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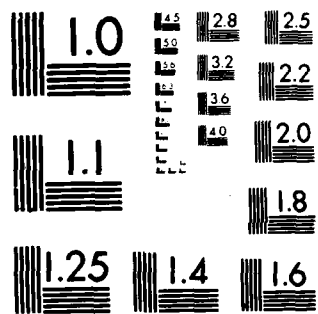
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LATTICE GAS MODELS FOR CHEMISORPTION ON STEPPED SURFACES*

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We consider the theory of chemisorption on stepped surfaces for systems for which a lattice gas in thermodynamic equilibrium is an appropriate model. Using statistical mechanics we demonstrate that by comparing LEED (Low Energy Electron Diffraction) results for flat and stepped substrates one can determine the change in adsorption energy at terrace edges. Thus one can answer the important question of whether adatoms bind more or less strongly at this kind of defect site. We also examine some new and interesting features of LEED spot shapes and integrated intensity behavior for adsorption on stepped substrates when the overlayer is partially disordered. In a companion paper, we consider O on a certain stepped W(110) surface. We demonstrate there, via Monte Carlo calculations, that the binding energy is less strong on either terrace edge for this particular adsorbate, surface and defect. ↗

I. Introduction

The detailed behavior of adsorption at steps is a question of fundamental importance to surface physics. The growth kinetics and equilibrium shape of crystals can be determined by whether adsorption occurs at step edges or on the flat surface. Overlayer ordering can be strongly influenced by terraces if domains of different azimuthal ordering are crystallographically equivalent on the flat surface but distinguished by step edge direction. Reactions in heterogeneous catalysis are often associated with "active sites" at defects, and the reaction kinetics may be profoundly influenced by adsorption energies at those sites.

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In this paper we present a detailed theory of LEED results for certain chemisorbed systems on stepped surfaces. We also show how information about changes in adsorption energies at terrace edge sites may be extracted from those results.

Section II presents a general theory of LEED scattering from overlayers on stepped surfaces, including the effects of disorder in the overlayer when a lattice gas model is appropriate. We consider the overlayer spot splitting and integrated intensity in the kinematic (single-scattering) approximation and also point out that qualitatively new LEED features may appear at low or high coverages.

Our general conclusions are illustrated with a model adsorption system calculation at $T = 0$ in Section III. We consider the effects of the change in edge site adsorption energy on overlayer LEED spot splitting and intensity as a function of coverage.

In a companion paper¹, we apply the theory developed here to O on a certain stepped $W(110)$ surface. Using experimental results and existing models for the stepped and flat surface adsorption systems as input in a Monte Carlo calculation, we show that the edge site adsorption energy is less strong at either terrace edge than for the flat surface.

The lattice gas theory employed here makes use of the properties of thermodynamic equilibrium. This has some important advantages in surface systems that have not been fully exploited, especially in chemisorption studies. First, properly chosen systems are characterized by only a few parameters. Since there exist several well-developed methods for calculating thermodynamic quantities, one can determine these parameters with considerable confidence. For instance, in an adsorption system many observable effects, such as LEED results, depend only on the adsorption energy and adatom-adatom (AA) interactions. This is a consequence of the general fact that all kinetic effects are irrelevant to equilibrium properties. This situation is especially advantageous when one is dealing with a lattice gas model with finite range AA forces. There are only

a few energy parameters in the problem, since the adatoms sit at discrete sites and are only influenced by a few near neighbors. Second, although equilibrium studies certainly cannot solve all the important questions in surface physics, they can provide a secure starting place from which to attack other more difficult problems in complicated systems. One such application of equilibrium studies on a flat surface is demonstrated in the companion paper on O on stepped W(110), and we believe it will not be the last.

II. LEED Scattering from Overlayers on Stepped Surfaces

In this section we present a theory of LEED scattering from overlayers on stepped surfaces. There have been several treatments of LEED scattering from stepped surfaces², but to our knowledge none of them have considered the effects due to partial ordering of the adlayer that we present below. Our treatment uses the single scattering (kinematic) approximation throughout. While multiple-scattering (dynamic) effects constitute a very important part of the LEED signal, in certain cases they may be ignored when considering an overlayer beam and a small angular region around it. Previous work has shown that overlayer spot shapes and trends in the intensity, rather than their absolute numerical values³, are well approximated by the single scattering approximation.

Now consider a stepped surface. We assume that this surface is composed of identical terraces, with equivalent points on neighboring terraces separated by a fixed vector $\underline{g}$, and that there are N_s such terraces within the coherence length ξ of the LEED apparatus. If $\underline{k}$ is the momentum transfer (scattering) vector ($\underline{k} = \underline{k}_f - \underline{k}_0$, $\underline{k}_0(f)$ = incoming (scattered) electron wave vector, $|\underline{k}_0| = |\underline{k}_f|$) then the total scattering amplitude $A(\underline{k})$ is

$$A(\underline{k}) = \sum_{j=1}^{N_s} A_j(\underline{k}) \exp(i \underline{k} \cdot \underline{g}_j) \quad (1)$$

Here $A_j(\underline{k})$ is the amplitude due to the j th terrace, and $\underline{g}$ is a (real space) vector connecting identical points on adjacent terraces. For monatomic height steps and uniform terraces $\xi \approx N_s g$. If the terraces are identical and we use the single scattering approximation

$$A_j(\underline{k}) = f(\underline{k}) = \sum_{\ell=1}^N n_{\ell} \exp(i \underline{k} \cdot \underline{R}_{\ell}) \quad (2)$$

In Eq (2) we have made the important assumption that the overlayer can be described by a lattice gas model. This means the adatoms on a given terrace sit on a fixed set of N equivalent sites ℓ , with occupation variable $n_{\ell} = 0(1)$ for an unoccupied (occupied) site. These sites are at positions $\underline{R}_{\ell}$ with respect to the origin of $\underline{g}$. (Note that the location of these adatom sites with respect to the substrate is irrelevant in the lattice gas picture). Some of the other assumptions involved in using a lattice gas model are reviewed by Domany et al⁴. In writing Eq. (2) we have ignored an overall multiplicative factor - the adatom scattering cross-section - which is usually sufficiently slowly varying with scattering angle to be taken constant, in the vicinity of any diffraction feature.

Now the LEED intensity for the beam $\underline{k}$ is just

$$I(\underline{k}) = \langle |A(\underline{k})|^2 \rangle = \sum_{j, \ell=1}^{N_s} \langle f(\underline{k}) f^*(\underline{k}) \rangle \exp(i \underline{k} \cdot \underline{g}(j-\ell)) \quad (3)$$

In Eq. (3) the angular brackets denote an average over adlayer configurations. We assume from this point on that the adlayer is in thermodynamic equilibrium, which means that at a given temperature T and coverage θ the average will be determined by adatom-adatom (AA) forces and any variation in the adatom adsorption energy ϵ (AS force) due to the steps. Now in the case of strong chemisorption, ϵ is generally several eV (for O/W, $\epsilon \sim 5$ eV). Further, ϵ is mainly determined by the few substrate atoms surrounding an adsorption site. Since the configuration of neighbors is different for a site just below or just above a step, one expects a change $\delta\epsilon$ in adsorption energy there on the order of one eV, so that $\delta\epsilon \gg kT$.

Hence terrace edge sites for which $\delta\epsilon > 0$ will be the last to be occupied as the coverage θ is increased. On the other hand, sites for which $\delta\epsilon < 0$ will be occupied first, and can serve as nucleation sites for overlayer domains. This distinction can have a strong effect on the θ dependence of the LEED scattering, which we examine in detail below. Such effects can then be used to determine the sign of $\delta\epsilon$ from LEED results for a given stepped chemisorption system.

Now for many important adsorption systems the AA interactions are short ranged⁵. Since the adsorption sites immediately on either side of a step will be either occupied or empty according to whether $\delta\epsilon \gtrless 0$, the only AA interactions that can "cross" a step and influence the next terrace will be long range and hence quite weak. Thus we assume that the statistical average in Eq(3) can be taken independently on each terrace. Hence

$$I(k) = N_s \langle |f(k)|^2 \rangle + \sum_{\substack{j,l=1 \\ j \neq l}}^{N_s} \langle f(k) \rangle^2 \exp(i k \cdot g(j-l)) \quad (4)$$

$$= N_s \left(\langle |f(k)|^2 \rangle - |\langle f(k) \rangle|^2 \right) + h(N_s, k \cdot g) |\langle f(k) \rangle|^2 \quad (5)$$

In Eqs. (4) and (5) the statistical average refers to a single terrace, and the interterrace interference is expressed via

$$h(N_s, x) \equiv \sum_{j,l=1}^{N_s} \exp(i x(j-l)) = \sin^2(N_s x/2) / \sin^2(x/2) \quad (6)$$

This function is familiar from the simple diffraction grating. For $N_s > 1$ it has peaks of height N_s^2 and width $2\pi/N_s$ centered at $x = 0, \pm 2\pi, \pm 4\pi$, and is quite small in between. The peak area rapidly approaches $2\pi N_s$ as N_s grows.

Eq (5) is a central result of our theory. Its first term refers to a single terrace and is non-zero only if there is some degree of statistical disorder of the adatoms. This term contains some new physics that to our knowledge has not been examined previously. The second term in Eq (5) includes the effects of interterrace interference via the function h . If one has a

"complete" (perfect) adlayer then $\langle |\rho|^2 \rangle = |\langle \rho \rangle|^2$ and the peaks in h express the condition of constructive interference between steps. This gives rise to a characteristic splitting of the LEED spots in the g direction from which the average step width and height may be determined². If there is disorder in the adlayer, the situation is more complicated. In general, the second or "split" term in Eq(5) will be non-zero. In addition there will also be a contribution to the LEED intensity from the first term, due to the disorder, that refers to one terrace only and is not split. In what follows we consider the influence of the two terms in Eq(5) on overlayer LEED spot splitting and integrated intensity. As we will see, the sign of $\delta\epsilon$ (the change in adsorption energy at terrace edge sites) plays an important role in these effects.

It is interesting to compare Eq(5) with the van Hove expression for thermal neutron scattering.⁶ The first term in Eq(5) corresponds to the incoherent neutron scattering cross-section and ρ corresponds to the (spin dependent) neutron-single nucleus scattering length.

We now consider uniform terraces that are long compared to their width. Then we need only consider two $\delta\epsilon$, on either long edge. In general, for small widths and attractive $\delta\epsilon$ on one or both edges, one would expect most adatoms to be "frozen" in a single ordered configuration as long as θ and T are not too large (i.e. for $T \lesssim T_c$, where T_c = ordering temperature on the flat surface and $\theta \lesssim \theta_c$ where θ_c is the coverage of a "complete" ordered overlayer on the flat surface). In this case the second term in Eq(5) will be more important and splitting may be observed. The first term, which is a measure of adlayer disorder, will in general be relatively small. If both edges are repulsive, the situation is more complicated. Then for $\theta \lesssim \theta_c$, one can have "floating" regions of ordered adlayer, with a random phase relation so that $|\langle \rho_k \rangle|^2 \approx 0$ and there will be little or no splitting. As θ grows, there are two possibilities. If the terrace width is commensurate with an integral number of adlayer unit meshes the overlayer "locks in" to a single ordered arrangement so that $|\langle \rho \rangle|^2 \approx \langle |\rho|^2 \rangle$

and the spot is split. If the width is incommensurate with an integral number of adlayer unit meshes, one can have $|\langle \rho \rangle|^2 \approx 0$ even for $\theta \approx \theta_c$. On a real surface one expects a distribution of terrace widths so that a combination of both these possibilities will occur. These various cases are illustrated by our model in Section III.

It is also instructive to consider the limit of Eq(5) for infinite terrace width. In this case the number of sites $N \rightarrow \infty$, and the number of terraces $N_s \rightarrow 1$ as the width approaches the LEED coherence length ξ . When this happens, the interterrace interference function $h \rightarrow 1$ and the right hand side of Eq(5) reduces to $\langle |\rho|^2 \rangle$, which is the proper limit. For $N \rightarrow \infty$, this function will be independent of $\delta\epsilon$ except in certain special cases. Note also that as N grows, $\langle |\rho|^2 \rangle \rightarrow 0(N^2)$, $|\langle \rho \rangle|^2 \rightarrow 0(N^2)$, and $\langle |\rho|^2 \rangle - |\langle \rho \rangle|^2 \propto N T \chi$, where χ is the susceptibility of $\langle \rho(k) \rangle$ to a field coupling to $\rho(k)$. One has $\chi = 0(1)$, but χ may become large near an incipient phase transition (a true phase transition cannot occur in a two dimensional system with finite range forces). Hence for N large but not infinite the first term in Eq(5) may become important.

Because of finite instrumental response function effects, an important quantity for comparison with LEED experiments is the integrated intensity

$$I = \iint_{\underline{a}} I(\underline{k}) \frac{d(\underline{k} \cdot \underline{a})}{2\pi} \frac{d(\underline{k} \cdot \underline{b})}{2\pi} \quad (7)$$

where $\underline{a}$ and $\underline{b}$ are unit mesh vectors and the integral extends over an area $\underline{a}$ in reciprocal space around the overlayer diffraction beam. $\underline{a}$ is defined by instrumental parameters and beam energy. It is apparent from Eq(5) that even if $|\langle \rho \rangle|^2$ is sizable its contribution to I may be relatively small, depending on $\underline{a}$ and the shape of $|\langle \rho(k) \rangle|^2$ as a function of $\underline{k}$. For instance, suppose $|\langle \rho \rangle|^2 \approx \text{constant}$. Then since

$$\int_{-\pi}^{\pi} (h(N_s, x) - N_s) dx = 0 \quad (8)$$

there is a tendency for the two contributions of $|\langle \rho \rangle|^2$ to cancel. To understand this point in more detail let $\underline{k}_0$ define an adlayer beam and $\hat{i}$ be a unit vector parallel to the projection of $\underline{g}$ onto a terrace. Then, if $|\langle \rho(\underline{k}) \rangle|^2 \cong$ constant for $\underline{k}$ in the range $\underline{k}_0 \pm \frac{\pi}{g} \hat{i}$ and if there is a maximum of h at $x = \underline{k}_0 \cdot \underline{g}$, the contribution of $|\langle \rho \rangle|^2$ to h will be small if the integrated intensity is measured over this range of $\underline{k}$ values. Notice that for N_s reasonably large (>2 or 3) and for sufficiently wide terraces, the peaks in h will be quite narrow ($\Delta k \approx \frac{2\pi}{N_s g}$). Hence h will act like a delta function in the $\underline{g}$ direction and its effect on h will be to single out one $\underline{k}$ value. Further, one expects $|\langle \rho(\underline{k}) \rangle|^2$ to "spread out" as a function of $\underline{k}$ for g small enough. Hence it may happen that the LEED instrument response function is such that the net contribution of $|\langle \rho \rangle|^2$ to h is small. This in fact occurs in the model calculation for O/stepped W(110) reported in the companion paper.¹

There is an interesting possibility of new LEED features appearing in the stepped chemisorption systems we are considering. Suppose $\delta\epsilon < 0$ for a certain edge. Then the sites along that edge will fill up first, while all others on the terrace remain empty. Since the substrate configuration is quite different at the edge than elsewhere in the terrace, one would expect the adatom-adatom (AA) interactions to be different as well. If the AA edge energies favor a particular one-dimensional order and the temperature is not too large, new LEED spots will appear. If one edge has $\delta\epsilon < 0$ and the terrace is D sites wide, these spots will reach a maximum intensity for some coverage $0 < \theta < \frac{1}{D}$. The spots will be streaked in the direction perpendicular to the step edge, since they are due to one-dimensional order. There should also be a spot splitting in this direction due to the fixed phase relation between edge sites. If the terraces are randomly distributed in the direction parallel to the step edge, there will be no splitting in that direction. For a repulsive edge ($\delta\epsilon > 0$) similar effects can occur for coverages $1 - \frac{1}{D} < \theta < 1$. Note that the two terrace edges are different, hence one can have two new sets of AA interactions. The

corresponding LEED features will occur simultaneously at low θ if both $\delta\epsilon < 0$, at high θ if both $\delta\epsilon > 0$, or separately at low and high θ , if $\delta\epsilon < 0$ for one edge and $\delta\epsilon > 0$ for the other. To our knowledge such LEED features have neither been predicted nor observed previously, and we urge that experiments be done to confirm these ideas.

III. Model Calculation

We illustrate the general points made above with a model calculation at $T = 0$. Consider a square lattice of adsorption sites with terraces of width D sites in the $[1,0]$ direction and length L sites in the $[0,1]$ direction. Suppose the adatom-adatom (AA) interactions are such that (2×1) adlayer ordering occurs. The "perfect" (complete) overlayer has an adatom occupying every other site in the $[1,0]$ direction, and every filled site is part of a filled row in the $[0,1]$ direction. A simple (but not unique!) set of AA interactions giving rise to this type of order is nearest neighbor attraction on the $[0,1]$ direction along with nearest neighbor repulsion and second neighbor attraction on the $[1,0]$ direction.

We restrict ourselves to $T = 0$ to be able to calculate analytically. In general, we expect the conclusions we draw at $T = 0$ will be valid for a considerable range of finite temperatures. This expectation is born out by the results for our finite temperature calculation for O on stepped $W(110)$ in the companion paper¹. There may well be more subtle effects near incipient phase transitions, but we are not concerned with them here.

We now consider several aspects of the LEED scattering predicted by our model at $T = 0$. The features of interest are (i) the behavior of the quantities $\langle |\rho|^2 \rangle$ and $\langle |\rho\rangle|^2$ and the LEED intensity I vs. coverage θ for the overlayer beam, (ii) LEED spot splitting effects and (iii) the relative size of the contributions of $\langle |\rho|^2 \rangle$ and $\langle |\rho\rangle|^2$ (cf. Eq(5)) to the integrated LEED intensity at certain θ values. There are three possibilities for the change in adsorption energy at

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terrace edge sites: (a) both $\delta\epsilon > 0$ (both edges less attractive than the terrace) which we denote ++, (b) both $\delta\epsilon < 0$ (both edges more attractive than the terrace, denoted --, and (c) one edge with $\delta\epsilon > 0$ and one with $\delta\epsilon < 0$, denoted +-. Further we distinguish in each case whether D is even or odd since this difference can be significant. We make no assumptions here about AA interactions along the edges and therefore do not consider the possibility of new LEED spots mentioned at the end of Section II.

Now let $\underline{a}$ ($\underline{b}$) be a vector between neighboring adsorption sites in the $[1,0]$ ($[0,1]$) direction. A (2×1) overlayer beam may be defined by $\underline{k}_0$, where $\underline{k}_0 \cdot \underline{a} = \pi$, $\underline{k}_0 \cdot \underline{b} = 0$. If the experiment is set up so that $\underline{k}_0 \cdot \underline{g} = (2n+1)\pi$, $n = \text{integer}$, the second term in Eq(5) will not contribute to the intensity of the overlayer beam $I(\underline{k}_0)$. When considering splitting we will also be interested in a nearby beam $\underline{k}_1$ chosen to coincide with a maximum of h in Eq(5), $\underline{k}_1 = \underline{k}_0 + \Delta \underline{k} \cdot \underline{g} = \pm \pi$. There is a third overlayer beam defined by $\underline{k} = \underline{k}_0'$ that is of interest; for this beam $(N_s, \underline{k}_0' \cdot \underline{g}) = N_s$. One can always find such a $\underline{k}$ vector since $0 \leq h \leq N_s^2$. This beam is useful in discussing the intensity I since by Eq(5)

$$I(\underline{k}_0') = N_s \langle |f(\underline{k}_0')|^2 \rangle = N_s \langle |f(\underline{k}_0)|^2 \rangle \quad (9)$$

The last equality holds because the statistical average is independent of the component of $\underline{k}$ perpendicular to the terrace.

Now we consider case (a), ++, for $D = \text{odd}$. At low θ , there is considerable cancellation in $|\langle \rho(\underline{k}_0) \rangle|^2$, since the (2×1) domains may nucleate anywhere except at an edge site. The maximum value of this quantity comes at $\theta_m = 1/2 \frac{D-1}{D} < 1/2$. $\langle |\rho(\underline{k}_0)|^2 \rangle$ will be larger than $|\langle \rho \rangle|^2$ at low θ , but will also reach a maximum with the same value as $|\langle \rho(\underline{k}_0) \rangle|^2$ at θ_m . This may be seen easily by finding the state(s) of minimum energy at each θ . Note that the maximum LEED intensity for a flat surface (2×1) overlayer comes at $\theta = 1/2$. Now $I(\underline{k}_0)$ will go to zero at θ_m , but

$I(\underline{k}_0')$ will have a maximum there. Since $\theta_m = 1/2 - \frac{1}{2D}$ for the ++
 $D = \text{odd}$ case, the maximum in $I(\underline{k}_0')$ is shifted to lower coverage values than
 for the flat surface. This is simply a consequence of the fact that less
 adsorption sites are available, which implies a "complete" adlayer forms at
 a lower θ value. By our arguments in Section II, one can expect similar results
 for the integrated intensity - if the integration area is properly chosen,
 since the contribution of $|\langle \rho \rangle|^2$ may be quite small. This is confirmed in the
 companion paper¹.

For $\theta = \theta_m$ one has

$$\langle |f|^2 \rangle = |\langle f \rangle|^2 = L^2 \sin^2(1/2 (D-1) \underline{k} \cdot \underline{a}) / \sin^2(\underline{k} \cdot \underline{a}) \quad (10)$$

Hence, using $g \cong Da$, one finds

$$I(\underline{k}_i) \cong L^2 N_s^2 D^2 / \pi^2 \quad (11)$$

Since $I(\underline{k}_0) = 0$, the overlayer spot is strongly split (for a real system various
 effects that we are ignoring such as multiple and diffuse scattering will make
 $I(\underline{k}_0) > 0$). If one calculates the integrated intensity

$$I = \int_{\pi - 2\pi/D}^{\pi + 2\pi/D} I(k) \frac{d(k \cdot a)}{2\pi} \quad (12)$$

where the integral is along a line including $\underline{k}_0$ and $\underline{k}_1$, one finds that the $\langle |\rho|^2 \rangle$
 term in Eq(5) contributes about 5/4 of the total integrated intensity for $D = 11$.

For case (a), ++ and $D = \text{even}$ the behavior of $\langle |\rho(\underline{k}_0)|^2 \rangle$ is similar to
 that above, except that its maximum is at $\theta_m = 1/2 \frac{D-2}{D}$, further below 1/2
 than for the $D = \text{odd}$ case. $|\langle \rho(\underline{k}_0) \rangle|^2$, however, goes to zero at θ_m due to
 phase cancellation effects. Thus both $I(\underline{k}_0)$ and $I(\underline{k}_0')$ show maximum at $\theta = \theta_m$.
 At this coverage, one finds

$$\langle |f|^2 \rangle = L^2 \sin^2(1/2 (D-2) (\underline{k} \cdot \underline{a})) / \sin^2(\underline{k} \cdot \underline{a}) \quad (13)$$

$$|\langle f \rangle|^2 = \cos^2 1/2 (\underline{k} \cdot \underline{a}) \langle |f|^2 \rangle \quad (14)$$

Hence

$$\begin{aligned} I(k_0) &\cong N_s (D-2/2)^2 \\ I(k_1) &\cong N_s (1 - (\pi/D)^2) (D/\pi)^2 + N_s^2 (\pi/D)^2 (D/\pi)^2 \\ &= N_s ((D/\pi)^2 - 1) + N_s^2 \end{aligned} \quad (15)$$

so that

$$I(k_1)/I(k_0) \cong \frac{(D/\pi)^2 - 1 + N_s}{(D-2/2)} = 7/8$$

if we take $D = 10$, $N_s = 5$. Therefore the overlayer spot is not split. Defining ρ as in Eq(12) one finds that the contribution of the $|\langle \rho \rangle|^2$ term in $I(k)$ is about 10% and the $|\langle \rho \rangle|^2$ h term about 2% of the total.

For case (b), -- and $D = \text{even}$, there is only one overlayer arrangement possible at low T and $\langle |\rho(k)|^2 \rangle = |\langle \rho(k) \rangle|^2$ for all k . Also, $\langle |\rho(k_0)|^2 \rangle$ is very small due to phase cancellation effects. For $D = \text{odd}$, the maximum in either term comes at $\theta_m = 1/2 \frac{D+1}{D} = 1/2 + \frac{1}{2D}$. On a real surface with both $\delta\epsilon < 0$ one would expect a mixture of odd and even width terraces. Hence the maximum in $I(k_0')$ or will occur for coverages above the flat surface value of $1/2$.

For case (c), +-, there is again only one overlayer arrangement possible, so $\langle |\rho|^2 \rangle = |\langle \rho \rangle|^2$. For $D = \text{even}$ the maximum comes at $\theta_m = 1/2$, for $D = \text{odd}$ at $\theta_m = 1/2 \frac{D-1}{D} = 1/2 - \frac{1}{2D}$.

Notice that one can distinguish between the three cases, ++, -- and +- (both edges less attractive, more attractive, or one of each) by simply looking at the coverage θ_m at which the observable quantity $I(k_0')$ peaks vs. the flat surface value ($\theta = 1/2$ here). Assuming an even mixture of odd and even terrace widths one finds

$$\begin{aligned} \theta_m &\cong 1/2 - 3/4 D \quad \text{for } ++ \\ &\cong 1/2 + 1/2 D \quad \text{for } -- \\ &\cong 1/2 - 1/4 D \quad \text{for } +- \end{aligned} \quad (17)$$

For $D \approx 10$ which is achievable by cutting crystals at an angle, the difference between these three cases is easily within the resolution of Auger spectroscopy. Thus one can determine whether terrace edge sites adsorption energies are greater or less than on the terrace by looking at changes in the coverage dependence of appropriately chosen LEED features. Note that θ_m is respectively less than, greater than or close to the flat surface value depending on whether there are effectively fewer, more, or the same number of adsorption sites available on the stepped surface than the flat surface. Thus we expect the shift induced by the changes in adsorption energy on the stepped surface to be a very general effect, determined only by the sign of the two $\delta\epsilon$ and not specific to the model calculation presented here. Further consequences of this argument for theory and experiment are explored in the companion paper¹.

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