1
Peculiarities of the Metallic Surface

1.1
Surface Energy and Surface Stress

The first law of thermodynamics states that

$$dQ = dU + dW \tag{1.1}$$

where dQ is the increment in the heat energy of the system, dU is the increment in the internal energy and dW is a work that the system has performed. Only dU is the total differential and it is independent of the method of system transition from one state to another.[1)] dQ and dW are simply infinitesimal quantities. In fact, (1.1) is the law of the energy conservation for an isolated system.

Substituting $dQ = T\,dS$ and $dW = p\,dV$ in (1.1) one arrives at

$$dU = T\,dS - p\,dV \tag{1.2}$$

where S is the entropy, T is the temperature, p is the pressure, V is volume of the system.

The internal energy of the system depends also on the number N of particles, that is, atoms or molecules. Thus, one should add the corresponding term:

$$dU = T\,dS - p\,dV + \mu\,dN \tag{1.3}$$

where μ is the chemical potential. The chemical potential is defined as a change in the internal energy when the number of particles varies at constant entropy and volume:

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} \tag{1.4}$$

1) If the internal energy is a function of the pressure and the temperature, $U = U(p,T)$, then the infinitesimal increment in the internal energy is given by $dU = \left(\frac{\partial U}{\partial p}\right)_T dp + \left(\frac{\partial U}{\partial T}\right)_p dT$.

Strained Metallic Surfaces. Valim Levitin and Stephan Loskutov

ISBN: 978-3-527-32344-9

The internal energy U increases (or, on the contrary, decreases) if

- the system receives (returns) the heat or
- mechanical work is done under the system (the system does mechanical work) or
- the number of particles in the system increases (decreases).

Turning to the free energy. The Helmholtz free energy F is known to be equal to

$$F = U - TS \tag{1.5}$$

Differentiating (1.5) and combining with (1.3) we obtain

$$dF = -S\,dT - p\,dV + \mu\,dN \tag{1.6}$$

At constant temperature and volume the increment in the free energy varies linearly with increase in the particle number,

$$dF = \mu\,dN \tag{1.7}$$

with the proportionality factor $\mu = \mu(T, V)$.

The Gibbs thermodynamic potential $G = F + pV$ is expressed as

$$dG = -S\,dT + V\,dp + \mu\,dN \tag{1.8}$$

The difference between the Helmholtz free energy and the Gibbs thermodynamic potential is insignificant under atmospheric pressure for a bulk solid.

Molecules of the surface layer in a homogeneous liquid are known to be attracted by other molecules within the liquid. Unlike in the body of the liquid the attraction of surface molecules is not compensated. Liquids turn out to be covered by an elastic stretched film and so the concept of surface tension is used for them.

The thermodynamic approach can also be applied to the surface of solids. J. W. Gibbs was the first to note that the surface contributes to the free energy. He also considered the cleavage process of a bulk body.

In order to create a free surface one must break the bonds between neighboring atoms. This implies that the creation of an additional piece of surface costs the system extra energy. The surface energy is equal to the work necessary in order to form the unit area of surface by a process of division of the solid into parts. This process is assumed to be thermodynamically reversible.

The reversible work dW required for an external force to create an infinitesimal area dA of the surface is directly proportional to this area

$$-dW = \gamma\,dA \tag{1.9}$$

where γ is a proportionality factor. It is dependent on temperature, volume, and the particle number.

The minus in (1.9) implies that the work performed by an external force is expended for increase in the Helmholtz free energy of dF. Since, for a reversible and equilibrium process, $dF = -dW$, the surface contribution to the free energy must be proportional to the increment in the surface area,

$$dF = \gamma\, dA \tag{1.10}$$

The factor of proportionality γ can be identified as the excess of the free energy per unit area. Thus, the surface energy γ is also defined as

$$\gamma = \left(\frac{dF}{dA}\right)_{T,V,N} \tag{1.11}$$

The temperature, the volume of crystal and the number of atoms are assumed to be constant. The reversibility requirement in the definition of γ implies that the composition in the surface region is also in thermodynamic equilibrium. Recall also that distances between atoms remain unchanged.

The unit of surface energy is $\mathrm{J\,m^{-2}}$ or $\mathrm{N\,m^{-1}}$.

A variation in the free energy of a solid through the equilibrium cleaving process, in a general case, is given by

$$dF = -S\, dT - p\, dV + \mu\, dN + \gamma\, dA \tag{1.12}$$

Gibbs pointed out that, for solids, there is another important quantity to be considered. It is the work per unit area needed to elastically stretch (or compress) a pre-existing surface. Solid surfaces exhibit a surface stress which is similar to surface tension in a liquid.

As long ago as 1950 Shuttleworth [9] emphasized the distinction between the surface Helmholtz free energy, and the surface stress. The surface energy is the work necessary to form unit area of a surface by a process of splitting up, the cleavage. The surface stress is the tangential stress (force per unit length) in the surface layer; this stress must be balanced either by external forces or by volume stresses in the body. For crystals, the surface stress is not equal to the surface energy. Both quantities have the same units, but the surface stress is a second-rank tensor, whereas the surface energy is a scalar quantity.

The broken interatomic bonds cause the surface stress. The atomic configuration at the surface is dissimilar to that within the body. Surface atoms therefore have a different arrangement than if they were constrained to remain in the interior of the solid. Therefore, the interior atoms are viewed as exerting a stress on the surface (moving them out of the positions they would otherwise occupy).

The cleavage of a body creates new surfaces. The excess in the surface free energy dF_s consists of two parts,

$$dF_s = dF_{s1} + dF_{s2} \tag{1.13}$$

or

$$dF_s = d(\gamma A) = \gamma\, dA + A\, d\gamma. \tag{1.14}$$

The first term $dF_{s1} = \gamma\, dA$ describes the work needed to break down interatomic bonds and to create the surface area dA. The average area per atom is unchanged, but the number of atoms on the surface increases.

The second term $dF_{s2} = A\, d\gamma$ contributes the free energy due to changes in the interatomic distances on new surfaces. These changes are balanced in the macroscopic and microscopic areas. The number of atoms on the surfaces remain unchanged. The stressed surface contributes a surface energy with an increment $d\gamma$.

A change in the surface area may be considered in a macroscopic sense as the consequence of stresses acting on surface atoms [6]. A tensor with components σ_{ij} (where $i, j = 1, 2$) defines the stresses on the surface in an approximation of elasticity theory. The strain tensor has components ε_{ij}. It is used to express the elastic deformation of the solid surface.

Consider a plane normal to the surface and label the normal to the plane as the direction j. σ_{ij} is the force per unit length which atoms exert across the line of intersection of the plane with the surface in the $i - th$ direction. The strain tensor ε_{ij} is defined in a similar way.

The work done in the surface can be expressed as the change in the elastic energy

$$dF_s = A \sum_{i,j=1}^{2} \sigma_{ij} d\varepsilon_{ij} \tag{1.15}$$

The increment in the surface is given by

$$dA = A \sum_{i=1}^{2} d\varepsilon_{ii} = A \sum_{i,j=1}^{2} \delta_{ij} d\varepsilon_{ij} \tag{1.16}$$

The total differential of the surface stress γ is written as

$$d\gamma = \sum_{i,j=1}^{2} \frac{\partial \gamma}{\partial \varepsilon_{ij}} d\varepsilon_{ij} \tag{1.17}$$

Combining (1.14)–(1.17) and making the coefficients at $d\varepsilon_{ij}$ equal one obtains

$$\sigma_{ij} = \gamma \delta_{ij} + \frac{\partial \gamma}{\partial \varepsilon_{\,ij}} \tag{1.18}$$

The surface stress σ_{ij} and the stress-induced elastic strain are tensors related to each other by (1.18).

For most surfaces, the off-diagonal components are equal to zero in appropriate coordinates, that is, the surface stress is isotropic. In this case, the surface stress can be viewed as a scaler quantity

$$\sigma = \gamma + \frac{d\gamma}{d\varepsilon} \tag{1.19}$$

This indicates that the difference between the surface free energy and the surface stress is the change in the free energy per unit change in the elastic strain of the surface. A better way is to consider σ as the force per unit length (or work per unit area) exerted on a surface during elastic deformation; and to consider γ as the force per unit length (or work per unit area) exerted on a surface during plastic deformation [6].

The surface energy depends on the crystal plane orientation. The value γ is a function of $\vec{n}$, $\gamma = f(\vec{n})$, where $\vec{n}$ is perpendicular to a plane (hkl) in the crystal lattice.

The experimental measurement of the surface energy for solids is extremely difficult. There are few data about values of γ in the literature. However, several efforts to calculate the surface energy have been made.

The authors of [11] used the density functional theory to establish a database of surface energies for low index surfaces of 60 metals from the periodic table. The absolute values are of the order of several $\mathrm{J\,m^{-2}}$. The values vary when the surface orientation changes.

Some data are presented in Table 1.1.

Table 1.1 Surface energies for different crystal planes in some metals, $\mathrm{J\,m^{-2}}$.

Metal	(100)	(110)	(111)	Ref.
Al	1.35	1.27	1.20	11
Au	1.63	1.70	1.28	11
Mo	3.34	2.92	3.24	10
W	4.64	4.01	4.45	11

1.2 Crystal Structure of a Surface

A scheme of some characteristic rearrangements of surface atoms for the cubic crystal lattice is presented in Figure 1.1. A compression or an extension of the topmost layer leads to change in interatomic spacing. The bulk spacing c_{bulk} decreases to values c_2 and c_1. This variation is normal to the surface and is called the relaxation (Figure 1.1a).

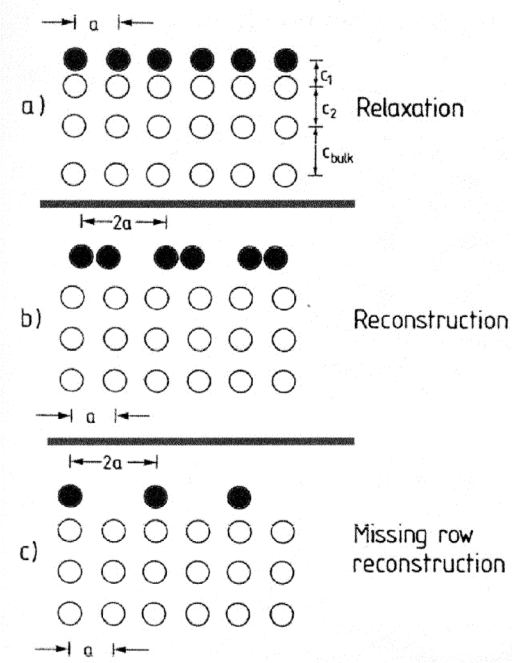

Fig. 1.1 Schematic view of characteristic rearrangements of surface atoms in a cubic crystal lattice. a is the crystal lattice constant. Reprinted from [4] with permission from Springer.

The atomic configuration shown in Figure 1.1b is related to a shift in the atoms parallel to the surface. This type of atomic rearrangement is called reconstruction. Missing row reconstruction is also possible (Figure 1.1c).

In Figure 1.1 only idealized models of atom distributions are shown. In reality, the atomic rearrangements are more complex. The atom structure of the surface is dependent on the bond type. It is different in semiconductors with their directed covalent bonds and in metals, which have delocalized electronic bonds. In many semiconductors, which are tetrahedrally bonded, such as silicon, germanium, GaAs, and InP, the directedness of bonds in the bulk has a dramatic effect and may result in directed bonds at the surface.

There are no convincing experimental data on surface relaxation [1]. Calculations on the relaxation of the surface layer for metallic crystals have been made using models in which the bonds between pairs of atoms were considered.

The results for copper obtained using a Morse interaction potential are shown in Figure 1.2. It is found that the surface layer is displaced by 5–20%. The displacement of atoms from equilibrium positions decreases exponentially with the layer number. The greater the atom density in the crystal plane the less atomic displacements there will be in the surface layers.

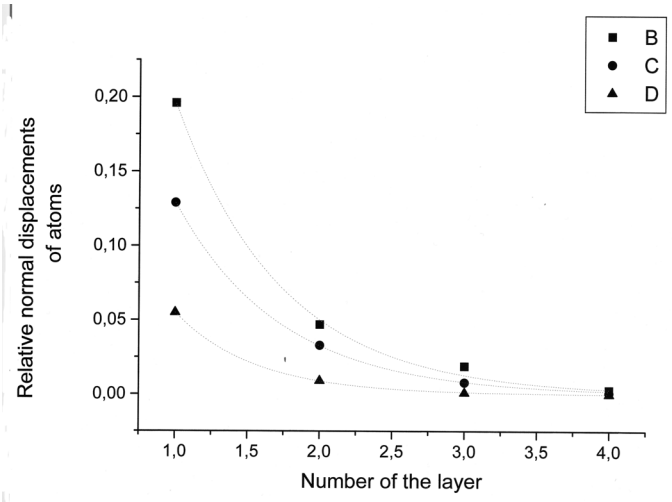

Fig. 1.2 Displacements of atom layers near the surface of copper. B, crystal plane (110), the atom density equals 10.86 at. nm^{-2}; C, plane (100), 15.36 at. nm^{-2}; D, plane (111), 17.74 at. nm^{-2}. The calculated data from [12] are plotted in the graph.

The structure of the first crystal plane differs from that of the underlying planes even in an ideal clean surface. Such a structure is in fact a superstructure (the overlayer structure). One uses a special notation in order to designate the dimensions, nature and orientations of the unit cell of the first plane relative to the underlying ones. These notations are useful also when an ordered adsorbed layer is present at the surface.

The position of an atom at the surface is given by the vector $\vec{r}$

$$\vec{r} = m\vec{a} + n\vec{b} \tag{1.20}$$

where $\vec{a}$ and $\vec{b}$ are the translation vectors of the solid and m and n are integers. Then the superstructure can be labeled by E $\{hkl\}p(m \times n)$ or E $\{hkl\}c(m \times n)$. E is a chemical element, p represents a primitive cell, c denotes a centered one. The surface unit cell can be rotated with respect to the substrate unit cell. The ratio of the dimensions of these cells cannot be an integer. The notation $E\{hkl\}c(m \times n)R\theta$ means a surface structure that is obtained from the surface plane unit cell by a rotation trough an angle θ, the length of the basis vectors being multiplied by m and n, respectively.

For instance, a clean surface {100} for nickel is denoted by $\mathrm{Ni}\{100\}c(1 \times 1)$. The superstructure formed by the absorbtion of oxygen atoms on this surface is the $\mathrm{O}\{100\}c(2 \times 2)$ structure.

Matrix notation is also used for the occurring superstructure.

The relationship between the vectors of an overlayer structure $\vec{a_2}, \vec{b_2}$ and basis vectors $\vec{a_1}, \vec{b_1}$ that correspond bulk layers is given by

$$\vec{a_2} = G_{11}\vec{a_1} + G_{12}\vec{b_1}; \tag{1.21}$$

$$\vec{b_2} = G_{21}\vec{a_1} + G_{22}\vec{b_1}. \tag{1.22}$$

Thus, vectors $\vec{a_2}, \vec{b_2}$ of an overlayer structure can be obtained from basis vectors $\vec{a_1}, \vec{b_1}$ by the conversion

$$\begin{pmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{pmatrix} \tag{1.23}$$

Figure 1.3 presents an example of the notations.

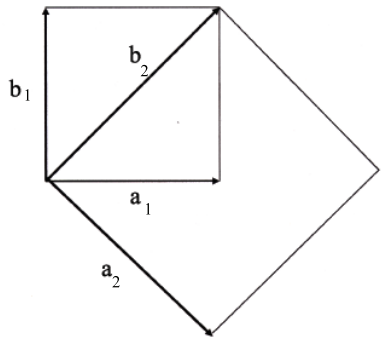

Fig. 1.3 Vectors $\vec{a_2}$ and $\vec{b_2}$ define the superlattice, vectors $\vec{a_1}$ and $\vec{b_1}$ are the vectors of the plane inside the bulk. The surface superstructure has a possible notation E $\{100\}c(\sqrt{2} \times \sqrt{2})\ R45^\circ$ or $\left(\begin{smallmatrix} 1 & \bar{1} \\ 1 & 1 \end{smallmatrix}\right)$.

In such a case

$$\vec{a_2} = \vec{a_1} - \vec{b_1};$$

$$\vec{b_2} = \vec{a_1} + \vec{b_1}.$$

Consequently, the corresponding matrix is

$$\begin{pmatrix} 1 & \bar{1} \\ 1 & 1 \end{pmatrix} \tag{1.24}$$

1.3 Surface Defects

Defects always exist on real surfaces. Figure 1.4 shows, schematically, defects of different dimensionality. Defects of zero dimension are vacancies, adatoms,

ledge adatoms, and kinks. Their sizes in three dimensions are of the order of the interatomic distance. On the surface of a compound crystal one can distinguish between adatoms of the same kind or foreign adatoms. The step is a one-dimensional defect, in which the ledge separates two terraces from each other. In many cases steps of the single atomic height prevail over steps of several atomic heights. There are also groups of defects such as divacancies, and steps of some interatomic distances in height.

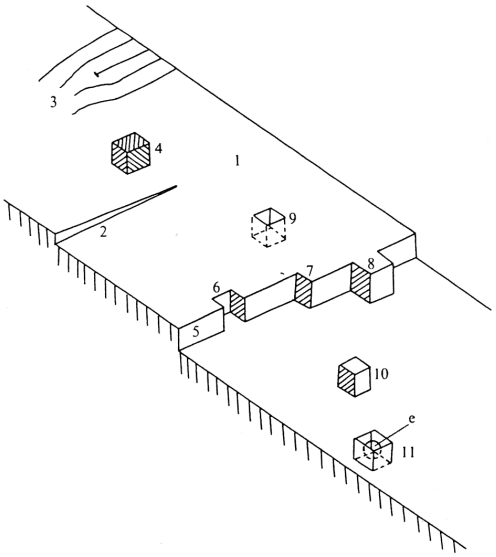

Fig. 1.4 Various defects that may occur on a solid surface: 1, a terrace, i.e. the perfect flat face itself; 2, an emerging screw dislocation; 3, the intersection of an edge dislocation with the terrace; 4, an impurity adatom; 5, a monoatomic step; 6, a vacancy in the ledge; 7, a step in the ledge–a kink; 8, an adatom of the same kind as the bulk atoms situated upon the ledge; 9, a vacancy in the terrace; 10, an adatom on the terrace; 11, a vacancy in the terrace where an electron is trapped. Reprinted from [2] with permission from Oxford University Press.

Different positions of atoms have various numbers of neighboring atoms. For example, an atom on a terrace has the largest number of neighbors. Atoms on steps and adatoms have the least number of neighbors.

Other important defects are dislocations which can be generated by the strained surface. (Figure 1.5). An edge dislocation penetrating into a surface with the Burgers vector oriented parallel to the surface, creates a point defect. In a typical well-annealed single crystal the density of dislocation–surface interactions is of the order of $10^8 - 10^{10}\ \mathrm{m}^{-2}$.

Formation of steps at the surface is shown schematically in Figure 1.6. The sources of the dislocations are situated along slip lines. Dislocations emitted by sources move along the slip planes and appear on the surface.

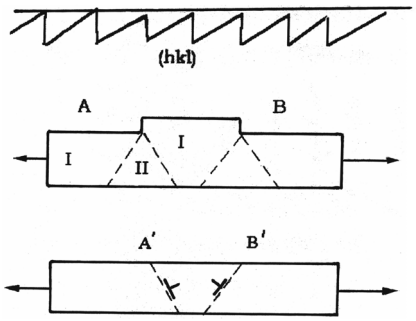

Fig. 1.5 Generation of dislocations at a surface. The surface roughness on a plane (hkl) is shown. During deformation the surface acts as a dislocation source. A' and B' are slip planes, A and B are steps that have opposite signs, I and II are shifted parts of the crystal.

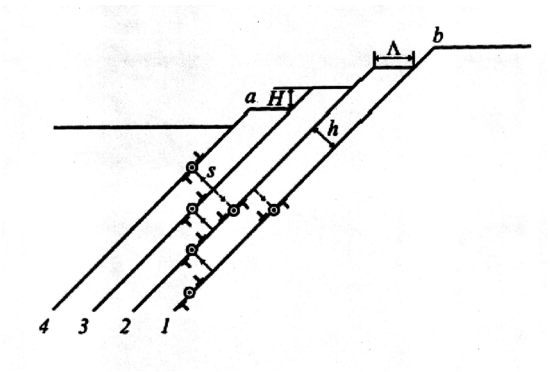

Fig. 1.6 Formation of steps at the metallic surface. ab is a slip band, 1 - 4 are slip lines, s are dislocation sources, h is the mean distance between slp lines, H is the mean hight of steps.

The surface is known to attract a dislocation with the force $F = -\mu b^2/4\pi l$, where μ is the shear modulus, b is the Burgers vector and l is the distance from the free surface. A step is formed at the surface. Many dislocations take part in the formation of a step. However, polyatomic steps are unstable energetically and transform to monatomic steps.

The microscopic structure of the surface is changed as a result of deformation. The technique of tunnel microscopy enables one to reveal the formation and change in the nanometric defects on the surface of thin polished films of copper [13].

The applied stress leads to the generation of four ensembles of surface nanometric defects. These ensembles differ from one another in dimension and energy of formation. They have the shape of a prism. One of the walls is per-

pendicular to the surface, another one is inclined at 30°. Figure 1.7 shows an example of a nanometric surface defect. Walls of nanodefects consist of steps with a width of from 5 to 50 nm. Their walls are formed as a consequence of the output of dislocations along planes of the light slip. Sources of dislocations belong also to a set of four ensembles. The authors [13] believe that when the concentration of nanodefects amounts to $\sim 5\%$ part of them resolves. Another part enlarges into defects of the next ensemble.

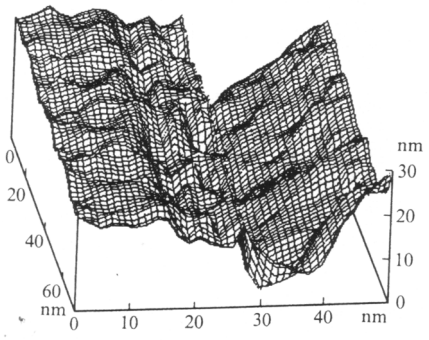

Fig. 1.7 The nanometric defect on the surface of strained copper (after [13]).

Steps are important in the formation of vicinal surfaces, that is, high-index surfaces. Such vicinal surfaces are formed by small low-index terraces and a high density of regular steps. The steps in a simple cubic structure are shown in Figure 1.8. The normal to the surface is slightly inclined to the [001] direction. The inclination angle ϑ to the [001] axes is given by $\tan\vartheta = 1/4$.

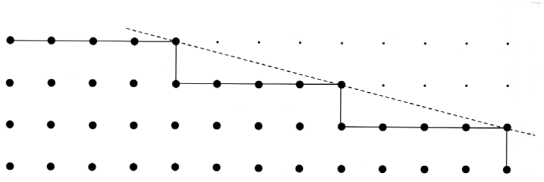

Fig. 1.8 Terraces, ledge atoms and steps in a simple cubic crystal. Terraces are located along (001) plane, steps are parallel to (010). The surface plane is (014). Reprinted from [6] with permission from Springer Science.

A convenient notation was proposed [14] for the geometrical structure of steps. A stepped surface is denoted by

$$p(hkl) \times (h'k'l'),$$

where hkl are the Miller indices of the terraces, $(h'k'l')$ are the indices of the ledges, and p gives the number of atomic rows in the terrace parallel to the

edge. In Figure 1.9a $6(111) \times (001)$ stepped surface is presented. A series of six-atom terraces are separated by $(100) \times (111)$ steps in the face-centered cubic crystal lattice.

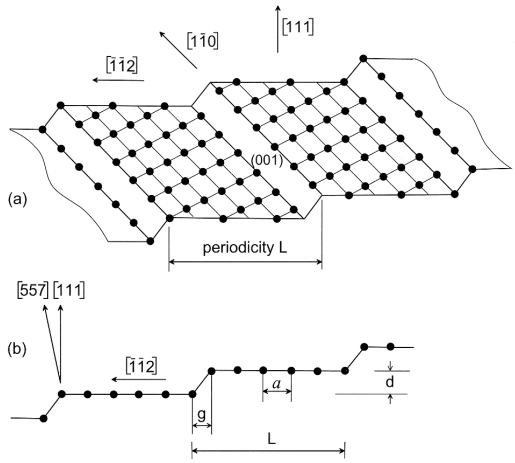

Fig. 1.9 Steps on the (557) surface of a face-centered cubic crystal. (a) Positions of the lattice points in a $6(111) \times (011)$ stepped surface. (b) The characteristic length and heights are shown. Reprinted from [6] with permission from Springer Science.

This type of stepped surface is obtained by cutting the crystal along a plane making a small angle ($\leq 10^\circ$) with a low-index plane. Such surfaces show a periodic succession of steps of monoatomic height and flat terraces.

On metal surfaces the step tends to be smoothed out by the gas of free electrons, which forms dipole moments due to the spatially fixed positive ion cores.

In semiconductors the different dangling (free) bonds might modify the electronic energy levels near the steps.

Surface defects are centers of chemical activity. The degree of adsorption increases exponentially with an increase in the defect density.

The resistance of the material to deformation is strongly affected by films on the surface. The scheme in Figure 1.10 is an illustration of the decrease in strength of a crystal with an active liquid on the surface (the Rebinder effect). Other surface films can increase the strength.

1.4 Distribution of Electrons near the Surface

Many microscopic phenomena on the surface result from special features of the electron subsystem. Properties of the electronic structure near the surface

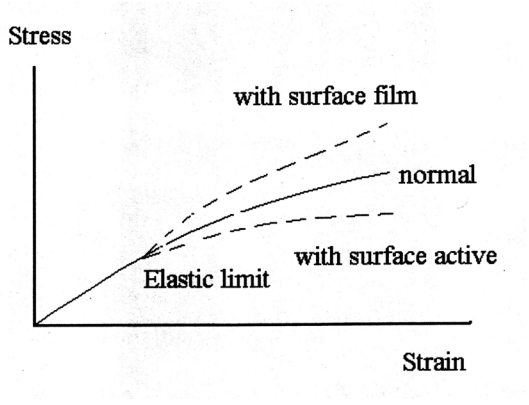

Fig. 1.10 The dependence of stress on strain for the different surface states.

are somewhat different from those inside the bulk. This is mainly because part of interatomic bonds are broken at the surface. These broken bonds are called dangling bonds. This means that unpaired electrons tend to bond with each other or with foreign atoms. The neighboring atoms can form pairs that are called dimers.

In Figure 1.11 the bonds between the surface atoms are shown. The lattice parameter of the surface crystal cell increases to twice its length in one direction, compared with the perpendicular direction. This effect is termed the 2×1 reconstruction.

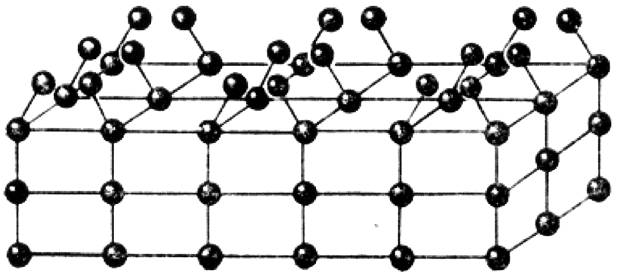

Fig. 1.11 Formation of atomic dimers on the surface. Reconstruction 2×1.

There is still no reliable experimental technique for the unequivocal determination of the atomic structure of the topmost surface layer. One has therefore to consider various models of the surface structure. As usual, the calculations based on the model have to be compared with experimental data.

A quantum-mechanical description of the electronic properties has been worked out for simple metals. It begins with the description of a gas of free electrons. In order to describe the basic properties of the surface one examines the problem of many bodies in the framework of density functional theory. This theory was developed in order to discuss the basic electronic properties of metals.

Here we follow the approach of Blakely [1] as well as that of Lüth [4] and Kiejna and Wojciechowsky [5].

1.4.1 Model of Free Electrons in Solids

Let us consider a cubic box of size $L \times L \times L$ of a monovalent metal. Inside the metal crystal the electrostatic potential $V(\vec{r})$ is a periodic function of the distance. However, electrons are trapped by the metallic ions inside the metal. According to the Sommerfeld idea one can represent the bonding between ions and electrons by an infinite potential barrier at the metal surface. In that case the electrostatic potential $V(\vec{r})$ =const =a in the box and $V(\vec{r}) = \infty$ elsewhere. The positive charge is distributed inside the cubic box with a constant density $\varrho_+(r) = ne$, where n is the number of ions per unit volume and e is the charge of the electron. The state of each electron is described by the Schrödinger wave equation

$$\left[-\frac{\hbar}{2m}\nabla^2\psi + V\psi\right] = E\psi \tag{1.25}$$

where $\hbar = h/2\pi$, h is the Planck constant, m is the mass of an electron, ψ is the wave function, V is the potential due to all the other electrons and the positive charge in the system and E is the total energy of the electron[2)].

The motion of the electron is limited by the surface. The energy E of the electron in a bound state varies discretely.

The wave function squared, ψ^2, determines the local position of the electron in space. For example, in the one-dimensional case the probability w to find an electron in a segment dz is given by

$$w(z) = \psi^2(z)\,dz$$

The function $w(z)$, as any probability function, has a property

$$\int_{-\infty}^{+\infty} \psi^2(z)\,dz = 1$$

2) Atomic units are used in quantum physics. The Bohr radius $a_0 = 0.529177 \times 10^{-10}$ m is a unit of length. The mass of the electron is equal to $m = 9.109534 \times 10^{-31}$ kg. The electron charge $e = 1.602169 \times 10^{-19}$ C, and the Planck constant $\hbar = 1.054589 \times 10^{-34}$ J s. In order to convert SI units into atomic units one has to put $m = \hbar = e = 1$.

The boundary conditions $\psi(x, y, z) = 0$ must be justified on the surfaces of the box under consideration. The solution of (1.25) is given by

$$\psi(x, y, z) = \left(\frac{8}{L^3}\right)^{1/2} sin\left(\frac{\pi n_x x}{L}\right) sin\left(\frac{\pi n_y y}{L}\right) sin\left(\frac{\pi n_z z}{L}\right) \tag{1.26}$$

where positive integers $n_x, n_y, n_z = 1, 2, 3 \ldots$. On the surface of the cube, the boundary conditions $\psi(x, y, z) = 0$ are fulfilled.

The energies of the electron can have only discrete quantities. They are given by

$$E = \frac{\pi^2 \hbar^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right) \tag{1.27}$$

The possible kinetic energies of the electron can also be expressed as

$$E = \frac{\hbar}{2m}\vec{k}^2 = \frac{\hbar}{2m}(k_x^2 + k_y^2 + k_z^2) \tag{1.28}$$

where k_x, k_y, k_z are components of the wave vector $\vec{k}$:

$$k_x = \frac{\pi n_x}{L}$$

and similarly for k_y and k_z.

The lowest energy level is equal to

$$E(1, 1, 1) = \frac{\pi^2 \hbar^2}{2mL^2}(1 + 1 + 1) \tag{1.29}$$

Only two electrons can have the same energy level. According to the Pauli principle, successive electrons have to occupy higher levels. The energy of the electrons of the highest occupied state at $T = 0$ is called the Fermi energy E_F. It is related to the concentration of electrons:

$$E_F = \frac{\hbar^2}{2m}(3\pi^2 \overline{n})^{2/3} \tag{1.30}$$

where $\overline{n}$ is the average electron density. The available energetic states are filled at $T = 0$ K up to a maximum value of $|\vec{k}|$. This is denoted by k_F and is called the Fermi momentum.

$$k_F = (3\pi^2 \overline{n})^{1/3} \tag{1.31}$$

Thus

$$E_F = \frac{\hbar^2}{2m}k_F^2 \tag{1.32}$$

A characteristic volume falling on one electron is equal to

$$\frac{4}{3}\pi r_0^3 = \frac{L^3}{N} \tag{1.33}$$

In units of the Bohr radius a_0 the so called Wigner–Seitz radius r_s is given by

$$r_s = \frac{r_0}{a_0} = \frac{(3/4\pi\overline{n})^{1/3}}{a_0} \tag{1.34}$$

where r_s is measured in atomic units.

In Table 1.2 parameters of the electron subsystem in some metals are presented. The parameters were calculated based on the valency of metals and volumes of their crystal unit cells.

Table 1.2 Parameters of the electron subsystem in some metals. Z is the number of the element in the periodic table. fcc is the cubic face-centered crystal lattice, bcc is the cubic body-centered, hcp is the hexagonal close-packed, cc is the cubic complicated crystal lattice. $\overline{n}$ is the electron concentration, E_F is the Fermi energy, r_s is the characteristic radius, k_F is the Fermi momentum.

Metal	Z	Crystal lattice	Valency	$\overline{n}, 10^{29}$ m^{-3}	E_F, eV	r_s, a.u.	$k_F, 10^{10}$ m^{-1}
Na	11	bcc	1	0.254	3.15	3.99	1.75
Mg	12	hcp	2	0.867	7.14	2.65	1.37
Al	13	fcc	3	1.81	11.7	2.07	1.75
Ti	22	hcp	4	3.02	16.5	1.75	2.08
V	23	bcc	5	3.58	18.4	1.65	2.20
Cr	24	bcc	6	5.03	23.1	1.47	2.46
Mn	25	cc	2	1.65	10.9	2.14	1.70
Fe	26	bcc	2	1.70	11.1	2.12	1.71
Co	27	hcp	2	4.82	22.7	1.50	2.43
Ni	28	fcc	2	1.84	11.8	2.06	1.81
Cu	29	fcc	1	0.847	7.0	2.67	1.36
Nb	41	bcc	5	2.80	15.6	1.79	2.02
Mo	42	bcc	6	3.84	19.3	1.61	2.25
Ag	47	fcc	1	0.586	5.49	3.02	1.20
W	74	bcc	6	3.81	19.1	1.62	2.24
Au	79	fcc	1	0.590	5.53	3.01	1.21
Pb	82	fcc	4	1.32	9.47	2.30	1.58

The concentration of electrons in metals varies in the range $(0.25 - 5.03) \times 10^{29}$ m^{-3}. The Fermi energy ranges from 5.5 to 20 eV. The five and six-valency metals with the body-centered crystal lattice V, Cr, Nb, Mo, W have larger values of $\overline{n}$ than do metals with the face-centered crystal lattice Al, Ni, Cu, Ag, Pb, Au.

It is worth considering the correlation between the concentration of the electrons $\overline{n}$ in a metal and the parameters of strength of the crystal lattice.

We may choose a mean-square amplitude of the atom vibrations $\overline{u^2}$ as a measure of the interatomic bonds. The temperature dependence of this value $\overline{du^2}/dT$ is a characteristic of the crystal lattice strength of solid metals. The vibration of the atoms can be compared if one takes into account the different mass m of the atoms. The value of $\overline{u^2}$ was found to be inversely proportional to the atomic mass [15]. Consequently, it is expedient to exclude the mass effect by multiplying values $\overline{du^2}/dT$ by the mass of one atom.

Thus, we have found [15] the reduced amplitude, that is, the parameter η, which characterizes the strength of the interatomic bonds,

$$\eta = m\frac{\overline{du^2}}{dT} \tag{1.35}$$

The less the reduced amplitude η, the greater the strength of the crystal lattice.

In Figure 1.12 the correlation between the electron concentration and the parameter η is presented.

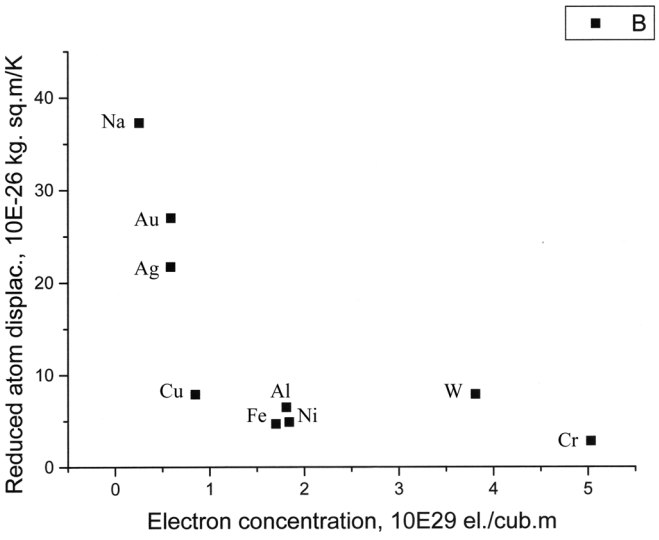

Fig. 1.12 Correlation between the electron concentration in metals and the reduced amplitude of atomic vibrations.

The interatomic bonds in metals are realized by free electrons. From this point of view the correlation in Figure 1.12 seems to be logical. Also Figure 1.12 shows chromium as a material with strong interatomic bonds. Similar properties are indicated by the values of η and $\bar{n}$ for tungsten, nickel, iron, and aluminum. It is no surprise that these metals are most favored in modern practice.

1.4.2 Semi-Infinite Chain

A simple model consists of a monoatomic linear chain fastened at one end. The end of the chain represents the surface. Assume that the axis Oz is directed perpendicular to the surface, the point $z = 0$ is the abscissa on the surface.

The total potential of the electron is a periodic function of the distance. Thus, we can write

$$V(z + r) = V(z). \tag{1.36}$$

The dependence of the potential along the chain is assumed to be the cosine function,

$$V(z) = \begin{cases} 2V_0 \cos(2\pi z/a), & z < 0 \\ V_{vac}, & z \geq 0, \end{cases} \tag{1.37}$$

where a is the parameter of the crystal lattice.

One tries then to solve the Schrödinger equation (1.25).

Far away from the surface, at $z \ll 0$, the electronic wave function in the lower-order approximation can be taken as a superposition of two plane waves:

$$\psi(z) = A \exp(ikz) + B \exp\left[i\left(k - \frac{2\pi}{a}\right)z\right] \tag{1.38}$$

where A and B are constants, $k = 2\pi/\lambda$ is the absolute value of the wave vector in the normal direction and a is the crystal lattice parameter. Near the Brillouin zone boundaries characteristic band splitting occurs; an electron is scattered between states $k = +\pi/a$ and $k = -\pi/a$. The dependence of the energy of the electron on the wave vector is parabolic and splits near $k = \pm\pi/a$.

Let us briefly consider the solutions of the Schrödinger equation near a solid surface. The two solutions (for $z < 0$ and $z \geq 0$) have to coincide at the surface $z = 0$. The same requirement is imposed on the derivation $d\psi/dz$. It turns out that under the surface, the solution is a superposition of both an incoming and a reflected wave. Thus, a standing wave is formed near the surface.

In Figure 1.13 one can see the dependence of the squared wave function on distance. The peak at the surface indicates that the electron is attracted by the surface. At $z > 0$ the wave function decreases exponentially. The electronic tail is spread out the surface as far as 0.1 nm.

One can imagine the electron distribution near the surface as shown in Figure 1.14. A dipole layer is formed at the surface. The surface atoms are unbalanced because they have neighbors on one side and none on the other.

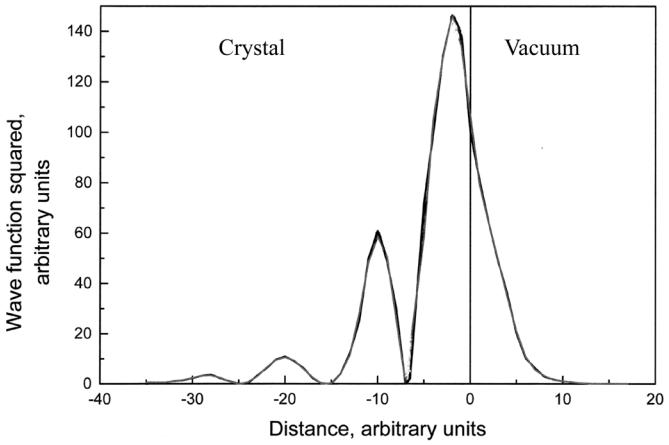

Fig. 1.13 Squared wave function of an electron near the surface.

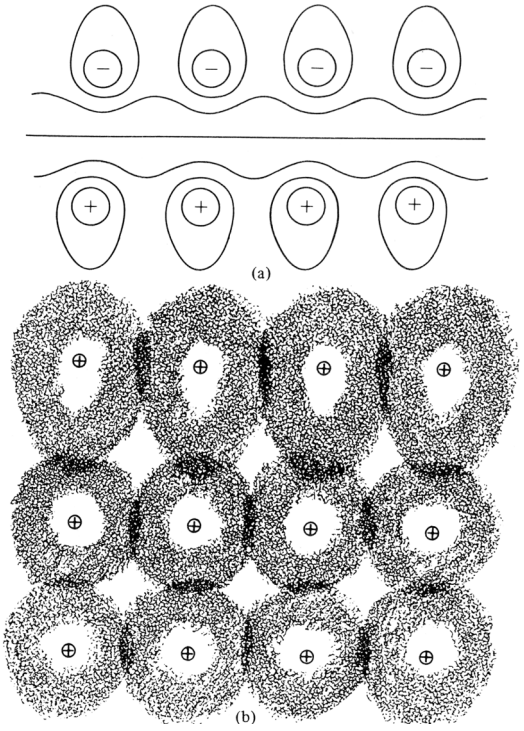

Fig. 1.14 The distribution of electrons near the surface: a, equipotential lines in an electric double layer; b, distortion of the charge in a model simple cubic lattice. Reprinted from [2] with permission from Oxford University Press.

Therefore the electron distribution around them is an asymmetrical one with respect to the positive ion cores. This leads to a double electric layer as shown in Figure 1.14a. The dipoles are directed into the metal from the vacuum.

The graph in Figure 1.13 is a section of Figure 1.14b with a plane passing through ions parallel to the surface.

If the surface has steps the electronic charge tends to smooth them out (Figure 1.15).

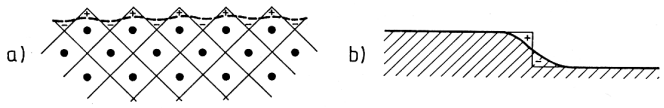

Fig. 1.15 Formation of electronic surface dipoles at the metal surface: a, smearing out of the charge distribution. Rectangles are the Wigner–Seitz cells; b, smearing out of the electronic charge distribution at a step. The increase in the negative charge (an electron cloud) is formed near the step. Reprinted from [4] with permission from Springer.

1.4.3 Infinite Surface Barrier

One can further complicate the Sommerfeld model (perhaps more realistically).

The next step in the model of free electrons is to introduce a potential barrier at the surface. This barrier confines the electronic charge.

It is appropriate to replace the metallic cube by a slab of thickness L in the z-direction which extends infinitely in the x- and y-directions [5]. One assumes that a discontinuity in the potential at the planes $z = 0$ and $z = L$ is described by

$$V(\vec{r}) = \begin{cases} 0, & \text{for } 0 \le x \le L, \quad -\infty \le y,\ z \le \infty, \\ \infty, & \text{elsewhere} \end{cases} \tag{1.39}$$

This means that one sets infinitely high potential walls at $x = 0$ and $x = L$.

Further, one replaces the actual infinite set of wave functions by a finite number, imposing boundary conditions, characterized by a period L in the y and z directions and a fixed boundary at $x = L$.

In this case the appropriate wave functions have the form

$$\psi_k(x, y, z) = \left(\frac{2}{L^3}\right)^{1/2} \sin(k_x x) \exp[i(k_y y + k_z z)] \tag{1.40}$$

where $k_y = (2\pi n_y)/L$, $k_z = (2\pi n_z)/L$, $n_{y,z} = 0, \pm 1, \pm 2, \ldots$, $k_x = (\pi n_x)/L$; $n_x = 1, 2, 3 \ldots$

The density of electrons is given by

$$\varrho_- = -|e| \sum_k |\psi_k|^2 \tag{1.41}$$

The variation in the density of the electronic charge can be expressed [1,5] as

$$\varrho_- = -n|e|B_r = -n|e| \left[1 + \frac{3\cos(2k_F\, z)}{(2k_F\, z)^2} - \frac{3\sin(2k_F\, z)}{(2k_F\, z)^3}\right] \tag{1.42}$$

where z is the distance in the normal direction to the surface.

In Figure 1.16 the distribution of the electric charge near the surface is presented for two metals. The dependencies have been calculated in accordance with (1.42). The dependence exhibits some oscillations near the surface relative to the average bulk value. The wave length of the oscillations is equal to $\pi/2k_F$. The electron tails jut out of the metal surface for ≈ 0.08 nm.

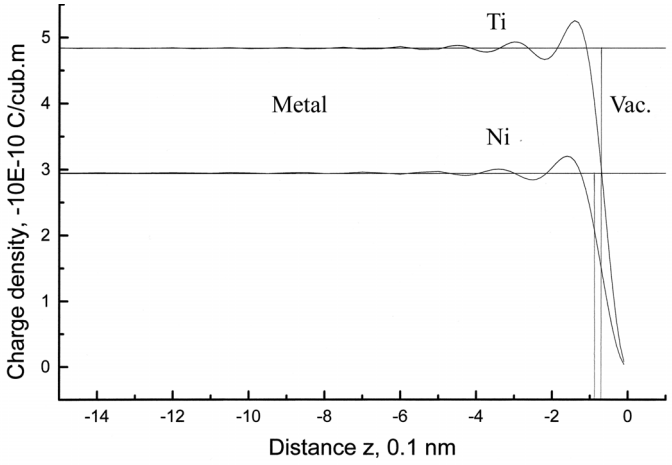

Fig. 1.16 Distributions of the electric charge near the surface in nickel and titanium. The positive charge is assumed to be uniform inside the metal. The electron density oscillates in the metal near the surface. Dipoles are directed into the metal from the vacuum.

1.4.4
The Jellium Model

The energy of two subsystems in metals determines the most characteristic features of electronic structure of a clean solid surface. This energy consists of the kinetic energy of the electrons, the energy of attraction between the electrons and the ions and the energy of electron repulsion.

Let us assume that a semi-crystal system consists of N electrons and N ions. The position of each ion is determined by the vector $\vec{R}$.

In quantum mechanics, the Hamiltonian is known to correspond to the total energy of a system. It is given by:

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{\vec{R}} \sum_{i=1}^{N} \frac{Ze^2}{\mid \vec{r}_i - \vec{R} \mid} + \frac{1}{2} \sum_{i,j}^{N} \frac{e^2}{\mid \vec{r}_i - \vec{r}_j \mid} \tag{1.43}$$

where p_i, m, and e are the momentum, the mass and the charge of the electron, respectively, Z is the charge of the nucleus and $\vec{r}_{i,j}$ are radius vectors of the electrons. The first term of (1.43) is the sum of the energies of the electrons. The second and third terms represent the Coulomb ion–electron and the electron–electron interactions. The presence of the last term makes the solution of (1.43) intractable.

The jellium model is a realistic approximation for simple metals. In this case the conduction electrons scatter only very weakly from the screened ion core pseudopotentials. In this model the positive charge is considered to be a homogenous medium forming a sort of jelly. The positive background charge has a density equal to the spatial average ion charge distribution. For the metal surface the distribution of the positive charge can be modeled by a step function:

$$n_+(z) = \begin{cases} \overline{n}, & z \leq 0 \\ 0, & z > 0 \end{cases} \tag{1.44}$$

The axis z is normal to the surface. The average electron concentration according to (1.31) is given by

$$\overline{n} = \frac{k_F^3}{3\pi^2} \tag{1.45}$$

The uniform positive charge density $\overline{n}$ is often expressed in terms of an inverse sphere volume,

$$\frac{1}{\overline{n}} = \left(\frac{4\pi}{3}\right) r_s^3 \tag{1.46}$$

The sum of the positive and negative charges must be equal to zero, so

$$\int [n(z) - n_+(z)]\, dz = 0,$$

where $n(z)$ is the electron density.

Replacement of the discrete lattice of ions and conducting electrons by the uniform positive background, leads to an error. However, the estimation shows that this error in energy is of the order of 10^{-7} eV which is much smaller than the Fermi energy.

The electron density variation perpendicular to the surface reveals two features. First, electrons jut out (spread out) into the vacuum ($z > 0$). In this way electrons create an electrostatic dipole layer at the surface. The electron distribution has no sharp edge. One should distinguish between the physical and the geometric surface. The first one denotes the location of the barrier, the second is the place where the positive charge background vanishes. The electron density decreases exponentially with the distance from the surface.

Second, the function $n(z)$ oscillates as it approaches an asymptotic value and compensates for the uniform positive charge in the bulk. The potential step keeps the electron within the crystal.

Figure 1.17 illustrates the dependence of the electron density upon the distance for two values r_s. At the higher electron densities ($r_s = 2$) the electrons extend further beyond the positive charge and the oscillations in the electron density are greatly diminished.

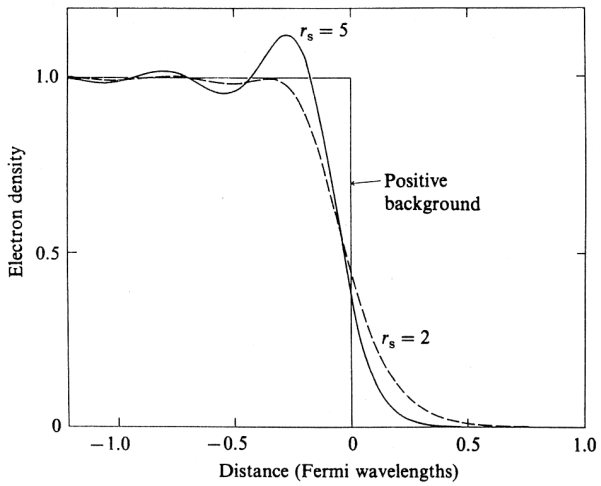

Fig. 1.17 Electron density profile at a jellium surface. r_s is the characteristic (Wigner–Seitz) radius. Data of Lang and Kohn. Reprinted from [3] with permission from Cambridge University Press.

We have already seen an analogous calculated dependence for nickel and titanium in Figure 1.16.

The distribution of the electron density near the monoatomic step is noteworthy. The electrons jut out as before but, in addition, they tend to smooth out the sharp step along the surface. Figure 1.18 presents the electrostatic potential near the monoatomic step for the jellium model. An electrostatic dipole appears oriented oppositely to the jut-out value. The net dipole moment is reduced relative to the flat-surface value.

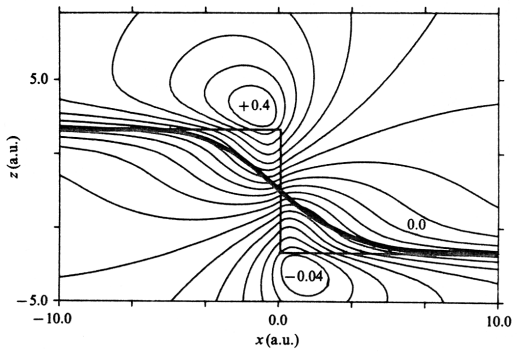

Fig. 1.18 Electrostatic potential near a jellium step. The heavy solid curve indicates the smoothed electron surface. Data of Thomson and Huntington. Reprinted from [3] with permission from Cambridge University Press.

1.5 Summary

The surface energy γ is equal to the work necessary to form the unit area of surface by a process of cleavage of the solid into parts.

Variation in the Helmholtz free energy of a solid by the equilibrium cleaving process, in a general case, is given by

$$dF = -S\,dT - p\,dV + \mu\,dN + \gamma\,dA + A\,d\gamma \tag{1.47}$$

The fourth term on the right-hand side describes the work needed to break down interatomic bonds and to create the surface area dA. The average area per atom is unchanged, but the number of atoms on the surfaces increases. The fifth term contributes the free energy due to changes in the interatomic distances on the new surfaces. These changes are balanced in the macroscopic and microscopic areas. The number of atoms on the surfaces remains unchanged. The stressed surface contributes a surface energy by an increment $d\gamma$.

A rearrangement of atoms occurs in the topmost layers of the surface. One uses a special notation to denote the surface superstructure. The notation reveals the dimensions, the nature and the orientation of the unit cell in the first plane relative to the underlying ones.

Defects always exist on real surfaces. Defects of zero dimension are vacancies, adatoms, ledge adatoms, and kinks. Their sizes in three dimensions are of the order of the interatomic distance. The step is a one-dimensional defect, in which the ledge separates two terraces from each other. Steps of the single atomic height prevail over steps of several atomic heights. There are also groups of defects such as divacancies, and steps of some interatomic dis-

tances in height. Other defects are related to dislocations. The applied stress and strain leads to the generation of ensembles of surface nanometric defects. These ensembles have the shape of prisms and differ from one another by dimension and energy of formation. Walls of nanodefects consist of steps of width from 5 to 50 nm. The walls are formed in consequence of an output of dislocations along planes of the light slip on the surface.

The parameters of the electron subsystem in some metals have been calculated based on the valency of the metals and the volumes of their crystal cells. The concentration of electrons in metals varies in the range $(0.25 - 5.03) \times 10^{29}$ m^{-3}. The Fermi energy ranges from 5.5 to 20 eV.

The electron concentration correlates with a parameter of the strength of the crystal lattice

$$\eta = m\frac{\overline{du^2}}{dT}$$

where $\overline{u^2}$ is the mean-squared amplitude of the atomic vibration, m is the atom mass and T is the temperature.

The free electrons in the metals are attracted by the surface. The electron density oscillates near the surface. At $z > 0$ the wave function squared decreases exponentially. The electronic tail juts (spreads) out on the surface as far as 0.08–0.10 nm. The electron distribution around the surface atoms is asymmetrical with respect to the positive ion cores. A dipole layer is formed at the surface. The dipoles are directed into the metal from the vacuum.

The jellium model is a realistic approximation for simple metals. In this case the conduction electrons scatter very weakly from screened ion core pseudopotentials. In this model the positive charge is considered to be a homogenous medium forming a sort of jelly. The positive background charge has a density equal to the spatial average ion charge distribution. For the metal surface the distribution of the positive charge can be modeled by a step function.

The electron density near the monoatomic surface step tends to smooth out the sharp step along the surface. An electrostatic dipole appears to be oriented opposite to the jut-out value.