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ORIENTATIONAL EPITAXY IN ADSORBED MONOLAYERS

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The ground state for adsorbed monolayers on crystal-line substrates is shown to involve a definite relative orientation of the substrate and adsorbate crystal axes, even when the relative lattice parameters are incommensurate. The rotation angle which defines the structure of the monolayer-substrate system is determined by the competition between adsorbate-substrate and adsorbate-adsorbate energy terms, and is generally not a symmetry angle. Numerical predictions are presented for the rare gas-graphite systems, whose interaction potentials are rather well known. Recent LEED data for some of these systems appear to corroborate these predictions.

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Introduction

Monolayer films grown on uniform crystalline substrates can be divided into two classes. In the registered (or commensurate) structures the lattice parameters of the adsorbed film lock into integral multiples or submultiples of those of the substrate surface. There is a well-defined combined adsorbate-substrate surface unit cell (which may involve one or more inequivalent adsorbate atoms (molecules),⁽¹⁾ implying that the adsorbate lattice must be oriented along a symmetry axis of the substrate.

On the other hand, if lateral dependence of the adsorbate-substrate potential is sufficiently weak compared to adsorbate-adsorbate interactions, the two structures will have incommensurate lattice parameters, with the orientation unrelated to symmetry. An example is silver on mica,⁽²⁾ where small (~ 100 Å) islands are observed to be aligned about $\frac{1}{2}^\circ$ off the mica axis. This type of misorientation has been attributed to edge effects,⁽³⁾ and to crystal-size-dependent lattice coincidences involving dislocations.⁽⁴⁾

The phenomenon we consider here, however, exists in infinite crystallites, and is related in a simple way to the dynamical response of the lattices. It involves the creation of static distortion waves (SDW) in the interfacial region, caused by the adsorbate-substrate interaction potential. These distortions are close analogues to the charge-density wave phases of bulk solids.⁽⁵⁾ The amplitudes of these waves and the corresponding energy terms

depend upon the mismatch of the two lattices, their relative orientation, the lattice dynamics of the monolayer lattice, and the shape of the potential well presented to the adatom by the substrate. The order parameters for the distorted structures are the amplitudes of the SDW waves, the number of order parameters reflecting the Fourier components describing the adsorbate-substrate interaction, as well as the symmetry of the system.

Static Distortion Waves

We treat here a particularly simple case of a monolayer adsorbed on a rigid substrate crystal face at $T=0$ K. Only lateral effects are treated, making the problem two-dimensional.

The adatom-adatom Hamiltonian for the monolayer in the harmonic approximation is

$$\hat{H}_0 = E_L + \sum_j \frac{1}{2M} \hat{p}_j^\alpha \hat{p}_j^\alpha + \sum_{ij} \frac{1}{2} \phi_{ij}^{\alpha\beta} \hat{u}_i^\alpha \hat{u}_j^\beta, \quad (1)$$

where E_L is the ideal lattice potential energy, and $\hat{p}_j^\alpha$ and $\hat{u}_j^\alpha$ the α -components of the momentum and position operators for the atom at lattice site j . Summation over α and β is implicit. This lattice has a set of direct lattice vectors denoted by $\{\vec{R}_j\}$ and a set of reciprocal lattice vectors $\{\vec{\tau}\}$. The adatom-adatom potential then produces longitudinal and transverse coupling constants $\phi_{ij}^{\alpha\beta}$. The corresponding dynamical matrix has eigenfrequencies $\omega_\ell(\vec{q})$ and eigenvectors $\epsilon_\ell^\alpha(\vec{q})$. These then define the usual transformation to phonon

creation and destruction operators $\hat{a}_{\vec{q},l}^\dagger$ and $\hat{a}_{\vec{q},l}$ via

$$\hat{u}_j^\alpha = \frac{1}{\sqrt{N}} \sum_{\vec{q},l} \varepsilon_l^\alpha(\vec{q}) e^{i\vec{q} \cdot \vec{R}_j} \left[\frac{\hbar}{2M\omega_l(\vec{q})} \right]^{1/2} \left[\hat{a}_{\vec{q},l} + \hat{a}_{-\vec{q},l}^\dagger \right]. \quad (2)$$

Introduction of the adatom-substrate potential $\phi(\vec{r})$ is treated as a perturbation $\hat{H}_1$. This approximation is reasonable for incommensurate phases, where the adatom-adatom term is obviously dominant. $\hat{H}_1$ is also expanded in a power series in $\hat{u}_j^\alpha$:

$$\hat{H}_1 = \sum_j \phi(\vec{R}_j) + \sum_j \phi^\alpha(\vec{R}_j) \hat{u}_j^\alpha = \sum_j \frac{1}{2} \phi^{\alpha\beta}(\vec{R}_j) \hat{u}_j^\alpha \hat{u}_j^\beta + \dots \quad (3)$$

The substrate energy $\phi(\vec{r})$ is expanded in a Fourier series with $\phi(\vec{r}) = \sum_{\vec{G}} \phi_{\vec{G}} \exp(i\vec{G} \cdot \vec{r})$, $\{\vec{G}\}$ being the set of reciprocal lattice vectors for the substrate direct lattice vectors $\{\vec{R}\}$. If $\hat{H}_1$ term is truncated after the linear term, we have that

$$\begin{aligned} H = E_L + \frac{1}{2} \sum_{\vec{q},l} \hbar \omega_l(\vec{q}) + \sum_{\vec{q},l} \hbar \omega_l(\vec{q}) a_{\vec{q},l}^\dagger a_{\vec{q},l} + \frac{N \sum \phi_{\vec{G}}}{G} \delta_{\vec{G},\vec{0}} \\ + i \sqrt{N} \sum_{\vec{q},l} \left\{ g_{\vec{q},l} \hat{a}_{\vec{q},l} - g_{-\vec{q},l}^* \hat{a}_{-\vec{q},l}^\dagger \right\} \end{aligned} \quad (4a)$$

$$g_{\vec{q},l} = \sum_{\vec{G}} \phi_{\vec{G}} G^\beta \varepsilon_l^\beta(\vec{q}) \delta_{\vec{G}+\vec{q},\vec{0}} \left\{ \frac{\hbar}{2M\omega_l(\vec{q})} \right\}^{1/2} = -g_{-\vec{q},l}^* \quad (4b)$$

The Hamiltonian in Eq. (4a) is that of a set of uncoupled displaced oscillators in momentum space with the corresponding coordinates being the amplitudes of the normal modes of the original monolayer lattice. The ground state

is characterized by non-zero average values for these coordinates. (6) A consequence of this is that the atoms in the monolayer are statically displaced from their ideal lattice sites. The substrate lattice is now assumed to have an inversion symmetry about the point $\vec{r} = +\vec{A}$, and the Fourier coefficients written as $\phi_{\vec{G}} = \phi_{\vec{G}} \exp(-i\vec{G} \cdot \vec{A})$ where $\phi_{\vec{G}}$ is real and symmetric in $\vec{G}$. After some algebra, one finds that this static displacement is given by

$$\langle \hat{u}_j^a \rangle = \sum_{\vec{G}, l} \epsilon_l^a(\vec{G}) \eta_l(\vec{G}) \sin \vec{G} \cdot (\vec{R}_j - \vec{A}) \quad , \quad (5)$$

$$\eta_l(\vec{G}) = \frac{\phi_{\vec{G}} G^{\beta} \epsilon_l^{\beta}(\vec{G})}{M \omega_l^2(G)} \quad (6)$$

in the extended Brillouin zone scheme. Note that $\eta_l(\vec{G})$ is real and antisymmetric in $\vec{G}$, and the set of $\eta_l(\vec{G})$ form the order-parameter set for the SDW phase. The atom at the j^{th} site is statically displaced from its ideal site. This displacement varies in a sinusoidal fashion from lattice site to lattice site, and is just the linear response of the monolayer lattice to the external periodic field imposed by the substrate surface.

The energy terms associated with the SDW phase can be evaluated in a straightforward manner. The lock-in term $N \sum_{\vec{G}} \sum_{\vec{\tau}} \phi_{\vec{G}} \delta_{\vec{G}, \vec{\tau}}$ is zero for incommensurate lattices. The strain energy it costs to produce the SDW phase is $N \sum_{\vec{q}, l} \hbar \omega_l(q) \xi_{\vec{q}, l}^* \xi_{\vec{q}, l}$ where $\xi_{\vec{q}, l} = i g_{\vec{q}, l}^* / \hbar \omega_l(q) = \xi_{-\vec{q}, l}^*$ and the corresponding

adatom substrate potential energy term is $\sum_j \phi^{\alpha}(\vec{R}_j) \langle \hat{u}_j^{\alpha} \rangle$. Since the second-order terms in $\phi(\vec{r})$ have been ignored in this level of approximation, there is no change in the phonon frequencies or polarization vectors. Assembling all energy terms we have

$$E = E_L + \frac{1}{2} \sum_{\vec{q}, l} \hbar \omega_l(\vec{q}) - \frac{1}{2} N \sum_{\vec{G}, l} \phi_{\vec{G}}^{\alpha} \epsilon_l^{\alpha}(\vec{G}) \eta_l(\vec{G}) . \quad (7)$$

The total energy is translationally invariant, but the last term does depend upon the relative orientation of the monolayer and substrate lattices. It is this SDW term which produces the orientational locking of the two lattices. The origin of the effect is illustrated by Fig. 1, which shows two triangular reciprocal lattices oriented at some angle. The SDW energy term has its largest negative value when the $\eta_l(\vec{G})$ are largest. The specific value of this angle depends upon two competing factors in Eq. (6). The $\omega_l^2(\vec{q})$ term tends to align the $\vec{G}$ vector with the nearest $\vec{\tau}$ vector since this minimizes the $\vec{q} = \vec{G} - \vec{\tau}$ vector which defines the mode. This term favors long wavelength distortions, corresponding to low frequency phonons. However, each $\eta_l(\vec{G})$ contains a weight factor $G^{\beta} \epsilon_l^{\beta}$ which affects the manner in which each mode can contribute to the distortions. Since transverse modes have lower frequencies than longitudinal modes, this term tends to produce an orientation of the $\vec{G}$ and $\vec{\tau}$ lattices so as to take maximum advantage of these transverse modes. Again

referring to Fig. 1, the $\omega_q^2(q)$ term tends to align the lattices at $\theta=0$, since that minimizes q . However, when $\theta=0$, only longitudinal modes can contribute. Initially, rotation away from $\theta=0$ causes transverse response without increasing the magnitude of q (since $\left. \frac{\partial |q|}{\partial \theta} \right|_{\theta=0} = 0$).

Thus the energy is always lowered by rotating off the symmetry direction. As θ becomes larger, however, $|\vec{q}|$ begins to increase, causing stiffened response. There will then be some non-zero, non-symmetry, angle at which the total energy is minimal.

The undistorted monolayer lattice shows Bragg reflections for scattering vectors $\vec{Q}$ equal to reciprocal lattice vectors $\vec{\tau}$. The clearest signature of the SDW phase is the appearance of satellite peaks around the $\vec{Q} = \vec{\tau}$ parent peaks. There are many such satellite peaks, but the strongest or primary ones occur at $\vec{Q} = \vec{\tau} + \vec{q}_n$ where $\vec{q}_n$ is any one of the SDW wave vectors. The structure of these satellite peaks is similar to those found in bulk incommensurate solids, although the two-dimensional nature of the monolayer should affect the satellites in a manner much like the effect on the parent peaks.⁽⁷⁾ To avoid this difficulty, we will describe the case where the scattering vector is in the plane of the monolayer. For this case, the results are identical to the 3-D results, except that all vectors are 2-D vectors instead of 3-D vectors. Following the work of Pynn, Axe, and Thomas⁽⁸⁾ we find that the parent peak is

reduced in intensity by the introduction of static distortion and the missing intensity shows up in the form of satellite peaks. The lattice structure factor is proportional to

$$\left[\prod_{\vec{G}} J_0(Q^\beta \epsilon_{\vec{G}}^\beta(\vec{G}) \eta_{\vec{G}}(\vec{G})) \right] \Delta(\vec{Q}) + \sum_{\vec{G}_1} \left[\prod_{\vec{G} \neq \vec{G}_1} J_0(Q^\beta \epsilon_{\vec{G}}^\beta(\vec{G}) \eta_{\vec{G}}(\vec{G})) \right] J_1(Q^\alpha \epsilon_{\vec{G}_1}^\alpha(\vec{G}_1) \eta_{\vec{G}_1}(\vec{G}_1)) \Delta(\vec{Q} + \vec{G}_1)$$

where J_0 and J_1 are the Bessel functions of the first kind of order zero and one and $\Delta(\vec{Q})$ is the periodic delta function given by $\Delta(\vec{Q}) = \sum_{\vec{r}} \delta_{\vec{r}, \vec{Q}}$. The leading term is the parent peak, the second term is the primary satellite peak. The parent term is modified by a factor which acts much like a Debye-Waller factor for small η and Q . The primary satellite peak has a rather small intensity for small Q and η because of the J_1 term. The intensity of the peak is proportional to $(Q^\alpha \epsilon_{\vec{G}_1}^\alpha \eta_{\vec{G}_1})^2$. The higher order terms are even smaller, being proportional to higher powers of $(Q^\alpha \epsilon_{\vec{G}_1}^\alpha \eta_{\vec{G}_1})$. (5)

Rare Gases on Graphite

The simplest, and most studied, experimental systems are rare gas monolayers on the graphite (001) surface, (9-11) whose interactions are to a good approximation pairwise additive. (12) Furthermore the graphite lattice is considerably stiffer than the adsorbed film and thus its effect on the adsorbate is mainly that of a static external field.

Steele⁽¹²⁾ has estimated the Fourier coefficients of the rare gas-graphite interaction using known Lennard-Jones rare gas potentials and an approximation for the rare gas-carbon atom-atom potential. This unlike atom-atom potential is taken to be of the Lennard-Jones form, but constrained to fit measured heats of adsorption and the usual combining rules ($2\sigma_{AB} = \sigma_{AA} + \sigma_{BB}$, $\epsilon_{AB}^2 = \epsilon_{AA}\epsilon_{BB}$).

In our calculations we have used only the lowest Fourier components, as listed in Table I. From the measured structure and dynamics of Ar on graphite⁽¹³⁾ we know that these potentials are reasonable approximations to the experimental situation, at least in this one case. Fig. 2 shows the SDW energy for a fixed lattice constant as a function of θ , the deviation from the $\sqrt{3} \times \sqrt{3}$ 30° registered phase direction, for Ne, Ar, Kr, and Xe monolayers. Note that the further the nearest-neighbor distance is from registry, the greater is the angular deviation. Ne, some 25% out of registry in lattice parameter, has $\theta_{\min}$ between 15° and 20° , while Ar, approximately 10% out of registry, has $\theta_{\min} = 3.5^\circ$. The values for Kr and Xe are even closer to the registered orientation. This is physically sensible since q changes more rapidly with θ as the registered lattice parameter is approached, thus stiffening the response as per Eq. (6).

In Fig. 3 we display the total energy at $\theta_{\min}$ for Ar as a function of the nearest-neighbor spacing a . On the same plot is the corresponding curve for E_0 , the energy in

absence of substrate. It is seen that, in addition to lowering the energy, the substrate potential causes a slight lattice expansion, bringing it closer to the registered distance.

Particularly interesting is the rotation of the ground state with change in lattice parameter, displayed for Ar at $T=0$ K in Fig. 4. As the lattice expands to approach registry it also rotates toward the registered orientation. This phenomenon should manifest itself in real systems at finite temperatures through thermal expansion. The linear response calculation used here will not be applicable very close to registry, so it is not possible to conclude from these results whether the registry-incommensurate transition should be continuous or first order. We note, however, that because of the continuum of possible order parameter values, the transition can in principle be a continuous one.

Discussion

The orientational epitaxy discussed here appears to have been observed experimentally. LEED studies on the heavy rare gases Ar and Xe,⁽¹⁰⁾ as well as Kr⁽¹¹⁾ show a definite crystal orientation close to $\theta=0$. More recently preliminary high resolution work on Kr and Ar indicates that, at least at some temperatures and coverages, the value of θ is non-zero as predicted for incommensurate

structures (CHINN M. and FAIN S. C., 1977, private communication). Our results for Kr must be considered a model calculation for some assumed potential form. The Kr results are sensitive to the potential parameters chosen, and the question of whether or not Kr is in or out of registry at $T=0$ K and zero pressure may depend upon how the Kr-Kr potential is affected by the graphite surface. Never-the-less, the fixed orientation at a small rotation angle, the static distortions, and the dependence of rotation angle upon lattice parameter are relevant to the incommensurate state which has been observed at elevated pressures.

The appearance of satellite peaks due to the static strain has not as yet been observed as far as we know. Although the calculations appear reasonably realistic for rare gas monolayers on graphite, treatment of more general cases requires consideration of relaxation effects in the substrate, as well as thicker adsorbate films.⁽¹⁴⁾ As pointed out earlier, the approach to registry involves nonlinear terms, considerably complicating the theory.

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TABLE I

PARAMETERS FOR SDW CALCULATION

Adatom	Atomic Mass [AMU]	Adatom-Adatom		ϕ_{G_1} for Graphite [Kelvin]
		ϵ [Kelvin]	σ [Å]	
Ne	20	35.6	2.78	-3.75
Ar	36	120.0	3.40	-4.62
Kr	84	158.0	3.60	-5.00
Xe	131	226.0	4.05	-4.62

FIGURE CAPTIONS

Figure 1. The reciprocal lattice vectors for the monolayer lattice $\{\vec{T}\}$ and the graphite lattice $\{\vec{G}\}$. The angle θ is the angle of rotation relative to the superlattice.

Figure 2. The energy of the SDW phase relative to the energy of the undistorted lattice with the same lattice constant. The curves are for ^{20}Ne (.....) with $a = 3.12 \text{ \AA}$, ^{36}Ar (——) with $a = 3.86 \text{ \AA}$, ^{84}Kr (---) with $a = 4.05 \text{ \AA}$, and ^{131}Xe (-.-.-) with $a = 4.55 \text{ \AA}$. The substrate is the graphite (001) surface. The angle of rotation is that shown in Fig. 1.

Figure 3. The energy per atom for ^{36}Ar as a function of lattice constant. The E_0 curve is the energy in the absence of the static distortions. The E_T curve includes the SDW energy evaluated at $\theta_{\min}$. The arrow to the far left indicates the point of minimum energy using only E_L , the next indicates the point of minimum energy with zero point energy included, and the last indicates the point where the total energy is a minimum.

Figure 4. The value of $\theta_{\min}$ as a function of lattice parameter for ^{36}Ar . The arrow indicates the point where the total energy is a minimum. The question mark indicates that the linear response approximation is beginning to fail because of the large amplitudes of the distortion waves.

Figure 4 (cont).

At $a = 3.95 \text{ \AA}$, the rms deviation of an atom from its ideal lattice site is about 4% of the lattice parameter.