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# X-ray-standing-wave-analysis of noncommensurate adsorbate structures

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We describe an application of the x-ray-standing-wave technique to analyzing noncommensurate surface adsorbate structures. Coherent fractions larger than zero are generally expected if the adsorbate reflects the substrate surface corrugation or potential. We explicitly calculate standing-wave results for an in-plane incommensurate, corrugated adsorbate and for a two-dimensional lattice gas, using a model adsorbate-substrate interaction potential.

In the present study we calculate x-ray-standing-wave (XSW) results for noncommensurate adsorbate systems. As we shall show, adsorbate phases may be incommensurate, liquid, or even a two-dimensional gas and will nevertheless yield substantial coherent fractions for selected diffraction vectors. The only condition is in fact that there is some substrate-adsorbate interaction which leads either to a corrugation of the adsorbate in the direction perpendicular to the surface or to a modulated adsorbate distribution function along the surface or both.

By now the XSW technique[1] is an established tool for the analysis of the structure of surface adsorbates.[2] The structure of simple adsorbate systems with one atom per surface unit cell is determined with ease which has been demonstrated in a number of studies.[3] However with increasing success of the method and an increasing range of applications, more complicated problems are being tackled or encountered by chance. Surface vibrational amplitudes in-plane and normal to the surface have been studied for different adsorbate systems as a function of surface temperature.[4] Adsorbate structures characterized by a peculiar low-energy-electron-diffraction pattern have been analyzed[5,6] and found to consist of a more or less regular superlattice of domains, the interior lattice of which is incommensurate with the substrate lattice. An attempt was even made to study the structure of an overlayer, which was suspected of being liquid.[7] For this particular study of the high coverage phase of Pb on Si(111) at slightly elevated temperature, a "tilted" XSW measurement, i.e., a measurement using a diffraction vector with a pronounced in-plane component, yielded an XSW coherent fraction much larger than zero. On this basis the investigators rejected the hypothesis of a liquid overlayer, which was not necessarily a correct conclusion as we will show in our present study.

Many surface-adsorbate systems are characterized by a rich variety of phases and structures resulting from the reduction in dimensionality.[8] Among all possible phases, commensurate structures are only one particular class. Thus for the application of the XSW technique in surface science it is important to understand which results are characteristic of the different classes of adsorbate structures. Here we calculate typical XSW results for the large subgroup of noncommensurate surface adsorbate structures.

The principles of the XSW technique are described in a number of publications[9,10] which the interested reader should consult if our following brief description does not provide enough information. An x-ray interference field is generated by Bragg reflecting a plane x-ray wave of a perfect single crystal. The physics of this process is described by the dynamical theory of x-ray diffraction (DTXD).[11] The nodal (antinodal) planes of the wave field ("standing wave") resulting from the coherent superposition of incident and scattered x-ray waves are parallel to and match exactly the periodicity of the chosen set of diffraction planes. It is important to note that the position of the standing-wave planes can be manipulated. The standing-wave pattern moves by exactly half. a diffraction plane spacing while scanning through the range of strong Bragg reflection either in angle or energy. For core excitations (of adsorbate atoms in our case), which are very well described in the dipole approximation, the photoexcitation probability is directly proportional to the wave field intensity at the center of the atom. Decay channels such as fluorescence reflect this proportionality and the fluorescence yield $Y_F$ of an adsorbate atom at the position $\mathbf{r}_A$ is then given by

$$Y_F = 1 + R + 2\sqrt{R}\cos(v - 2\pi\mathbf{H}\cdot\mathbf{r}_A), \qquad (1)$$

where the reflectivity $R$ and the phase $v$ between the $E$ field of the incident and reflected wave are both functions of the angle of incidence or x-ray energy. The diffraction vector is given by $\mathbf{H}$.[12] The phase $v$ changes by $\pi$ while passing through the range of Bragg reflection and both $R$ and $v$ can be calculated with the help of the DTXD.

Equation (1) gives the expected XSW result for one adsorbate atom at one particular position $\mathbf{r}_A$. In realistic situations we will be dealing with a large number $N$ of positions because (i) we are averaging over time and (ii) we are usually dealing with a large number of adsorbate atoms.[13] Thus the fluorescence yield will be expressed by

$$Y_F = 1 + R + 2\sqrt{R}N^{-1}\sum_{i=1}^{N}\cos(v - 2\pi\mathbf{H}\cdot\mathbf{r}_i) \ . \quad (2)$$

We can express Eq. (2) via a distribution function $G(\mathbf{r})$ with $\int G(\mathbf{r})d\mathbf{r} = 1$ as

$$Y_F = 1 + R + 2\sqrt{R}\int G(\mathbf{r})\cos(v - 2\pi\mathbf{H}\cdot\mathbf{r})d\mathbf{r} \ . \quad (3)$$

In Eq. (1) the dot product $\mathbf{H}\cdot\mathbf{r}_A$ in the argument of the cosine function can be simplified as follows:

$$\mathbf{H}\cdot\mathbf{r}_A = |\mathbf{H}|z_A = P_A^{\mathbf{H}} \ (\mathrm{mod}\, 1),$$

where $z_A$ is the component of $\mathbf{r}_A$ parallel to $\mathbf{H}$ and $0 \le P_A^{\mathbf{H}} < 1$. Thus $P_A^{\mathbf{H}}$ measures the adsorbate position relative to a diffraction plane of the set defined by $\mathbf{H}$ normalized to the diffraction plane spacing $d_{\mathbf{H}}$. Equations (2) and (3) are equivalent to the following expression:

$$Y_F = 1 + R + 2\sqrt{R}F^{\mathbf{H}}\cos(v - 2\pi P^{\mathbf{H}}). \quad (4)$$

This can easily be understood since a sum (integral) of cosine functions of the same variable $v$ will yield again a cosine function of $v$, the amplitude of which also depends on the relative phases of the individual cosine functions (i.e., the $2\pi\mathbf{H}\cdot\mathbf{r}_i$'s). Thus every result of an XSW measurement on a surface adsorbate has the functional form of Eq. (4) with the two fitting parameters $F^{\mathbf{H}}$ and $P^{\mathbf{H}}$ plus a third fitting parameter necessary for overall normalization.[9] The other parameters $R$ and $v$ are calculated using the DTXD. $P$ and $F$ are commonly called coherent position and coherent fraction, respectively. For a commensurate adsorbate with a primitive surface unit cell $F$ will be close to unity—less than unity actually only via the effect of its vibrational amplitude[9]—and $P$ will give directly the distance of the adsorbate from a diffraction plane in units of $d_{\mathbf{H}}$. This is schematically shown in Fig. 1. To pinpoint the surface position of an adsorbate with one atom per unit cell would need in principle three different XSW measurements with non-coplanar $\mathbf{H}$ vectors. In practice, using, e.g., symmetry arguments, two measurements suffice and in situations where other information is available even one measurement can solve the problem.[3]

For a commensurate adsorbate with more than one atom per surface unit cell [compare Fig. 1(b)], $F$ can be significantly smaller than unity, possibly even close to zero, and $P$ will describe the average position of the adsorbate with respect to the used diffraction planes.[14,15]

What is now the situation if we measure a noncommensurate adsorbate system? If we use a set of diffraction planes parallel to the crystal surface, it is clear that we will end up with a coherent fraction larger than zero since any monolayer adsorbate structure will exhibit a relatively well-defined surface distance in order to keep bond lengths reasonable. Along the surface, however, basically all possible positions are occupied by a noncommensurate adsorbate. This is schematically shown in Fig. 1(c). Thus, if the diffraction vector $\mathbf{H}$ is not normal to the surface, the yield function given by Eq. (2) is characterized by a summation over cosine functions with random phases, which causes $F$ to vanish. As we will show in the following, even for a uniform in-plane distribution, this is only the case if the overlayer shows no perpendicular corrugation in phase with the planar lattice structure of the substrate surface.

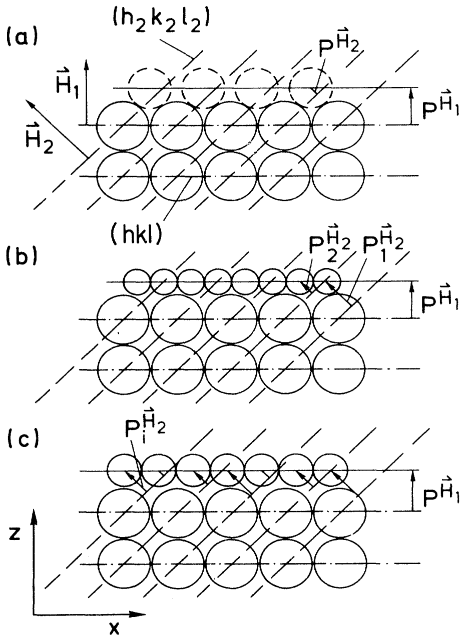

FIG. 1. Adsorbate atoms on the surface of a crystal with a simple-cubic lattice structure in side view. Two different sets of diffraction planes $(h_1k_1l_1)$ and $(h_2k_2l_2)$ characterized by diffraction vectors $\mathbf{H}_1$ and $\mathbf{H}_2$, respectively, are indicated. The adsorbate positions relative to the diffraction planes are characterized by $P$. (a) A commensurate adsorbate with one atom per surface unit cell. (b) A commensurate adsorbate with a nonprimitive surface unit cell. (c) Simple scheme for an incommensurate adsorbate characterized by one particular distance normal to the surface.

As substrate we choose a primitive cubic lattice of period $a$ and we assume the corrugation to be sinusoidal with peak to peak amplitude $4ca$. Thus the XSW yield function is given by Eq. (3) where $G$ reduces to a $\delta$ function of $z$

$$G(\mathbf{r}) = \frac{1}{a^3}\delta\left(c\cos\left(\frac{2\pi}{a}x\right) + c\cos\left(\frac{2\pi}{a}y\right) - \frac{z}{a}\right) , \quad (5)$$

and we can express the XSW result as

$$\begin{aligned} F^{hkl}\cos\left(v - 2\pi P^{hkl}\right) &= \int_0^a \frac{dx}{a}\int_0^a \frac{dy}{a}\cos\left(v - 2\pi\left\{\frac{hx}{a} + \frac{ky}{a} + lc\left[\cos\left(\frac{2\pi}{a}x\right) + \cos\left(\frac{2\pi}{a}y\right)\right]\right\}\right) \\ &= \cos\left(v + \frac{h+k}{2}\pi\right) J_h\left(2\pi lc\right) J_k\left(2\pi lc\right) \ , \end{aligned} \quad (6)$$

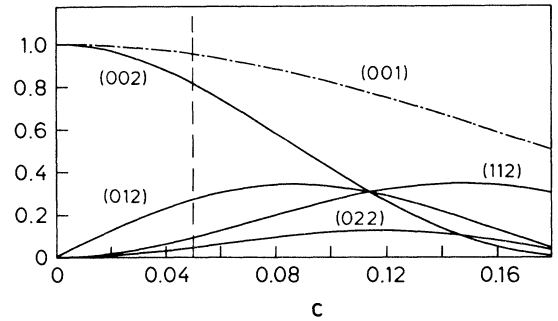

FIG. 2. Coherent fraction $F$ as a function of adsorbate corrugation amplitude for five different diffraction planes and a simple-cubic substrate crystal. The peak-to-peak amplitude of the sinusoidal corrugation is $4ca$ where $a$ is the substrate lattice constant.

where $\mathbf{H} = (1/a)(h,k,l)$ is the diffraction vector, $c$ is the adimensional normalized corrugation amplitude, and the $J$'s are Bessel functions of the first kind.[16] In Fig. 2 we show calculated $F$ values for several sets of diffraction planes as a function of $c$, the crystal surface orientation being [001].

It is important to realize that an XSW measurement will in general yield a coherent fraction larger than zero independent of any interaction or correlation between the adsorbate atoms. What is needed, in fact, is a correlation of the adsorbate location with the substrate lattice or surface potential. To elucidate this point we consider a particle on the surface constrained by a relatively simple substrate-adsorbate interaction potential $U(\mathbf{r})$. For the $x, y$ dependence we consider only the lowest-order Fourier components of the substrate-adsorbate interaction, i.e., a sinusoidal dependency. In the $z$ direction (surface normal) we treat the interaction in the harmonic approximation taking only the quadratic term of the expansion into account. With these approximations the interaction potential can be expressed as

$$\frac{U(\mathbf{r})}{k_B T} = w\left[\cos\left(\frac{2\pi}{a}x\right) + \cos\left(\frac{2\pi}{a}y\right)\right] + s\left\{c\left[\cos\left(\frac{2\pi}{a}x\right) + \frac{2\pi}{a}y\right] - \frac{z}{a}\right\}^2 . \tag{7}$$

With this potential we can express the coherent part of the XSW yield function as

$$F^{hkl}\cos\left(v - 2\pi P^{hkl}\right) = \frac{\int d\mathbf{r}\left[e^{-U(\mathbf{r})/k_B T}\cos\left(v - \frac{2\pi}{a}(hx + ky + lz)\right)\right]}{\int d\mathbf{r}\left(e^{-U(\mathbf{r})/k_B T}\right)} . \tag{8}$$

The spatial distribution of the adsorbate (averaged, e.g., over time) is simply given by a Boltzmann distribution. Solving the integral numerically we calculate the expected XSW results in terms of $F$. We do not list the obtained $P$ values since they depend on the average adsorbate-surface distance which is not of interest for the present considerations. The potential given by Eq. (7) is very convenient since it allows us, via tuning the interaction potential parameters $w$, $s$, and the corrugation amplitude parameter $c$, to study several qualitatively different adsorbate distribution functions as shown in Table I and discussed in the following.

For column one of Table I the "spring constant" $s$ of the adsorbate for vibrations normal to the surface is infinitely strong ($s \to \infty$) and the strength of the potential shows no $x, y$ dependence ($w \to 0$). The result is a sinusoidally corrugated ($c = 0.05$) overlayer, distributed in $x$ and $y$ uniformly. Thus, this case corresponds exactly to the sinusoidally modulated adsorbate of Eq. (6) above. The adsorbate distribution is shown schematically in Fig. 3(a). The $F$ values which are listed in column one of Table I correspond to the corrugation value indicated in Fig. 2 by the dashed line.

For column two we have $w \to 0$, $s = 400$, and $c = 0.05$ which also corresponds to a situation where the in-plane distribution is uniform. Different from the case discussed before, the potential in the $z$ direction is characterized now by a reasonable, finite value, leading to a distribution in the $z$ direction due to vibrations. This is shown schematically in Fig. 3(b). The effect of vibrations is a reduction of $F$ most pronounced for the diffraction vectors with the largest components in the $z$ direction.

In column three, all parameters $w$, $s$, and $c$ are characterized by reasonable finite values. The potential in the $z$ direction, as in the previous case, is relatively stiff but there is now an additional, in-plane modulation ($w = 0.2$). As a result, the in-plane adsorbate distribution is no longer uniform but modulated and thus peaked at certain lattice locations. This is indicated in Fig. 3(c). The main effect is a slight increase in $F$ for all diffraction vectors and, in particular, a nonvanishing coherent fraction for diffraction vectors parallel to the surface.

In column four we listed for comparison the results obtained choosing $w = 0.2$, $s = 400$, and $c \to 0$ which corresponds to the distribution discussed in the last paragraph except that the overlayer is now perfectly flat without any corrugation perpendicular to the surface ($c \to 0$). Just because of the $x, y$ dependence of the potential an XSW measurement using diffraction vectors with an in-plane component will still show coherent fractions larger than zero. However, the missing corrugation leads to an increase of the coherent fractions for diffraction vectors normal to the surface whereas the coherent fractions for all other diffraction vectors are decreased.

The substrate-adsorbate interaction potential which we have chosen and our classical thermodynamical treatment of the particle localization are as simple as possible. Nevertheless, our model calculations show that

TABLE I. Coherent fraction $F$ for a number of different diffraction vectors. Four different sets of parameters $w$, $s$, and $c$ for the surface-adsorbate interaction potential given by Eq. (7) lead to four different adsorbate distribution functions.

| $h\ k\ l$ | $F^{hkl}$ | | | |
|---|---|---|---|---|
| 1 0 0 | 0.000 | 0.000 | 0.100 | 0.100 |
| 1 1 0 | 0.000 | 0.000 | 0.010 | 0.010 |
| 0 0 1 | 0.952 | 0.928 | 0.929 | 0.976 |
| 1 0 1 | 0.151 | 0.148 | 0.174 | 0.097 |
| 1 1 1 | 0.024 | 0.023 | 0.027 | 0.005 |
| 2 0 1 | 0.012 | 0.012 | 0.016 | 0.005 |
| 0 0 2 | 0.817 | 0.740 | 0.742 | 0.906 |
| 1 0 2 | 0.270 | 0.245 | 0.256 | 0.090 |
| 1 1 2 | 0.089 | 0.081 | 0.088 | 0.009 |
| 2 0 2 | 0.043 | 0.039 | 0.043 | 0.005 |
| 0 0 3 | 0.624 | 0.500 | 0.504 | 0.801 |
| 1 0 3 | 0.332 | 0.266 | 0.272 | 0.080 |
| 1 1 3 | 0.177 | 0.142 | 0.147 | 0.008 |
| 2 0 3 | 0.081 | 0.065 | 0.068 | 0.004 |
| $w$ | 0 | 0 | 0.2 | 0.2 |
| $s$ | $\infty$ | 400 | 400 | 400 |
| $c$ | 0.05 | 0.05 | 0.05 | 0 |

any adsorbate-surface interaction will lead in general to a modulated particle density distribution which will yield characteristic XSW results. In particular, the lack of isotropy will bring about coherent fractions larger than zero.

Since for an XSW measurement we do not require a correlation among the adsorbate atoms, we can choose the surface particle density or adsorbate coverage so low that we can effectively neglect adsorbate-adsorbate interactions. Note in this context that the results shown in Table I are in fact the same for the time average over the motion of a *single* particle on the surface as for the configuration average of many (independent) particles. Our model adsorbate-substrate interaction potential did, of course, not take any adsorbate-adsorbate interactions into account. Trying to separate the effects of adsorbate-adsorbate and adsorbate-surface interaction is in our opinion a fascinating prospect for the future. With the XSW technique this can in principle be done by varying coverages from the monolayer range to such low values that adsorbate-adsorbate interactions can be neglected.

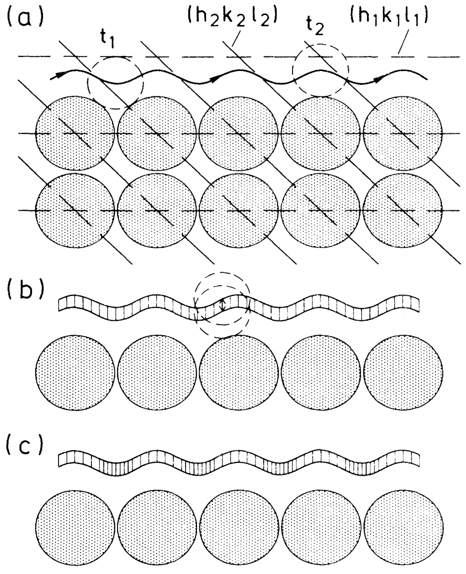

FIG. 3. An adsorbate atom on a simple-cubic substrate in side view. (a) The adsorbate is moving on the surface along the indicated sinusoidal path. Shown is the position of the adsorbate at two particular times $t_1$ and $t_2$. Averaged over time the atom can be found with equal probability at any point along its path. Two sets of diffraction planes are indicated. (b) Same as in (a) but the atom is now vibrating leading to a broadening of its path normal to the surface. (c) Same as in (b) but the adsorbate atoms residence time varies now on the surface which is indicated by different densities of the line pattern.

To summarize, the present investigation has shown two things very clearly. First, we do not generally determine structure factors of an adsorbate with the XSW technique but rather test the correlation of adsorbed atoms with the substrate lattice. This is not a new finding but something which is frequently misunderstood. Second, for any set of diffraction planes and adsorbates with any coverages up to the monolayer range, coherent fractions larger than zero are not really the exception. The response of the adsorbate to the underlying substrate potential should lead in general to a modulated distribution of the adsorbate which yields coherent fractions larger than zero, possibly further enhanced by the correlation between the vertical and in-plane adatom coordinates.

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[12] $\mathbf{H}$ is related to a reciprocal-lattice vector $\mathbf{G}$ simply by $\mathbf{G} = 2\pi\mathbf{H}$.

[13] One monolayer corresponds roughly to $10^{14}$ atoms per $\mathrm{cm}^2$ and XSW measuring times are of the order of minutes, which is very long compared to typical time scales for surface diffusion and vibrations.

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[15] E. Vlieg, E. Fontes, and J.R. Patel, Phys. Rev. B **43**, 7185 (1991).

[16] This result can be obtained using the identity

$$e^{i\rho\cos\phi} = J_0(\rho) + 2\sum_{n=1}^{\infty} i^n J_n(\rho)\cos(n\phi);$$

see *Bateman Manuscript Project, Higher Transcendental Functions*, edited by A. Erdélyi (McGraw-Hill, New York, 1953), Vol. II, paragraph 7.2.4.