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Surprises in the physics of metal surfaces*

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Abstract

Metal surfaces sometimes exhibit surprisingly complex properties, such as complicated surface structures, vibrational anisotropies, and a strongly enhanced surface anharmonicity, which result in drastic changes in properties as a function of temperature. Some examples are discussed in detail: the strong temperature dependence of interlayer spacings for Ag(111), the complicated herringbone reconstruction of Au(111), and reversed vibrational anisotropies and thermal contraction on unreconstructed FCC(110) surfaces. It is shown that *ab initio* density functional theory calculations can shed useful insight on these puzzling phenomena.

Keywords: Metal surfaces, surface physics, nanotechnology.

1. Introduction

The scientific investigation of the properties of solid surfaces is motivated both by questions of basic scientific interest and by the technological importance of surfaces. In recent years, there has been a spurt of activity and new discoveries in the field of surface physics. This is partly due to the development of new experimental techniques such as the scanning tunneling microscope (STM), which makes it possible to image individual atoms on a surface, thus providing access to a wealth of new experimental data. The increasing interest in surface science has also been spurred by the development of nanotechnology. The smaller an object is, the greater is the surface-to-volume ratio. Therefore, at nanoscales, surface properties become increasingly important, and the properties of very small objects are determined almost entirely by their surfaces.

Surface properties play a crucial role in many processes of technological importance, such as crystal growth, device physics and construction, and catalysis. Though, hithterto, one has frequently been forced to use a trial-and-error approach in determining factors such as growth environment or choosing catalysts, one has now approached a stage where theoretical calculations can provide useful input in deciding such issues.

The present state-of-the-art is to perform *ab initio* calculations based on density functional theory.[1] This is now a well-established technique, wherein the only input is the atomic numbers of the elements. These calculations are essentially exact (except for strongly correlated materials), offer predictive power, and enable one to study complex systems by separating out the various factors and processes involved. For example, a multi-step chemical reaction can be split up into various steps and each step can be well understood. While a possible drawback of the *ab initio* approach is that computational requirements of CPU time and memory can be

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very high, simpler (and less computer-intensive) theoretical treatments sometimes give wrong results. Moreover, the continually falling costs and increasing power of computers actually now make *ab initio* calculations cheaper, in some cases, than experiments!

Though all *ab initio* calculations have the same theoretical underpinnings, they can differ in technical details. The *ab initio* calculations presented in this paper all use a plane wave basis set (to expand the Kohn–Sham equations[2]) and the local density approximation to the exchange-correlation potential between electrons. Only degrees of freedom corresponding to the valence electrons are retained, and the interaction between the ion cores and valence electrons is described using a pseudopotential.

For large systems, one can sidestep heavy computational demands by using a model to describe the physics at larger length scales. However, instead of the model's parameters being determined empirically, they are obtained from microscopic *ab initio* calculations. Given below are three examples in which this approach is applied to studying interesting and surprising phenomena in the physics of metal surfaces.

Before attempting to investigate a complex phenomenon such as a chemical reaction or growth process, one would first like to understand a simple surface of a single crystal. Perhaps the simplest surfaces that one can consider are the low-index surfaces of face-centered-cubic (FCC) metals. The FCC structure is a simple one (with only one atom in the unit cell of the bulk lattice) and very commonly found in nature; the metals Al, Ca, Ni, Cu, Sr, Rh, Pd, Ag, Ir, Pt, Au and Pb all crystallize in this structure. Though the bulk structure is simple, the low-index surfaces of these metals display a surprising complexity in their structural and vibrational properties.

Upon cleaving a crystal to create a surface, bonds are broken near the newly-created surface. Due to these missing bonds, atoms near the surface are no longer in equilibrium at their bulk positions, and there are structural rearrangements of atoms near the surface. One can think of the crystal as being composed of layers of atoms parallel to the surface. In the simplest case, there is no shift in the positions of atoms within a layer; however, there are changes in interlayer distances. This process is known as *relaxation*. The first case I will discuss below is the relaxation of the Ag(111) surface, and how it changes with temperature. There can however also be, in addition, rearrangements in atomic positions within layers, leading to *reconstruction*. The second case I will discuss is the reconstruction of Au(111). Changes in surface structure also have an impact on the vibrational properties of surface atoms. The third case I will discuss is this connection between structure and vibrations for the surfaces of Ag(110), Cu(110) and Al(110).

2. Case 1: Thermal relaxation of silver (111)

A (111) surface is obtained when an FCC crystal is cut parallel to the layers of close-packed atoms. The Ag(111) surface does not reconstruct, but it does display a small amount of interlayer relaxation. At room temperature, the first interlayer spacing d_{12} is contracted by about 2.5% relative to d_B, the interlayer spacing in the bulk structure. Such a contraction is expected for metal surfaces; since surface atoms have lost some of their neighbours, they try to get closer to the neighbours they have left in the layer below. However, recent experiments[3] show a surprising reversal in this situation at high temperatures: as the crystal is heated, d_{12} expands considerably faster than d_B, so that at 1200 K it is actually expanded by 10% relative to d_B. This is a somewhat controversial experimental result, which moreover was contradicted by semi-empirical calculations using embedded-atom potentials.[4] One would therefore like to investigate this phenomenon by performing *ab initio* calculations.

Bond lengths change with temperature because of the *anharmonicity* of the interactions between atoms. If interatomic potentials were perfectly harmonic (i.e. varied quadratically with displacements), there would not be any thermal expansion. The experimental results on Ag(111) suggest that the surface anharmonicity must be considerably enhanced over the bulk anharmonicity. One consequence of anharmonicity is that phonon frequencies change with bond lengths. The structure at finite temperatures is determined by minimizing the free energy, which consists of the static (zero temperature) energy and a vibrational free energy that depends on temperature and bond lengths.

In order to investigate the anharmonicity on the Ag(111) surface, the key quantity to examine is how the frequencies of surface phonons change upon varying d_{12}. This is done by performing 'frozen-phonon' calculations, in which atoms are distorted from their equilibrium positions (simulating a vibration, which may or may not be a real phonon eigenmode of the system) and total energies and forces on atoms are calculated for a series of frozen snapshots of the vibration. The second derivatives of energy (or first derivatives of forces) with respect to atomic displacements provide force constants, which provide information about interatomic couplings.

First, the modes with surface wave vector $\mathbf{k} = 0$, in which the whole top layer moves as a whole, were investigated. Figure 1 shows how the frequency of these modes varies for the cases when the topmost layer vibrates along the x, y and z directions, with the directions defined as $\hat{x} = [1\bar{1}0]$, $\hat{y} = [11\bar{2}]$ and $\hat{z} = [111]$. It can be seen that for all three cases, the frequency decreases strongly with d_{12}. This implies that the surface can significantly reduce its vibrational free energy by increasing the value of d_{12}, thus favouring the thermal expansion of d_{12}. One

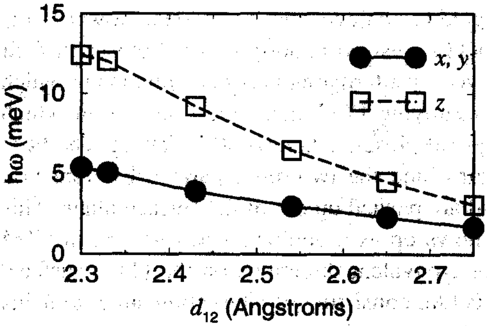

FIG. 1. *Ab initio* results for the change in frequency of the $\mathbf{k} = 0$ modes along the x, y and z directions, for Ag(111), upon increasing d_{12} beyond the zero-temperature value of 2.30 Å.

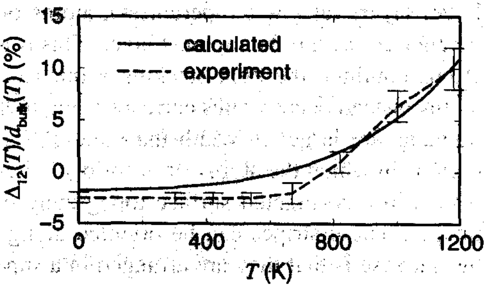

FIG. 2. Comparison of calculated and experimental values for the temperature-dependence of the percentage contraction/expansion of the first interlayer spacing d_{12} relative to the bulk spacing d_B, for Ag(111). Experimental values are from Statiris *et al.*[3]

notable feature is that the anharmonicity of the in-plane vibrations along x and y makes a crucial contribution, contradicting the frequently held belief that the main contribution comes from the anharmonicity of vibrations along z (normal to the surface).[5] In a similar way, the dependence on d_{12} of vibrations at the edges of the surface Brillouin zone were also studied.

A database of *ab initio* results for surface force constants and how they vary with d_{12} was thus set up. This database was then used to parametrize a simple form of interatomic potential $U(r)$, with pairwise radial and tangential terms between nearest-neighbour (NN) atoms; with the potential for surface NN bonds between two atoms in layer 1 or one atom in layer 1 and another in layer 2 differing from that of bulk-like bonds. This potential can then be used to set up a dynamical matrix for a slab, which can be diagonalized to obtain phonon frequencies $\omega_{\mathbf{k}\lambda}$ (where $\mathbf{k}$ denotes wave vectors and λ is a branch index). The optimum value of d_{12} at a temperature T is then obtained by minimizing the free energy, given by

$$F(d_{12},T)=E_{\text{stat}}(d_{12})+k_BT\sum_{k\lambda}\ln\left\{2\sinh\left(\frac{\hbar\omega_{k\lambda}(d_{12})}{2k_BT}\right)\right\}, \tag{1}$$

where $E_{\text{stat}}(d_{12})$ is the static contribution to the free energy; the second term on the right-hand side is F_{vib}, the vibrational part of the free energy; $\hbar$ the Planck constant, and k_B the Boltzmann constant.

Figure 2 shows the result thus obtained for the relative contraction/expansion of d_{12} as a function of temperature; it can be seen that the calculation confirms the experimental observation of a strongly enhanced surface thermal expansion of d_{12}, with the initial contraction at lower temperatures getting reversed to an expansion at higher temperatures. This is accompanied (and driven) by a notable softening of the frequencies of surface phonons, and a concomitant increase in the amplitudes of vibration of surface atoms.[6]

3. Case 2: Reconstruction of gold (111)

As for the Ag(111) surface, atoms on the Au(111) surface would like to be closer to their neighbours. While atoms in the top layer of Ag(111) achieve this by relaxing towards the lower layers (at low temperatures), atoms on Au(111) instead choose to come closer to their neighbours within the topmost layer. This is achieved by alternating between domains in which atoms continue the bulk stacking sequence by occupying FCC sites, and domains in which atoms instead occupy sites corresponding to hexagonal-close-packed (HCP) stacking. The FCC domains are larger in width than the HCP domains, and the two are separated by transition regions in which the atoms sit in 'bridge' sites, and are pushed up out of the surface plane. This results in a corrugated surface topography that shows up as a double-striped pattern in STM images. These stripes can be oriented along three equivalent directions on the (111) surface; the surprise is that they are arranged in a superstructure consisting of alternating superdomains of two out of the three possible orientations, resulting in a 'herringbone' pattern with an extremely large unit cell periodicity of about 300 Å.[7, 8]

The actual reconstruction observed results from a balance between two opposing forces: surface atoms would like to be closer together than they are in the bulk structure; this can be theoretically treated by visualizing them as being connected by springs of force constant k whose favoured length b is less than a, the nearest-neighbour spacing in the bulk. However, it costs energy if surface atoms lose registry with the bulk; the physics of this can be modelled by a corrugation potential $V_c(r)$ due to the substrate, in which the surface atoms sit. These two opposing factors (stretched springs between surface atoms and an external corrugation potential) form the ingredients of the well-known Frenkel–Kontorova model.[9] The equilibrium structure is then found by minimizing the corresponding Hamiltonian:

$$H = \sum_i \frac{1}{2} k(l_i - b)^2 + \sum_j V_c(r_j), \tag{2}$$

where i and j run over all bonds and atoms in the surface layer, respectively; l_i is the length of the ith bond and r_j the position of the jth atom.

The two-dimensional version of this model was first applied to study the double-striped reconstruction on Au(111) by Takeuchi *et al.*,[10] who obtained $V_c(r)$, k and b from *ab initio* calculations. They found it indeed favourable for the surface to reconstruct into the double-striped pattern, with an optimum periodicity of $20a$, which compares well with the experimentally observed periodicity of $22a$.

To understand why the stripes then arrange into the herringbone, one can apply the theory of 'stress domains'.[11, 12] The double-striped reconstructed surface has a very anisotropic surface stress, since surface atoms have come closer together along one direction (normal to the walls separating FCC and HCP domains) but not along the perpendicular direction. In such a case, due to the presence of long-range elastic interactions, it is always favourable to have alternating domains in which the anisotropy of the surface stress changes direction. The distance between successive walls separating these stress domains is given by

$$l_0 = \pi a_d e^{C_1/C_2+1} \tag{3}$$

where a_d and C_1 describe the width and the energy per unit length, respectively, of the domain walls, and C_2 is a measure of how anisotropic the surface stress is for the double-striped pattern. Upon substituting values corresponding to the Au(111) surface, one finds that l_0 lies between 140 and 980 Å, which is in accordance with the experimentally reported values which range between 125 Å and 162 Å.[13]

Figure 3 shows a simulated STM image for the reconstructed Au(111) surface, using the structure determined by the Frenkel–Kontorova model in combination with the theory of stress domains. This image is in excellent agreement with experimental STM images of the reconstructed surface.

4. Case 3: Vibrational anisotropies and thermal contraction of FCC(110) surfaces

A (110) surface is obtained when an FCC crysal is cut along the diagonal of one of the faces of the conventional cubic unit cell. The geometry of the surface is quite different from that of the (111) surfaces considered above, and as a result the properties also differ considerably. While some (110) surfaces of FCC metals do reconstruct, I will consider the cases of Ag(110), Cu(110) and Al(110), none of which reconstruct. However, they do exhibit a pronounced oscil-

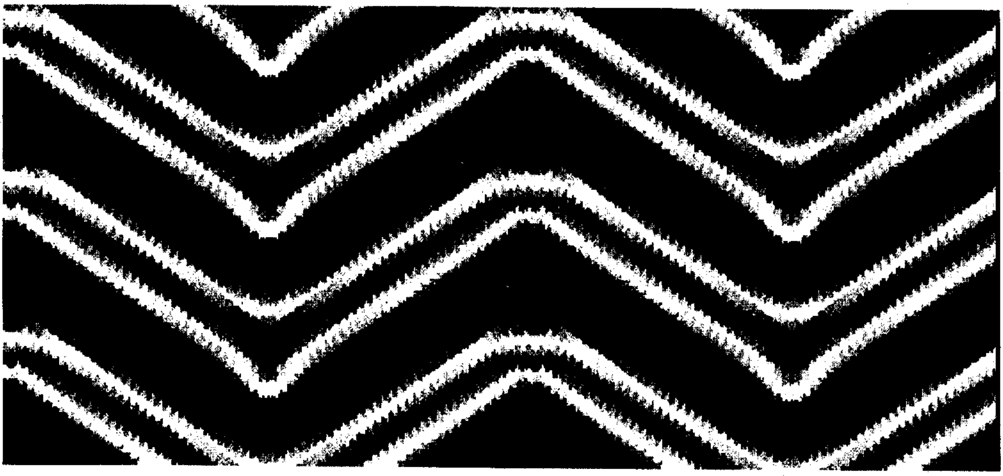

FIG. 3. Simulated STM image of the reconstructed Au(111) surface. Atoms are shaded according to the value of the corrugation potential at their coordinates. This mimics the surface corrugation measured by an STM.

latory relaxation of interlayer spacings, with successive interlayer spacings near the surface being alternately contracted and expanded.[14]

There are two main surprises in the thermal behaviour of these unreconstructed FCC(110) surfaces. One is the nature of the vibrational anisotropies for surface atoms.[15–17] Atoms in the surface layer are found to have larger amplitudes of vibration in the surface plane than normal to it, though one would expect the reverse to hold, given the absence of atoms in layers above. Also, one would expect vibrational amplitudes to decay monotonically as one goes from the surface to the bulk; however, the amplitude of vibration normal to the surface is larger for atoms in the second layer than for those in the first layer. The other surprise is the way in which the relaxation of interlayer spacings changes with temperature. While some interlayer spacings do indeed expand upon heating (as one would expect), the first interlayer spacing d_{12} for Al(110)[15, 18] and the second interlayer spacing d_{23} for Ag(110)[16] instead *contract* upon heating.

To understand the vibrational properties of these surfaces, one follows the same approach that was used above for Ag(111). Inter- and intralayer force constant tensors are obtained by performing *ab initio* frozen phonon calculations. One seemingly counter-intuitive result that emerges for all three (110) surfaces considered, upon following this procedure, is that if the topmost layer of atoms is moved along the z direction (normal to the surface), the force induced upon the *third* layer of atoms is found to be considerably larger than that on the second layer of atoms, and is almost twice as large as the corresponding value for the bulk crystal. However, it is notable that this result holds *only* for the relaxed surface, and not for the bulk-truncated surface (with all interlayer spacings fixed at bulk values).[19]

This implies that NN bonds between atoms in layers 1 and 3 (which are present on (110) surfaces but not on (111) surfaces) are extremely stiff, which can qualitatively explain the anomalous thermal features that are observed experimentally. The stiffness of these bonds significantly reduces the vibration normal to the surface of atoms in the topmost layer, leading to the reversed anisotropies observed experimentally, and also makes it very unfavourable to change the value of $d_{13} = d_{12} + d_{23}$. Thus, if d_{12} expands then there is a tendency for d_{23} to contract, and *vice versa*.

Quantitative results for vibrational amplitudes are obtained by following the same procedure as was used for Ag(111), first establishing a large database of *ab initio* results for inter- and intralayer force constants, and then using this to parametrize a model interatomic potential. One important difference for (110) surfaces is the additional presence of the crucial NN bonds between layers 1 and 3. This is then used, as before, to determine phonon frequencies $\omega_{\mathbf{k}\lambda}$ and eigenvectors $e_{i\alpha}^{\mathbf{k}\lambda}$, and the mean-squared displacement (MSD) at temperature T of atoms in layer i along the direction α is then given by

$$\left\langle u_{i\alpha}^{2}(T)\right\rangle = \frac{1}{N}\sum_{\mathbf{k}\lambda}\frac{\hbar}{M\omega_{\mathbf{k}\lambda}}\left(e_{i\alpha}^{\mathbf{k}\lambda}\right)\left(n_{\mathbf{k}\lambda}+\tfrac{1}{2}\right), \tag{4}$$

where the summation runs over all wave-vectors **k** in the surface Brillouin zone and all phonon branches λ, $\hbar$ is Planck's constant, M the atomic mass and $n_{\mathbf{k}\lambda}$ the Bose–Einstein distribution factor. Table I gives some values of MSDs computed using this formula. It is seen that the anisotropies are indeed reversed, in agreement with experiment and earlier molecular dynamics simulations using either *ab initio* (for Al(110))[20] or embedded atom (for Cu(110) and Ag(110))[21] potentials.

A simple geometric justification can be provided for the large enhancement in the radial force constant coupling NN atoms in layers 1 and 3 (Fig. 4). An atom in layer 1 of an FCC (110) surface has NN bonds to atoms in layers 1, 2 and 3. For the bulk-truncated surface, the lengths of these 1-1, 1-2 and 1-3 NN bonds are equal. When the surface relaxes, the contraction in d_{12} results in a shortening of the 1-2 and 1-3 bond lengths; the geometry of the surface is such that the 1-3 bond (which is normal to the surface) is shortened by a larger amount than

Table I
Selected values of mean squared displacements (in Å^2) for atoms in the two topmost layers T is the temperature in Kelvin

Material	Method	$T(K)$	$\langle u_{1y}^2\rangle$	$\langle u_{1z}^2\rangle$	$\langle u_{2y}^2\rangle$	$\langle u_{2z}^2\rangle$
A1(110)	This work	400	0.027	0.022	0.014	0.032
	AI-MD	400	0.028	0.019	0.013	0.030
	LEED	400		0.032		0.030
	MEIS	330	0.027	0.018	0.015	0.015
Ag(110)	This work	300	0.021	0.014	0.010	0.026
	EAM	300	0.020	0.013		
	MEIS	300	0.048	0.026	0.022	0.026
Cu(110)	This work	300	0.009	0.010	0.007	0.010
	EAM	300	0.019	0.013	0.010	0.014
	HAS	300		0.012		

The values are compared with results from *ab initio* molecular dynamics (AIMD, Marzari *et al.*[20]) and embedded atom method (EAM, Yang and Rahman[21]) simulations, and experiments using MEIS (Busch and Gustafsson[16, 17]), LEED (Goebel and von Blanckenhagen[18]) and helium atom scattering (HAS, Zeppenfeld[22]).

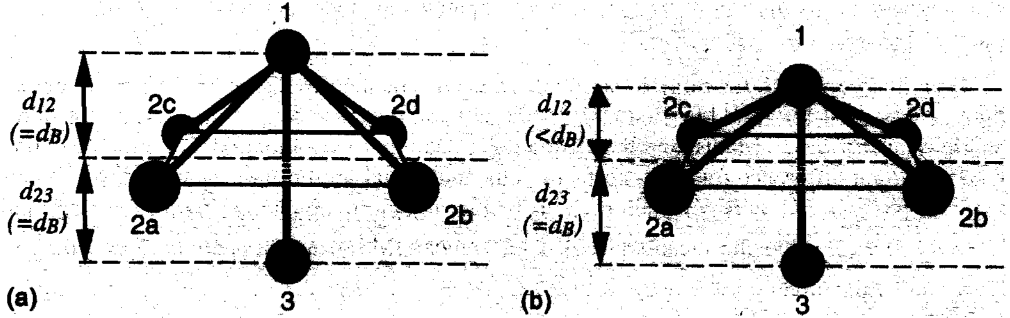

FIG. 4. Bond geometry for FCC(110) surfaces: interlayer bonds involving atoms in the topmost layer for (a) the bulk-truncated (unrelaxed) surface and (b) surface with first interlayer spacing d_{12} relaxed. Atom 1 is in the topmost layer, atoms 2a, 2b, 2c and 2d are in the second layer, and atom 3 is in the third layer.

the 1-2 bond (which lies at an angle to the surface). Since bond stiffnesses scale as a high power of bond lengths, it is reasonable that, while both 1-2 and 1-3 NN bonds become stiffer, the much larger effect is for the 1-3 bond. These geometric arguments are independent of specific features of the electronic structure and should therefore also apply in general to other unreconstructed (110) faces of FCC metals.

5. Conclusions

It is seen that even supposedly 'simple' surfaces—of elemental metals with simple bulk structures—exhibit complex structural and thermal behaviour. Many of these phenomena are the outcome of a delicate balance between different terms in the energy, which can be reliably determined by *ab initio* calculations. Temperature is found to play an important role. These results will have important implications in growing overlayers on surfaces of these metals and in their use as catalysts.

References

1. HOHENBERG, P. AND KOHN, W.	*Phys. Rev. B*, 1964, **136**, 864.
2. KOHN, W. AND SHAM, L. J.	*Phys. Rev. A*, 1965, **140**, 1133.
3. STATIRIS, P., LU, H. C. AND GUSTAFSSON, T.	*Phys. Rev. Lett.*, 1994, **72**, 3574.
4. LEWIS, L. J.	*Phys. Rev. B*, 1994, **50**, 17693.
5. NARASIMHAN, S. AND SCHEFFLER, M.	*Z. Phys. Chem.*, 1997, **202**, 253.
6. NARASIMHAN, S.	*Surf. Sci. Lett.*, 1998, **417**, L1166.
7. HUANG, K. G., GIBBS, D., ZEHNER, D. M., SANDY, A. R. AND MOCHRIE, S. G. J.	*Phys. Rev. Lett.*, 1990, **65**, 3313.
8. BARTH, J. V., BRUNE, H., ERTL, G. AND BEHM, R. J.	*Phys. Rev. B*, 1990, **42**, 9307.
9. FRENKEL, Y. I. AND KONTOROVA, T.	*Zh. Eksp. Reor. Fiz.*, 1938, **8**, 1340.

10. Takeuchi, N., Chan, C. T. and Ho, K. M. *Phys. Rev. B*, 1991, **43**, 13899.
11. Marchenko, V. I. *JETP Lett.*, 1981, **33**, 381.
12. Alerhand, O. L., Vanderbilt, D., Meade, R. D. and Joannopoulos, J. D. *Phys. Rev. Lett.*, 1988, **68**, 1973.
13. Narasimhan, S. and Vanderbilt, D. *Phys. Rev. Lett.*, 1992, **69**, 1564.
14. Barnett, R. N., Landman, U. and Cleveland, C. L. *Phys. Rev. B*, 1983, **27**, 6534.
15. Mikkelsen, A., Jiruse, J. and Adams, D. L. *Phys. Rev. B*, 1999, **60**, 7796.
16. Busch, B. W. and Gustafsson, T. *Surf. Sci.*, 1998, **407**, 7.
17. Busch, B. W. and Gustafsson, T. *Phys. Rev. B*, 2000, **61**, 16097.
18. Goebel, H. and von Blanckenhagen, P. *Phys. Rev. B*, 1993, **47**, 2378.
19. Narasimhan, S. *Phys. Rev. B*, 2001, **64**, 125409.
20. Marzari, N., Vanderbilt, D., De Vita, A. and Payne, M. C. *Phys. Rev. Lett.*, 1999, **82**, 3296.
21. Yang, L. and Rahman, T. S. *Phys. Rev. Lett.*, 1991, **67**, 2327.
22. Zeppenfeld, P. *Phase transition and dynamics of solid surfaces and physisorped layers*, Ph. D. Thesis, Kernforschungsanlagel, Jülich, 1989.