Atom positions on the vicinal face of a fcc crystal

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An approximate expression for the free energy of a single crystal is derived to determine equilibrium positions of atoms on vicinal faces of a fcc crystal at various temperatures thermodynamically. The obtained free energy has a peculiarity (critical temperature) in all the considered cases: infinite crystal, low-index face, adatom on a low-index face, and vicinal face. The physical meaning of the critical temperature is special for each case. The calculated temperature dependence of the lattice constant agrees well with experiment, and the critical temperature for an infinite crystal corresponds to the melting temperature of the crystal. The variance of the thermal vibrations near this critical point of the free energy agrees with the empirical Lindemann criterion. For an adatom on a low-index face, the critical temperature corresponds to its becoming delocalized (spread over the surface). Similarly, there is a temperature at which an atom at a step edge breaks away and becomes a delocalized adatom.

I. INTRODUCTION

The study of thermodynamical equilibrium positions of atoms on the surface and in the bulk of a crystal attracts interest in the context of purely practical applications (microelectronics, for example) and in view of the necessity to understand the processes occurring on the crystal surface and in the layers near the surface (melting, roughening, etc., see, for example, Ref. 1). A theoretical description of surface thermodynamics helps reveal the general mechanisms underlying the surface phase transitions, and can often serve as the starting point for numerical experiments and lead to a better understanding of the nature of these phenomena. Thermodynamical equilibrium parameters of a statistical system (in particular, a crystal with a surface) can be found by minimization of its free energy (by the free energy we mean the Helmholtz free energy) or any other thermodynamical potential. An exact expression for the free energy can be calculated only in a few specific cases.[2] More real (but simple enough) structures, such as a geometrically ideal three-dimensional monocrystal with interaction of some neighbors, are usually described by various approximations of the free energy,[3–9] which are found either theoretically from the perturbation theory,[6–9] or by extension over a parameter,[5] or by adding a semiempirical term to the known free energy.[3,4] We will derive an approximate expression for the crystal free energy in the framework of the thermodynamical perturbation theory which was used earlier to study some systems interacting via the Morse potential, and to find the first-order correction to the free energy of a system of harmonic oscillators for a rectilinear chain with an edge,[6] a three-dimensional ideal crystal,[7–9] and the second-order correction for these cases.[8] The main aim of this work is to determine some properties of crystal bulk and surface in thermodynamical equilibrium.

In an earlier work,[10] we considered equilibrium positions of atoms on two vicinal faces [near the (001) and (111) planes] of a Ni single crystal at $T=0$ K using the pairwise Morse potential

$$U(r)=D(e^{-2\alpha(r-r_0)}-2e^{-\alpha(r-r_0)}),\qquad(1)$$

where parameters were found by fitting (minimizing the root-mean-square deviations between calculated and experimental values; for more details see, for example, Ref. 11) the lattice constant, the elastic constants, and the binding energy to their experimental values. In this work we consider a potential with attraction,

$$U(r)=e^{a-r/b}-De^{-\alpha(r-r_0)^2},\qquad(2)$$

which was used earlier in sputtering simulations.[9] This expression is continuous with all derivatives, and correctly describes the interatomic interaction in the range from thermal energies to few keV; this is important for sputtering simulation, as pointed out in Ref. 9. The upper limit is defined by applicability of the Born-Mayer potential, i.e., the repulsive part in Eq. (2). Any other exponential form for the repulsive part in Eq. (2) can be used, such as the Moliere approximation of the Thomas-Fermi-Firsov potential, for example. In these cases potential (2) is also available for the calculation of the free-energy approximation in closed form. As a matter of fact, the closed-form approximation to the free energy of a crystal can be calculated for any exponential-type potentials.

The approximations for the free energy of a monocrystal based on potentials (1) and (2) will be derived in Sec. II. We will use this approximation to describe the temperature dependence of the lattice constant and the variance of thermal vibrations (in this work abbreviated as VTV) of an infinite fcc crystal. The temperature behavior of (001) and (111) faces' first-layer relaxation, the adatoms on these faces, and atoms on the vicinal face slightly tilted from the (001) face, will be considered in Secs. III A, III B, and III C. Section IV presents brief conclusions. The numerical calculations will be carried out for a fcc copper single crystal.

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TABLE I. Calculated parameters of potential (2) for some metals. The data on the lattice constant (d), elastic constants (C_{11}, C_{12}) and binding energy (E_0) at $T=0$ K were taken from Ref. 13. The calculated values are given in brackets.

	Cu	Ag	Au	Pt	Ni	Pd
E_0 (eV/at.)	3.5(3.5)	2.96(2.96)	3.78(3.78)	5.852(5.852)	4.435(4.435)	3.94(3.94)
d (Å)	3.61	4.09	4.08	3.924	3.524	3.89
C_{11} (eV/Å^3)	1.101(1.101)	0.82(0.82)	1.26(1.26)	2.167(2.167)	1.63(1.63)	1.46(1.46)
C_{12} (eV/Å^3)	0.78(0.78)	0.61(0.64)	1.06(0.97)	1.57(1.57)	0.94(0.94)	1.10(1.10)
a	9.863	8.113	10.637	11.347	9.995	10.738
D (eV)	0.597	0.492	0.704	1.303	0.481	0.839
α(Å^{-2})	0.659	2.506	1.693	0.830	0.565	1.024
r_0 (Å)	2.33	2.90	2.77	2.37	2.88	2.444

II. APPROXIMATE EXPRESSION FOR THE FREE ENERGY OF A CRYSTAL

Let us consider a crystal (system of atoms) with a pairwise additive interatomic interaction. The coordinate origin will be set in one of the atoms of the system. The potential energy of this atom is $u(r)=\frac{1}{2}\Sigma_{i=1}^{N}u(r_i)$ where the interaction potential will be chosen in the form of Eq. (2).

Potential (2) is convenient for a closed-form calculation of the correction to the free energy. The first term in Eq. (2) is a repulsive Born-Mayer-type potential, and the second one is a Gaussian. Obviously, potential (2) is more localized than the Morse potential [Eq. 1)]. This is of importance in simulations involving a large number of particles. The potential was truncated at the point R_{tr} [depending, of course, on the parameters in Eq. (2)] in calculations. In this paper we assume $|U(R_{tr})|=0$ eV (at this point $R_{tr}=[r_0+1/(2\alpha b)]+\sqrt{(1/\alpha)[(r_0/b)+(1/4\alpha b)-a+\ln(D)]}=9.3$ Å, values for Cu from Table I was used). Function (2) and all its derivatives are smooth in the region of function definition. We note that the constant b in Eq. (2) was fixed (for Cu we used the values $=0.219$ Å,[12] which are often used in crystal sputtering simulations). a, α, D, and r_0 from Eq. (2) were chosen so as to fit the experimental data on the elastic constants, and to satisfy the condition of zero pressure in the crystal bulk (diagonal elements of the stress tensor are null). Two elastic constants C_{11} and C_{12} ($C_{44}=C_{12}$ in cubic crystals with additive pairwise interactions) and the binding energy were varied during the fitting. Table I lists the values of constants from expression (2) for some metals. The data on the lattice constants, binding energy, and elastic constants were taken from Ref. 13. Minimization of the potential energy and the free energy was performed by the simplex method and was corrected by a quasi-Newton algorithm.[11]

An approximate free-energy expression is derived for a system of particles interacting according to Eq. (2) (in what follows we will call this, for convenience, the total system) in the same way as for the Morse system.[8] As an origin system we used a system of harmonic oscillators whose free energy is known. The potential energy of a harmonic oscillator is taken as $U_0(r_\alpha)=\frac{1}{2}\Sigma_{\alpha=1}^{N_d}\lambda_\alpha r_\alpha^2$, where $N_d=1$, 2, and 3 is the spatial dimension of the system; $\alpha=x,y,z$; λ_α is the corresponding force constant of the oscillator (when the index is unessential we will simply write λ); and r_α^2 is the square of the corresponding coordinate. In what follows the term ''free energy'' will be used to mean the configurational part of the free energy, since the kinetic free-energy part is known exactly and is the same for the total and the origin systems. Following the thermodynamical perturbation theory, we write $F=F_0+\Delta F$, where F_0 is the known free energy of the origin system $F_0=-N_d\theta N\ln(C\sigma^2)$, where N is the number of particles; $\theta=kT$; C is a constant (depending on the system dimensions and the atomic mass and independent of the VTV and the lattice constant); and σ^2 is the VTV of the atoms. The correction $\Delta F=\langle U-U_0\rangle_0$, where $\langle\cdots\rangle_0$ means averaging over $e^{-U_0/\theta}$. It is seen that the calculation of the correction is reduced to the calculation of integrals of the form $\int e^{f(x)}e^{-U_0/\theta}$, where x stands for the appropriate set of variables. In the case of the potential function (2), such integrals are calculated in closed form for a one-dimensional system and under standard assumption of small atomic displacements from equilibrium positions for two- and three-dimensional systems. The result of the calculations can be formulated as follows. The specific (per one atom) free energy of a system of atoms interacting according to Eq. (2) is $f=f_0+\frac{1}{2}\Sigma U'(r_i)$, where $U'(r_i)$ is the same as in Eq. (2), but with temperature-dependent constants (primed)

$$U'(r)=\sum_i A'e^{-r_i/b}-D'e^{-\alpha'(r_i-r_0)^2}), \quad A'=e^{a+(\mu_i/2b^2)},$$

$$\mu_i=n_x^2(\sigma_{x_0}^2+\sigma_{x_i}^2)+n_y^2(\sigma_{y_0}^2+\sigma_{y_i}^2)+n_z^2(\sigma_{z_0}^2+\sigma_{z_i}^2), \quad (3)$$

$$D'=\frac{D}{\sqrt{1+2\alpha\mu_i}}, \quad \alpha'=\frac{\alpha}{1+2\alpha\mu_i}.$$

Here the subscript 0 indicates the specified atom at the coordinate origin; r_i is the radius vector of the ith atom; n_x, n_y, and n_z are direction cosines of the radius-vector; and σ_{lm} are the components of the VTV [the first subscript stands for the Cartesian coordinate $(x.y.z)$, and the second is the number of the atom]. For the Morse potential [Eq. (1)], the free-energy expression with accuracy up to the first-order correction is[8]

$$U'(r)=\sum_i [D'(e^{-2\alpha(r_i-r_0')}-2e^{-\alpha(r_i-r_0')})],$$

$$\lambda_i=\alpha^2[n_x^2(\sigma_{x_0}^2+\sigma_{x_i}^2)+n_y^2(\sigma_{y_0}^2+\sigma_{y_i}^2)+n_z^2(\sigma_{z_0}^2+\sigma_{z_i}^2)],$$
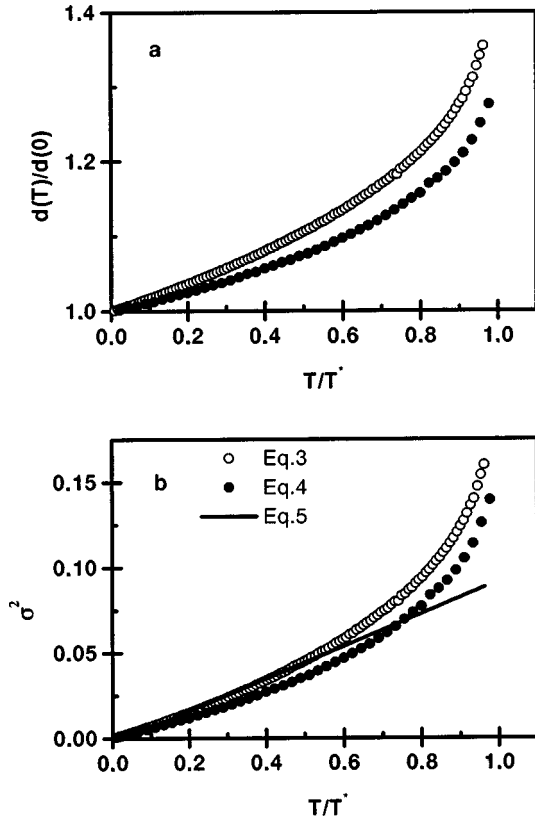$$(4)$$

FIG. 1. Temperature dependence of the lattice constant (a) and the variance of thermal vibrations (b) of an infinite fcc copper crystal. The lattice constant is normalized to a value of 0 K. The temperature is normalized to a critical valve. Open circles, Eq. 3; closed circles, Eq. (4); solid line, Eq. (5).

$$D' = De^{-\lambda_i/2}, \quad r_0' = r_0 + \frac{3\lambda_i}{2\alpha},$$

where parameters n, σ_{im}, and r_i are the same as in Eq. (3).

Equilibrium thermodynamical parameters of the total system can be found by minimization of the approximate free-energy expressions (3), (4) with respect to a given parameter. Figures 1(a) and 1(b) show the temperature dependencies of the lattice constant and the VTV of the atoms of an infinite copper crystal for both free-energy approximations (3) and (4). The minimum of the free energy with respect to these parameters exists only within a finite-temperature range, and disappears at a temperature $T = T_v^*$, which below will be referred to as the bulk critical temperature. This critical point is the point of a first-order phase transition because the first-order derivatives of free energy are discontinuous in this point. On the basis of the universality and scaling hypotheses (see, for instance, Ref. 14) we scale the calculated critical temperature to the melting temperature, and expect that we may obtain an appropriate qualitative description of the behavior of the lattice constant and the VTV of the total system over the whole temperature range below melting point. There are some arguments in favor of this method.

(a) The calculated critical temperature is higher than the real one. However, taking into account the fact that the second-order correction decreases the system critical temperature while not affecting the qualitative system's behavior, and that it is of the same order as the first-order correc-

tion (as we determined earlier in Ref. 8), it appears to be reasonable to use the temperature scaling.

(b) The calculated value of the VTV in the vicinity of the critical point is in agreement with Lindemann's criterion obtained in Ref. 15.

Since our model is an Einstein-type model with unharmonic interatomic interactions, we can compare our results with the classical one. In a harmonic Einstein model, introducing the Einstein temperature θ_E, $\sigma^2(T)$ is given by

$$\sigma^2(T) = \frac{\hbar^2}{2\mu k_b \theta_e} \coth\left(\frac{\theta_e}{2T}\right), \tag{5}$$

where μ is reduced mass of the atom pair (Cu-Cu in our case). As shown in Ref. 16, Eq. (5) valid for a quantum-mechanical Einstein model based on anharmonic effective pair potential. Our results for $\sigma^2(T)$ [Fig. 1(b), θ_E from Ref. 17] are close to Eq. (5) (solid line) far from critical point.

One can note also the sharp growth of the lattice constant and VTV as $T \Rightarrow T_v^*$ [Figs. 1(a) and 1(b)]. Mathematically, this means that function $f(T, d, \sigma^2)$ has no minimum as a function of variables d and σ^2 above critical temperature. Obviously, when the free energy has more parameters [as in the case with an adatom on the (001) face considered below in Sec. III A), some of them will not have a peculiarity like $T \Rightarrow T^*$. The physical meaning of such a behavior of the free energy in these cases will be discussed below.

The relation of the critical point in Eq. (3) to the physical parameters of a real crystal, in particular to a phase transition (melting in case of crystal volume), requires a more detailed study of expression (3). In this paper we will restrict ourselves to the temperature dependence of the lattice constant and the VTV, and will not consider the behavior of other critical parameters or the derivatives of the free energy.

III. TEMPERATURE DEPENDENCE OF THE ATOM POSITIONS ON THE VICINAL FACE OF A FCC CRYSTAL

First, let us consider a low-index (001) face of a fcc crystal at $T = 0$ K. As in the case of Ni,[10] let us consider a vicinal (119) face with steps of one-atom height close to the (001) face, such that the step edge contains $[\bar{1}10]$ chains and the length of the terraces is such that the face makes an angle of about 9° with the initial low-index face. Decreasing the angle of (001) face rotation around the $[\bar{1}10]$ axis does not change the behavior of the atoms which are far from the terrace edges as compared with the (001) plane. The equilibrium position of atoms on a (119) face at $T = 0$ K is found by minimization of the system's potential energy. During minimization we vary the positions of atoms in the five topmost layers near the surface, and the problem becomes two dimensional because the crystal is symmetric in the direction normal to the step edge. Displacements of atoms interacting according to expression (2) are much smaller (no more than 0.2 Å) than in the case of the Morse potential.[10] On the whole, the displacements of atoms at the step edge are directed toward each other so that the step is smoothed out, which is in qualitative agreement with the results of Ref. 10.

Now we know the atomic positions on the low-index and vicinal faces at $T = 0$ K. Our further steps are as follows:

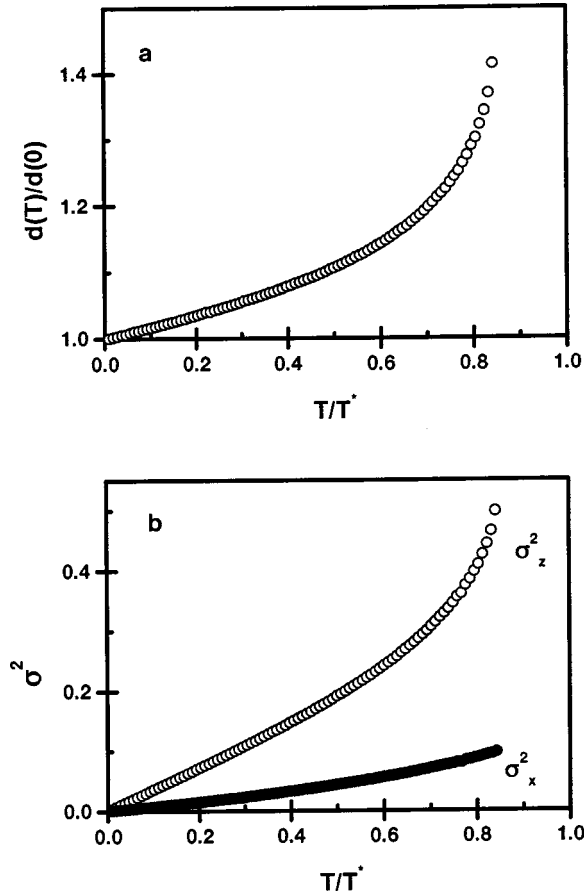(1) We shall find the equilibrium thermodynamical pa-

FIG. 2. The normalized first interlayer distance $d_{12}(T)/d_{12}(0)$ (a) and the components of the variance of thermal vibrations $\sigma_x^2 = \sigma_y^2 \neq \sigma_z^2$. (b) Dependence of atoms of the (001) face of a Cu crystal on the reduced temperature T/T_v^*.

FIG. 3. The dependence of thermal vibrations anisotropy $\gamma = \sigma_z^2/\sigma_x^2$ of atoms on the (001) face of Cu on the reduced temperature T/T_v^*.

rameters [in our case, the lattice constant $d(T)$, and the $\sigma^2(T)$] of an ideal infinite crystal at various temperatures. At this step the VTV [i.e., $\sigma^2(T)$] is assumed to be isotropic. This was done is Sec. II.

(2) We consider the atomic layers near the crystal surface as a statistical system in a thermostat. The thermostat is the part of the crystal under the surface for which $d(T)$ and $\sigma^2(T)$ are already known from step (1). Here $\sigma^2 = (\sigma_x^2, \sigma_y^2, \sigma_z^2)$ and, at least for the uppermost atomic layer, $\sigma_z^2 \neq \sigma_x^2 = \sigma_y^2$.

The accuracy to which the critical temperature is determined depends on the temperature increment used when finding the minimum of the free energy (in this work, 25 K).

A. (001) and (111) faces

Let us start our analysis with the first layer of the (001) and (111) faces. We will assume for this topmost layer that $\sigma_z^2 \neq \sigma_x^2 = \sigma_y^2$, and that the first interplanar distance differs from the bulk value. For simplicity we consider the case when the lattice constant varies with temperature in the face plane in the same way as in the bulk of the crystal. Taking into account a larger number of near-surface layers changes the result by only a few percent.

The behavior of the first interplanar distance and the VTV is shown in Figs. 2(a) and 2(b). As in Refs. 8 and 9, the
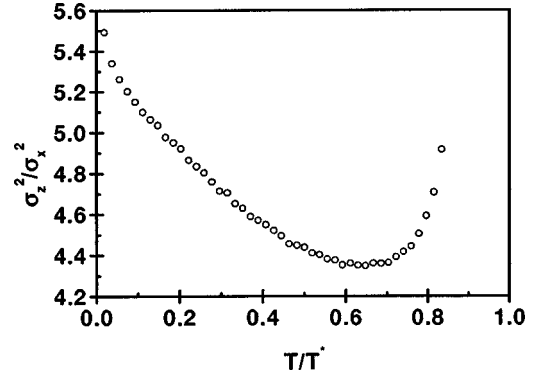
critical temperature of the uppermost atomic layer differs from the bulk one and is equal to $0.85T_v^*$ for the (001) face (it agrees with $0.845T_v^*$ in Ref. 18) and $0.75T_v^*$ for the (111) face. The physical sense of critical temperature in this case differs from the same for the case of crystal volume. Since one of the VTV components has a peculiarity, surface atoms are delocalized in this direction. In our case this means the beginning of a roughening transition, i.e., the surface column height is changed.

A considerable difference of the critical temperature of low-index faces of a fcc crystal from the bulk value was reported earlier[18] for some fcc crystals, including Cu. The calculations were performed by the molecular dynamics (MD) and Monte Carlo methods.[5] In Ref. 18 it was found that critical temperature for the (001) plane in Cu is higher than for the (111) plane. The values of critical temperatures found in our work differ from those calculated in Refs. 7, 15, and 18 because we used different approaches and interaction potentials. However, the difference between bulk and surface critical temperatures is in qualitative agreement with the results of Refs. 15 and 18. Note that determining thermodynamical parameters and critical temperatures by the proposed method does not require time-consuming MD calculations (not reliable near the critical point of system), and involves only the finding of the minimum of a function of a few (2–10) variables.

The anisotropy of the thermal vibrations is expressed as $\gamma = \sigma_z^2/\sigma_x^2$, and presents a nonmonotonic function of temperature (Fig. 3) for both the (001) and (111) faces, but $\gamma_{001} > \gamma_{111}$. In view of the lack of any reliable experimental data on the anisotropy of thermal vibrations of atoms on the crystal surface over a wide temperature range, we cannot verify this result. It may be suggested that the sharp increase in the anisotropy of thermal vibrations in the vicinity of the critical point corresponds to the earlier observed[19] abrupt increase in the anharmonicity at temperatures near $0.8T_v^*$. This result qualitatively corresponds to the fact that a noticeable deviation from the linear growth of $\sigma^2(T)$ occurs near these temperatures [Fig. 2(b)].

B. Adatom on the (001) and (111) faces

Now let us consider one adatom on a (001) face of copper [qualitatively, adatom behavior on the (111) face is the same
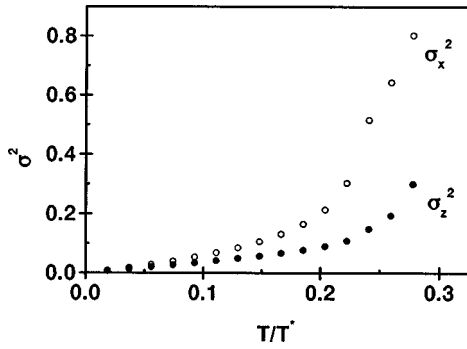
FIG. 4. The dependence of the components of the variance of the thermal vibrations of an adatom on the (001) face of Cu on the reduced temperature T/T_v^*.

as on the (001) face]. We assume that $\sigma_z^2 \neq \sigma_y^2 = \sigma_x^2$. In this case, one has to vary three coordinates of the adatom and two components of the VTV when minimizing the free energy.

An interesting question is which particular component of adatom's VTV has a peculiarity as a function of temperature [more precisely, we mean a singularity of a free-energy derivative on $\sigma^2(T)$] when $T \rightarrow T^*$. Figure 4 shows the behavior of the normal $[\sigma_z^2(T)]$ and tangential $[\sigma_x^2(T)]$ components of the VTV with temperature. The critical temperature is $T_a^* = 0.28 T_v^*$ in the case of the (001) face, and $T_a^* = 0.29 T_v^*$ for the (111) face. However, in contrast with the cases considered above, only the tangential component of the VTV has a peculiarity as $T \rightarrow T_a^*$ (we recall that was assumed $\sigma_y^2 = \sigma_x^2$). The physical meaning of this result lies in the fact that at $T \gtrsim T_a^*$ the adatom loses its bonding to a particular place on the crystal surface, i.e. although it does not yet evaporate, it moves freely from one potential pit to another on the crystal surface. This picture is similar to exceed cluster atom behavior (Cu_{14} and Cu_{13}) in Ref. 20. The upper limit of adatom stability on the crystal face is the lower limit of island formation; i.e., when $T > T_a^*$, delocalized adatoms are conjugated and islands begin to grow.

C. Surface of the vicinal face

Let us now consider the upper atomic layer of the (119) face. In contrast with the case of a low-index face, the displacements in the X and Z directions (the X axis lies in the face plane and is perpendicular to the step edge, and the Z axis is perpendicular to the face) can be different, so $\sigma_z^2 \neq \sigma_y^2 \neq \sigma_x^2$. The problem of the free-energy minimization for a system composed of several uppermost atomic layers of the vicinal face being in contact with a thermostat (the underlying part of the crystal) is essentially similar to the one discussed earlier, but requires much more elaborate calculations. The reason is that, as the number of variables grows, the stipulation of function minimization problem deteriorates very fast. In this work we used an iteration procedure in which the free energy is minimized for each individual atom. There are a total of nine such atoms in each layer, and we should consider no less than four layers. At each iteration the position and VTV of each atom were found. The procedure was terminated when the sum of the absolute values of the displacements of all the atoms from their positions on the previous iteration step became smaller than 0.01 Å.

As in the case of an adatom on the crystal surface, not all thermodynamic parameters, but only one of them, exhibit a peculiarity with increasing temperature. At $T_c^* = 0.66 T_v^*$ the component σ_x^2 of the VTV has a peculiarity, and, at higher temperatures, there is no free-energy minimum. Physically, this means that there is a temperature at which an atom loses its bonds to the step edge atoms, and since this critical temperature is higher than the temperature of the adatom delocalization, the adatom breaks away from the step edge and moves freely over the crystal surface. These results are in good agreement with Ref. 21 for vicinal faces (113), (115), and (117) of Al (in Ref. 21, step mobility was increased near $T_c^* = 0.64 T_v^*$). This abrupt increase of step mobility appears to be the first stage in the melting of a crystal's vicinal face.

The displacements of atoms at the step edge slowly change with temperature, and the tendency for smoothing out of the step (occurring already at 0 K) becomes more pronounced. But at the critical temperature atomic displacements become so large (up to 1 Å at the step edge) that there is no sharp step at all, but rather a smooth transition from one terrace to another.

IV. CONCLUSIONS

Function (2) suggested for the description of the pairwise part of the interatomic interaction not only enables one to derive a closed-form approximate expression for the free energy, but also offers a unified description of the interatomic interaction in a wide energy range (from thermal energies to few keV). Note that function (2) is infinitely smooth over the entire definition region, unlike the commonly used sewed potentials.

Displacements of atoms on vicinal faces of a fcc crystal close to the (001) face (which were found by minimization of the potential energy) are directed so that the step is smoothed out as the edge atom and the bottom atom moves toward each other. Minimization of the expression obtained for the crystal free energy enables one to find the equilibrium thermodynamic parameters such as the lattice constant and the VTV of atoms. These equilibrium thermodynamic parameters exist only below a certain (critical) temperature T^*. At temperatures higher than T^*, the free energy is a monotonic function of these parameters and has no minimum.

The critical temperature T_s^* is lower for the (001) and (111) faces than T_v^* for an infinite crystal. The degree of thermal vibration anisotropy of surface atoms on these faces varies nonmonotonously with temperature, reaching a maximum at 0 K and T_s^*. The tangential (parallel to the face plane) component of the adatom's VTV σ_x^2 has a peculiarity at $\simeq T_v^*/4$, which testifies that long before the premelting of the face ($\simeq 4 T_v^*/5$) adatoms on the surface become delocalized and freely move over the surface.

The only equilibrium thermodynamic parameter to exhibit a peculiarity as a function of temperature is the component σ_x^2 of the VTV of an atom at the step edge (the X axis is perpendicular to the step edge). This means that the first stage in the surface melting (or, more precisely, the change of the surface structure) is the "breaking away" of an atom from the step edge. Since this "breakaway" temperature ($\simeq 2 T_v^*/3$) is higher than the temperature of delocalization, it

seems that at this temperature the step mobility may increase sharply and a considerable number of adatoms may appear on the surface. Thus three temperature ranges can be distinguished for a vicinal crystal face: $T < T_a^*$, adatoms occupy localized sites at the surface and step edges are stable; $T_a^* < T < T_c^*$, adatoms move freely along the surface and couple to islands or step edges, but step edges are stable yet; and $T > T_c^*$, step edges are unstable. The proposed approximate expression for the free energy of a system of atoms interacting according to Eq. (2), and the approach to the study of temperature dependences of equilibrium thermodynamical parameters of a crystal by minimization of this expression, may be useful in the study of the surface properties of crystals at various temperatures.

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