

Interplay of surface misfit and monatomic steps on crystal surfaces.

III. Model for the $\{110\}$ surface of an anisotropic bcc crystal

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This paper generalizes the model that has been introduced in part I of this series to describe the interplay between surface misfit [limited to the surface monolayer (ML)] and steps on the cube faces of isotropic crystals with simple cubic structure, to the $\{110\}$ surfaces of anisotropic bcc crystals. The generalization involves (i) modeling of the ML crystal periodic interaction in terms of a truncated Fourier series containing a scale factor W to allow for a variable strength of interaction, and coefficients F_i , all adapted to yield a meaningful description of the activation energy Q of surface adatom migration, and (ii) the introduction of anisotropic elasticity to model the atomic interaction within the ML. The primary objective of modeling the surface stresses associated with steps on $\{110\}$ bcc surfaces has been accomplished. The results have been expressed in terms of the dimensionless parameters $\sigma = Q/W$ and (anisotropy ratio) A , and a crystal parameter G , depending on geometry and the stiffness constant c_{44} . The application of certain consistency requirements has yielded valuable relations for the F_i . The significance of these results lies in the fact that they are in great demand in the description of a wide variety of surface phenomena. For isotropic crystals, Q is shown to be given by the simple relation $Q = 3G$. This yields for $\{110\}$ tungsten a value of $Q = 1.1$ eV in good agreement with the empirical value of 0.92 eV. Although the model is somewhat crude, it is a sound phenomenological one and is believed to yield predictions which constitute useful guidelines for more accurate calculations.

I. INTRODUCTION

The phenomenon of surface misfit, its consequence for the formation of a monatomic step on a crystal surface with quadratic symmetry (the cubic face of a crystal with simple cubic structure), and a phenomenological model for its description have been dealt with in detail previously.^{1,2} Use was made of the techniques applied to boundary-value problems on linear elasticity theory. A primary problem had been to construct the boundary conditions; specifically the expressions for the relevant surface stresses. These comprise the shear stresses τ and τ^c , associated with the upper and lower terraces on either side of the step, and a normal stress N .

The derivation of τ employed the theoretical techniques developed by Frank and van der Merwe³ and van der Merwe⁴ to describe the behavior of epitaxial monolayers (ML's) on surfaces with rectangular and quadratic symmetries, treating the ML's as isotropic elastic sheets. In this paper we consider the $\{110\}$ surface of a bcc crystal, i.e., a surface with rhombic symmetry. We allow for elastic anisotropy with principle stiffness constants c_{11} , c_{12} , and c_{44} and anisotropy ratio A . The construction of τ now involves the generalization of the more complicated analysis, introduced by van der Merwe and his co-workers⁵ for the isotropic rhombic case, to the anisotropic rhombic case.

The initial goal is again to express the distribution of surface stresses in terms of the relevant parameters: (i) the stiffness constants, providing for anisotropy, (ii) the surface misfits (f_x and f_y within, and f_z normal to, the

$\{110\}$ plane), which we limit to the surface ML, and (iii) the symmetry and bond strength of the ML-substrate interaction which we embed in a truncated Fourier series V . The bond strength is included through the introduction of a scale factor W , approximately proportional to the energy of desorption E_{des} .⁵ In order to be physically meaningful, certain constraints could be imposed on the Fourier coefficients F_i .^{6,7} There are to be only three stationary values: an absolute minimum, an absolute maximum, and a saddle point. The latter defines the activation energy Q of surface migration.

As to atomic interactions, we assumed that the crystal surface layers could be approximated by a truncation of the bulk. This implies that the shear modulus that one obtains for the $\{110\}$ bcc surface from a transformation of the cubic stiffness constants be (nearly) equal to that which one may derive from V . By combining these consistency relations with the constraints imposed on V , it is possible to derive some useful relations for the F_i and the scale factor W . All quantities could be expressed in terms of Q (or W), $\sigma = Q/W$, A , and the materials parameter $G = \Omega c_{44} / 4\pi^2$, in which Ω is the volume per atom in the ML. The introduction of interaction ratios L_x and L_y , as measures of the relative ML-atom-ML-atom to ML-atom-substrate interactions, also came as a natural consequence of the analysis. L_x and L_y differ, because of anisotropy and rhombic (deviating from quadratic) symmetry.

The considerations are dealt with in the paper as follows: the construction of V and its properties in Sec. II, the anisotropic elastic description (including the transfor-

mation to local coordinates in the $\{110\}$ plane) in Sec. III, the construction and solution of the equations governing the atomic displacements in the ML of the upper terrace in Sec. IV, the definitions and derivation of the interfacial shear moduli and surface stresses in Sec. V, and considerations on surface parameters, including the Fourier coefficients, in Sec. VI. The results are discussed and summarized in Sec. VII.

II. SUBSTRATE INTERACTION POTENTIAL

The combination of misfitting monolayer (ML) of the upper terrace and the underlying crystal is equivalent to a misfitting epitaxial ML on a crystalline substrate.^{1,4} The ML-atom-substrate interaction V must display the two-fold symmetry of the rhombic unit cell of the $\{110\}$ bcc atomic plane⁷ displayed in Fig. 1. This symmetry may be built into a Fourier representation of V that has previously been written in the truncated form⁵

$$V(u, v) = W(1 - B\{\cos[\pi(v+u)] + \cos[\pi(v-u)] + C_1\cos(2\pi u) + C_2\cos(2\pi v)\}) , \quad (1a)$$

$$x_{lk} = (l + u_{lk})a_x/2, \quad y_{lk} = (k + v_{lk})a_y/2, \quad l, k = 0, \pm 1, \pm 2, \quad (1b)$$

$$a_x = 2a \sin\alpha, \quad a_y = 2a \cos\alpha, \quad \tan\alpha = \sqrt{2}. \quad (1c)$$

In Eqs. (1) (x_{lk}, y_{lk}) are the Cartesian coordinates of the ML atom (l, k) , enumerated from a position $(0, 0)$ of perfect registry with the minimum of V , and $(a_x u_{lk}, a_y v_{lk})/2$ the components of displacement of this atom from the corresponding trough (l, k) . For simplicity we have written l, k, u, v, B, C_1 , and C_2 instead of $\bar{l}, \bar{k}, \bar{u}, \bar{v}, A/3, c_1^2$, and c_2^2 , respectively, as were used in Ref. 5. Note that the scale factor W that defines the strength of interaction is also the constant term in the Fourier series. The products WB , WBC_1 , and WBC_2 are the coefficients of the higher-order harmonic terms. (The ensuing calculations

are more simply carried out in terms of the separate parameters W, B, C_1 and C_2 .)

The topography of the potential surface is of interest. The relations $\partial V/\partial u = 0 = \partial V/\partial v$, determining the stationary values of V , yield the simultaneous equations

$$\begin{aligned} \sin(\pi u)[\cos(\pi v) + 2C_1\cos(\pi u)] &= 0, \\ \sin(\pi v)[\cos(\pi u) + 2C_2\cos(\pi v)] &= 0. \end{aligned} \quad (2)$$

These equations suggest the following possible extrema for $V(u, v)$:

$$V(0, 0) = 0, \quad \text{minimum}, \quad (3a)$$

$$V(1, 0) = V_m, \quad \text{maximum}, \quad (3b)$$

$$V(\frac{1}{2}, \frac{1}{2}) = Q, \quad \text{saddle}, \quad (3c)$$

$$V(0, v') = V', \quad \cos(\pi v') = -1/2C_2. \quad (3d)$$

Q is the activation energy of surface migration. Equations 3(a)–3(c) yield, in conjunction with (1a), the relations

$$B = 1 - \sigma/2, \quad (C_1 + C_2) = 2(\sigma - 1)/(2 - \sigma), \quad (4a)$$

$$V_m = 4BW = 2(2 - \sigma)W, \quad Q/V_m = \sigma/2(2 - \sigma), \quad (4b)$$

$$\sigma = Q/W, \quad 0.4 \leq \sigma < \frac{4}{3} \quad (4c)$$

in terms of the important parameters Q, W , and σ .

Also, in view of our assumption that $V(0, 0) = 0$ and $V(1, 0) = V_m$ are, respectively, the absolute minimum and absolute maximum of the interaction potential $V(u, v)$ in Eq. (1a), the assumption that V' in (3d) is an intermediate extremum requires that C_i ($i=1, 2$) be simultaneously greater than $\frac{1}{2}$ and less than $-\frac{1}{2}$. This assumption is therefore inconsistent and rules out the possibility of an additional stationary value. This is also topographically evident. The assumption that $V(\frac{1}{2}, \frac{1}{2}) = Q$ is the saddle value, i.e., that $0 < Q < V_m$, implies, as may be seen from Eqs. (4), that $0 < \sigma < \frac{4}{3}$. We believe that σ is not far from unity; bounded above by $\sigma = \frac{4}{3}$ and below, possibly by about 0.4.

III. STRAIN ANALYSIS FOR $\{110\}$ bcc MONOLAYER

The main objective of this section is to find a description of the elastic relaxation of the surface ML resulting from the interplay of surface misfit and steps. The main purpose is to derive an expression for the relevant surface shear stress¹ τ_x . The misfits are defined by the ratios¹¹

$$f_y = f_x = \frac{a_x^0 - a_x}{a_x} = \frac{a^0 - a}{a} = r - 1, \quad r = a^0/a \quad (5a)$$

$$f_z = (a_z^0 - a_z)/a_z. \quad (5b)$$

The superscripts in a_x^0 and a_y^0 designate the equilibrium lateral spacings for a ML, when the substrate interaction is cut off and a_z^0 the relaxed interlayer spacing. It has been assumed that the equilibrium overlayer has the same symmetry ($\alpha^0 = \alpha$) as the truncated crystal. Thus f_x and f_y are equal, though different from f_z , which is deter-

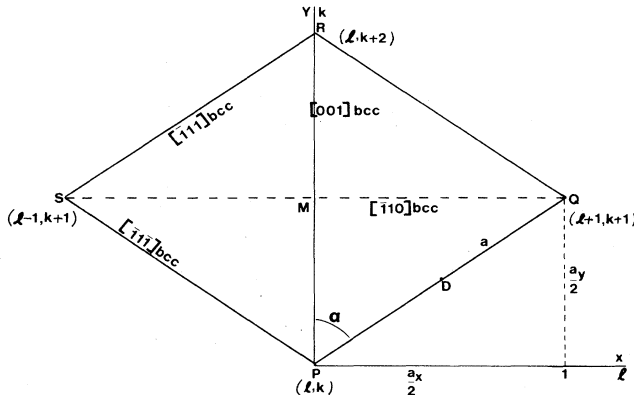


FIG. 1. Diagram displaying the $\{110\}$ bcc surface unit cell, having side length b , diagonal lengths a_x and a_y , and vertex angle α . The atomic positions are defined by the integers l and k .

mined by the multilayer relaxation. Also, the present considerations are aimed at cases in which the surface misfit is small and $r \approx 1$. We accordingly take $r=1$ unless it appears as $r-1$, for example, in f_y above.

We adopt the conventional notation c_{11} , c_{12} , and c_{44} for the contracted stiffness constants, referred to the cube axes, and

$$A = 2c_{44}/(c_{11} - c_{12}), \quad (6)$$

for the anisotropy ratio.^{6,8,9} The transformation matrix $\bar{T}$ from the cube axes to the local axes (x, y, z) on the (110) plane (see Fig. 1) has been given as⁶

$$\bar{T} = (t_{IJ}) = \begin{bmatrix} -1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 0 & 0 & 1 \\ 1/\sqrt{2} & 1/\sqrt{2} & 0 \end{bmatrix}, \quad I, j = 1, 2, 3, \text{ or } x, y, z. \quad (7)$$

Although the details for other planes in the set {110} will be different the results are equivalent.

The stiffness constants c_{ijkl} , constituting a fourth-rank tensor, accordingly transform as

$$\bar{c}_{IJKL} = t_{Ii} t_{Jj} t_{Kk} t_{Ll} c_{ijkl}, \quad (8a)$$

yielding in contracted notation⁶

$$\begin{aligned} \bar{c}_{11} &= \bar{c}_{33} = (c_{11} + c_{12} + 2c_{44})/2, \\ \bar{c}_{12} &= c_{12}, \quad \bar{c}_{13} = (c_{11} + c_{12} - 2c_{44})/2, \\ \bar{c}_{22} &= c_{11}, \quad \bar{c}_{44} = \bar{c}_{66} = c_{44}, \quad \bar{c}_{55} = (c_{11} - c_{12})/2. \end{aligned} \quad (8b)$$

All other elements are either zero or determined by the symmetry $\bar{c}_{IJ} = \bar{c}_{JI}$.

In the considerations below we need expressions (in local coordinates) for (i) the shear stresses $\bar{\sigma}_{13} \equiv \tau_{xz}$ and $\bar{\sigma}_{23} \equiv \tau_{yz}$, acting on the (110) crystal plane, (ii) the tensions $\bar{T}_x$ and $\bar{T}_y$ (per unit length) in the ML, and (iii) the strain energy ϵ per ML atom. We have the following.

(i) Using Hooke's law $\bar{\sigma}_{IJ} = \bar{c}_{IJKL} \bar{\epsilon}_{KL}$

$$\tau_{xz} = \bar{c}_{55} \gamma_{xz}, \quad \tau_{yz} = \bar{c}_{44} \gamma_{yz}. \quad (9)$$

(ii) Using conventional expressions for the strain energy density, and ignoring the z dependence for the ML,

$$\epsilon = \frac{1}{2} \Omega (D_{11} e_x^2 + D_{22} e_y^2 + 2D_{12} e_x e_y + D_{33} \gamma_{xy}^2); \quad (10a)$$

$$D_{11} = (\bar{c}_{11}^2 - \bar{c}_{13}^2)/\bar{c}_{11}, \quad D_{22} = (\bar{c}_{11} \bar{c}_{22} - \bar{c}_{12}^2)/\bar{c}_{11}, \quad (10b)$$

$$D_{21} = D_{12} = (\bar{c}_{11} \bar{c}_{12} - \bar{c}_{13} \bar{c}_{12})/\bar{c}_{11}, \quad D_{33} = \bar{c}_{44}; \quad (10c)$$

where Ω is the volume per ML atom and we have written $e_x, e_y, \dots$ for the strains $\epsilon_{11}, \epsilon_{22}, \dots$.

(iii) Using the stresses in combination with Hooke's law

$$\begin{aligned} T_x &= a_z (D_{11} e_x + D_{12} e_y), \\ T_y &= a_z (D_{22} e_y + D_{12} e_x), \\ T_{xy} &= a_z D_{33} \gamma_{xy}. \end{aligned} \quad (11)$$

The subsequent analysis also requires that the strains be expressed in terms of the atomic coordinates defined in Eq. (1). These may be written down⁵ in the local system, most simply, with reference to Fig. 1, as

$$\begin{aligned} e_x &= \frac{x(Q) - x(S) - a_x^0}{a_x^0} = \frac{(u_{l+1, k+1} - u_{l-1, k+1} - 2f)}{2r}, \\ e_y &= \frac{y(R) - y(P) - a_y^0}{a_y^0} = \frac{(v_{l, k+2} - v_{l, \bar{k}} - 2f)}{2r}, \\ \gamma_{xy} &= [x(R) - x(P)]/a_y^0 + [y(Q) - y(S)]/a_x^0 \\ &= \frac{(u_{l, k+2} - u_{lk}) \sin \alpha}{2r \cos \alpha} + \frac{(v_{l+1, k+1} - v_{l-1, k+1}) \cos \alpha}{2r \sin \alpha}. \end{aligned} \quad (12)$$

We take $r=1$ in accordance with the "small-misfit" assumption.

In the analysis below use will be made of the continuum approximation,³ in which, for example,

$$\begin{aligned} u_{l+1, k+1} &\simeq u(l+1, k+1) \\ &= u(l, k) + \frac{\partial u}{\partial l} + \frac{\partial u}{\partial k} \\ &\quad + \frac{1}{2} \left[\frac{\partial^2 u}{\partial l^2} + 2 \frac{\partial^2 u}{\partial l \partial k} + \frac{\partial^2 u}{\partial k^2} \right] + \dots, \end{aligned}$$

and second- or higher-order derivatives are neglected, as needed. In Eqs. (12), for example we retain only first-order derivatives and obtain⁵

$$\begin{aligned} e_x &= \frac{1}{r} \left[\frac{\partial u}{\partial l} - f \right], \quad e_y = \frac{1}{r} \left[\frac{\partial v}{\partial k} - f \right], \quad r=1 \\ \gamma_{xy} &= \frac{\tan \alpha}{r} \frac{\partial u}{\partial k} + \frac{\cot \alpha}{r} \frac{\partial v}{\partial l}, \quad r=1. \end{aligned} \quad (13)$$

IV. GOVERNING EQUATIONS AND RELEVANT SOLUTIONS

The equations governing the equilibrium displacements of ML atoms are approximately given by the minimization of the total energy

$$E_{\text{tot}} = \sum_{l, k} (V + \epsilon)_{l, k} \quad (14)$$

with respect to the components of atomic displacements u and v , after having substituted from Eqs. (1), (10), and (12). We obtain for a specific atom (l, k) , by differentiation with respect to $u_{l,k}$, and after some simplification, the result

$$0 = 2\pi WB [\sin(\pi u_{lk}) \cos(\pi v_{lk}) + C_1 \sin(2\pi u_{lk})] \\ - (\Omega/4r^2) \{ D_{11}(u_{l+2,k} - 2u_{lk} + u_{l-2,k}) + D_{33}[(u_{l,k+2} - 2u_{l,k} + u_{l,k-2}) \tan \alpha \\ + (v_{l+1,k+1} - v_{l-1,k+1} - v_{l+1,k-1} + v_{l-1,k-1}) \cot \alpha] \}, \quad (15)$$

where we take $r=1$. The analogous equation for the y component v_{lk} may be written down by symmetry considerations.

For a ledge normal to the x direction, the y component v_{lk} is constrained to the value $v_{lk} \equiv 0$. In the continuum approximation the governing equation (15) and its counterpart for the y direction thus become

$$\frac{d^2 u}{dl^2} = \frac{\pi}{2L_x^2} [\sin(\pi u) + C_1 \sin(2\pi u)], \quad (16a)$$

$$\frac{d^2 v}{dk^2} = \frac{\pi}{2L_y^2} [\sin(\pi v) + C_2 \sin(2\pi v)], \quad (16b)$$

$$L_x^2 = \frac{\Omega D_{11}}{4WBr^2}, \quad L_y^2 = \frac{\Omega D_{22}}{4WBr^2}, \quad r=1. \quad (17)$$

As before,^{1,2} we assume that the misfit f is subcritical, so that we need to consider only single dislocation solutions. Equation (16a) can be integrated twice,^{5(c)} yielding the results

$$\frac{du}{dl} = -\frac{\sqrt{2}}{L_x} \left[1 + 2C_1 \cos^2 \left[\frac{\pi u}{2} \right] \right]^{1/2} \sin \left[\frac{\pi u}{2} \right], \quad (18a)$$

$$\frac{(2D_1)^{1/2} \pi (l + l_0)}{L_x} \\ = -\ln \left[\frac{[1 + 2C_1 \cos^2(\pi u/2)] - (D_1)^{1/2} \cos(\pi u/2)}{[1 + 2C_1 \cos^2(\pi u/2)]^{1/2} + (D_1)^{1/2} \cos(\pi u/2)} \right], \quad (18b)$$

$$D_1 = 1 + 2C_1. \quad (18c)$$

The minus signs are a consequence of considering a "step-up" ledge when going in the positive x direction as in Fig. 1 of Ref. 1. Analogous results may be written down for v by replacing, respectively, u , l , x , C_1 , and D_1 by v , k , y , C_2 , and D_2 . Furthermore,¹ the origin for the variables l and k are taken at the ledge so that, if a complete dislocation existed, its center $u = -1$ would be at $l = -l_0$.

We again limit ourselves to cases in which the misfit is small; so small that also the ML atomic displacements are everywhere small enough for the approximations

$$\sin(\pi u/2) \simeq \pi u/2, \quad \cos(\pi u/2) \simeq 1 - \pi^2 u^2/8$$

to be acceptable. Equations (18a) and (18b) then approximate to

$$du/dl \simeq -[(2D_1)^{1/2}/2L_x] \pi u, \quad (19a)$$

$$\pi u \simeq -4(D_1)^{1/2} \exp[-\beta_x(l + l_0)], \quad (19b)$$

$$\beta_x = (\pi/L_x)(D_1/2)^{1/2}. \quad (19c)$$

The ledge located at $l=0$ [with $u(l_0)=u_0$] constitutes a free boundary of the strained ML. It accordingly follows for the boundary, using Eqs. (11), (13), and (19a), that

$$0 = T_x(u_0) \approx 2a_z \left[\frac{D_{11}}{r} \left[-\frac{(2D_1)^{1/2}}{2L_x} \pi u_0 - f \right] - \frac{D_{12}}{r} f \right], \quad r=1.$$

This gives

$$\pi u_0 \approx -r L_x (2/D_1)^{1/2} (D_{11} + D_{12}) f / D_{11}, \quad r=1. \quad (20)$$

Since u is a continuous function of l it may be inferred from (19b) and (20) that

$$\exp(-\beta_x l_0) \approx r L_x (D_{11} + D_{12}) f / 2(2)^{1/2} D_1 D_{11}. \quad (21)$$

This is a relation defining l_0 .

V. INTERFACIAL MODULI AND SURFACE STRESSES

In this section we define and calculate the force components (F_x, F_y) , experienced by a ML atom in the field V emanating from the substrate. We use these to define the shear stress components $(\bar{\tau}_{xz}, \bar{\tau}_{yz})$ induced by the relaxing ML on the crystal surface underneath. In view of the constraint $v \equiv 0$ for a ledge normal to the x direction we may write,¹ using Eqs. (1),

$$F_x = -\frac{2}{a_x} \left[\frac{\partial V}{\partial u} \right]_{v=0} \\ = -\frac{4\pi WB}{a_x} [\sin(\pi u) + C_1 \sin(2\pi u)]. \quad (22)$$

The corresponding relation for F_y , for a ledge normal to the y axis, is evident. We may now define the shear stress (force per unit area) $\bar{\tau}_{xz}$ by

$$\bar{\tau}_{xz} = -\frac{2F_x}{a_x a_y} = \frac{8\pi WB}{a_x^2 a_y} [\sin(\pi u) + C_1 \sin(2\pi u)], \quad (23)$$

where $a_x a_y / 2$ is the area per ML atom, as may be inferred by inspection of Fig. 1.

If we introduce the small-misfit assumption employed in Eqs. (19), Eq. (23) reduces to

$$\bar{\tau}_{xz} = \frac{8\pi WBD_1}{a_x^2 a_y} \pi u \quad (24a)$$

$$= \frac{8\pi^2 WBD_1}{a_x^2 a_y} \frac{2a_z^0}{a_x} \frac{a_x u}{2} \frac{1}{a_z^0} \equiv \frac{8\pi^2 WBD_1}{a_x^2 a_y} \bar{\gamma}_{xz} . \quad (24b)$$

In Eq. (24b) $a_x u/2$ is the ML atomic displacement parallel to the crystal surface, and a_z^0 the height of the atom above the underlying atomic plane. These define $(a_x u/2)/a_z^0$ as the shear strain $\bar{\gamma}_{xz}$. In the present, somewhat crude approximation, we take $a_z^0 = a_z$. We also apply this approximation to a_x^0 and a_y^0 , unless their differences, as in Eqs. (5), are involved. By Eq. (1c), also $2a/a_x = 1$. In accordance with Hooke's law, Eq. (24b) thus defines an interfacial shear modulus

$$\mu_{ix} = 8\pi^2 WBD_1 / a_x^2 a_y . \quad (25)$$

We likewise obtain

$$\mu_{iy} = \frac{8\pi^2 WBD_2}{a_x a_y^2} \frac{2a_z^0}{a_y} = \frac{8\pi^2 WBD_2}{a_y^3} , \quad (26a)$$

$$D_2 = 1 + 2C_2 . \quad (26b)$$

Furthermore, by substituting from Eqs. (19b) and (21) for πu into (24a), it follows that

$$\bar{\tau}_{xz} = -\tau_{0x} \exp(-\beta_x l) , \quad (27a)$$

$$\tau_{0x} = 8\pi(2D_1)^{1/2} WBL_x (D_{11} + D_{12}) f / D_{11} a_x^2 a_y . \quad (27b)$$

We likewise find

$$\bar{\tau}_{yz} = -\tau_{0y} \exp(-\beta_y k) , \quad (28a)$$

$$\tau_{0y} = 8\pi(2D_2)^{1/2} WBL_y (D_{12} + D_{22}) f / D_{22} a_x a_y^2 , \quad (28b)$$

$$\beta_y = (\pi/L_y)(D_2/2)^{1/2} . \quad (28c)$$

We still need to find expressions for the shear stress τ_x^c induced by the ML of the lower terrace, and the normal stress N_x , induced by the "multilayer relaxation." As in Ref. 1 we write

$$\tau_x^c = \begin{cases} (\tau_{0x}^c/d) \cos(\pi x/d) & \text{for } |x| \leq d/2 \\ 0 & \text{for } |x| > d/2. \end{cases} \quad (29a)$$

The quantity τ_{0x}^c is defined by the requirement, that the integrated value of τ_x^c must balance that due to $\bar{\tau}_{xz}$, or simply by T_x far from the step, i.e., at $u=0=du/dl=v=dv/dk$. We obtain from (11), (13), and (29)

$$\tau_{0x}^c = \frac{\pi}{4} \frac{a_x}{r} (D_{11} + D_{12}) f , \quad r=1 . \quad (29b)$$

We also assume that $d \sim a_x$.

As in Ref. 1 we write

$$N_x = \begin{cases} (2N_0/b) \sin(2\pi x/b) & \text{when } |x| \leq b/2 \\ 0 & \text{when } |x| > b/2, \end{cases} \quad (30a)$$

and find N_0 from the requirement that the integrated force per unit length,

$$F_N = \int_0^{b/2} N_x dx ,$$

of the couple defined by N_x must balance with the shear force per unit length

$$F_z = \gamma \mu_{zx} a_z = \frac{a_z^0/2 - a_z/2}{a_x} \mu_{xz} a_z .$$

We obtain

$$N_0 = \pi \mu_{zx} a_x f_z / 16 . \quad (30b)$$

As in Ref. 1 we assume that $b \sim a_x$. Furthermore, we may identify μ_{zx} with $\bar{c}_{55}$ in Eq. (8),

$$\mu_{zx} = \bar{c}_{55} . \quad (30c)$$

VI. SURFACE PARAMETERS

Important goals for this section are to relate the various unknowns and to select appropriate independent variables. The main unknowns are the four parameters contained in the interaction potential $V(u,v)$ in Eq. (1), i.e., the scale factor W as a measure of the strength of the ML-crystal interaction and the Fourier coefficients expressed as the products WB , WBC_1 , and WBC_2 of the quantities W , B , C_1 , and C_2 . The activation energy Q of surface migration is an observable, and hence Eqs. (3a) and (3b) provide two equations, relating the four unknowns. Two more equations, though not independent (see the end of this section), follow from the requirement of consistency, namely, that the τ_{xz} and γ_{xz} of Eqs. (9) are, respectively, the same as $\bar{\tau}_{xz}$ and $\bar{\gamma}_{xz}$ in Eq. (24b). This implies that $\bar{c}_{55}$ in Eqs. (9) and μ_{ix} in Eq. (25) be the same, and likewise for $\bar{c}_{44}$ and μ_{iy} in Eq. (27a). Hence, on using Eq. (8b), we obtain

$$8\pi^2 WBD_1 / a_x^2 a_y = (c_{11} - c_{12})/2 , \quad (31a)$$

$$8\pi^2 WBD_2 / a_y^3 = c_{44} . \quad (31b)$$

For convenience we rewrite Eqs. (31) in the forms

$$\frac{D_2}{D_1} = \frac{1+2C_2}{1+2C_1} = \frac{c_{44}}{c_{11}-c_{12}} = \frac{A}{2} , \quad (32a)$$

$$WBD_2 = WB(1+2C_2) = \Omega c_{44} / 4\pi^2 \equiv G . \quad (32b)$$

The anisotropy ratio A and the volume Ω per ML atom, have been defined in Eqs. (6) and (10c) and G is an important materials parameter depending on geometry and stiffness.

From Eqs. (4), (6), and (32), we solve for W , B , C_1 , and C_2 . We write the results, together with L_x and L_y , given in Eqs. (17), as

$$W = \frac{Q}{\sigma}, \quad Q = \frac{2+A}{A}G, \quad B = 1 - \frac{\sigma}{2}, \quad (33a)$$

$$C_1 = \frac{A\sigma + 6\sigma - 2A - 4}{2(2-\sigma)(2+A)}, \quad (33b)$$

$$C_2 = \frac{3A\sigma + 2\sigma - 2A - 4}{2(2-\sigma)(2+A)}, \quad (33c)$$

$$\frac{c_{44}}{\pi^2 D_{11}} L_x^2 = \frac{c_{44}}{\pi^2 D_{22}} L_y^2 = \frac{A\sigma}{(2-\sigma)(2+A)}. \quad (33d)$$

The result $Q = (2+A)G/A$ is an exciting one in that it relates observable quantities and accordingly allows an assessment of the reliability and accuracy of the approach. The relations in Eqs. (33) must, however, be viewed with some caution. They are based on Eqs. (31), which firstly assume that the ML is a true truncation of the macroscopic crystal, ignoring the reasons for surface misfit, and secondly, derives the force constants μ_{ix} and μ_{iy} in Eqs. (25) and (26), as second-order derivatives [compare Eqs. (22)–(24)] of a potential which is truncated at second-order harmonics. For the latter procedure, it has been shown⁷ that several higher-order harmonics have to be included in order to obtain reliable values. We, nevertheless, believe that the results are accurate enough to be useful.

In order to establish the nature of the solutions it is necessary to determine the boundary lines $\sigma_1(A)$ and $\sigma_2(A)$ in (A, σ) space between positive and negative values of C_1 and C_2 , respectively, and the regions in which $1/|2C_1|$ and $1/|2C_2|$ exceed unity so that no stationary values of the kind defined by Eq. (3d) exist. It follows from Eq. (33b) that

$$C_1 \leq 0 \quad \text{for } \sigma \leq \sigma_1(A) = 2(A+2)/(A+6), \quad (34a)$$

$$C_2 \leq 0 \quad \text{for } \sigma \leq \sigma_2(A) = 2(A+2)/(3A+2), \quad (34b)$$

$$1/|2C_1| > 1 \quad \text{for } 0 < \sigma < \bar{\sigma}_1(A) = 2(A+2)/(A+4), \quad (35a)$$

$$1/|2C_2| > 1 \quad \text{for } 0 < \sigma < \bar{\sigma}_2(A) = (A+2)/(A+1). \quad (35b)$$

Curves of the boundary lines are displayed in Fig. 2. The allowed values, according to Eqs. (35), fall within the shaded region. It is seen that the extreme allowed values of σ , namely 0 and $\frac{4}{3}$, are exactly those specified in Eq. (4c). Of further interest is that C_1 and C_2 are equal but opposite in sign for $\sigma = 1$, i.e.,

$$C_1 = -C_2 = (2-A)/2A, \quad \sigma = 1, \quad (36)$$

as may be seen from Eqs. (33). Three-dimensional displays of $V(u, v)$ in Eq. (1) for $(A, \sigma) = (1, 1)$ and $(2, \frac{1}{2})$ are shown in Fig. 3.

Whereas the anisotropy ratio A , is a specified quantity for a given material, the parameter σ is unknown, except

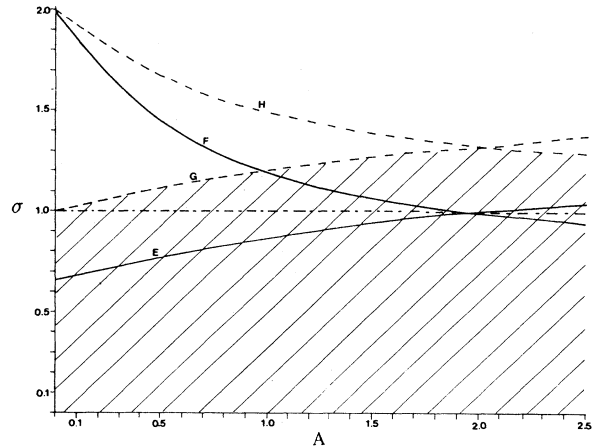


FIG. 2. The diagram displays the boundary (solid) lines in (A, σ) space where C_1 and C_2 change sign [see Eqs. (34a) and (34b)]: curve E for C_1 , i.e., $\sigma_1(A)$ and curve F for C_2 , i.e., $\sigma_2(A)$. It also displays the region of allowed values [see Eqs. (34c) and (34d)]: within the shaded area [below both of the dashed curves: G for $\sigma_1(A)$ and H for $\bar{\sigma}_2(A)$] there are no other stationary values in V [Eq. (1)] other than the absolute maximum, the absolute minimum, and the saddle point [see Eq. (4)]. On the dashed-dotted line $\sigma = 1$, $C_2 = -C_1$ [see Eq. (36)].

that it is limited to the interval $0 < \sigma < \frac{4}{3}$, or more precisely, the shaded area in Fig. 2. That σ is a variable parameter reflects the fact that the four equations are not fully independent; the left-hand sides of Eqs. (32) are effectively derivatives of the same function, namely the potential V in (1a). The fact that they are not independent also demonstrates the consistency of the considerations. If the truncation were at higher-order harmonics there would have been more undetermined parameters. With the present Fourier truncation we need one more observed (or calculated) quantity, e.g., W or C_1 or C_2 , in order to specify uniquely a value of σ . Calculated values of the Fourier coefficients as obtained from W , WB , WBC_1 , and WBC_2 , as well as the interaction ratios L_x and L_y , for a number of bcc metals (for which the stiffness constants are known) are tabulated in Table I for selected values for σ in the range $0.4 - \frac{4}{3}$.

VII. DISCUSSION AND CONCLUSIONS

The primary aim of this paper had been to derive the surface stresses needed to calculate the stress and strain fields due to the interplay of surface misfit f and atomic steps on $\{110\}$ surfaces of anisotropic bcc crystals. We have accomplished this goal for the case in which f is limited to the surface ML. We have expressed the surface stresses [see Eqs. (27)–(30)] in terms of the transformed stiffness constants and f , providing for lateral, as well as, normal misfits.

The analysis has two legs. The one is to develop a truncated Fourier series V for the ML-substrate interac-

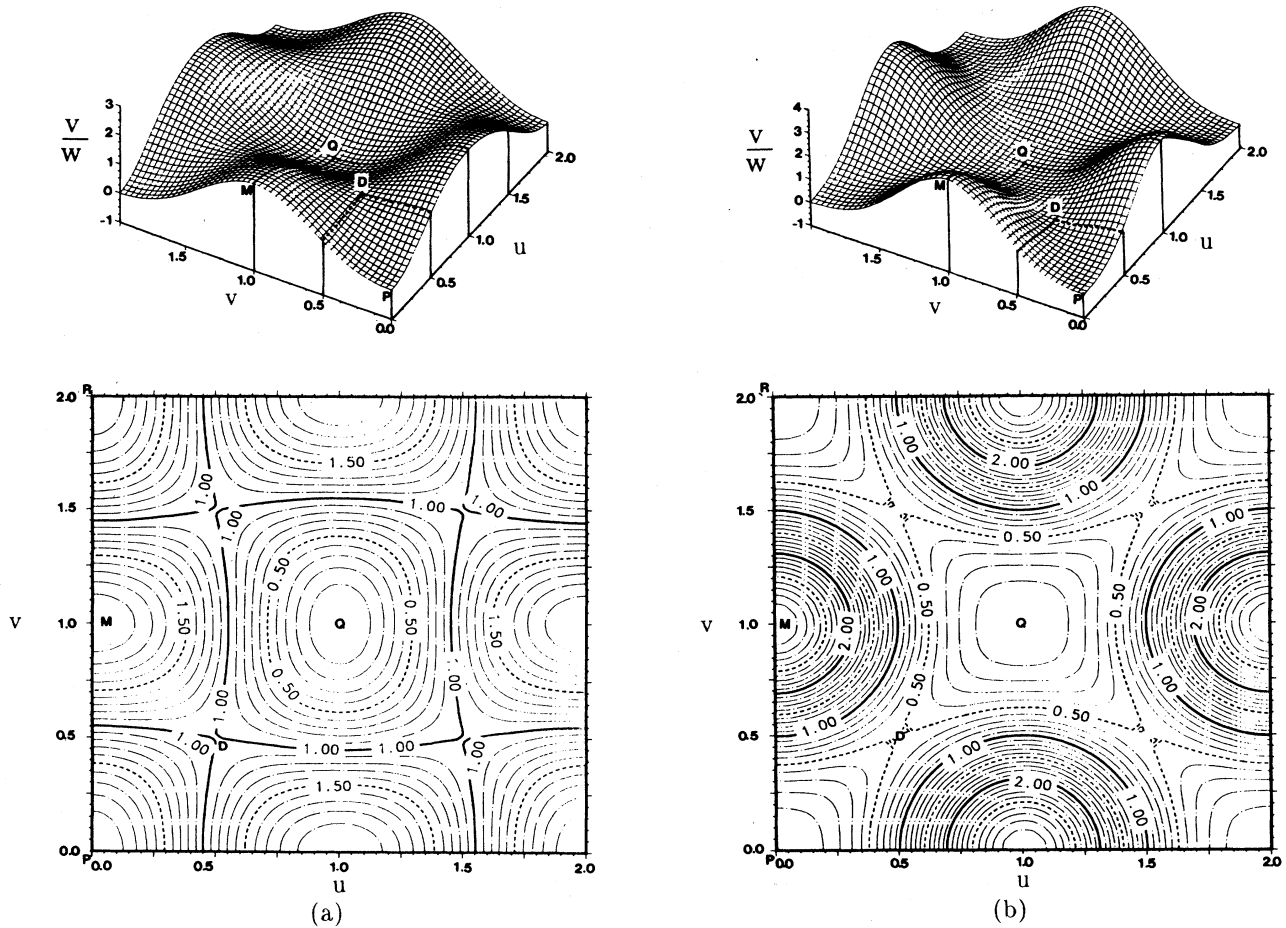


FIG. 3. Three-dimensional display of the dependence of the interaction potential V [Eq. (1)], in units of W , on displacement (u, v) within a unit cell (a) for $A=1=\sigma$, i.e., $Q=W$ and (b) for $A=2$, $\sigma=\frac{1}{2}$, i.e., $Q=2W$. Correlate points P (minimum), D (saddle), and M (maximum) with corresponding points in Fig. 1.

tion. V contains a scale factor W , to tune the strength of interaction. The Fourier coefficients as given by W , WB , WBC_1 , and WBC_2 are chosen such that there are only three stationary values; one absolute minimum, one absolute maximum, and a saddle point. The saddle defines the activation energy Q of surface migration. The other leg is to model the atom-atom interaction within the ML in terms of anisotropic elasticity (harmonic approximation) with stiffness constants c_{11} , c_{12} , and c_{44} and anisotropy ratio A .

Apart from finding expressions for the surface stresses, the analysis has led naturally to deriving valuable relations for the coefficients F_i in terms of the physical properties of the ML-crystal system. The relations [see Eqs. (33)] are expressed in terms of the variable parameter $\sigma=Q/W$, the anisotropy ratio A in Eq. (6) and the parameter G in Eq. (32).

Important details of the predictions, summarized in Fig. 2, are (i) the allowed values of A and σ which are limited to the shaded area; (ii) the regions of positive and negative values of C_1 and C_2 —below line $\sigma_1(A)$ both are

negative, between $\sigma_1(A)$ and $\sigma_2(A)$ they are of opposite sign, and above $\sigma_2(A)$ they are both positive; (iii) on the line $\sigma=1$, C_1 and C_2 are equal but of opposite sign, and (iv) the positions of the metals for which the stiffness constants, and accordingly A , are known, fall on the vertical line through the corresponding value of A (so that any special values of σ can be identified).

A very important result is the relation $Q=(2+A)G/A$ for the activation energy of surface migration Q in terms of the crystal parameters A and G . Since all three quantities are observables this relation can be used to assess the reliability and accuracy of the approach. For $\{110\}$ W , Q has been measured as 0.92 eV.¹⁰ Otherwise, by substituting for G and A , we obtain 1.1 eV. This is as good an agreement as one can hope for with such a rather crude model. More data is needed, of course, to make a true assessment.

In Table I we have tabulated values of the Fourier coefficients F_i (expressed in eV), the activation energy Q , and the interaction ratios L_x and L_y (expressed in terms of the value 2π , estimated for surfaces with quadratic

TABLE I. Calculated values of (i) the anisotropy ratio A enclosed in parentheses, (ii) the Fourier coefficients as given by the products W , WB , WBC_1 , and WBC_2 in units of eV, and (iii) the interaction ratios L_x and L_y expressed in units of 2π [the value obtained for cube faces of a simple-cubic crystal (Ref. 1)] for values of σ ($=0.4, 1$, and 1.1). At $\sigma=1$, $W=Q$ [see Eq. (33a)]. The stiffness constants are taken from Ref. 9.

	σ	W	BW	WBC_1	WBC_2
Fe (2.427)	0.4	0.986	0.789	-0.305	-0.286
	1	0.395	0.196	-0.001	0.001
	1.1	0.358	0.161	0.008	0.027
Ta (1.56)	0.4	1.340	1.072	-0.386	-0.418
	1	0.536 ^a	0.268	0.016	-0.016
	1.1	0.487	0.219	0.041	0.030
W (1)	0.4	2.842	2.274	-0.758	-0.947
	1	1.137 ^a	0.568	0.094	-0.094
	1.1	1.033	0.465	0.146	-0.043
V (0.78)	0.4	1.840	0.672	-0.215	-0.289
	1	0.336 ^a	0.168	0.368	-0.368
	1.1	0.305	0.137	0.052	-0.021
Mo (0.775)	0.4	2.412	1.929	-0.617	-0.830
	1	0.965 ^a	0.483	0.107	-0.107
	1.1	0.877	0.395	0.150	-0.062
Nb (0.55)	0.4	0.968	0.775	-0.235	-0.345
	1	0.387 ^a	0.194	0.055	-0.055
	1.1	0.352	0.158	0.072	-0.037

^a $W=Q$.

symmetry¹⁾ for the metals considered. They are arranged in order of decreasing value of A . The tabulation is for values of σ selected from the range $0.4 < \sigma < \frac{4}{3}$. It is seen that $L_x > L_y$ for $A > 1$ and vice versa.

The findings may be summarized thus.

(1) The goal, expressing the surface stresses for the $\{110\}$ surface of an anisotropic bcc crystal in terms of the surface misfit and other crystal parameters, has been accomplished.

(2) Valuable relations for the Fourier coefficients F_i of the surface-monolayer-substrate-crystal interaction V have been obtained some of which have been summarized in the diagram of Fig. 2. Because of the great variety of surface phenomena that depend on V this result is of great significance.

(3) When the activation energy Q of surface self-diffusion is known empirically or otherwise, the F_i are known in terms of the crystal parameter G , determined by crystal geometry and elastic properties and a variable parameter $\sigma = Q/W$. The latter can only be determined if additional data become available.

(4) A valuable result is that $Q = (2 + A)G/A$, which relates observables and can accordingly be used to assess the reliability and accuracy of the approach. The fact that this predicts a value of $Q = 1.1$ eV for a $\{110\}$ tungsten surface, as compared to the experimental value of 0.92 eV, is very encouraging.

(5) Although it is a somewhat crude phenomenological model, it has a sound physical basis, and is believed to offer excellent guidelines for more accurate calculations.

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