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Surface energy and surface stress on vicinals $Cu(1\,1\,n)$

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Abstract

The step energy and the step stresses are calculated as a function of the distance L between steps for vicinals $Cu(1\,1\,n)$. In addition to the well-known Marchenko-Parshin model where the steps behave as dipole forces, we show that the steps are displaced in the direction parallel to the terrace with respect to the dipolar displacements. This results from the application at the step of a monopole force, F_b, whose modulus decreases as $1/L$. The extra displacement due to F_b does not modify the step energy with respect to the MP model but is linked to the presence of the interaction term in the step stresses, that vary as $1/L$. Because the step stress is calculated with respect to the nominal surface stress, we calculate the diagonal surface stresses in both the vicinal system (x, y, z) where z is normal to the vicinal and the projected system (x, b, c) where c is normal to the nominal terrace. Moreover, we calculate the surface stresses by using two methods: the first called the '*Force*' method, from the surface pressure forces and the second called the '$\Delta\ E$' method, by homogeneously deforming the vicinal in the parallel direction, x or y, and by calculating the surface energy excess proportional to the applied strain. We confirm that the variation of the step stress in the tensor direction $'xx'$ is the same between the two methods while it is different in the direction $'yy'$. In the '*Force*' method, the step stress in the direction $'yy'$ is the sum of the two step stresses in the directions $'bb'$ and $'cc'$. In the '$\Delta\ E$' method, the step stress in the direction $'yy'$ equals this calculated in the direction $'bb'$ (parallel to the terrace) in the '*Force*' method, this in the normal direction $'cc'$ being excluded.

Key words: Semi-empirical models and model calculations, Stepped single crystals surfaces, Surface energy, Surface stress, Cu(001)

1. Introduction

Stepped surfaces are widely used as templates in various experimental and theoretical studies, as well as in numerical simulations. Surface steps and kinks (step defects) play an important role in catalytic reactions, growth kinetics, crystal morphologies, faceting, and roughening transitions [1, 2, 3]. Steps can have direct evidence in both adsorption and reaction properties of surfaces. Moreover, vicinals can be used as support for better arrangement of quantum wires during their growth, as in the case of vicinals of $InP(001)$ with $InAs$ quantum wires [4].

In the paper, we study the surface energies and surface stresses of $Cu(1\ 1\ n)$ vicinals and their dependency on the distance between steps L (L is the distance in the projected direction, that is, parallel to the (001) terrace). The surface stresses are calculated by using two different coordinate systems (x, y, z) and (x, b, c) as showed in Fig. 1. The (x, y, z) reference system is called the one *vicinal* while this (x, b, c) is called the one *projected*. Contrary to the step energies, the calculation of the step stresses depend on the directions in the two reference systems. The vicinals of type $(1\,1\,n)$ are more often used in experiment

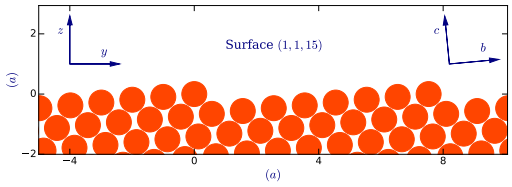

Figure 1: Side view of the $Cu(1\,1\,15)$ vicinal. Here we present the two reference systems used in the paper. The reference system (x, y, z) is this *vicinal* while the reference system (x, b, c) is this *projected*. The direction b is parallel to the (001) terrace. The direction x is not presented because it is directed along the steps. The vicinal angle is the tilt angle between the two reference systems. The length unit a is the distance between nearest atoms in the direction b. The unit a is also the real distance between nearest neighbours in bulk.

than the vicinals of type $(0\ 1\ M)$ [5, 6, 7, 8]. The $Cu(0\ 1\ M)$ vicinals were first examined [9, 10] because the three principal directions of the terrace are the principal directions of the

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fcc cell and thus, the understanding of findings are less laborious. The interactions being limited to nearest neighbours, the geometric simplifications have helped us a lot in the study of vicinals of type $(0\,1\,M)$, and notably when studying the surface stresses. In addition, the difficulties linked to the anisotropy of the fcc metal are avoided at best. For $Cu(0\ 1\ M)$ vicinals, the components of the dipole force $\mathbf{f} = (0, f'_y, f_z)$ that characterizes the step in the Marchenko-Parshin (MP) model [11] have the same modulus ($f'_y = f_z = -0.15\ naN$).

For $Cu(1\,1\,n)$ vicinals, the direction normal to the terrace, c, is unchanged ((001) terrace) while the directions x and b are parallel to the diagonals of the faces of the fcc cell. So, the directions x and b correspond to the two dense directions of the terrace. With respect to $Cu(0\,1\,M)$ vicinals, we will see in this way that the component f'_b is multiplied by $\sqrt{2}$ while the component f_c does not change.

The step stresses are calculated in the diagonal directions of the two reference systems, on the one hand in the directions $'xx'$, $'bb'$ and $'cc'$, and on the other hand in the directions $'yy'$ and $'zz'$. By using the five diagonal directions, we will understand why the interaction stress between steps is different in the direction $'yy'$ when using two methods of calculation of the step stresses. In the first method called the '*Force*' method, we directly calculate the interaction forces between atoms in the first surface monolayers while they are nonexistent in bulk. The step stress is always zero in the direction normal to the vicinal surface 'zz'. In the second method called the '$\Delta\ E$' method, we calculate the step stress by deforming all the system in one direction parallel to the vicinal surface, $'xx'$ or $'yy'$. From the energy excess proportional to the applied strain, we can easily deduce the step stress in the two directions $'xx'$ and $'yy'$. The use of the two methods will show that the interaction stress in the direction $'yy'$ is different while it is the same for the direction parallel to the steps $'xx'$. The difference will be explained in the paper.

The paper is organized as follows: Section 2 presents the potential chosen in our simulations as well as the minimization method of the total energy of the periodic system at $T = 0K$. Section 3 explains how to calculate the step energy and the step stress for vicinals. The two methods, the one '*Force*' and the one '$\Delta\ E$', are detailed in this section as well as the Shuttleworth relationship between the two fundamental surface quantities, the surface

energy and the surface stress [12]. Section 4 gives the step energy of vicinals $Cu(1\ 1\ n)$ and the surface displacements with respect to the nominal surface. Section 5 is devoted to the step stresses of vicinals $Cu(1\ 1\ n)$ for different diagonal directions in the two reference systems cited above (this *vicinal* and this *projected*). Section 6 demonstrates why the step stress in the diagonal direction $'yy'$ is different between the two methods of calculation of step stresses. Section 7 displays the conclusion.

2. Simulation model and *RGL* potential adapted to *Cu*

The equilibrium configurations of the flat and vicinal surfaces at $T = 0K$ are obtained by the quenched molecular dynamics method [13]. All our calculations use a slab delimited by two identical surfaces. Periodic boundary conditions are applied along the surface directions x and y. In the direction z, the slab is sufficiently large enabling to correctly reproduce the bulk properties in the center of the slab. Between the two surfaces, the number of planes perpendicular to the direction c is larger than 200. We use the RGL potential which is a many-body potential [14]. This potential has been adjusted to the bulk elastic constants and the cohesive energy. The lattice constant is equal to the value determined in experiment. For Cu, it is equal to $a\sqrt{2} = 3.61$ Å. The length unit a is the distance between nearest neighbours in the dense row direction (direction x or b). The interactions between atoms are limited to their nearest neighbours. For this cut-off radius, the parameters of the RGL potential are given in Ref. [14]. We use this potential because this reference shows that the agreement with the experiment has proven to be good for low and intermediate temperatures ($< 900K$ for Cu).

3. Calculating step energy and step stress

In bulk, the cohesive energy is calculated by using the RGL potential and by adding up the interaction energies between one atom and its twelve neighbours. For Cu, the cohesive energy equals $-3.5\ eV$. For $T = 0K$ and at zero pressure, the atomic energy is minimum and consequently, the pressure forces between the bulk atom and its neighbours are zero.

For the $Cu(001)$ surface, the atoms of the first monolayer have lost four neighbours with respect to bulk. At equilibrium, we note that the two first monolayers are contracted in the direction normal to the surface z. The surface is relaxed in the direction z in order to cancel the diagonal surface stress $\overline{\sigma^0_{zz}}$, in the direction normal to the surface. Due to the loss of four neighbours in the first monolayer and because in the direction parallel to the surface, the distance between surface atoms cannot vary with respect to bulk; the diagonal surface stress parallel to the surface is not cancelled: $\overline{\sigma^0_{xx}} = \overline{\sigma^0_{yy}} = 0.367\ eV/a^2$. Here, we consider that the non-diagonal surface stresses are nonexistent for the nominal surface and their vicinals ($\overline{\sigma^0_{\alpha\beta}}$ with $\alpha \neq \beta$ is nonexistent). The surface energy is the energy excess with respect to bulk energy. It is calculated per surface area unit and is added up along the z axis from the surface up to bulk. For $Cu(001)$, the surface energy γ_0 is equal to $0.455\ eV/a^2$.

The surface stress is the sum of pressure forces that exist on the surface and are null in bulk. The pressure forces are $r_{mn\alpha} \times F_{mn\alpha}$ where $r_{mn\alpha} = (R_{m\alpha} - R_{n\alpha})$ is the position of atom m relative to the neighbour n in the direction α and $F_{mn\alpha}$ is the partial force applied on the atom m due to the neighbouring atom n in the direction α. The diagonal pressure forces between the atoms m and n are calculated as minus half of $r_{mn\alpha}$ multiplied by the derivative of the potential of the atom m with respect to $r_{mn\alpha}$. When deforming the surface in the diagonal direction parallel to the surface and when omitting the variation of the surface energy due to the variation of the atomic surface area (we omit, therefore, the term γ_0 in the Shuttleworth relation [12]), the method of Ackland and Finnis [15] writes that the surface stress $\overline{\sigma^0_{\alpha\alpha}}$ can be calculated in numerical methods in the atomic scale as

$$\begin{aligned} \overline{\sigma^0_{\alpha\alpha}} &= \frac{1}{A_0}\left.\frac{\partial A_0\gamma_0}{\partial\epsilon_{\alpha\alpha}}\right|_{\epsilon_{\alpha\alpha}=0} = \frac{1}{A_0}\frac{\partial\sum_m \Phi_m}{\partial\epsilon_{\alpha\alpha}} \\ &= \frac{1}{2A_0}\sum_m\sum_{n\neq m} r_{mn\alpha}\frac{\partial\Phi_m}{\partial r_{mn\alpha}} = -\frac{1}{2A_0}\sum_{m,n\neq m} r_{mn\alpha}\ F_{mn\alpha} \end{aligned} \tag{1}$$

where A_0 is the periodic surface area and Φ_m is the potential energy of the atom m. This equation gives the diagonal surface stress $\overline{\sigma^0_{\alpha\alpha}}$ by calculating the pressure forces that exist when the surface is not homogeneously deformed by $\epsilon_{\alpha\alpha}$. Therefore, the derivative of the energy $A_0\gamma_0$ with respect to $\epsilon_{\alpha\alpha}$ is taken at $\epsilon_{\alpha\alpha} = 0$. Here, $\epsilon_{\alpha\alpha}$ is called the homogeneous

strain when it is applied everywhere, in the periodic system. In the following, the homogeneous strain is called $\epsilon^h_{\alpha\alpha}$ instead of $\epsilon_{\alpha\alpha}$. This method for calculating the surface stress $\overline{\sigma^0_{\alpha\alpha}}$ is called the '*Force*' method (calculation of the pressure *forces* for $\epsilon^h_{\alpha\alpha}=0$).

When the system (surface and bulk) is deformed by a factor of $(1+\epsilon^h_{\alpha\alpha})$ in the direction α, the equilibrium energy excess due to the strain $\epsilon^h_{\alpha\alpha}$ is

$$\Delta E = \Delta E_{1o} + \Delta E_{2o} + \cdots \tag{2}$$

where ΔE_{1o} and ΔE_{2o} are the first and the second-order energies as a function of the deformations due to $\epsilon^h_{\alpha\alpha}$. In this paper, we treat only the first-order energy ΔE_{1o} because the quantity ΔE_{1o} is enough to explain the presence of the surface stress for the nominal surface and the corresponding vicinals. By using the reference system (x,y,z), the first-order energy ΔE_{1o} is written as

$$\begin{aligned}\Delta E_{1o} &= \sum_{m,n} K_{1,x,m,n}\ \Delta(x_m - x_n) + K_{1,y,m,n}\ \Delta(y_m - y_n) + K_{1,z,m,n}\ \Delta(z_m - z_n) \\ &= \Delta E_{xx} + \Delta E_{yy} + \Delta E_{zz}.\end{aligned} \tag{3}$$

Between the initial (I) and final (F) configurations, $\Delta(\alpha_m - \alpha_n)$ is the *local* deformation between two atoms m and n in the direction α ($\Delta(\alpha_m - \alpha_n) = [(\alpha_m - \alpha_n)_F - (\alpha_m - \alpha_n)_I]/(\alpha_m - \alpha_n)_I$). The constants $K_{1,\alpha,m,n}$ are the first-order elastic constants calculated in the initial configuration I. For the nominal surface, the configuration I is the non-deformed flat surface. For the vicinal, and by using the reference system (x,b,c) (Fig. 1), the configuration I corresponds to two $Cu(001)$ relaxed surfaces that are distant, at the step position ($b=0$), from $a/2$, the step width $l=a/2$ and the step height $h=a/\sqrt{2}$ in the directions x, b and c, respectively.

For the nominal surface, under homogeneous strain parallel to the surface ($\alpha = x$ or y), the surface energy $\gamma(\epsilon_{\alpha\alpha})$ is

$$\begin{aligned}\gamma(\epsilon_{\alpha\alpha}) &= \gamma_0 + \left.\frac{\partial\gamma_0}{\partial\epsilon_{\alpha\alpha}}\right|_{\epsilon_{\alpha\alpha}=0} \times \epsilon_{\alpha\alpha} + \cdots \\ &= \gamma_0 + \left(\overline{\sigma^0_{\alpha\alpha}} - \gamma_0)\right) \times \epsilon_{\alpha\alpha} + \cdots\end{aligned} \tag{4}$$

In Eq. (4), the term $-\gamma_0 \times \epsilon_{\alpha\alpha}$ results from the fact that the surface energy is defined per *constant* surface area unit, a^2 here, while the atomic surface varies by a factor of $(1+\epsilon_{\alpha\alpha})$. This term is necessary in order to respect the matter conservation rule in the calculation of $\gamma(\epsilon_{\alpha\alpha})$. In the following, we suppose that the quantity of matter is not corrupted, and if so, we omit the term $-\gamma_0 \times \epsilon_{\alpha\alpha}$. The term $\overline{\sigma^0_{\alpha\alpha}} \times \epsilon_{\alpha\alpha}$ in Eq. (4) is the first-order energy as a function of the deformations, i.e ΔE_{1o} in Eq. (2).

When we deform the $Cu(001)$ flat surface under the strain ϵ^h_{yy}, for example, the first-order energy is $\Delta E_{1o} = \Delta E_{yy}$ with $\Delta(y_m - y_n) = \epsilon^h_{yy}$. The sum of the elastic constants $K_{1,y,m,n}$ is equal to the surface stress $\overline{\sigma^0_{yy}}$. ΔE_{xx} is zero because $\Delta(x_m - x_n)$ is zero and ΔE_{zz} is zero because the elastic constants $K_{1,z,m,n}$ and their sum $\overline{\sigma^0_{zz}} = 0$ are zero. From the first-order energy ΔE_{1o}, we can therefore deduce the surface stress $\overline{\sigma^0_{yy}}$ by using the relation $\Delta E_{1o} = \overline{\sigma^0_{yy}} \times \epsilon^h_{yy}$. We call this method of calculation of $\overline{\sigma^0_{yy}}$ the '$\Delta\ E$' method that consists of deforming the system by $\epsilon^h_{\alpha\alpha}$ and then deducing the first-order energy excess ΔE_{1o} due to $\epsilon^h_{\alpha\alpha}$.

On vicinals, we calculate the surface stresses by using both calculation methods (the '*Force*' method and the '$\Delta\ E$' method). Because the step stress is the stress excess with respect to the surface stress of the nominal surface, we calculate, firstly, the step stresses in the projected reference system (x, b, c). From this system, we can then, and more easily, deduce the step stresses in the vicinal reference system (x, y, z), knowing that the $'zz'$ step stress is zero in the direction normal to the vicinal surface, irrespective of the vicinal angle θ.

We note that the two calculation methods, the '*Force*' and the '$\Delta\ E$', give the same quantity for the stress, with the exception of the interaction stress between steps in the direction perpendicular to the step (diagonal direction $'yy'$). A part of the interaction stress calculated by using the '*Force*' method is not used when we deform the system in the direction $'yy'$ [10]. This shows that the equivalence between the two methods is not valid only for the interaction stress in the direction $'yy'$ while it is valid for the direction $'xx'$, parallel to the step. We will explain this difference in a later section (section 6).

4. Step energy on vicinals $Cu(1\,1\,n)$

Fig. 2 gives the step energy E_{St} as a function of the distance L between steps for $Cu(11n)$ vicinals. The step energy has been fit with two functions $G_{23}(L) = G_0 + G_2\ L^{-2} + G_3\ L^{-3}$

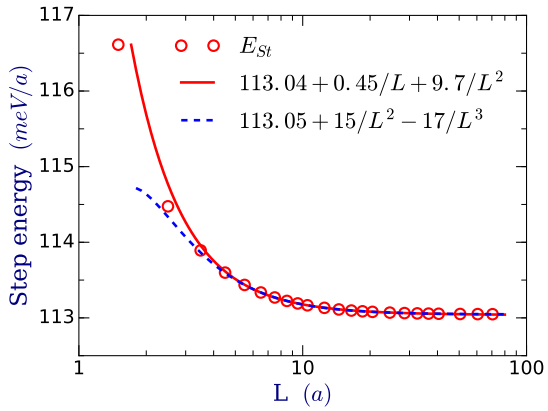

Figure 2: Step energy E_{St} as a function of the distance L between steps. It is adjusted to two different functions $G_{23}(L) = G_0 + G_2\ L^{-2} + G_3\ L^{-3}$ and $H_{12}(L) = H_0 + H_1\ L^{-1} + H_2\ L^{-2}$. The function G_{23} is the one used in the MP model for which the term of order $O(1/L)$ is not present. The second function takes into account the variation of order $O(1/L)$ because the step deformation in the diagonal direction $'bb'$, $\epsilon_{bb}(0)$, includes a term proportional to $1/L$.

and $H_{12}(L) = H_0 + H_1\ L^{-1} + H_2\ L^{-2}$. In the function $G_{23}(L)$, the term proportional to $1/L$ is not present. The use of $G_{23}(L)$ results from the MP model [11]. In the MP model, the step behaves as one dipole line applied upon a flat surface. If the applied force per length unit is $\mathbf{f} = (0, f_b, f_c)$ and if it is applied at the origin line $b = 0$, the MP model gives the surface displacement $\mathbf{u}(b)$ as follows

$$\mathbf{u}(b) = -\frac{2(1-\nu^2)}{\pi E}\frac{\mathbf{f}}{b} = -\Lambda\frac{\mathbf{f}}{b} \tag{5}$$

where ν is Poisson's ratio and E is Young's modulus. In the MP model and from Eq. (5), the interaction energy between steps can be easily deduced. It is

$$\Gamma^{MP} = \sum_{n=1}^{\infty} \Lambda\frac{\mathbf{f}^2}{(nL)^2} = \frac{\pi^2}{6}\Lambda\frac{(f_b^2 + f_c^2)}{L^2}. \tag{6}$$

The interaction energy between steps Γ^{MP} results from the product at the step position ($b = 0$) of the dipole force multiplied by the sum of the displacements due to neighbouring steps located at $y = nL$, n being a non-zero integer. In addition, Γ^{MP} supposes that the work of the surface forces W is twice that minus the second-order energy as a function of the deformations due to lines of dipole forces ($W = -2\ E_{2o}$). The energy E_{2o} is calculated by using the deformations within the entire periodic vicinal system.

When forces are applied upon a flat surface, the first-order energy due to forces, E_{1o}, does not exist. On vicinals, the first-order energy E_{1o} is present and it is calculated by using the deformations in only a few surface monolayers. As for the forces applied upon a flat surface, the equilibrium verifies to a good approximation the relation $E_{1o} = -2E_{2o}$ and consequently, the sum $E_{1o} + E_{2o} \approx -E_{2o}$ (we ignore here the third-order energy and more).

Because the terrace between steps tends to contract ($\overline{\sigma^0_{yy}} > 0$), Eqs. (5) and (6) are modified with respect to the MP model. Consequently and in the paper, we instead use the following equations [16]

$$\begin{aligned} u_b(b) &= -\Lambda \frac{f_b(1+X)}{b} = -\Lambda \frac{f'_b}{b} \\ u_c(b) &= -\Lambda \frac{f_c}{b} \end{aligned} \tag{7}$$

$$\Gamma^{MP'} = \frac{\pi^2}{6} \Lambda \frac{(f_b^2(1+2X)^2 + f_c^2)}{L^2} \tag{8}$$

where X corresponds to the recursive extra contraction of the terrace with respect to the MP model when the dipole lines $\mathbf{f}$ are applied on the flat surface: $X = -\lambda f_b(1 - \lambda f_b(1 - \lambda f_b(\ldots))) = (-\lambda f_b/(1 + \lambda f_b))$. For $Cu(001)$, we use the constant $\lambda = 0.8\ naN^{-1}$ [16]. Note that the parallel component f_b is replaced by the component f'_b while the corresponding component in the step energy $\Gamma^{MP'}$ is not proportional to $f'^2_b = f_b^2(1+X)^2$ but to $f_b^2(1+2X)^2$. This shows that the difference between Γ^{MP} and $\Gamma^{MP'}$ results from the fact that the surface tends to contract at equilibrium due to the existence of the surface stress in the direction parallel to the terrace. The normal component f_c is not modified because the surface stress is zero in the direction normal to the surface.

Fig. 3 gives the surface displacements in the two directions b and c for $L = 32.5\ a$. By

adjusting these displacements to the sum of the displacements due to neighbouring steps, we find that the elastic constant Λ and the dipole force f_c are identical to those deduced in vicinals $Cu(0\,1\,M)$ [10], namely $\Lambda = 0.0683\ a^2/naN$ and $f_c = -0.15\ naN$. Concerning the component parallel to the terrace, we find that f'_b is equal to $f_c \times \sqrt{2}$, that f_b is $-0.18\ naN$ and X is 0.17. Because the width and the height of the step are, respectively, $l = a/2$ and $h = a/\sqrt{2}$, we can write that $f'_b \times l$ is equal to $f_c \times h$.

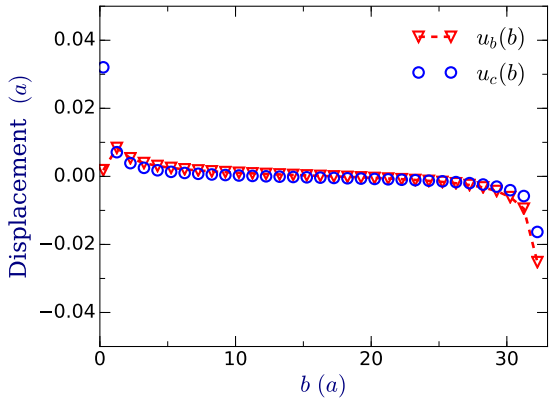

Figure 3: Surface displacements on a $Cu(1\,1\,n)$ vicinal with $n = 65$. The displacements are calculated with respect to the atomic positions of the nominal surface $Cu(001)$. The b and c directions are respectively parallel and normal to the terrace (see Fig. 1). The positions on both sides of the terrace, $b = a/4$ and $b = L - a/4$, are those of the lower and upper corners of the step. From these displacements, we can deduce the dipole force $\mathbf{f}' = (0, f'_b, f_c)$ in the modified MP model. To a good approximation, $f'_b = f_c \times \sqrt{2}$ and $f_c = -0.15\ naN$.

Since we have the values of Λ, X, f_b and f_c, we can calculated the step-step interaction energy $\Gamma^{MP'}$ in Eq. (8). It is equal to $+15\ a^2/L^2\ meV/a$. In Fig. 2, we have adjusted the step energy, E_{St}, to the function $G_{23}(L)$) with $G_2/L^2 = +15\ a^2/L^2\ meV/a$. The agreement with the modified MP model is therefore good. The contribution due to the parallel component f_b is 2.6 with respect to the contribution due to the normal component f_c. If the modified MP model was not used, the contribution due to f_b would be twofold with respect to the contribution due to f_c because we should have the relation $f_b = f_c\sqrt{2}$ instead of $f_b(1+X) = f_c\sqrt{2}$. The difference is thus important between the MP model and this modified model

due to the tendency to contraction of the terrace between steps.

The step-step interaction energy $\Gamma^{MP'}$ is almost 3/2 times larger for $Cu(1\,1\,n)$ vicinals than for $Cu(0\,1\,M)$ vicinals. Because $f'_b = f_c\sqrt{2}$, the contribution due to the parallel component f'_b is twice for $Cu(1\,1\,n)$ vicinals.

To a good approximation, we can deduce the step-step interaction energy $\Gamma^{MP'}$ for other fcc metals. There is a direct link between the component f'_b and the nominal surface stress $\overline{\sigma^0_{yy}}$. The link is $f'_b \approx \overline{\sigma^0_{yy}} \times a$. Then, we deduce the component $f_c = f'_b/\sqrt{2}$. The values of Λ and X in Eq. (8) are given in Ref. [16] for different fcc metals. So, we can have a good estimate of the interaction energy $\Gamma^{MP'}$ for vicinals of type $(1\,1\,n)$, by using the modified MP model.

In order to understand the usefulness of the other adjustment function $H_{12}(L)$ in Fig. 2, we give here the behavior of $Cu(11n)$ vicinals with respect to $Cu(001)$ surfaces with opposite steps, i.e for which the component f_c changes sign between neighbouring steps. This was shown by studying $Cu(0\,1\,M)$ vicinals [9].

Fig. 4 and Fig. 5 give the variations of the step deformations as a function of the distance L. For clarity, we write the step deformations $\epsilon_{bb}(0)$ and $\epsilon_{cb}(0)$ with respect to the length unit used here $(= a)$ as

$$\begin{aligned} \epsilon_{bb}(0) &= \frac{u_b(+a/4) - u_b(-a/4)}{a} \\ \epsilon_{cb}(0) &= \frac{u_c(+a/4) - u_c(-a/4)}{a}. \end{aligned} \tag{9}$$

For vicinals and assuming that only the modified MP model allows one to describe the surface displacements $u_b(b)$ and $u_c(b)$ from Eq. (7), $\epsilon_{bb}(0)$ and $\epsilon_{cb}(0)$ should vary as $(\pi^2/3)\Lambda f'_b/L^2$ and $(\pi^2/3)\Lambda f_c/L^2$, respectively [9]. They are respectively equal to $-0.048\ a^2/L^2$ and $-0.034\ a^2/L^2$. For surfaces with opposite steps, only the component f_c changes sign between neighbouring steps, and we can write that the parallel step deformation $\epsilon_{bb}(0)$ should be identical to those calculated for vicinals. However, Fig. 4 shows that the variations are different between vicinals and surfaces with opposites steps. On vicinals, we note that the step deformations include a component of order $O(1/L)$ in addition to the component of order $O(1/L^2)$ in the modified MP model. This is checked because in Figs. 4 and 5, different

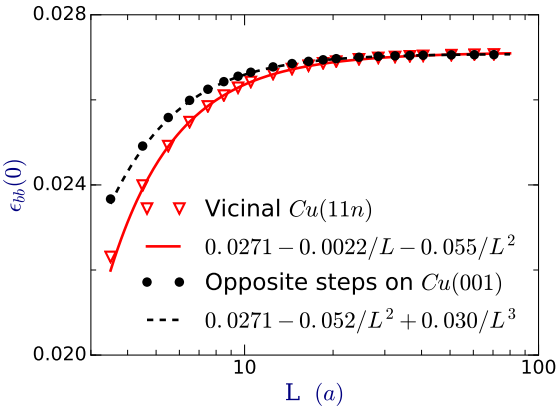

Figure 4: Step deformations $\epsilon_{bb}(0)$ on the first monolayer for $Cu(1\,1\,n)$ vicinals and surfaces with opposite steps, as a function of the distance L. The step deformations are calculated by using Eq. (9). They are calculated over the length unit a while the two corners of the step are distant from $a/2$ in the direction b. They are adjusted to the function $C_0 + C_1/L + C_2/L^2$ for vicinals and to the function $C_0 + C_2/L^2 + C_3/L^3$ for surfaces with opposite steps. The constant C_2 is close to the expected value $(\pi^2/3)\Lambda f'_b = -0.048\ a^2$.

adjustments of the component of order $O(1/L^2)$ are close to the values of $-(\pi^2/3)\Lambda f'_b/L^2$ and $-(\pi^2/3)\Lambda f_c/L^2$, whether the step is opposite or not.

With respect to the surfaces with opposite steps, the component of order $O(1/L)$ in the step deformations of vicinals results from the fact that the step is under the influence of a monopole force F_b in the direction b, in addition to the dipole force f_b, and that the modulus of F_b decreases as $1/L$ [9]. To confirm the presence of the term proportional to $1/L$ in the step deformations for vicinals, we can give the displacements of the atoms of the step (upper and lower corners of the step) as a function of the distance L after subtracting the displacements due to neighbouring steps in the modified MP model with $f_c = -0.15\ naN$ and $f'_b = f_c \times \sqrt{2}$. The reduced displacements are called the displacements $\Delta\omega_b(b)$ and $\Delta\omega_c(b)$ for the two directions b and c. At the positions of the step, $b = \pm a/4$, their variations as a function of L are showed in Fig. 6 and Fig. 7. They are fitted to the function of the form $C_0 + C_1/L + C_2/L^2$. We are particularly interested in the components of order $O(1/L)$. For surfaces with opposite steps, we have checked that the component of order $O(1/L)$ is absent in the corresponding $\Delta\omega_b(b)$. On vicinals, the components of order $O(1/L)$ in the

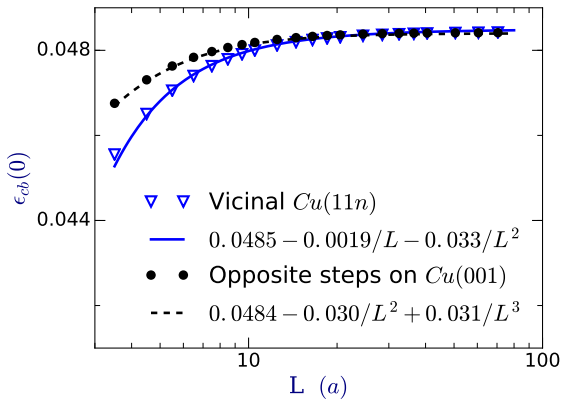

Figure 5: Step deformations $\epsilon_{cb}(0)$ on the first monolayer for $Cu(1\,1\,n)$ vicinals and surfaces with opposite steps, as a function of the distance L. The step deformations are calculated by using Eq. (9). They are calculated over the length unit a while the two corners of the step are distant from $a/2$ in the direction b. They are adjusted to the function $C_0 + C_1/L + C_2/L^2$ for vicinals and to the function $C_0 + C_2/L^2 + C_3/L^3$ for surfaces with opposite steps. The constant C_2 is close to the expected value $(\pi^2/3)\Lambda f_c = -0.034\ a^2$.

four displacements $\Delta\omega_b(\pm a/4)$ and $\Delta\omega_c(\pm a/4)$ are present. The difference between the two components of order $O(1/L)$ at the step positions, $b = \pm a/4$, reproduces the components of order $O(1/L)$ in the two step deformations $\epsilon_{bb}(0)$ and $\epsilon_{cb}(0)$. They are equal to $-0.002\ a/L$.

In addition, Fig. 8 gives the surface displacement $u_c(L/2)$ at the middle of the terrace. It varies as $-0.013a/L$ for large L while it is zero for surfaces with opposite steps. Because the three displacements $\Delta\omega_c(+a/4)$, $u_c(L/2)$ and $\Delta\omega_c(L - a/4)$ vary respectively as $-0.014/L$, $-0.013/L$ and $-0.012/L$, we can deduce that the normal surface displacement $u_c(b)$ includes an extra displacement $\Delta\omega_c^F(b)$ that varies linearly with the position b between $b = +a/4$ and $b = L - a/4$ as

$$\Delta\omega_c^F(b) = \frac{a}{L}(-\frac{u_1}{2} + \frac{u_1}{L}b + Q), \tag{10}$$

with $u_1 = 0.002\ a$ and $Q = -0.013\ a$. This is shown in Fig. 9 for $L = 9.5\ a$ as one example. Due to relevant differences between vicinals and surfaces with opposite steps, we conclude that the step is under the influence of the monopole force F_b in the direction of the descending steps and for which the modulus decreases as $1/L$ [17, 9].

In the step deformation $\epsilon_{bb}(0)$, the ratio between the component of order $O(1/L)$ and the

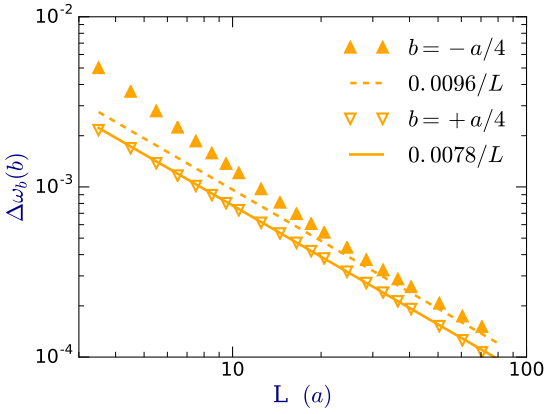

Figure 6: On $Cu(11n)$ vicinals and from the surface displacement $u_b(b)$, we have subtracted the displacements proportional to $1/b$ in the modified MP model with $f'_b = -0.15 \times \sqrt{2}\ naN$. This gives the reduced displacements $\Delta\omega_b(\pm a/4)$ for the two corners of the step. Their variations as a function of L are adjusted to the function $C_0 + C_1/L + C_2/L^2$ and then we plot the two functions C_1/L for the two step corners. The difference between the two functions C_1/L is close to the component of order $O(1/L)$ in the step deformation $\epsilon_{bb}(0)$ $(= +0.0022/L)$.

component of order $O(1/L^2)$ is *quantitatively* close to $f_z/f'_y = 1/\sqrt{2}$. Indeed, if we adjusted the step deformation $\epsilon_{bb}(0)$ to the function of the form $C_0 + C_2/L^2 + C_3/L^3$, the constant C_2 would be equal to $-0.081\ a^2$, which is close to $(\pi^2/3)\Lambda(f'_b + f_c)/L^2 = -0.081\ a^2/L^2$. Therefore, we consider that the component of order $O(1/L)$ in $\epsilon_{bb}(0)$ is limited *quantitatively* by the surface displacement normal to the terrace deduced in the modified MP model, i.e proportional to the component f_c of the dipole force $\mathbf{f}'$. The fit to $C_0 + C_2/L^2 + C_3/L^3$ for the step deformation of vicinals is not correct because C_2 is too high with respect to the modified MP model and because it is different from the constant C_2 adjusted for surfaces with opposite steps. This shows that for vicinals, the component of order $O(1/L)$ is present in the step deformation $\epsilon_{bb}(0)$.

On vicinals, the presence of the term proportional to $1/L$ in the step deformation $\epsilon_{bb}(0)$ is linked to the existence of the interaction stress which varies as $1/L$. No interaction stress between steps exists for surfaces with opposite steps. For surfaces with opposite steps, we can calculate the step energy from the MP model and by assuming that the first-order

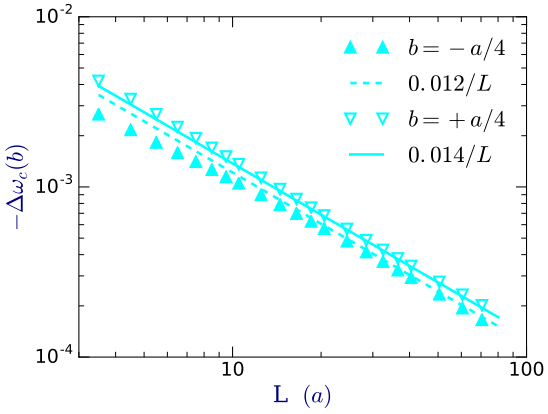

Figure 7: On $Cu(11n)$ vicinals and from the surface displacement $u_c(b)$, we have subtracted the displacements proportional to $1/b$ in the modified MP model with $f_c = -0.15\ naN$. This gives the reduced displacements $\Delta\omega_c(\pm a/4)$ for the two corners of the step. Their variations as a function of L are adjusted to the function $C_0 + C_1/L + C_2/L^2$ and then we plot the two functions C_1/L for the two step corners. The difference between the two functions C_1/L is close to the component of order $O(1/L)$ in the step deformation $\epsilon_{cb}(0)$ $(= +0.0019/L)$.

energy E_{1o} is equal to $-2E_{2o}$. For vicinals, the interaction stress between steps should be taken into account in the step energy. Our calculations of the first-order energy show that the step energy can be adjusted to the two fit functions $G_{23}(L)$ and $H_{12}(L)$. The function $G_{23}(L)$ corresponds to the MP model and is the elastic response of the bulk against the action of the steps on surface. The first-order energy E_{1o} is close to $-2 \times \Gamma'_{MP}$ in Eq. 8 by using the relation $E_{1o} \approx -2E_{2o}$. The function $H_{12}(L)$ takes into account the term of order $O(1/L)$ in the step deformation $\epsilon_{bb}(0)$. In this case, the first-order energy $E_{1o} \approx -2H_{12}(L)$ has been adjusted to the step deformation $\epsilon_{bb}(0)$ multiplied by a specific step stress that we call $\sigma_{bb}^{S,1o}$: $E_{1o} \approx \sigma_{bb}^{S,1o} \times \epsilon_{bb}(0)$. The adjustment of E_{1o} is made within a constant, and we find that $\sigma_{bb}^{S,1o}$ is equal to $-0.40\ eV/a$. When supposing that the constant $\sigma_{bb}^{S,1o} = -0.40\ eV/a$ is calculated in the first surface monolayer and over the distance a, it corresponds to a dipole force in the direction b, applied at the step position and equal to $-0.25\ naN$.

Due to the equilibrium relation $E_{1o} \approx -2E_{2o}$, we have thus the equilibrium relation

$$\frac{\pi^2}{3}\Lambda\frac{(f_b^2(1+2X)^2 + f_c^2)}{L^2} \approx \sigma_{bb}^{S,1o}\epsilon_{bb}(0), \tag{11}$$

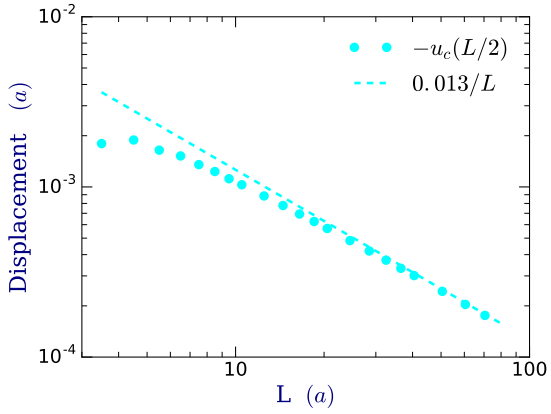

Figure 8: Surface displacement $u_c(b)$ at the middle of the terrace $b = L/2$ for $Cu(1\,1\,n)$ vicinals. It is adjusted to the function $-0.013\ a^2/L$ for large L. The constant -0.013 is almost the middle between the two constants C_1 deduced from the reduced displacements $\Delta\omega_c(\pm a/4)$ of the two step corners in Fig. 7 ($-0.012\ a^2/L$ and $-0.014\ a^2/L$).

within a constant. A close link exists between the normal component of the dipole force f_c/L^2 and the component of order $O(1/L)$ in the step deformation $\epsilon_{bb}(0)$. We have adjusted the interaction step deformation $\epsilon_{bb}(0)$ to $-0.0022/L - 0.055/L^2$ (Fig. 6) or *quantitatively* to $C_2/L^2 + C_3/L^3$ for which C_2 is close to $(\pi^2/3)\Lambda(f'_b + f_c)/L^2$ (see above). Within an 11% margin, the agreement is good between the two quantities $(f_b^2(1+2X)^2 + f_c^2)$ and $\sigma_{bb}^{S,1o} \times (f_b(1+X) + f_c)$ with $\sigma_{bb}^{S,1o}$, f_b, f_c and X respectively equal $-0.25\ naN$, $-0.18\ naN$, $-0.15\ naN$ and 0.17. On the one hand, the term of order $O(1/L)$ is omitted in the fit to the function $G_{23}(L)$ because the MP model takes into account only the displacements due to neighbouring steps and is calculated in all the system (surface + volume). More specifically, when excluding the deformations due to the origin step, the second-order interaction energy due to lines of monopole force F_b does not vary as $1/L$ but rather as $1/L^2$ and is small with respect to the modified MP model [17, 9, 10]. On the other hand, the component of order $O(f_c^2/L^2)$ is not taken into account in the fit to the function $H_{12}(L)$ because the step-step interaction stress is zero in the direction normal to the surface.

Because the two functions $H_{12}(L)$ and $G_{23}(L)$ are almost equal in quantity, we consider that the presence of the component of order $O(1/L)$ in the step deformation $\epsilon_{bb}(0)$ is fully

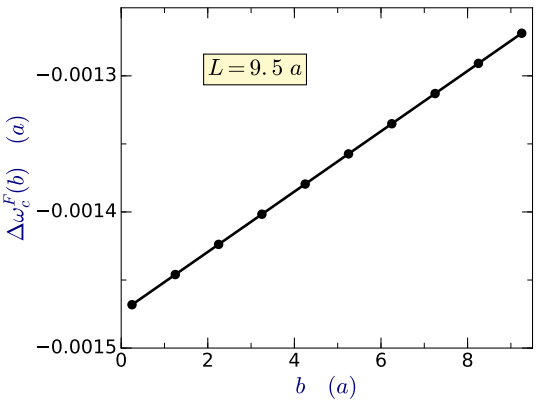

Figure 9: For $L = 9.5\ a$, this figure gives the linear variation of $\Delta\omega_c^F(b)$ in Eq. (10). It varies as $0.002a^2/L^2b$. The displacement is normal to the terrace and proves that the step is under the influence of a monopole force F_b in the direction parallel to the terrace, towards the descending steps and for which the modulus decreases as $1/L$. The small derivative at the middle of the terrace shows that its contribution in the second-order energy is negligible with respect to the modified MP model [17, 9].

screened by the component of order $O(f_c^2/L^2)$ in the modified MP model. Consequently, the presence of the interaction stress between steps does not modify the interaction energy between steps calculated from the modified MP model. It is only masked because the energy calculated from the modified MP model is regulated by the presence of the bulk and the two components of the dipole force $\mathbf{f}'$ are closely related to each other and to the nature of the step.

The original MP model does not show that the surface displacement can be modified in order to decrease the surface stress on the terrace between steps [16]. When supposing that this effect is nonexistent (original MP model), the component of the dipole force parallel to the terrace should be equal to f_y^0 whose intensity is equal to that of $f_c \times \sqrt{2}$. By accounting the effect due to the surface stress, the intensity of the parallel component f_b' is not equal to the intensity of $f_b^0(1+X)$ but rather to that of f_y^0. So the strong relation between the two components of the dipole force $\mathbf{f}'$ still holds, namely $f_b' = f_b(1+X) = f_c \times \sqrt{2}$. It is as if the effect due to the surface stress should be nonexistent. In contrast, the paper [9] shows that the equilibrium relation $E_{1o} \approx -2E_{2o}$ is slightly modified with respect to the original

MP model because the corresponding interaction energy due to f'_y is not proportional to $f_b^2(1+X)^2$ but to $f_b^2(1+2X)^2$. This has been confirmed by the presence of the oscillations of the surface displacement near the step for vicinals $Au(0\,1\,M)$ for which the constant X is equal to 0.40 instead of 0.17 for Cu. We conclude that the surface energy and the surface stress must be studied separately in order to better understand the physics of surfaces. The modification due to the surface stress may not be visible in the surface energy with respect to the configuration where the surface stress should be absent. In next section, we study the surface stress of $Cu(1\,1\,n)$ vicinals.

5. Step stress on vicinals $Cu(1\,1\,n)$

In this section, we give the surface stress on vicinals $Cu(1\,1\,n)$. In the paper [10], the same calculations were also made on vicinals $Cu(0\,1\,M)$.

5.1. The 'Force' method

The step stresses are stress excesses with respect to the nominal surface stress $\overline{\sigma^0_{xx}} = \overline{\sigma^0_{yy}}$. As for the flat surface, the step stress normal to the vicinal surface always vanishes and the non-diagonal stresses are nonexistent. On vicinals, we study the step stresses in the two reference systems, this vicinal (x, y, z) and this projected (x, b, c). Thus, we study the diagonal step stresses σ^{St}_{xx}, σ^{St}_{yy}, σ^{St}_{bb} and σ^{St}_{cc}. The step stress σ^{St}_{zz} in the direction $'zz'$ vanishes over the period. This is an important characteristic of the step stress in the equilibrium of vicinal surfaces. Because $\sigma^{St}_{zz} = 0$, we have the relation $\sigma^{St}_{yy} = \sigma^{St}_{bb} + \sigma^{St}_{cc}$.

Fig. 10 gives the variation of the step stresses as a function of the distance between steps L. The step stresses σ^{St}_{xx}, σ^{St}_{yy}, σ^{St}_{bb} and σ^{St}_{cc} vary as

$$\sigma^{St}_{\alpha\alpha} = \sigma^{IS}_{\alpha\alpha} + \frac{\sigma^{Int}_{\alpha\alpha}}{L} \tag{12}$$

where $\sigma^{IS}_{\alpha\alpha}$ is the isolated step stress and $\sigma^{Int}_{\alpha\alpha}/L$ is the interaction stress between steps. The interaction stresses are linked to the presence of the components of order $O(1/L)$ in the step deformations $\epsilon_{bb}(0)$ and $\epsilon_{cb}(0)$ when the vicinals are not deformed by ϵ^h_{xx} or by ϵ^h_{yy}. So, the interaction stresses result from the presence of the monopole line F_b that is added to the

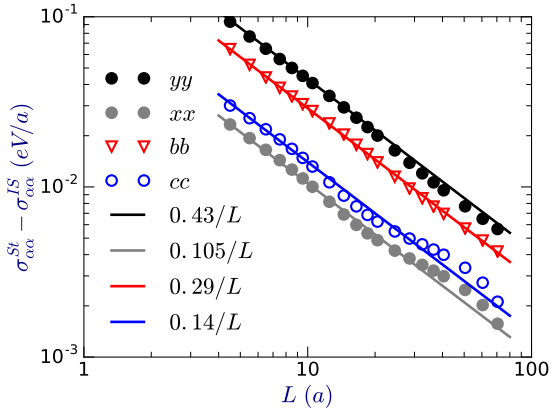

Figure 10: Step stress $\sigma^{St}_{\alpha\alpha}$ as a function of the distance L. The step stress is calculated in the three directions of the vicinal system (x, y, z) on the one hand and in the directions b and c of the projected system (x, b, c), on the other hand. Each isolated step stress $\sigma^{IS}_{\alpha\alpha}$ is subtracted. It is equal to $+0.055$, -0.42 and 0.0 eV/a for the directions x, y and z, respectively. The values of $\sigma^{IS}_{\alpha\alpha}$ do not change for the corresponding directions in the projected system x, b and c. Except for the normal z where $\sigma^{St}_{zz} = 0$, the step stresses vary as $\sigma^{Int}_{\alpha\alpha}/L$. The constants $\sigma^{Int}_{\alpha\alpha}$ are equal to 0.105, 0.43, 0.29 and 0.14 eV for the directions x, y, b and c, respectively. We also note that σ^{Int}_{yy} is the sum of the constants σ^{Int}_{bb} and σ^{Int}_{cc}.

dipole line $\mathbf{f}'$ at the step position (see previous section). The monopole force F_b is present when the vicinal is not homogeneously deformed, and its modulus decreases as $1/L$ and disappears for infinite L.

In this section, we homogeneously deform the vicinals by a factor of $(1+\epsilon^h_{xx})$ or $(1+\epsilon^h_{yy})$, and we give the differences in the step deformations with respect to the non-deformed vicinals. They are called $\Delta\epsilon_{bb}(0)$ and $\Delta\epsilon_{cb}(0)$. In next section (the 'Δ E' method), we will give the excesses in the step energy that are proportional to ϵ^h_{xx} or ϵ^h_{yy}. When the vicinals are homogeneously deformed by ϵ^h_{xx} or by ϵ^h_{yy}, a monopole force proportional to the homogeneous strain is added to the monopole force F_b. We call it F_ϵ, which does not depend on the distance L. For $\epsilon^h_{xx} < 0$ or $\epsilon^h_{yy} < 0$, F_ϵ is directed towards the descending steps, and we consider that its direction is parallel to the terrace as for F_b. Under homogeneous strain, the monopole force F_ϵ is responsible for the terms of order $O(1/L)$ in the extra step deformations $\Delta\epsilon_{bb}(0)$ and $\Delta\epsilon_{cb}(0)$. Figs. 11 and 12 give the variations of $\Delta\epsilon_{bb}(0)$ and $\Delta\epsilon_{cb}(0)$ as a function

of L for the strains $\epsilon^h_{yy} = -10^{-3}$ and $\epsilon^h_{xx} = -10^{-3}$, respectively. For $\epsilon^h_{yy} = -10^{-3}$, Fig. 11

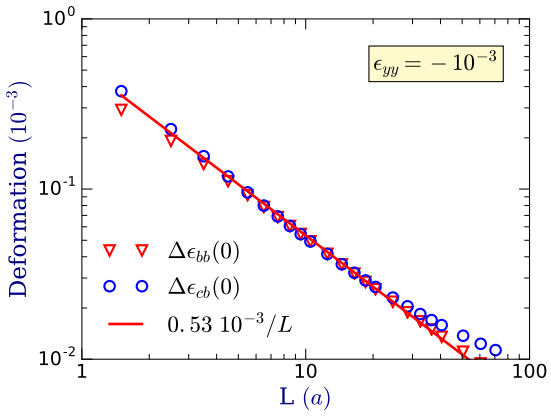

Figure 11: Step deformations $\Delta\epsilon_{bb}(0)$ and $\Delta\epsilon_{cb}(0)$ due to homogeneous strain $-\epsilon^h_{yy} = 10^{-3}$. They vary as $-0.68\ 10^{-3} + 0.53\ 10^{-3}/L$ and $-0.73\ 10^{-3} + 0.52\ 10^{-3}/L$ for the tensor directions $'bb'$ and $'cb'$, respectively.

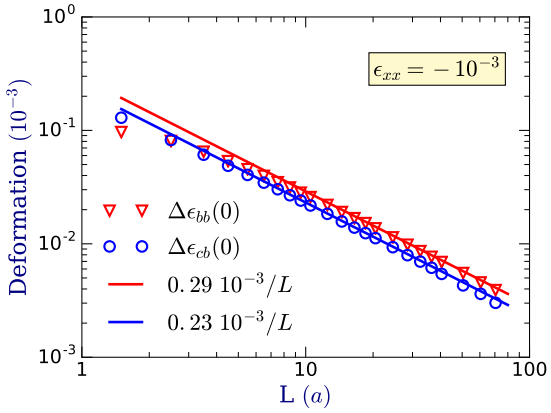

Figure 12: Step deformations $\Delta\epsilon_{bb}(0)$ and $\Delta\epsilon_{cb}(0)$ due to homogeneous strain $-\epsilon^h_{xx} = 10^{-3}$. They vary as $-0.0625\ 10^{-3} + 0.29\ 10^{-3}/L$ and $-0.53\ 10^{-3} + 0.23\ 10^{-3}/L$ for the tensor directions $'bb'$ and $'cb'$, respectively.

shows that $\Delta\epsilon_{bb}(0)$ and $\Delta\epsilon_{cb}(0)$ vary as $1/L$ by almost the same factor ($0.53/L$ and $0.52/L$). For $\epsilon^h_{xx} = -10^{-3}$ (strain parallel to the steps), the parallel and normal deformations $\Delta\epsilon_{bb}(0)$ and $\Delta\epsilon_{cb}(0)$ vary as $0.29/L$ and $0.23/L$, respectively.

5.2. The 'Δ E' method

As for the nominal surface, we can calculate the surface stress when we homogeneously deform the vicinal surface in the direction parallel to the surface, and we calculate the energy excess proportional to the applied strain (see section 3). We will see that a difference exists between the two methods concerning the interaction stress for the applied strain perpendicular to steps ϵ^h_{yy}. We note that we calculate only the first-order energy excesses proportional to ϵ^h_{xx} or ϵ^h_{yy} in order to deduce the step stresses. The first-order energies ΔE_{1o} are firstly calculated in the two directions $'bb'$ and $'cc'$, $\Delta E_{1o} = \Delta E_{bb} + \Delta E_{cc}$ and with respect to the deformed nominal surface. Then and by rotation transformations, we can deduce the components in the vicinal directions, $\Delta E_{1o} = \Delta E_{yy} + \Delta E_{zz}$. For ϵ^h_{xx}, we omit the component in the direction $'xx'$ because it does not contribute to the interaction stress between steps.

For the applied strain $\epsilon^h_{yy} = -10^{-3}$, Fig. 13 gives the variation as a function of L of the first-order energies ΔE_{bb}, ΔE_{cc} and their sum ΔE_{1o} by using the deformations in the projected reference system. As for the extra step deformations $\Delta\epsilon_{bb}(0)$ and $\Delta\epsilon_{cb}(0)$, the two energies ΔE_{bb} and ΔE_{cc} vary as $1/L$ by the same factor. Within a constant, ΔE_{bb} and ΔE_{cc}

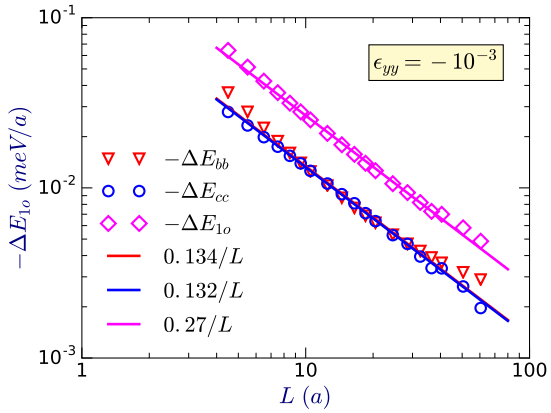

Figure 13: Variation as a function of L of the first-order energy ΔE_{1o} and their components in the projected system (x, b, c) for the vicinals under homogeneous strain $\epsilon^h_{yy} = -10^{-3}$. In the plot log-log, the constants proportional to ϵ^h_{yy} are subtracted. The component ΔE_{bb} varies as $[-0.20 + 0.134/L] \times \epsilon^h_{yy}\ eV/a$ and the component ΔE_{cc} varies as $[-0.27 + 0.132/L] \times \epsilon^h_{yy}\ eV/a$. The sum ΔE_{1o} varies as $[-0.47 + 0.27/L] \times \epsilon^h_{yy}\ eV/a$.

are equal to $K \times \Delta\epsilon_{bb}(0)$ and $K \times \Delta\epsilon_{cb}(0)$, respectively, with $K = -0.255\ eV/a$.

In the vicinal system for which the surface stress vanishes in the direction $'zz'$, Fig. 14 gives the variation of the corresponding first-order energies ΔE_{yy}, ΔE_{zz} and the same sum ΔE_{1o} as for the projected system. From this figure, we consider that the variation of ΔE_{zz}

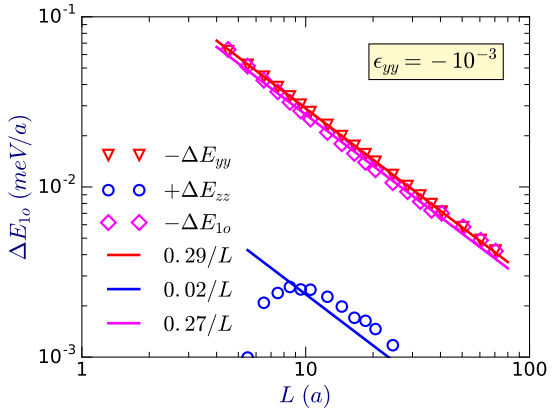

Figure 14: Variation as a function of L of the first-order energy ΔE_{1o} and their components in the vicinal system (x, y, z) for the vicinals under homogeneous strain $\epsilon^h_{yy} = -10^{-3}$. In the plot log-log, the constants proportional to ϵ^h_{yy} are subtracted. They are identical to those calculated in the projected system. The component ΔE_{yy} varies as $[-0.20+0.29/L]\times\epsilon^h_{yy}$ eV/a and the component ΔE_{zz} varies as $[-0.27-0.02/L]\times\epsilon^h_{yy}$ eV/a. The sum ΔE_{1o} varies as $[-0.47+0.27/L]\times\epsilon^h_{yy}$ eV/a.

is negligible with respect to the variation of ΔE_{yy}. To a good approximation, we write that the variation of ΔE_{1o} is that of ΔE_{yy}, i.e in the direction of the applied strain ϵ^h_{yy}.

By applying the rotation transformations in the step deformations $\Delta\epsilon_{bb}(0)$ and $\Delta\epsilon_{cb}(0)$, we deduce the step deformation $\Delta\epsilon_{yy}(0)$ in the direction of the homogeneous strain $'yy'$. When neglecting the terms of $O(1/L^2)$ and by writing that $\sin(\theta)$ varies as $\sqrt{2}/2L$, we have

$$\begin{aligned}\Delta\epsilon_{yy}(0) &= \Delta\epsilon_{bb}(0)\cos(\theta) - \Delta\epsilon_{cb}(0)\sin(\theta)\\ &\approx \Delta\epsilon_{bb}(0) - \Delta\epsilon_{cb}(0)\frac{\sqrt{2}}{2L}.\end{aligned} \tag{13}$$

This is shown in Fig. 15 for $\epsilon^h_{yy} = -10^{-3}$. It makes clear that $\Delta\epsilon_{yy}(0)$ varies as $-1.04\ (a/L)\times\epsilon^h_{yy}$ instead of $-0.53\ (a/L)\times\epsilon^h_{yy}$ for the variation of $\Delta\epsilon_{bb}(0)$. Because the interaction energy ΔE_{zz} is negligible in the variation of ΔE_{1o}, we can write that the variation of ΔE_{1o} is equal to a constant multiplied by the variation of $\Delta\epsilon_{yy}(0)$. Here the constant is equal to

$-0.27/1.04 = -0.26\ eV/a$. In this case, it is correct to write that the variation of the step stress depends on the variation of the step deformation $\Delta\epsilon_{yy}(0)$ in the direction of the applied strain, $'yy'$, rather than this in the direction $'bb'$. In next section, we will see that it is also correct to write that the same variation also depends on the variation of the step deformation $\Delta\epsilon_{bb}(0)$ in the direction parallel to the terrace $'bb'$ because the contribution in the direction normal to terrace $'cc'$ is excluded.

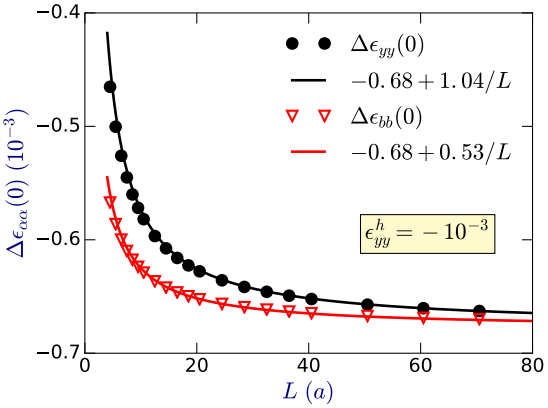

Figure 15: Step Deformation $\Delta\epsilon_{yy}(0)$ and $\Delta\epsilon_{bb}(0)$ as a function of the distance L for $\epsilon^h_{yy} = -10^{-3}$.

To validate the calculations made by using the first-order energies ΔE_{1o}, we can calculate the step energies from the sum of the atomic potentials for the two signs of the applied strain $\epsilon^h_{yy} = \pm 10^{-3}$. Because $|\epsilon^h_{yy}|$ is small, we can ignore the terms from the third-order onwards. For a given vicinal angle θ, we call the surface energy of the nominal $Cu(001)$ and that of the θ vicinal surface per projected area unit γ_0^+ and $\gamma_P^+(\theta)$, the two surfaces being deformed with $\epsilon^h_{yy} > 0$. Likewise, we call γ_0^- and $\gamma_P^-(\theta)$ the corresponding surface energies for the negative sign of the strain $\epsilon^h_{yy} < 0$. The quantity $[\gamma_P^-(\theta) - \gamma_0^-][L(1+\epsilon^h_{yy})]$, with $\epsilon^h_{yy} < 0$, is the step energy $\Gamma^-(L)$. We do the same for $\epsilon^h_{yy} > 0$, which gives $\Gamma^+(L)$. Because $|\epsilon^h_{yy}|$ is small, half the difference of the step energies for the two signs of ϵ^h_{yy}, $[\Gamma^+(L) - \Gamma^-(L)]/2$ gives, to an excellent approximation, $\sigma^{St}_{yy} \times |\epsilon^h_{yy}|$. Their variation as a function of L is given in Fig. 16. The interaction stress is close to that calculated by using the 'Δ E' method (Fig. 13 or Fig. 14). This makes sure that the method using the first-order energies, ΔE_{1o},

is correct.

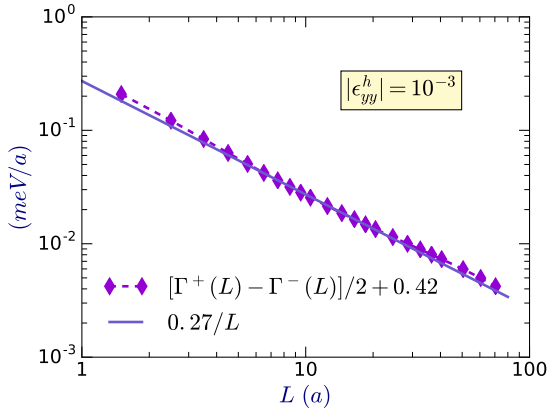

Figure 16: $[\Gamma^+(L) - \Gamma^-(L)]/2$ as a function of L. By deforming the vicinals and calculating their step energy, this figure shows that the step stress equals $-0.42 + 0.27\ a/L\ eV/a$.

As for $Cu(0\,1\,M)$ vicinals [10], the interaction stress between steps is different between the two calculation methods, the '*Force*' and the '$\Delta\ E$', only for the homogeneous strain in the direction $'yy'$. In the strain direction parallel to the step, $'xx'$, we have checked that the interaction stresses are identical for the used methods ($= 0.11 \pm 0.01\ a/L\ eV/a$). For the direction perpendicular to the steps $'yy'$, it is equal to $0.43\ a/L\ eV/a$ for the '*Force*' method while it is equal to $0.27\ a/L\ eV/a$ for the '$\Delta\ E$' method.

Different results for the applied strain parallel to steps, $\epsilon^h_{xx} = -10^{-3}$, are not illustrated in the paper. They are summarized and compared with the previous strain perpendicular to steps in Table 1.

6. Why σ^{Int}_{yy} is different

In the '*Force*' method, we calculate the forces that exist on the surface when it is not deformed ($\epsilon^h_{xx} = \epsilon^h_{yy} = 0$). This gives the step stresses that are calculated in the directions of the two reference systems. They are stress excesses with respect to the nominal surface. In the direction $'zz'$, the step stress σ^{St}_{zz} is always zero. Because it is zero, we have the equivalence between the two reference systems $\sigma^{St}_{yy} = \sigma^{St}_{bb} + \sigma^{St}_{cc}$. For infinite L, the step

Table 1: At the top, we give the step deformations $\Delta\epsilon_{bb}(0)$ and $\Delta\epsilon_{cb}(0)$ divided by the homogeneous strain ϵ^h_{xx} and ϵ^h_{yy} for the two strain directions $'xx'$ and $'yy'$, respectively (from Figs. 11 and 12). At the bottom, we list the step stresses calculated by using the two methods. By using the '*Force*' method, the variation of the step stresses are showed in Fig. 10. They vary as $\sigma^{Int}_{\alpha\alpha}/L$. We note that the constant σ^{Int}_{yy} is different when using the '$\Delta\ E$' method with respect to the '*Force*' method, while the constant σ^{Int}_{xx} is identical by using the two methods.

	$\epsilon^h_{yy} = -10^{-3}$	$\epsilon^h_{xx} = -10^{-3}$
$\Delta\epsilon_{bb}(0)/\epsilon^h_{\alpha\alpha}$	$0.68 - 0.53\ a/L$	$0.73 - 0.52\ a/L$
$\Delta\epsilon_{cb}(0)/\epsilon^h_{\alpha\alpha}$	$0.062 - 0.29\ a/L$	$0.53 - 0.23\ a/L$
	$\sigma^{St}_{\alpha\alpha}\ (eV/a)$ '*Force*' method	$\sigma^{St}_{\alpha\alpha}\ (eV/a)$ '$\Delta\ E$' method
xx	$+0.055 + 0.105\ a/L$	$+0.05 + 0.12\ a/L$
bb	$-0.42 + 0.29\ a/L$	
cc	$-0.000 + 0.14\ a/L$	
yy	$-0.42 + 0.43\ a/L$	$-0.47 + 0.27\ a/L$

stresses are the isolated step stresses $\sigma^{IS}_{\alpha\alpha}$ for the five diagonal directions $\alpha = x, y, z, b$ and c. For infinite L, the direction b and c are the direction y and z. In addition, we have therefore the equivalence between the isolated step stresses: $\sigma^{IS}_{cc} = \sigma^{IS}_{zz} = 0$ and $\sigma^{IS}_{bb} = \sigma^{IS}_{yy}$.

When using the '$\Delta\ E$' method, we calculate the step energy excess proportional to the applied strain ϵ^h_{xx} or ϵ^h_{yy}. When deforming a vicinal by the applied strain ϵ^h_{yy}, the first-order step energy excess is $\sigma^{St}_{yy} \times \epsilon^h_{yy}$ but we note that the step stress σ^{St}_{yy} is not equal in the two calculation methods. We find that the step stress σ^{St}_{yy} in the '$\Delta\ E$' method is equal to the step stress σ^{St}_{bb} in the '*Force*' method. The step stress σ^{St}_{cc} calculated in the direction $'cc'$ in the '*Force*' method is thus excluded when we use the '$\Delta\ E$' method. For a given direction $'\alpha\alpha'$, the interaction term of the first-order step energy excess corresponds to a constant multiplied by the interaction term of the step deformation proportional to the applied strain. We call this constant the step stress $\sigma^{\Delta E}_{\alpha\alpha}$ that exists when the vicinal is not deformed. In the direction normal to the terrace $'cc'$, $\sigma^{\Delta E}_{cc}$ is always zero as for $\sigma^{\Delta E}_{zz}$. This explains why the step stress σ^{St}_{cc} is excluded when using the '$\Delta\ E$' method.

In addition, we note that the two step stresses $\sigma^{\Delta E}_{yy}$ and $\sigma^{\Delta E}_{bb}$ are not equal because the interaction terms of the step deformations $\Delta\epsilon_{bb}(0)/\epsilon^h_{yy}$ and $\Delta\epsilon_{yy}(0)/\epsilon^h_{yy}$ are not. When admitting that the interaction term of σ^{St}_{yy} is equal to $\sigma^{\Delta E}_{bb}$ multiplied by the interaction term of $\Delta\epsilon_{bb}(0)/\epsilon^h_{yy}$ as well as to $\sigma^{\Delta E}_{yy}$ multiplied by the interaction term of $\Delta\epsilon_{yy}(0)/\epsilon^h_{yy}$, we have $\sigma^{\Delta E}_{bb} = -0.51\ eV/a$ and $\sigma^{\Delta E}_{yy} = -0.26\ eV/a$. The values of $\sigma^{\Delta E}_{bb}$ and $\sigma^{\Delta E}_{yy}$ correspond to the dipole forces $f' \times 1.51$ and $f' \times 0.76$ in the direction b and y, respectively. The difference between $\sigma^{\Delta E}_{bb}$ and $\sigma^{\Delta E}_{yy}$ results from both the fact that the step stress is calculated with respect the nominal surface (normal to the terrace is c) and the step stress is always zero in the direction normal to the vicinal surface (direction $'zz'$).

7. Conclusion

By the molecular dynamics method at $T = 0K$, we have calculated the equilibrium configurations of the $Cu(1\,1\,n)$ vicinals, their step energies and step stresses. By varying the distance between steps L, we have given the step energies and stresses as a function of L. The step energy has been adjusted to two functions $G_{23}(L) = G_0 + G_2\ L^{-2} + G_3\ L^{-3}$ and

$H_{12}(L) = H_0 + H_1\ L^{-1} + H_2\ L^{-2}$. The difference between $G_{23}(L)$ and $H_{12}(L)$ is marked by the presence or absence of a term proportional to $1/L$. In the well-known MP model, the steps behave as dipole forces $\mathbf{f}' = (0, f'_b, f_c)$ that are applied upon a flat surface (the directions b and c are respectively parallel and normal to the terrace). For $Cu(11n)$ vicinals, the components of the dipole force are linked by the relation $f'_b = \sqrt{2}\ f_c$ where the modulus of f_c is the same as in $Cu(0\ 1\ M)$ vicinals. From the equilibrium relaxation due to the dipole forces, the step energy has been adjusted to the function $G_{23}(L)$ where the component proportional to $1/L^2$ is close to that given by the MP model (G_2/L^2 is equal to $+15\ a^2/L^2\ meV/a$). It corresponds to the elastic energy minimization of the vicinal system (surface + bulk) due to the presence of the dipole forces. Nevertheless, this energy minimization cannot predict that a monopole force F_b is applied in addition to the dipole force at the step position. The force monopole F_b is parallel to the terrace, is directed towards the descending steps and its modulus decreases as $1/L$. It is responsible of the terms of order $1/L$ that are present in the step deformations in the two directions b and c while they are absent in the MP model. Finally, it is linked to the variation as $1/L$ in the step stress in the tensor directions $'bb'$, $'cc'$, $'yy'$ and $'xx'$. Because the surface stress is zero in the direction $'zz'$, the step energy has been adjusted to the function $H_{12}(L)$ that corresponds to a specific step stress multiplied by the step deformation in the direction $'bb'$. This effect due to the step stress is considered as masked in the step energy because the two functions $H_{12}(L)$ and $G_{23}(L)$ are quantitatively equivalent. In particular, the component of order $O(1/L)$ in the step deformation in the direction $'bb'$ is limited (obscured) by the displacement normal to the terrace deduced in the MP model. In addition to the step energy of vicinals, it is therefore essential to study the step stress and its variation as $1/L$ for better understanding of the equilibrium of vicinals.

The step stresses in the directions $'bb'$, $'cc'$, $'yy'$ and $'xx'$ vary as $1/L$ (the direction x and y are the directions of the vicinal surface parallel and perpendicular to the steps, respectively). They are calculated by using two calculation methods. The '*Force*' method directly calculates the surface pressure forces. The '$\Delta\ E$' method calculates the energy excess proportional to the applied strain $\epsilon^h_{\alpha\alpha}$ when the vicinal is homogeneously deformed by a factor of $(1 + \epsilon^h_{\alpha\alpha})$, the direction $'\alpha\alpha'$ being parallel to the vicinal surface ($\alpha = x$ or y).

We note that the step stress is identical by using the two methods in the direction parallel to the steps $'xx'$ but not in that perpendicular $'yy'$.

In the '*Force*' method, we calculate the pressure forces that exist on the vicinal surface. The step stresses (sum of the pressure forces) vary as $\sigma_{\alpha\alpha}^{IS} + \sigma_{\alpha\alpha}^{Int}/L$. The step stress in the direction $'yy'$ is the sum over the two step stresses in the directions $'bb'$ and $'cc'$. For infinite L, the step stress in the direction $'cc'$ is zero (it is equal to this in the direction $'zz'$).

In the 'Δ E' method, we calculate the energy excess proportional to the strain applied. The interaction term in the energy excess corresponds to the crossed term located at the step position between an isolated step stress and the deformation due to neighbouring steps. For the direction $'cc'$, the isolated step stress is zero. Therefore, the step stress in the direction $'yy'$ does not include the step stress calculated in the direction $'cc'$ by using the '*Force*' method. In the 'Δ E' method, the step stress in the direction parallel to the vicinal surface $'yy'$ is the step stress calculated in the direction parallel to the terrace $'bb'$ by using the '*Force*' method. This explains why the step stress is different in the direction $'yy'$ when using the two methods.

In the direction $'yy'$, we summarize that the step stress calculated by the '*Force*' method corresponds to pressure forces that are present on surface. It includes two components parallel and normal to the terrace: $\sigma_{yy}^{St} = \sigma_{bb}^{St} + \sigma_{cc}^{St}$. When we deform the vicinal by a factor of $(1 + \epsilon_{yy}^{h})$, we can calculate the energy excess proportional to the strain ϵ_{yy}^{h} by using the step stress σ_{yy}^{St}. However, the normal component σ_{cc}^{St} is excluded for this energy calculation even if the surface stress is really the sum of pressure forces present on non-deformed surface.

Finally, we must consider the surface pressure forces not only for calculating the energy excesses when the surface is deformed but also in the understanding of equilibrium of surfaces. Only, the minimization of the total energy does not allow to determine the equilibrium structure of surfaces. The surface stress can modify the equilibrium structure of surfaces without decreasing the total energy. Again, we write that the steps are repulsed by both the step energy and the step stress due to their decreasing when increasing L. The step stresses parallel to the vicinal surface correspond to pressure forces that must be as small as possible.

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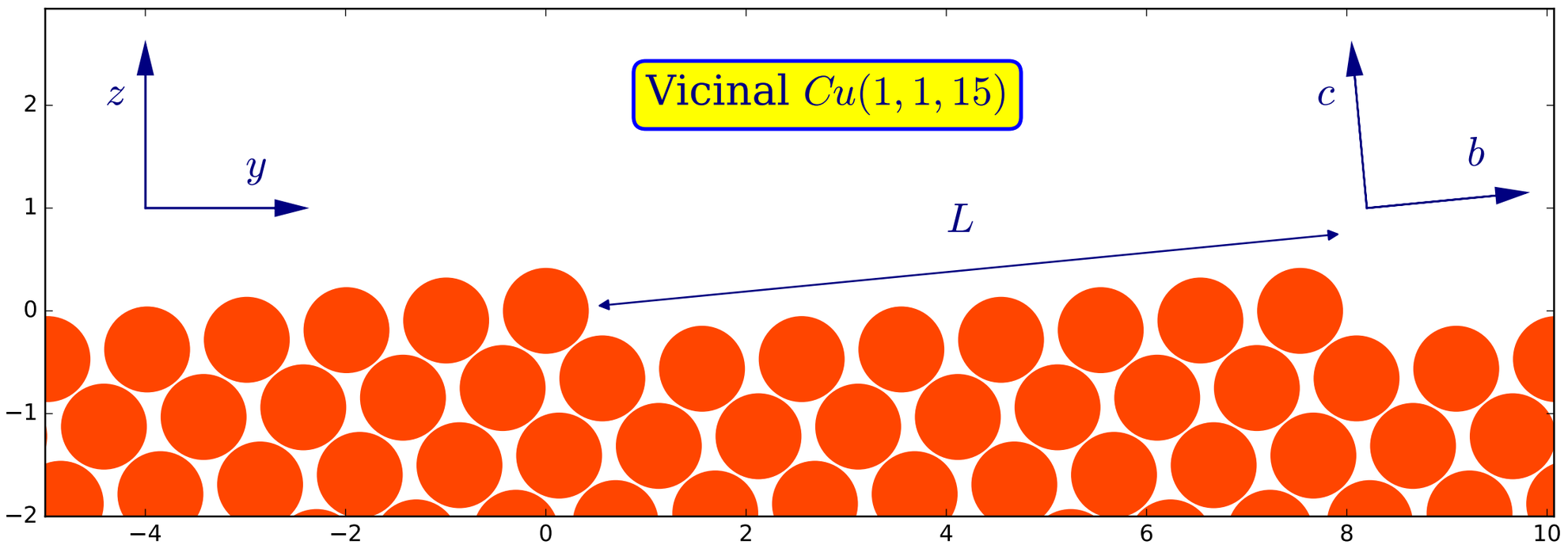
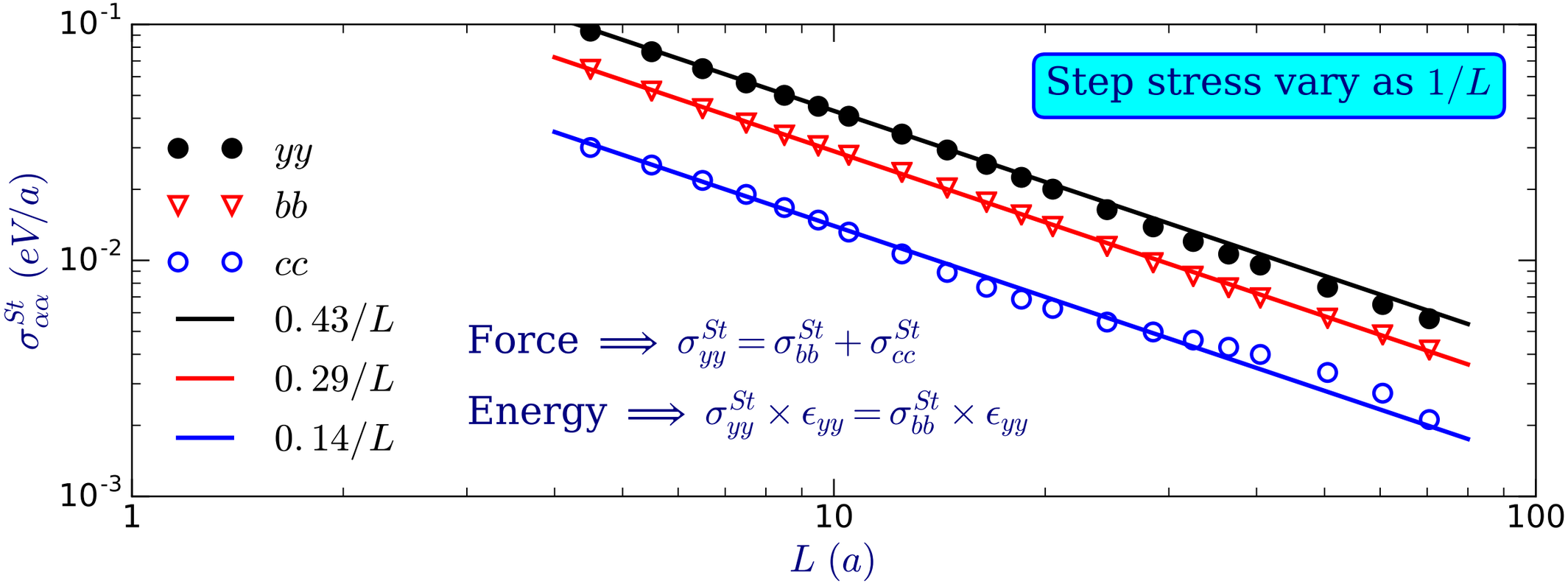

Vicinal $Cu(1,1,15)$
z
y
c
b
L
2
1
0
−1
−2
−4
−2
0
2
4
6
8
10


Step stress vary as $1/L$
yy
bb
cc
$0.43/L$
$0.29/L$
$0.14/L$
Force $\Longrightarrow$ $\sigma^{St}_{yy} = \sigma^{St}_{bb} + \sigma^{St}_{cc}$
Energy $\Longrightarrow$ $\sigma^{St}_{yy} \times \epsilon_{yy} = \sigma^{St}_{bb} \times \epsilon_{yy}$
$\sigma^{St}_{\alpha\alpha}\ (eV/a)$
10^{-1}
10^{-2}
10^{-3}
1
10
100
$L\ (a)$