane surfaces.

One difficulty in the parametrization of a many-body model is the large number of structural parameters which should be fitted to describe the lattice anisotropy; there are two lattice constants (and not one as in cubic metals), five elastic constants (and not three) and two equilibrium stresses (and not one) to consider. Moreover, in a pair-functional approach, differentiating between f.c.c. and h.c.p. structures requires considering interactions out to $3^{1/2}$ times the nearest-neighbour distance.

Early h.c.p. models ignored these complexities (for a review of work with pair potentials, see Bacon (1988)). Using short-ranged second-neighbour potentials it is possible to make the f.c.c. and h.c.p. structures equal in energy and to set the c/a ratio to its ideal value of 1.633. These potentials were intended for simple demonstration

purposes only and fulfil this role admirably; however, for many purposes their inadequacies are unacceptable. Equality of h.c.p. and f.c.c. energies leads to a zero basal stacking-fault energy and the infinite dissociation of dislocations. The large discrepancies in c/a ratio from ideal and elastic constants from isotropic will affect favoured interstitial sites, dislocation structure and splitting, and surface reconstructions. In various metals the c/a ratio varies from 1.856 (Zn) to 1.568 (Be) (Pearson 1967). These same two materials show the extreme values of the anisotropy ratio C_{44}/C_{66} between pure shear constants at 0.649 (Zn) and 1.222 (Be). Ti has more modest deviations with a c/a of 1.588 and anisotropy ratio of 1.128.

Dislocation splitting in Ti is rarely observed, which suggests that the stacking-fault energy is rather large, in accordance with previous tight-binding calculations (Legrand 1984). This is very difficult to account for within a short-range pair-functional approach such as the present, because the first departure from bulk value of the radial distribution about an atom near to the stacking fault occurs at $(8/3)^{1/2}$ times the near-neighbour spacing.

Recently, a concerted effort at parametrizing stable h.c.p. potentials (Igarashi, Khantha and Vitek 1991) with exact fits to cohesive energy, vacancy formation energy, two lattice parameters and five elastic constants resulted in potentials with an unappealing oscillatory nature. This makes their application to alloy calculations impossible (Kulp, Egami, Vitek and Ackland 1992). They also had very strong repulsion at distances shorter than first neighbours so that interstitial energies are too high, and it has proved impossible to soften the core without destabilizing the h.c.p. structure.

In this paper we adopt a different approach to parametrization; we fitted the potential parameters as if the material were f.c.c with a negative stacking-fault energy. This can be done because the radial distributions of the first 18 neighbours in f.c.c. and h.c.p. structure are identical and the potentials are short short-ranged, encompassing only 12 nearest and six second neighbours in the f.c.c. structure. The range includes two more distant neighbours in the h.c.p. structure (i.e. 20 total) whose additional contribution is weak enough to be treated as a perturbation. This has the consequence of making the fits to the h.c.p. properties inexact, but by reducing the number of fitting parameters we obtain a non-oscillatory form for the potentials. The c/a ratio arises from a fitted net attraction at range c as does the stacking-fault energy. All five elastic constants turn out to be well fitted.

Once the potential has been constructed, the relaxed vacancy and interstitial formation energies are used as a partial check of the validity of the model. Subsequently, we carry out a thorough study of surface energies, stresses and reconstructions. Finally we investigate various stacking-fault energies; these are important in determining the nature of the non-basal slip systems which control ductility in h.c.p. materials.

§2. CONSTRUCTION OF THE POTENTIALS

We use the Finnis–Sinclair (1984) formalism of the second-moment approximation to the tight-binding theory (Ackland *et al.* 1988). Mathematically this turns out to be equivalent to the embedded-atom (Daw and Baskes 1984), effective-medium (Norskov and Lang 1981), local-volume (Voter and Chen 1987) and glue (Ercolessi *et al.* 1988) models which have been successful in metallic modelling. The basic equation for the energy of an atom is

$$E_i = \frac{1}{2} \sum_j V(r_{ij}) - \rho_i^{1/2}, \quad (1)$$

where

$$\rho_i = \sum_j \phi(r_{ij}), \quad (2)$$

where V and ϕ are pairwise functions between atom i and one of the other atoms j a distance r_{ij} away. In the second-moment approximation, V is a short-range potential accounting for ion-ion repulsion as in standard tight-binding approaches while ϕ is interpreted as the square of the hopping integral and accounts for the valence band cohesion, ϕ can be thought of as an effective coordination; the scaling of energy with the square root of the coordination has recently been demonstrated by *ab-initio* calculations (Robertson and Heine 1992).

The implicit assumption behind all potentials of this nature is that the energy can be expressed in terms of short-range pair functionals with no explicit angular dependence. An implicit angular dependence is included in the near-neighbour potential, corresponding to a 60° angle, in the second-neighbour potential (90°) and so forth. This assumption often has no justification beyond computational convenience, but with the h.c.p. structure it is possible to test because it predicts relations between the elastic constants. Such a test is impossible with cubic structures because the same relations arise from symmetry.

With the Finnis-Sinclair formulation the elastic constants (derived from isotropic strains) can be written analytically in Cartesian coordinates with Z perpendicular to the basal plane as

$$\left. \begin{aligned} \Omega C_{11} &= 2Y_{2xx} - 2\rho_0^{-1/2}\rho_{2xx} + \rho_0^{-3/2}\rho_{1x}^2, \\ \Omega C_{22} &= 2Y_{2yy} - 2\rho_0^{-1/2}\rho_{2yy} + \rho_0^{-3/2}\rho_{1y}^2, \\ \Omega C_{33} &= 2Y_{2zz} - 2\rho_0^{-1/2}\rho_{2zz} + \rho_0^{-3/2}\rho_{1z}^2, \\ \Omega C_{12} &= 2Y_{2xy} - 2\rho_0^{-1/2}\rho_{2xy} + \rho_0^{-3/2}\rho_{1x}\rho_{1y}, \\ \Omega C_{23} &= 2Y_{2yz} - 2\rho_0^{-1/2}\rho_{2yz} + \rho_0^{-3/2}\rho_{1z}\rho_{1y}, \\ \Omega C_{13} &= 2Y_{2zx} + \rho_0^{-1/2}\rho_{1z}\rho_{1x}, \\ \Omega C_{44} &= 2Y_{2yz} - 2\rho_0^{-1/2}\rho_{2yz}, \\ \Omega C_{55} &= 2Y_{2zx} - 2\rho_0^{-1/2}\rho_{2zx}, \\ \Omega C_{66} &= 2Y_{2xy} - 2\rho_0^{-1/2}\rho_{2xy}, \end{aligned} \right\} \quad (3)$$

where Ω is the atomic volume,

$$\left. \begin{aligned} \rho_0 &= \sum_j \phi(r_{ij}^2), \\ \rho_{1x} &= \sum_j \phi'(r_{ij}^2)x_j^2, \\ \rho_{1y} &= \sum_j \phi'(r_{ij}^2)y_j^2, \\ \rho_{1z} &= \sum_j \phi'(r_{ij}^2)z_j^2, \\ \rho_{2xx} &= \sum_j \phi''(r_{ij}^2)x_j^4, \end{aligned} \right\} \quad (4)$$

$$\left. \begin{aligned} \rho_{2yy} &= \sum_j \phi''(r_{ij}^2) y_j^4, \\ \rho_{2zz} &= \sum_j \phi''(r_{ij}^2) z_j^4, \\ \rho_{2xy} &= \sum_j \phi''(r_{ij}^2) x_j^2 y_j^2, \\ \rho_{2yz} &= \sum_j \phi''(r_{ij}^2) y_j^2 z_j^2, \\ \rho_{2zx} &= \sum_j \phi''(r_{ij}^2) z_j^2 x_j^2, \end{aligned} \right\}$$

and

$$\left. \begin{aligned} Y_0 &= \sum_j V(r_{ij}^2), \\ Y_{1x} &= \sum_j V'(r_{ij}^2) x_j^2, \\ Y_{1y} &= \sum_j V'(r_{ij}^2) y_j^2, \\ Y_{1z} &= \sum_j V'(r_{ij}^2) z_j^2, \\ Y_{2xx} &= \sum_j V''(r_{ij}^2) x_j^4, \\ Y_{2yy} &= \sum_j V''(r_{ij}^2) y_j^4, \\ Y_{2zz} &= \sum_j V''(r_{ij}^2) z_j^4, \\ Y_{2xy} &= \sum_j V''(r_{ij}^2) x_j^2 y_j^2, \\ Y_{2yz} &= \sum_j V''(r_{ij}^2) y_j^2 z_j^2, \\ Y_{2zx} &= \sum_j V''(r_{ij}^2) z_j^2 x_j^2. \end{aligned} \right\} \quad (5)$$

V and ϕ have been written as functions of r_{ij}^2 to simplify the form of these equations.

From symmetry considerations, there are five independent elastic constants in h.c.p. metals. The nine above are reduced because the two coordinates in the basal plane (x and y) are equivalent; whence $C_{11} = C_{22}$, $C_{13} = C_{23}$, $C_{44} = C_{55}$. Furthermore, because of the hexagonal symmetry we find that

$$\sum_j x_j^4 = 3 \sum_j x_j^2 y_j^2,$$

which leads to the equality $2C_{66} = C_{11} - C_{12}$.

If we assume that the only interactions are between first and second neighbours, and that we have an ideal c/a ratio of $(8/3)^{1/2}$, then there are only three independent

elastic constants (analogous to f.c.c.). This arises from the following summations over h.c.p. near-neighbour shells.

Summing over the first 12 neighbours with the nearest-neighbour distance normalized to unity gives

$$\begin{aligned}\sum x^2 &= \sum y^2 = \sum z^2 = 4, \\ \sum x^4 &= \sum y^4 = \frac{5}{2}, \\ \sum z^4 &= \frac{8}{3}, \\ \sum x^2 y^2 &= \frac{5}{6}, \\ \sum x^2 z^2 &= \sum y^2 z^2 = \frac{2}{3}.\end{aligned}\tag{6}$$

The equivalent sums over the next six neighbours are

$$\begin{aligned}\sum x^2 &= \sum y^2 = \sum z^2 = 4, \\ \sum x^4 &= \sum y^4 = 4, \\ \sum z^4 &= \frac{8}{3}, \\ \sum x^2 y^2 &= \frac{4}{3}, \\ \sum x^2 z^2 &= \sum y^2 z^2 = \frac{2}{3}.\end{aligned}\tag{7}$$

In each case we note that

$$\sum x^2 = \sum y^2 = \sum z^2,\tag{8}$$

$$\sum z^4 + \sum y^2 z^2 = \sum x^4 + \sum x^2 y^2.\tag{9}$$

These two additional relations lead to the elastic constant equalities

$$C_{33} + C_{13} = C_{11} + C_{12},\tag{10}$$

$$C_{12} + C_{44} = C_{13} + C_{66}.\tag{11}$$

These are not related to the hexagonal symmetry; for the third shell of neighbours, $x_j = y_j = 0$, which contradict the above, nor are they equivalent to the Cauchy relations which apply to simple pairwise potentials of any range.

In the parametrization we shall assume these relations. Notwithstanding them, we extend the interaction to third neighbours; This will break these constraints and cause a non-ideal c/a ratio. The underlying assumption is that third-neighbour interaction is just a small perturbation. As we shall see, this assumption is reasonable.

The two constraints imposed on the h.c.p. elastic constants by the short-range approximation can be expressed as ratios as follows:

$$\frac{C_{33} + C_{13}}{C_{11} + C_{12}} = 1,\tag{12}$$

$$\frac{C_{12} + C_{44}}{C_{13} + C_{66}} = 1.\tag{13}$$

Values for these ratios for a variety of h.c.p. metals are given in table 1. The relations are well satisfied in most transition metals (cobalt, which has additional magnetic effects, being an exception) while being significantly violated in Cd, Zn and Be. This suggests a fundamental difference in the binding of the two groups; in particular it is clear that the

Table 1. Experimental ratios of elastic constants suggested by short-range pair-functional formalism: eqns. (13) and (14). Data from Simmons and Wang (1971).

	$\frac{C_{11} + C_{12}}{C_{33} + C_{13}}$	$\frac{C_{13} + C_{66}}{C_{12} + C_{44}}$
Zn	1.744	1.512
Mg	1.014	0.913
Co	1.021	0.720
Zr	1.006	0.909
Ti	1.016	0.823
Hf	0.980	0.917
Ru	0.945	0.962
Be	0.926	0.758

second group are unsuitable for modelling using short-ranged pair functionals. This is probably due to the p-like nature of the electrons at the Fermi level which introduces a strong directional dependence.

The relations do not include the effects of the inner elastic constants (Martin 1975) which arise because of the diatomic basis of the h.c.p. lattice. In § 3 these are shown to be of similar size to the perturbations arising from third neighbours and relaxation of c/a ; consequently neglecting them is fully consistent with our perturbation approach.

Hence a fitting strategy is determined. We shall fit to an ideal f.c.c. structure. We shall use the three independent (pair-functional short-range) elastic constants, one lattice parameter, the binding energy, vacancy formation energy (taken as 1.4 eV) and finally the stacking-fault energy (which will be negative). The vacancy formation energy allows us to incorporate the effect of undercoordination. The stacking fault will relate to the f.c.c. – h.c.p. energy difference. On applying the parameters to a h.c.p. structure we must recalculate all the properties. Unless they remain comparable with the fitted values, the perturbation assumption will be invalid. Fortunately, they do.

The 'cubic' elastic constants C_{11} , C_{12} and C_{44} to which we fit are simple averages of the appropriate h.c.p. constants $(2C_{11} + C_{33})/3$, $(2C_{13} + C_{12})/3$ and $(2C_{44} + C_{66})/3$. The single-crystal data was obtained from the compilation of Simmons and Wang (1971). Elastic constants for h.c.p. materials are difficult to calculate analytically because the structure has a diatomic basis and therefore contributions from 'inner' elastic constants (inhomogeneous strain). We describe the calculation of these in the next section.

The c/a ratio after relaxation is 1.592, slightly larger than the experimental value of 1.588 but much less than the ideal value of 1.633.

In common with previous workers, we parametrize the functions using a small number of cubic splines to guarantee continuity of the functions and their first and second derivatives (Ackland, Tichy, Vitek and Finnis 1987, Igarashi *et al.* 1991). This choice is purely arbitrary, and other workers have achieved satisfactory results with other functions. It is worth noting that the extrapolation of a cubic spline seldom gives a core hard enough at very close approach distances (Ackland and Thetford 1987, Rebonato, Welch, Hatcher and Billelo 1987, Foreman, Phythian and English 1991a, b). This is only a problem when dealing with atoms having kinetic energies of several electronvolts, such as the primary knock-on atom in a radiation damage cascade, and is well outside the range of problems considered here.

$$V(r) = \sum_{k=1} a_k (r_k - r)^3 H(r_k - r) \quad (14)$$

Table 2. Potential parameters and spline points (eqns. (15) and (16)) or the fitted lattice parameter (4.173061 Å deduced from the h.c.p. nearest-neighbour distance).

K Ω	A_k (eV)	B_k (Å)	a_k (eV)	r_k (Å)
1	39.795927	1.22	-57.099097	1.22
2	-40.061305	1.05	+80.735598	1.20
3			-21.761468	1.12
4			-10.396479	0.95
5			74.515028	0.80
6			35.921024	0.707107

and

$$\phi(r) = \sum_{k=1} A_k (R_k - r)^3 H(R_k - r), \quad (15)$$

where

$$H(x) = \begin{cases} 1, & \text{for } x > 0, \\ 0, & \text{for } x < 0. \end{cases}$$

The parameters a_k , r_k , A_k and R_k are given in table 2.

The reduction in the number of fitting parameters and the removal of explicit fitting to features dominated by neighbours beyond the first 18 makes it easy to fit suitable non-oscillatory functions for V and ϕ . Non-oscillatory positive functions ϕ are essential if the potentials are to be generalized for use in alloys because the overlap ϕ between different species is just the geometric mean of the elemental values (Ackland and Vitek 1990, Kulp *et al.* 1992); if one ϕ is negative, then the cohesive term could become imaginary! Occasionally, fits produce wildly oscillatory functions in which the oscillations in V and ϕ compensate to be reasonable at the neighbour spacings where the function is defined by the fit. This type of behaviour shows that the interpolation scheme is unphysical.

§ 3. ELASTIC CONSTANTS

Although the elastic constants were part of the fitting procedure, the parametrization was done using the approximations of short range, ideal c/a and no contribution from the 'inner elastic constants' (Martin 1975). All these approximations turn out to introduce small errors, and the actual elastic constants predicted by the model were evaluated by applying small strains to a molecular static block. This procedure automatically accounts for the internal elastic constants. Adding a PV term to the molecular statics energy enables calculation of the hydrostatic bulk modulus $K = -VdP/dV$ which in the h.c.p. case results in anisotropic strains. The calculated values of the elastic constants are then

$$C_{11} = 1.1235 \text{ eV } \text{\AA}^{-3} (1.0992 \text{ eV } \text{\AA}^{-3}),$$

$$C_{33} = 1.3547 \text{ eV } \text{\AA}^{-3} (1.1891 \text{ eV } \text{\AA}^{-3}),$$

$$C_{44} = 0.3208 \text{ eV } \text{\AA}^{-3} (0.3171 \text{ eV } \text{\AA}^{-3}),$$

$$C_{66} = 0.2899 \text{ eV } \text{\AA}^{-3} (0.2812 \text{ eV } \text{\AA}^{-3}),$$

$$C_{12} = 0.5452 \text{ eV } \text{\AA}^{-3} (0.5424 \text{ eV } \text{\AA}^{-3}),$$

$$C_{13} = 0.4782 \text{ eV } \text{\AA}^{-3} (0.4263 \text{ eV } \text{\AA}^{-3}).$$

The values in parentheses are the single-crystal experimental data obtained by Simmons and Wang (1971). The bulk modulus was found to be 11.7 Pa with the strain along z only about 80% of that in the basal plane. This suggests that, as the pressure increases, the c/a ratio moves towards ideal, in accordance with experiment.

The excellent agreement is actually better than might be expected from the average 'f.c.c.' values which were fitted. It is interesting to note that the difference between the 'fitted' and calculated values (due to allowing the structure to relax to a h.c.p. structure with non-ideal c/a and to including the 'inner' elastic constants) is in the same direction as the discrepancy between the 'short-ranged' approximation and the experimental values. This gives even more confidence that the short-ranged hypothesis is valid.

§4. COMPUTATIONAL METHODOLOGY

The calculations of surface and defect calculations was carried out using the molecular dynamics program MOLDY (Ackland 1987, Finnis 1988). Although results are presented for static relaxation, the program can also be used for molecular dynamics at finite temperature. This latter capability was used to check the stability of each structure by simulated annealing; heating the crystal close to the melting point and then quenching. This breaks any residual symmetry from the initial configuration and allows the system to escape from local minima. Finite-size effects were dealt with by using periodic boundary conditions and performing each relaxation with four different sizes of the simulation block. This ensures that the energy of the block containing the defect is converged with respect to system size. The differences between constant-volume and constant-pressure simulations for the point defects can be accounted for using simple elastic theory (Ackland and Thetford 1987).

The sample block is constrained to remain in a parallelepiped with the free surface (where applicable) being in the x - y plane. In most cases the surface leads to a tetragonal block, but for the pyramidal planes it is necessary to introduce a small monoclinic distortion. This is because there are no pairs of mutually perpendicular lattice vectors perpendicular to $(1\bar{1}01)$ or $(1\bar{1}0\bar{2})$.

Surface calculations were carried out at a fixed length (the volume taken from the ideal lattice parameters) in the x and y planes with free boundaries above the z (surface) plane. It is important to use fixed lengths since the infinitesimal elastic compression of the bulk which balances the surface tensions is absent in a simulation containing only a few layers of bulk materials. Surface stresses were calculated by applying a small strain to the block in the plane of the surface (xy). The z direction still has free boundary conditions. Subsequent atomic relaxation of the surface was permitted and the surface stress was deduced from the change in energy, assumed linear in the strain. There was no evidence of any strain-induced reconstructions.

Stacking faults are calculated with constant-length periodic boundary conditions in the x and y directions, and with constant-pressure boundaries in the z direction. This compensates for the balancing of the grain-boundary tension by the bulk crystal but allows perpendicular expansion of the boundary layer. These constraints are analogous to the surface case.

§ 5. POINT DEFECTS

In addition to the intrinsic importance of the vacancy in diffusion processes and of the interstitial in radiation damage studies, calculation of the energy of these defects is an excellent test of any parametrization. Correct modelling of these defects requires tackling the problems of overcoordination and undercoordination, as well as relaxation and the hardness of the potential core.

The vacancy formation energy has been measured as 1.55 eV (Shestopal 1966) and as 1.27 eV (Hashimoto, Smirnov and Kino 1984). From diffusion data the combined formation and diffusion energy is 2.0 eV (Herzig, Willecke and Vieregge 1991). The present potential gives a value of 1.43 eV for the relaxed configuration. Relaxation of atoms around the vacancy is very small; the neighbouring atoms move towards the vacancy by only a few hundredths of an Ångström. This is in contrast with calculations using pair potentials in which the inward relaxation of the neighbours is much greater. The vacancy formation volume was 0.8 times the atomic volume, a value rather similar to that found in similar calculations with f.c.c. and b.c.c. metals (Harder and Bacon 1986, Ackland and Thetford 1987, Ackland *et al.* 1987).

There have been numerous suggested sites for interstitials, a standard notation being defined by Johnson and Beeler (1981). Different potentials have yielded different results. The dominant effects in determining energies are the core repulsion (which determines how much the surrounding atoms are pushed away) and the elastic constants, which describe how the energy of the strain field around the interstitial is taken up. The present potential gives a good description of all five elastic constants, but the core is a simple extrapolation. Although the atoms approach one another sufficiently closely to be outside the harmonic region, the sampling of the core is still comparable with what one might encounter in a molecular dynamics simulation.

The most stable configuration was found to be the basal crowdion, in contrast with the work of Igarashi *et al.* (1991) and Oh and Johnson (1988) which prefers the pyramidal plane crowdion and in contrast with pair potential calculations (Bacon 1988) which generally prefer the basal octahedral site. Even after relaxation the basal plane containing the interstitial remains flat. This basal crowdion has a simple low-energy one-dimensional migration path along a close-packed direction, with some possibility of being deflected through 60° on to another close-packed line. Thus the migration may be confirmed to one or possibly two dimensions which is a possible cause for the growth of void lattices in radiation-damaged samples. All the between-planes configurations were found to be unstable.

The interstitial has a very small formation volume of only 0.96 times the atomic volume. This is in sharp contrast with the Igarashi *et al.* potential and is due to the softer core repulsion and the low value of C_{66} which Ti exhibits.

It is interesting to compare the h.c.p. and f.c.c. interstitials. In the f.c.c. structure, almost irrespective of the method used for determination, the most stable configuration is the (100) split dumbbell (which has no h.c.p. analogue). In spite of this, the most important migration mechanism for the f.c.c. structure is via the excited (110) crowdion interstitial configuration, analogous to the basal crowdion in the h.c.p. structure. It is probable that the non-ideal c/a ratio is important in stabilising the basal crowdion, since it means that basal 'nearest neighbours' are slightly farther apart than those in adjacent planes. This may also explain why Oh and Johnson (1988) found the interplanar octahedral and pyramidal crowdion configurations to be more stable: their potential has the ideal c/a ratio.

The formation energy of the basal crowdion interstitial was 3.07 eV, well above the thermal energy at melting; so we would expect to find interstitial atoms only in radiation-damaged samples. The other possible sites generally have energies within 0.2 eV, and those in the basal plane are even closer. Consequently we expect to find rapid thermal migration, once the interstitials are formed. It should be noted that, while the absolute value of the interstitial formation energy is very sensitive to the hardness of the potential core, the relative energies depend more on the crystal structure and elastic constants. Hence the large discrepancy between the current value and those obtained with the similar potentials of Igarashi *et al.* (1991) (hard core) and Oh and Johnson (1988) (large C_{66}).

§6. SURFACE RELAXATION AND RECONSTRUCTION

In general, the dominant feature of the surface is the relaxation of the atoms so as to optimize their effective coordination, and in particular an inward relaxation of the upper layer. The close-packed layers tend not to exhibit reconstruction, because this would reduce their coordination, but for less closely packed layers it may be possible for reconstructions to occur which conserve or even increase the effective coordination. A well examined example of this is the 'missing-row' reconstruction of the (110) f.c.c. surface in Au. Here the average coordination is unchanged by the reconstruction, but relaxation of the surface layer stabilizes the reconstructed surface. The energy difference is small; the same reconstruction occurs in Pt and Ir but not in many other f.c.c. metals. The missing-row reconstruction involves a decomposition of the (110) plane into close-packed microfacets. With only one set of close-packed planes (the basal planes) this decomposition is not possible in the h.c.p. structure; the simplest is into basal and pyramidal microfacets.

In the h.c.p. structure there are five significant surfaces to examine: the basal plane, two prismatic planes ($1\bar{1}00$) and $(11\bar{2}0)$ and two pyramidal planes ($1\bar{1}01$) and $(1\bar{1}02)$.

6.1. Basal plane surface

This is the lowest-energy surface. The surface energy found for Ti is 993 mJ m^{-2} and the isotropic surface stress 960 mJ m^{-2} . The uppermost layer shows an inward relaxation of 0.7% while subsequent relaxations are insignificant. These results are in rather poor agreement with the experimental values of 1650 mJ m^{-2} ((Murr 1975) there is some debate about whether these experiments, which are carried out at a high temperature, measure surface energy or tension) and $2 \pm 2\%$ (Jona and Marcus 1988).

There has been some debate regarding the existence of a 'chevron'-type reconstruction of the surface (for example Pond (1991)). A plausible explanation of the chevron structure is that the surface is not perfectly basal. This slight misalignment leads to a surface with occasional localized steps. There are two possible types of step at which a new layer can begin on the basal surface, both being microfacets of the pyramidal surface. The more stable of these cross at 60° but combination with the other type allows 120° corners to the step. The less stable step structure is only slightly unfavourable, suggesting that, for a small misorientation in an arbitrary direction, obtusely cornered microsteps would be present, giving an overall chevron appearance. There is quite a large energy associated with formation of a corner, much more with a 60° rather than a 120° corner. Consequently it is energetically favourable for a surface close to (0001) to form large chevrons. The energy of the steps was found to be $0.10 \text{ eV } \text{\AA}^{-1}$ with the difference between the two types of step less than $0.005 \text{ eV } \text{\AA}^{-1}$.

Such steps are doubtless important in crystal growth on the basal face. It is possible to create a triangular island of adatoms bounded only by steps of the more stable type, but the atom at the apex of the 60° corner, with only five nearest neighbours (compare nine in the surface, seven in the step, and 10 or 11 for atoms at the foot of the step) is unstable with respect to sites ahead of the step. Thus the most energetically favourable growth mechanism on the basal plane consists of jogs along straight steps, with islands of adatoms bounded by 120° corners.

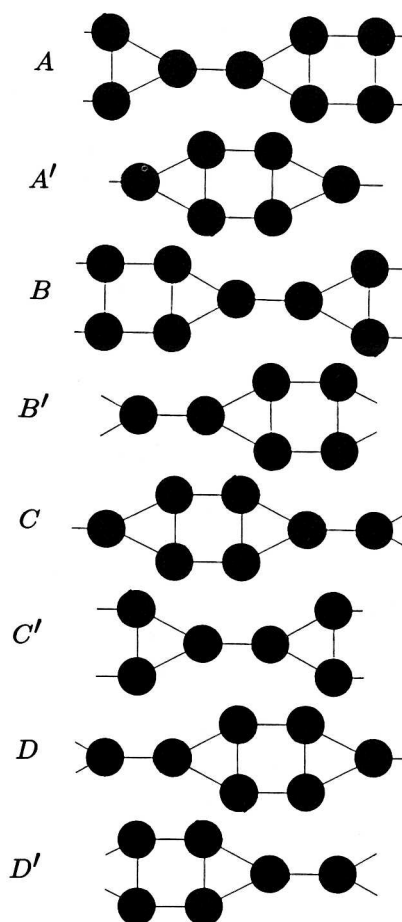
The possibility was also examined that the chevrons could be regions of stacking faults at the surface. These might increase the atomic and electron density at the surface and relax some of the surface stress. A region of stacking fault is most efficiently bounded by one-dimensional 'partial dislocation' in the two-dimensional surface layer. As with the steps, there are two possible types; again it is only possible to create a region of surface stacking fault bounded only by the more stable of the one-dimensional 'partials' if all the corners are at 60° . With the present potential, such stacking faults were not stable. This result might have been anticipated since low-energy stacking faults at the surface would lead to high residual dislocation densities when the material is grown from the melt.

6.2. Pyramidal plane surfaces

The $(1\bar{1}01)$ pyramidal planes are the second most densely packed planes in the h.c.p. structure, with surface atoms being either eightfold or ninefold coordinated. To obtain a parallelepiped unit cell for which one surface is a pyramidal plane it is necessary to have 32 atoms. The starting configuration was generated by relaxing unit cells in which the x - y planes formed a series of eight layers (as shown in the figure), initially flat, in an orthorhombic unit cell. The relaxation of this cell to the h.c.p. structure involves a corrugation of the planes and a small monoclinic distortion of the unit cell. The stacking order has been labelled AA'BB'CC'DD' for reference in the description of stacking faults. For surface calculations, each of these planes is identical.

Since the planes are not quite flat, there are theoretically two unreconstructed truncations: one containing all atoms of the corrugated plane, and the other containing only the lower half. In practice the first is preferred, with the outermost atoms having three nearest neighbours in the pyramidal plane below and five neighbours in the corrugated topmost layer. The formation energy of this pyramidal surface is 1039 mJ m^{-2} (if only the lower part of the corrugated plane is present the surface energy is 1433 mJ m^{-2}). Because of the low symmetry of this surface (the highest rotational symmetry is twofold) there are two components to the surface stress. The stress along the $\langle 11\bar{2}0 \rangle$ (close-packed) direction is 1116 mJ m^{-2} while along the (corrugated) $\langle \bar{1}10\bar{2} \rangle$ it is 725.4 mJ m^{-2} . This latter direction has a rather low surface tension because the increase in energy on stretching is balanced in part by the flattening of the surface layer. Various possible reconstructions were examined, based on oscillatory relaxations of top layer atoms, adatoms and missing rows, but none proved to be stable.

The $(1\bar{1}02)$ plane also has a low energy surface with a small repeat cell (computationally it is necessary to use a monoclinic unit cell to ensure that the $(1\bar{1}02)$ plane lies along one of the faces). There is only one possible termination. The atoms in the surface layer are sevenfold coordinated; so we might expect that the surface energy will be higher than in other cases and indeed it is found to be 1194 mJ m^{-2} . The surface tension in this plane is anisotropic, having components of 631 mJ m^{-2} along $\langle 11\bar{2}0 \rangle$ and 512 mJ m^{-2} along $\langle \bar{1}10\bar{1} \rangle$.



Sequence of $(1\bar{1}01)$ pyramidal planes in a perfect h.c.p. structure.

6.3. Prismatic $(1\bar{1}00)$ plane

This surface offers two possible terminations, which were found to have a large disparity in energy. The termination with a small spacing of 0.85 \AA between layers was much lower in energy (1061 mJ m^{-2}) than the termination with 1.7 \AA between layers (1359 mJ m^{-2}) in agreement with recent low-energy electron diffraction studies (Mischenko and Watson 1989a). This is entirely as one might expect from bond-breaking arguments, since in the small termination there are four missing nearest neighbours for each surface atom while for the larger termination there are eight.

The relaxation pattern of the layers follows the pattern typical of embedded-atom models (Chen *et al.* 1986, Ackland and Thetford 1987, Foiles 1987, Ackland *et al.* 1988, Ercolessi *et al.* 1988). For the stable surface the separation between the two outer (undercoordinate) layers is reduced by 5.6% (0.048 \AA) and the separation between the next two is also reduced by 0.8% (0.013 \AA); atoms in the second layer have two missing near neighbours and so are undercoordinated. Below this, in the fully coordinated region, the relaxation of the layers oscillates between expansion and contraction, getting smaller as one moves away from the surface. This relaxation is in very good

agreement with that found by Mischenko and Watson (1989a) who report an inward relaxation of the surface layer of 0.05 \AA .

This type of oscillatory relaxation is explained neatly by the effective-medium theory of Norskov and Lang (1981) (which reduces to a model equivalent to the present model). The n th layer moves to optimize its local electron density, inducing an opposite relaxation in the $(n+1)$ th layer, except, when a layer is undercoordinated; in this case it will move toward neighbouring layers so as to increase its effective coordination. This effect is more pronounced in the model of the hypothetical termination of the wider spaced surface layers. Here the relaxation of the spacing between the top two layers would be -6.4% (0.11 \AA). This large relaxation causes a compensatory expansion of the separation between second and third layers of 4.5% (0.038 \AA), a contraction between third and fourth of -1.7% (0.029 \AA) and subsequent damped oscillatory relaxations into the bulk.

For the stable surface the surface tension is 680 mJ m^{-2} along the $\langle 11\bar{2}0 \rangle$ direction and 481 mJ m^{-2} along $\langle 0001 \rangle$.

The other prismatic plane ($11\bar{2}0$) has six missing neighbours and an energy intermediate between the two ($1\bar{1}00$) types: 1187 mJ m^{-2} . Again the upper layer is contracted, this time by -4% (0.059 \AA), and subsequent layers show negligible relaxation. The surface tensions are somewhat higher, being 1019 mJ m^{-2} along $\langle 1\bar{1}00 \rangle$ and 915 mJ m^{-2} along $\langle 0001 \rangle$.

There has been some discussion about the possibility of a series of $N \times N$ reconstructions reported by Khan (1975). These were not found to be stable at zero temperature in the present model and were not observed by Mischenko and Watson (1989b) who attribute them to impurities.

§ 7. STACKING FAULTS

To study dislocations in h.c.p. materials it is important to know the energies of stacking faults which might enable splitting into partials. Most stacking faults have near-ideal coordination and so pair potential calculations might be expected to be reasonable. A thorough survey has been carried out by Bacon and Liang (1986) and the present potential gives similar results.

On the basal plane there are two intrinsic and one extrinsic stacking faults. I_1 corresponds to ABABCBCB, I_2 to ABABCACA, and E to ABABCABAB. For plasticity I_2 is the important fault, allowing dislocation splitting into Shockley partials. In an indirect way, the energy of the I_2 stacking fault is included in the fitting procedure; we actually fit the stacking fault in the f.c.c. form and assume this to have the same energy as the h.c.p. stacking fault, but with a different sign. The stacking fault on the pyramidal plane is not fitted, and indeed the very existence of a stable fault on the plane is not guaranteed by symmetry.

The relaxed stacking-fault energies on the basal plane were found to be as follows: I_1 , 33 mJ m^{-2} ; I_2 , 64 mJ m^{-2} ; E, 94 mJ m^{-2} . The associated expansion normal to the boundary plane are the following: I_1 , 0.0424 \AA ; I_2 , 0.076 \AA ; E, 0.027 \AA . The ratios of the stacking-fault energies are very close to the 1:2:3 ratio which would be expected from violation of second-neighbour layer order. More surprising is the low boundary expansion associated with the extrinsic fault. Note that these expansions are localized across one unit cell and are significantly smaller than the variation in the cell parameters due to non-ideal c/a ratio; to become ideal the c length would have to be increased by 0.122 \AA per unit cell.

On the pyramidal ($1\bar{1}01$) plane the most obvious stacking faults are

- (1) intrinsic type AA'BB'CC'CC'DD'AA', of energy 314 mJ m^{-2} ,
- (2) extrinsic AA'BB'CC'DD'BB'CC'DD', of energy 435 mJ m^{-2} and
- (3) the arrangement AA'BB'CC'DD'CC'DD'AA', of energy 359 mJ m^{-2} .

All stacking faults in which an odd number of layers is missing (added) are unstable because of the identical y coordinates of all (un)primed layers; atoms directly above others in the layer below are too close (figure). Unlike the basal faults, pyramidal plane faults do change the near-neighbour coordination of some of the atoms; in the lowest-energy intrinsic type, atoms in the boundary layer have 11 or 13 neighbours. On a simple bond-counting model this boundary would have a very low energy (overall there are an average 12 bonds per atom) but the many-body potential exposes the energy associated with both overcoordinated and under coordinated atoms.

In each case the stacking fault is associated with an expansion of the boundary layer. By analogy with grain boundaries we expect the largest expansion for the least stable arrangement, and within the pyramidal plane faults this is indeed found to be true, the relaxations being 0.038, 0.097 and 0.074 Å for types (1), (2) and (3) respectively. By contrast, the boundary layer expansion of the basal fault 0.076 Å, suggesting that this rule is valid only for similar faults.

§ 8. DISCUSSION

We have parametrized a semi-empirical Finnis–Sinclair-type potential for Ti. The model incorporates anisotropy in the shear constants and has a significant deviation from ideal c/a ratio. It uses smooth, monotonically decreasing functions. This has been achieved by a novel approach to the fitting procedure based on the idea that the deviation from ideal c/a and cubic elastic constants can arise as a perturbation due to weak interactions between neighbours separated by the c lattice parameter, applied to a model fitted to an unstable f.c.c. structure. This assumption can be tested, because it implies two relations between the elastic constants which are broken by the perturbation. These relations are experimentally observed in just those h.c.p. metals for which the second moment tight-binding approximation is best justified: those with partially filled sd bands.

Surface studies are generally in agreement with experiment, with no reconstruction found on any surface and a preference for the more densely packed termination of the prismatic plane. This is similar to what one might expect from analogous studies in f.c.c. materials and allows us to deduce some general rules governing the possibility of reconstruction of metallic surfaces.

- (1) Notwithstanding the importance of many-body forces for describing surface relaxations, the most important criterion for stability is the deviation from twelvefold coordination. In f.c.c. structures the 'missing-row reconstruction' of the (110) surface is the only possible reconstruction which conserves the number of broken bonds per unit area, while in h.c.p. structures there is no such reconstruction of any of the simple surfaces.
- (2) The secondary consideration is the possibility that the surface atoms relax more than in the unreconstructed case. This will generally be true in the cases where atoms are missing on the surface, but generally such cases will involve breaking extra bonds.
- (3) Surface relaxation is dominated by the motion of the undercoordinated surface atoms to increase their effective coordination. This leads to an inward

- relaxation of the top layer in all cases, the relaxation of which might set up compensatory oscillatory relaxations into the body of the material. The same effect causes surfaces to have a negative surface tension; the surface atoms would prefer greater overlap of their charge densities.
- (4) Relaxation of the surface tension could lead to large-scale reconstructions involving, for example, close-packed overlayers or widely separated extra row reconstructions. We have not examined this possibility here because of the large cell sizes required.

The surface stress has been found in all cases to be positive (the surface layer wishes to contract). It is not obvious that this should be so, but it is in accord with the theory of Ackland and Finnis (1986) that negative surface tension is associated with instability of the assumed crystal structure under the given potential.

The energy of the pyramidal surface was found to be lower than that of the prismatic surface (the basal plane being lowest of all). This is slightly surprising since the broken bond density is higher for the pyramidal surface (3.863 against 3.769, the basal being 3.464 bonds per nearest-neighbour distance squared). The discrepancy may be due to second-neighbour interactions.

The basal surface observations are similar to those of Chen (1992), who used a similar potential scheme including all elastic constants but with the ideal c/a ratio. One difference is that we correctly predict the large relaxation of the (1100) surface. This may well be related to the 'expanded' basal plane associated with the small c/a ratio.

A number of metastable stacking faults on the basal and pyramidal planes have been studied. The energy of the basal fault is strongly correlated with the f.c.c. — h.c.p. energy difference and is therefore loosely incorporated in the parametrization. Consequently not too much emphasis should be placed on the (reasonable) value found. Contrariwise, there is no implicit fitting of the pyramidal plane faults. Since their energy is dominated by the overcoordination or undercoordination of the boundary layer atoms, we would expect the present potentials which describe coordination effects well, to give good results here. In particular the absence of a stable fault with only one layer extra (or missing) is significant in making formation of partial dislocations for basal slip more difficult.

Defect energies are reasonable but the favoured interstitial site is at variance with previous potentials. There is, as yet, no experimental evidence for the preferred site. The choice of site is determined by two effects: the 'hardness' of the atomic core and the stiffness of the lattice to relax the strain energy. In the case of Ti the elastic energy for basal defects is rather low because of the anomalously low value of C_{66} , and the below-ideal value of c/a also means that there is more space between basal 'nearest neighbours' than between non-basal nearest neighbours. These two factors probably account for the non-basal site predicted by the potential of Oh and Johnson; they fit only an average shear constant and have the ideal c/a ratio. The non-basal site found by Igarashi *et al.* is probably a consequence of the very hard core to their potentials; it is the point in the lattice farthest from any atom site.

The closeness in the energies of the various sites implies that the migration path will be very complex, and that in reality several possible paths may need to be considered.

With respect to the time evolution of radiation-damaged samples, the small interstitial formation volume suggests that preferred migration to dislocation loops may be suppressed. From theoretical rate arguments this would tend to stabilize vacancy loops which have recently been observed (Griffiths 1991).

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