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Surface reconstructions on germanium

M C Payne[†], M Needels[‡] and J D Joannopoulos[‡]

[†] Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge
CB3 0HE, UK

[‡] Massachusetts Institute of Technology, Cambridge, MA 02139, USA

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Abstract. Total-energy pseudopotential calculations have been used to investigate a number of surface reconstructions on germanium. The system of buckled dimers on the (001) surface of germanium can be represented by a spin system. The interactions between the dimers are represented by interactions between the spins. The values of the interaction parameters in an effective Hamiltonian that describes the system of dimers have been determined by calculating the energies of the (2×1) , $c(4 \times 2)$, $p(2 \times 2)$ and $p(4 \times 1)$ arrangements of buckled dimers. The Hamiltonian gives a prediction of 380 ± 100 K for the temperature of the order–disorder phase transition on the surface. The mechanism responsible for stabilising the Takayanagi reconstruction of the (111) surface of germanium has been investigated by calculating the energies of the (3×3) Takayanagi structure and of sub-elements of this structure. It is shown that the Takayanagi reconstruction is stabilised by an interaction between the adatoms and the dimers in the second layer of atoms. The surface stresses of the complete Takayanagi structure and of the Takayanagi structure without adatoms have been calculated and it is found that the surface energy is not related to the magnitude of the surface stress. Preliminary results for the $c(2 \times 8)$ reconstruction of the (111) surface of germanium are presented.

1. Introduction

The ability to calculate total energies of different configurations of atoms is the first step towards understanding a wide range of physical properties of materials. One obvious application of total-energy calculations is to compute the energies of a number of different crystal structures and hence determine which structure is the most stable. Similarly the energies of a number of surface reconstructions can be calculated to determine which reconstruction has the lowest energy. However, there are many other physical properties of materials that can be related to total energies or to differences in total energies and these physical properties can be calculated using total-energy calculations. Any method that is used to calculate the total energies of structures that are not accessible experimentally must be accurate and reliable, because in these cases there is no direct experimental test of the accuracy of the computational results. Total-energy pseudopotential calculations have successfully predicted stable crystal structures, bulk moduli, phase transition pressures and phase transition temperatures (Yin and Cohen 1982, Rabe and Joannopoulos 1987). The calculations use no variable parameters and so they can be applied with confidence even when there are no experimental results to check the accuracy of the calculations.

A reliable method for calculating total energies allows computational experiments to be performed to study the physical properties of materials. To determine a physical property such as the bulk modulus the property must be related to the total energies of different configurations of atoms. A series of computations are performed to calculate these total energies and from the results of these computations the value of the physical property is deduced. However, in many cases the positions of the atoms are not precisely known. In the case of a surface reconstruction it is possible that only the periodicity of the reconstruction is known or that only the gross features of the structure have been found experimentally. If the lowest energy structure out of a range of possible structures is to be deduced computationally it is essential that the total energies are calculated for equilibrium configurations in which there are no forces on the atoms. The force on an atom is simply the derivative of the total energy with respect to the position of the atom. By calculating the change in the total energy on displacing an atom the forces on the atoms can be calculated. However, calculating forces in this way is extremely time-consuming, particularly if the system contains a large number of atoms. One advantage of pseudopotential methods which use plane wave basis sets is that the forces on all the atoms in the system can be calculated accurately from the results of a single total-energy calculation. If the forces on the atoms can be calculated the initial atomic configuration can be relaxed to equilibrium. Relaxation of the positions of the atoms is an essential part of a total-energy calculation for determining the lowest-energy crystal structure or surface reconstruction, because the total energy of a structure which is not in equilibrium gives no information as to which of a number of possible structures or reconstructions has the lowest energy and hence which is the most stable.

The paper illustrates a variety of applications of the total-energy pseudopotential technique. The total-energy pseudopotential method is briefly described in the following section. In § 3 it is shown that the dimers on the (001) surface of germanium can be represented by spins and that the interaction parameters in an effective Hamiltonian that describes the system of dimers can be extracted from total-energy calculations. The mechanism responsible for stabilising the Takayanagi reconstruction of the (111) surface of germanium is investigated in § 4 and in § 5 preliminary results for the $c(2 \times 8)$ reconstruction of the (111) surface are presented.

2. The total-energy pseudopotential method

The total energy of a solid can only be calculated with a number of simplifications. One method of simplifying the calculations is to use the pseudopotential approximation (Heine and Cohen 1976). This replaces the ions by an effective potential which reproduces the correct scattering properties. Using the pseudopotential approximation only the wavefunctions of the valence electrons have to be calculated. The pseudopotential and the screened ionic potential are identical outside the ion cores and the wavefunctions of the valence electrons in the two potentials are identical outside the regions occupied by the cores. However, the pseudo-wavefunctions are smooth in the core regions, in contrast to the true valence wavefunctions which oscillate rapidly in the core so that the wavefunctions remain orthogonal to those of the core electrons. The bonding energy in a solid is principally determined by the electron density in the regions outside the ion cores. Since the pseudo-wavefunctions and the pseudopotential in these regions are identical with the true wavefunctions of the valence electrons and the screened ionic potential respectively, bonding should be accurately described in the pseudopotential

approximation. As the pseudo-wavefunctions of the valence electrons are relatively smooth it is possible to expand them in a plane wave basis set, in which case the calculations have to be performed on a periodic system. Unfortunately, a surface does not possess the necessary three-dimensional periodicity. Calculations for surfaces with plane wave basis sets have to be performed using a slab geometry. In reality the total energy of a periodic array of crystal slabs is calculated and it is essential to ensure that the vacuum regions between the slabs are wide enough to prevent the surfaces of adjacent slabs interacting across the vacuum. Similarly, the slab must contain enough layers of atoms so that the two surfaces of the slab do not interact across the slab. Although the use of a periodic system is inconvenient for surface calculations, the advantage of calculating forces on the atoms, which is simple using pseudopotentials and plane wave basis sets, makes up for this inconvenience.

The most difficult problem in any electronic structure calculation is taking account of the effects of the electron–electron interaction. Hohenberg and Kohn (1964) have shown that the exchange–correlation energy of a system of interacting electrons is a unique functional of the electron density, and Kohn and Sham (1965) have shown that a system of interacting electrons can be mapped onto a system of non-interacting electrons moving in an effective potential, the exchange correlation potential V_{xc} , which takes account of the effects of the electron–electron interaction exactly. The exchange–correlation potential is related to the exchange correlation energy functional E_{xc} as follows:

$$V_{xc}(\mathbf{r}) = \delta E_{xc}[n(\mathbf{r})]/\delta n(\mathbf{r}) \quad (1)$$

where $n(\mathbf{r})$ is the density of the electron gas at position \mathbf{r} . Unfortunately, the form of the exchange correlation energy functional is unknown and so an exact mapping of the interacting electron system onto a system of non-interacting electrons cannot be performed. Remarkably, a very crude approximation for constructing the exchange–correlation potential, the local density approximation, gives good results for total energies. In the local density approximation the exchange–correlation potential at position \mathbf{r} is taken to have the value of the exchange correlation potential in a uniform electron gas which has the same density as the electron gas at \mathbf{r} . The local density approximation neglects all non-local contributions to the exchange–correlation potential and it is rather surprising that such a gross approximation works so well.

The calculation for the total energy proceeds by solving the Kohn–Sham equations

$$[(-\hbar^2/2m)\nabla^2 + V_{ion} + V_H + V_{xc}]\psi_i = \varepsilon_i\psi_i \quad (2)$$

where V_H is the Hartree potential, V_{ion} is the ionic potential, ψ_i are the Kohn–Sham eigenstates and ε_i are the Kohn–Sham eigenvalues.

The Kohn–Sham eigenstates must be calculated self-consistently so that the Hartree and exchange–correlation potentials that are used in the Kohn–Sham equations are those produced by the charge density generated by these eigenstates. Once the self-consistent solutions to the Kohn–Sham equations have been found the total energy can be calculated.

Significant advances have been made in the total-energy pseudopotential method by using iterative matrix diagonalisation schemes to solve the Kohn–Sham equations. Car and Parrinello (1985) suggested using a molecular dynamics approach for solving the Kohn–Sham equations in which the electronic wavefunctions are treated as dynamical variables. The electronic wavefunctions are allowed to evolve in time and if some form of damping is applied to the system the wavefunctions relax to the ones that minimise

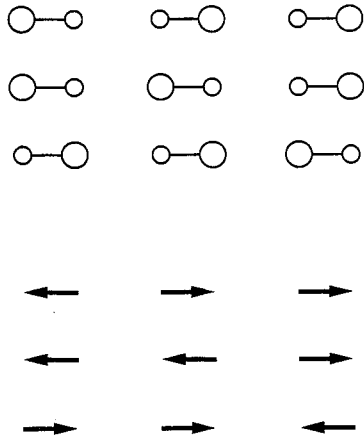


Figure 1. Schematic illustration of a configuration of buckled dimers on the (001) surface of Ge and the presentation of this configuration by a set of spins.

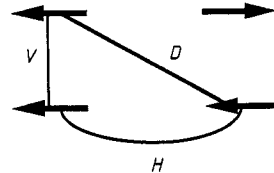


Figure 2. Schematic illustration of the interaction parameters in the effective Hamiltonian that describes the system of dimers on Ge (001).

the Kohn–Sham energy functional. In this method the positions of the ions and the size and shape of the unit cell can also be treated as dynamical variables, and if these degrees of freedom are allowed to relax at the same time as the electronic degrees of freedom the system will reach a global energy minimum. The advantage of iterative matrix diagonalisation schemes is that more basis states can be used in the calculations so that larger systems can be studied.

In the following sections some applications of the total-energy pseudopotential method will be described. No details of the actual calculations will be given because the authors believe that it is the physics that can be learnt by using the computational technique rather than the technique itself which is important.

3. Dimer reconstructions on the germanium (001) surface

The (001) surface of germanium forms a dimer reconstruction in which the dimers are buckled (Chadi 1979, Kubby *et al* 1987). An infinite number of reconstructions can be formed on this surface by varying the buckling directions of the dimers, and any finite number of calculations for the surface energies of different arrangements of buckled dimers cannot determine which is the most stable surface reconstruction. The effect of varying the buckling directions of the dimers is most clearly shown by replacing each dimer by a spin, where the spin points in the direction of the raised atom (see figure 1). Buckling a dimer in a particular direction will favour a particular arrangement of buckling for the neighbouring dimers and this interaction between the dimers can be described in the spin system by interactions between the spins. In principle the interaction between pairs of dimers could have an infinite range, but it is expected that the magnitude of the interaction will decrease rapidly as the distance between the dimers increases. An effective Hamiltonian can be written to describe the system of dimers in terms of the

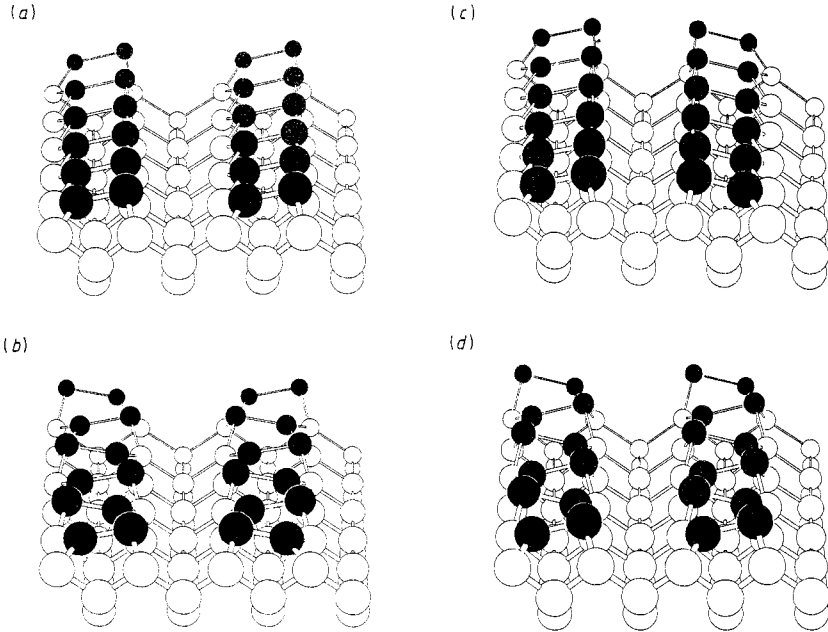


Figure 3. Buckled dimer reconstructions on the (001) surface of germanium: (a) $b(2 \times 1)$; (b) $c(4 \times 2)$; (c) $p(4 \times 1)$; (d) $p(2 \times 2)$.

Table 1. Total energy of buckled dimer reconstructions on the Ge(001) surface.

	Surface energy per dimer (eV)
$b(2 \times 1)$	0.0
$p(4 \times 1)$	0.037
$c(4 \times 2)$	-0.070
$p(2 \times 2)$	-0.073

spin variables. When only interactions between pairs of spins up to the second-nearest neighbours are included the effective Hamiltonian takes the following form

$$-\mathcal{H} = V \sum_{i,j} S_{i,j} S_{i,j+1} + H \sum_{i,j} S_{i,j} S_{i+1,j} + D \sum_{i,j} S_{i,j} S_{i+1,j+1} \quad (3)$$

where the subscripts i and j label the columns and rows of spins respectively. The parameters V , H and D refer to the interactions illustrated schematically in figure 2.

If this Hamiltonian is to describe the system of dimers on the germanium (001) surface the parameters V , H and D must be those appropriate to this system. These values of these parameters can be extracted from the energies of four different dimer reconstructions: the reconstructions chosen for our calculations were the $b(2 \times 1)$, $c(4 \times 2)$, $p(2 \times 2)$ and $p(4 \times 1)$ configurations which are illustrated in figure 3. Table 1 gives the surface energy per dimer for these arrangements of buckled dimers (Needels *et al* 1988). The results show that the $c(4 \times 2)$ and $p(2 \times 2)$ reconstructions in which the buckling direction alternates from dimer to dimer down the columns are lower in energy than the $b(2 \times 1)$ and $p(4 \times 1)$ reconstructions in which the buckling direction is the

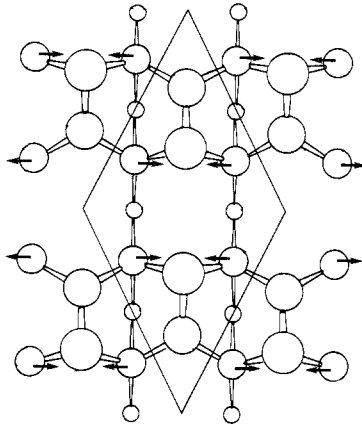


Figure 4. $c(4 \times 2)$ reconstruction on Ge (001). The arrows show the relaxation of the atoms in the first layer that stabilises alternation in the dimer buckling direction down the columns.

Table 2. Interaction parameters for the effective Hamiltonian describing the system of dimers on the (001) surface of Ge.

Coupling constant	meV
V	-43
H	10
D	4

same down the columns. The reduction in the surface energy when the buckling direction alternates from dimer to dimer down a column can be attributed to the relaxation of the atoms in the layer below the dimers. In the $c(4 \times 2)$ and $p(2 \times 2)$ reconstructions the atoms in this layer move towards the raised dimer atom and away from the lowered dimer atom. This relaxation is illustrated for the $c(4 \times 2)$ reconstruction in figure 4. The atoms also move in the planes perpendicular to the arrows but only the relaxation in the direction of the arrows distinguishes between the high- and low-energy reconstructions. The relaxation of the atoms in the directions shown in figure 4 maintains the lengths of the bonds between the dimer atoms and the first-layer atoms close to the bulk bond length, so that there is very little stretching of the bonds between the first-layer atoms and the dimers. This reduces the strain energy in these bonds and hence reduces the surface energy. The importance of this relaxation for stabilising reconstructions in which the buckling direction alternates from dimer to dimer down a column has been tested by imposing a constraint on the system. If the atoms in the first layer of the $c(4 \times 2)$ reconstruction are not allowed to move in the directions of the arrows but remain free to move in the planes perpendicular to the arrows, the energies of the $c(4 \times 2)$ and $b(2 \times 1)$ reconstructions become identical. The relaxation of the atoms in the first layer is, therefore, the mechanism that stabilises alternation in the direction of buckling of the dimers.

The values of the parameters V , H and D are given in table 2. The magnitude of the parameters decreases rapidly with the distance between the dimers, which suggests that the inclusion of interactions only up to second-nearest neighbours in the effective Hamiltonian is justified. A renormalisation group analysis of the effective Hamiltonian gives a prediction of 380 ± 100 K for the temperature of the order-disorder phase

transition on this surface (Needels *et al* 1988). This is slightly higher than the transition temperature measured experimentally (Kevan 1985, Culbertson *et al* 1986) but the observation of ordered clusters of dimers in STM images at room temperature (Kubby *et al* 1987) is consistent with the prediction of a weak second-order phase transition with the critical temperature quoted above.

4. The Takayanagi reconstruction

The structure of the (7×7) reconstruction observed on the (111) surfaces of silicon and strained germanium was deduced by Takayanagi *et al* (1985) using data obtained from transmission electron microscope experiments. An investigation of the mechanism responsible for stabilising the Takayanagi structure will be described in this section. The Takayanagi model for the (7×7) reconstruction can be generalised to a family of reconstructions which are formed in $(2m + 1) \times (2m + 1)$ (m integer) unit cells. All of the reconstructions share the same structural features, so the mechanism responsible for stabilising the structure can be deduced by studying the lowest member of the family of reconstructions. The calculations described later in this section were performed on the (3×3) reconstruction on the germanium (111) surface.

The Takayanagi reconstruction is extremely complex. The structure of the (3×3) reconstruction is illustrated schematically in figure 5. Figure 5(a) shows the positions of the atoms in the second layer below the surface, the crosses show the positions of the atoms in the bulk crystal. In this layer of the reconstruction there are missing atoms at the corners of the unit cell, and pairs of atoms along the edges and across the short diagonal of the unit cell move together to form the dimer bonds shown by the dark lines in figure 5(a). The dimer bonds form a triangular array. Higher members of the family of reconstructions have larger numbers of dimers between the missing corner atoms. Figure 5(b) shows the positions of the atoms in the first and second layers of the reconstruction. It can be seen that the atoms in the first layer form triangular islands in each half of the unit cell and that the islands in the two halves of the unit cell are rotated by 180° with respect to each other, which indicates the presence of a stacking fault over one-half of the unit cell. The reconstruction is terminated by adatoms which are shown in figure 5(c). The adatoms are the prominent features seen in scanning tunnelling microscope images of the reconstruction.

The difficulty in understanding the Takayanagi reconstruction arises from the fact that the reconstruction does not minimise the density of dangling bonds or the density of defects on the surface; yet the reconstruction has the lowest energy of all the reconstructions that can be formed on the (111) surfaces of silicon and strained germanium. This can only be the case if there is an interaction between the elements of the structure which is energetically favourable and lowers the energy of the complete reconstruction. The interaction that lowers the surface energy stabilises the Takayanagi structure. The interaction that is involved can be deduced by determining the energies of the elements of the reconstruction and of combinations of the elements. If the energy of a combination of elements is lower than the sum of the energies of the individual components, then the interaction between the elements is energetically favourable. Most of the structures whose energies are required to determine the favourable interaction cannot be obtained experimentally, and so the procedure for determining the favourable interaction can only be carried out computationally.

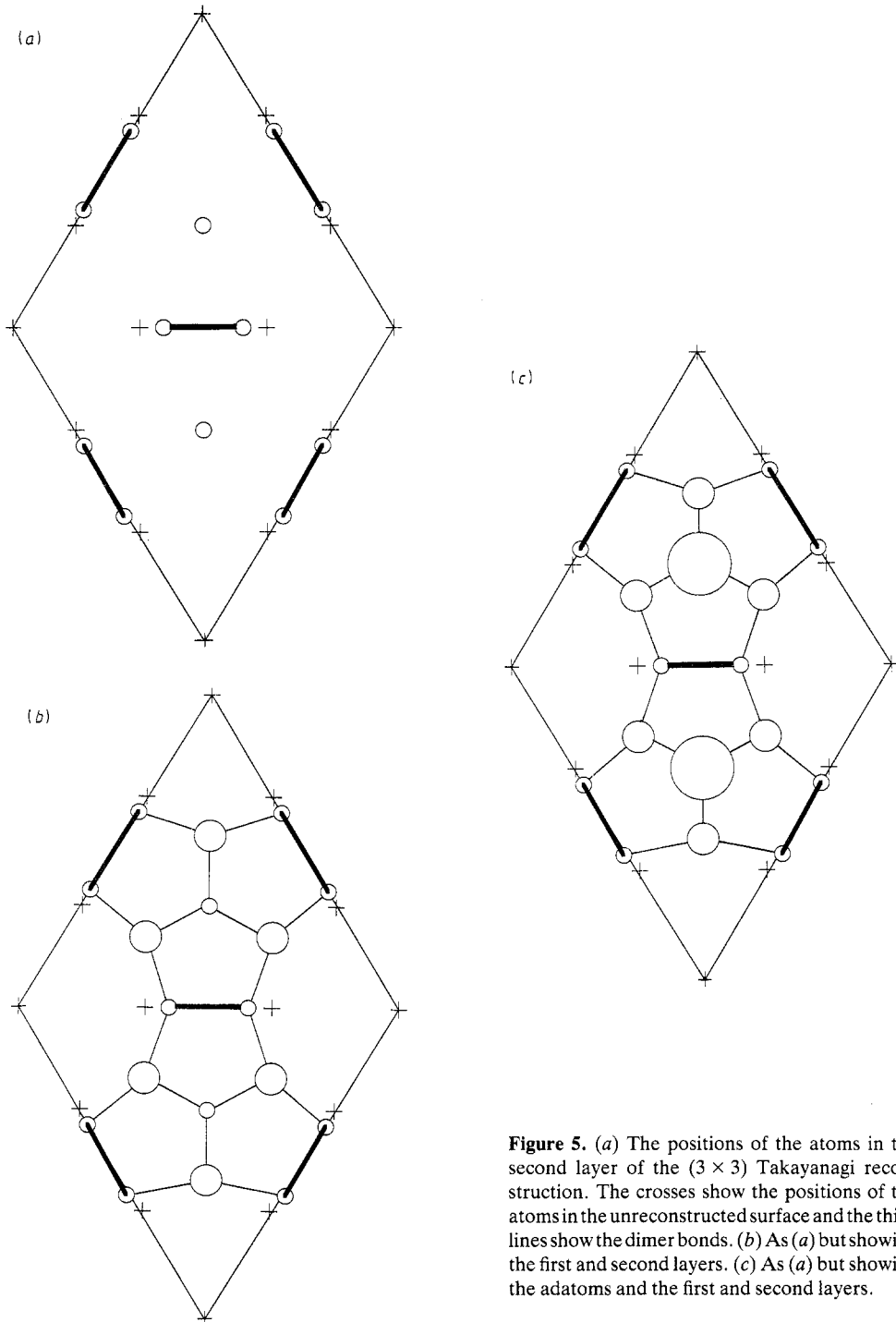


Figure 5. (a) The positions of the atoms in the second layer of the (3×3) Takayanagi reconstruction. The crosses show the positions of the atoms in the unreconstructed surface and the thick lines show the dimer bonds. (b) As (a) but showing the first and second layers. (c) As (a) but showing the adatoms and the first and second layers.

The results of calculations (Payne 1987) to deduce the role of the adatoms in the Takayanagi reconstruction are presented in table 3. To assess the importance of the adatoms in the Takayanagi structure the change in the surface energy on incorporating

Table 3. Total energies of reconstructions on the (111) surface of Ge.

	Energy per $n \times n$ unit cell (eV)	Energy per surface atom (eV)
1×1 unrelaxed	1.22	1.22
1×1 relaxed	1.15	1.15
2×2 adatom over second-layer atom	4.16	1.04
2×2 adatom over fourth-layer atom	4.50	1.13
3×3 Takayanagi without adatoms	10.06	1.12
3×3 Takayanagi	7.95	0.88

adatoms into the Takayanagi structure should be compared to the change in energy on adding adatoms to an unreconstructed surface. From the results in table 3 it can be seen that addition of adatoms to the unreconstructed surface does not significantly affect the surface energy. In the most favourable case when the adatoms are positioned over an atom in the second layer each adatom lowers the surface energy by 0.44 eV. This is much smaller than the value that would be expected from the reduction in the number of dangling bonds, and it shows that there is a large amount of strain energy associated with the adatoms. When the adatom is positioned over a fourth-layer atom the surface energy is reduced by only 0.10 eV per adatom. The results in table 3 also show that the Takayanagi structure without adatoms is not low in energy, which suggests that none of the interactions between the elements in this part of the structure is energetically favourable. If the addition of adatoms to the Takayanagi subsurface reduced the surface energy by only 0.44 eV per adatom, then the Takayanagi structure would have a high surface energy and it would not be a stable reconstruction of this surface. However, addition of the adatoms to form the complete Takayanagi structure actually reduces the surface energy by 1.06 eV per adatom. This shows that there is an interaction between the adatoms and an element of the reconstruction in the Takayanagi subsurface which is energetically favourable. If we compare the Takayanagi structures with and without adatoms we find that the length of the dimer bonds reduces from 2.60 Å to 2.56 Å on addition of the adatoms to form the complete Takayanagi structure. The bulk bond length in germanium is 2.45 Å, so that the dimer bonds are stretched in both structures. On addition of the adatoms the dimer bond length relaxes towards the bulk bond length, thus reducing the strain energy in the dimer bonds. This reduction in the strain energy causes the larger than expected reduction in the surface energy on adding the adatoms to the Takayanagi sub-surface. The pairing between the dimers and the adatoms is the mechanism which lowers the surface energy and stabilises the Takayanagi structure.

The reduction in the lengths of the dimer bonds on adding the adatoms to form the complete Takayanagi reconstruction reduces the strain in these bonds and it might be expected that this would reduce the magnitude of the surface stress. Table 4 shows the calculated surface stresses for the Takayanagi reconstruction with and without the adatoms. It can be seen that the surface stress increases on adding the adatoms to form the full Takayanagi structure, so that the surface stress increases as the surface energy decreases. In both cases the stresses are tensile, which shows that the surfaces wish to contract. These results reveal that the magnitude of the surface stress is not a direct measure of the magnitude of the surface energy. The unusual behaviour of the surface stress in this case is due to the complexity of the Takayanagi reconstruction. The surface

Table 4. Surface stresses for the (3×3) Takayanagi structures on the (111) surface of Ge.

	Surface stresses (eV/unit cell)	
3×3 Takayanagi without adatoms	30.0	16.8
3×3 Takayanagi with adatoms	33.6	33.6

Table 5. Total energies of adatom reconstructions on the (111) surface of Ge.

	Energy per surface atom (eV)
$c(2 \times 8)$ adatom over second-layer atom	1.0
$c(2 \times 8)$ adatom over fourth-layer atom	1.2
2×2 adatom over second-layer atom	1.04
2×2 adatom over fourth-layer atom	1.13

stress calculated is an average stress and the average stress is not necessarily a measure of the local stresses which are more directly related to the surface energy. The first and second layers of atoms in the Takayanagi structure are not continuously bonded across the surface and so they cannot directly transmit a surface stress. In the Takayanagi structure without adatoms the dimer bonds are highly strained and hence exert a large tensile stress. However, the tensile stresses in the dimers are opposed by contractive stresses in the first layer islands of atoms. These two local stresses partially cancel, leaving a residual surface stress which is smaller than the local stresses. The adatoms in the Takayanagi structure effectively reduce the equilibrium interatomic spacing in the first-layer islands of atoms. This reduces the magnitude of the contractive stress in the islands and allows the dimer bonds to contract. Although the local stress in the dimer bonds is reduced, this stress is no longer principally opposed by the contractive stress in the first layer islands, and so the surface stress increases even though the local stresses and hence the surface energy have decreased.

5. The $c(2 \times 8)$ reconstruction on Ge(111)

The unstrained (111) surface of germanium reconstructs in a $c(2 \times 8)$ structure which appears to be a simple adatom structure (Feidenhans'l *et al* 1988, Swartzentruber *et al* 1988). This is surprising because the simple (2×2) adatom reconstructions on the (111) surface were found to be considerably higher in energy than the Takayanagi structure. To determine the structure of the $c(2 \times 8)$ reconstruction, total-energy calculations will be performed for a variety of different models. Preliminary results for the simple adatom terminated structures are presented in table 5. Qualitatively the results for the $c(2 \times 8)$ structures are encouraging. The ordering of the energies of the $c(2 \times 8)$ structures is the same as that for the (2×2) structures, the energy being lowest when the adatoms are positioned over the second-layer atoms. The energy of the lowest-energy $c(2 \times 8)$ reconstruction is less than the energy of the lowest-energy (2×2) reconstruction, which shows that of these two dimer reconstructions the $c(2 \times 8)$ reconstruction is energetically favourable. However, the energy of this $c(2 \times 8)$ structure is higher than that of the

Takayanagi structure, which suggests that the simple adatom $c(2 \times 8)$ structures are not energetically favourable compared to the Takayanagi reconstruction.

It is possible that the $c(2 \times 8)$ reconstruction is not a simple adatom reconstruction and that an alternative model for the structure of the $c(2 \times 8)$ reconstruction might have lower energy than the Takayanagi structure, but this would contradict recent experimental results. The $c(2 \times 8)$ reconstruction could be stable with respect to the Takayanagi reconstruction if there were a mechanism for reducing the energies of the $c(2 \times 8)$ structures below the values shown in table 5. Preliminary calculations for the $c(2 \times 8)$ reconstruction show that the surface stress is highly anisotropic. If a surface has an anisotropic surface stress the surface energy can be reduced by the formation of domains (Alerhand *et al* 1988). The variation of the orientation of the unit cells between domains allows the surface unit cells to be strained without producing a uniform bulk strain. The very large anisotropy in the surface stress could lead to a significant reduction in the surface energy of the $c(2 \times 8)$ structures on domain formation. The cost in energy of forming the domain walls will be very small due to the simplicity of the adatom reconstruction. Alternatively, the $c(2 \times 8)$ reconstruction might be formed on cooling a system in which the adatoms are positioned randomly. A random adatom terminated surface would be stable with respect to the Takayanagi structure if the free energy of the system were lower than the free energy of the Takayanagi structure at the annealing temperature. The configurational entropy of the Takayanagi structure is effectively zero because of the very high cost in energy of making any change to the structure. In contrast the configurational entropy associated with randomly occupying adatom sites is relatively high. However, a simple calculation of the configurational entropy of the random adatom terminated surface shows that configurational entropy alone cannot overcome the difference between the energies of the simple adatom terminated surface and the Takayanagi structure.

6. Summary

Total-energy pseudopotential calculations have been used to investigate surface reconstructions on germanium. The applications illustrate a variety of uses of total-energy methods for determining the most stable surface structure, for evaluating parameters in effective Hamiltonians and for obtaining detailed microscopic information about the mechanisms responsible for stabilising particular reconstructions.

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