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Orientational Epitaxy—the Orientational Ordering of Incommensurate Structures

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A new class of structures is predicted to exist for monolayer films on solid surfaces. These structures involve two incommensurate lattices—the monolayer lattice and the surface lattice— which have a preferred relative orientation. The precise orientation depends upon the lattice constant and symmetry of each lattice. We believe this orientationally ordered incommensurate phase to be present in many physisorbed films. In particular, the existence of this phase appears to explain recent low-energy electron diffraction data for rare gases adsorbed on homogeneous substrates.

The growth of crystals on dissimilar substrates plays an important role in microelectronic device technology, and is also of considerable scientific interest. We discuss here aspects of the interactions of a monolayer film on a crystalline substrate and demonstrate the existence of a new class of epitaxy involving the relative orientations of substrate and adsorbate crystal axes for substances whose lattice parameters are mutually incommensurate. It is shown that, even for incommensurate systems, the ground state of the composite system is characterized by a definite relative orientation which is, in general, not a symmetry angle.

In many cases involving two crystals of differing bulk lattice parameters, distortions at the interface cause the crystals to be in registry.[1] That is, they have locally commensurate lattice parameters and relative orientations determined by symmetry. These results appear to obtain when adsorbate-substrate and adsorbate-adsorbate interactions are of comparable strength. There are, however, examples with weak adsorbate-substrate interactions in which the lattice parameters are incommensurate and the orientation is unrelated to symmetry. A well-studied one is silver on mica,[2] where the orientation of small (~100 Å) silver islands is about $\frac{1}{4}°$ out of registry with the mica. This misorientation has been attributed to edge effects,[3] and to crystal-size-dependent dislocation-induced lattice coincidences.[4]

The phenomenon that we consider here, however, exists even 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 analogs to the charge-density-wave phases of the bulk solids.[5] For purposes of illustration we here examine the simplest case, that of a monolayer adsorbed on a rigid substrate crystal face. The adsorbate monolayer crystal is assumed to be at zero kelvin, and its lattice dynamics are treated in the harmonic approximation.

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

$$\hat{H}_0 = E_L + \sum_j \frac{1}{2M}\hat{p}_j{}^\alpha \hat{p}_j{}^\alpha + \sum_{i,j} \tfrac{1}{2}\Phi_{ij}{}^{\alpha\beta}\hat{u}_i{}^\alpha \hat{u}_j{}^\beta, \tag{1}$$

where $\hat{p}_j{}^\alpha$ and $\hat{u}_j{}^\alpha$ are the α components of the momentum and position operators for the atom at lattice site j, and summation over α and β is implicit. The E_L term is just the ideal-lattice potential energy. 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 is then used to calculate the longitudinal and transverse coupling constants $\Phi_{ij}{}^{\alpha\beta}$, and the corresponding dynamical matrix is diagonalized to yield eigenfrequencies $\omega_l(\vec{q})$ and eigenvectors $\epsilon_l{}^\alpha(\vec{q})$. 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

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

The adatom-substrate potential $\varphi(\vec{r})$ is expanded in a power series in $\hat{u}_j{}^\alpha$ with the corresponding term $\hat{H}_1$ added to $\hat{H}_0$. This contribution to the Hamiltonian is

$$\hat{H}_1 = \sum_j \varphi(\vec{R}_j) + \sum_j \varphi^\alpha(\vec{R}_j)\hat{u}_j{}^\alpha + \sum_j \tfrac{1}{2}\varphi^{\alpha\beta}(\vec{R}_j)\hat{u}_j{}^\alpha \hat{u}_j{}^\beta +, \ldots . \tag{3}$$

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

$$\hat{H} = E_L + \tfrac{1}{2}\sum_{\vec{q},l} \hbar\omega_l(\vec{q}) + \sum_{\vec{q},l} \hbar\omega_l(\vec{q})\hat{a}_{\vec{q},l}{}^\dagger + N\sum_{\vec{\tau}}\sum_{\vec{G}} \varphi_{\vec{G}}\delta_{\vec{G},\vec{\tau}} + i\sqrt{N}\sum_{\vec{q},l} (g_{\vec{q},l}\hat{a}_{\vec{q},l} - g_{-\vec{q},l}{}^*\hat{a}_{-\vec{q},l}{}^\dagger), \tag{4a}$$

$$g_{\vec{q},l} = \sum_{\vec{\tau}}\sum_{\vec{G}} \varphi_{\vec{G}} G^\beta \epsilon_l{}^\beta(\vec{q})\delta_{\vec{G}+\vec{q},\vec{\tau}} \left[\frac{\hbar}{2M\omega_l(\vec{q})}\right]^{1/2} = -g_{-\vec{q},l}{}^*. \tag{4b}$$

The ground state of the Hamiltonian in Eq. (4a) is characterized by nonzero values for $\langle \hat{a}_{\vec{q},l}{}^\dagger \rangle$ and $\langle \hat{a}_{\vec{q},l} \rangle$, the average values of the phonon creation and destruction operators. These averages are easily calculated in a number of ways. For example, one may minimize the ground-state energy as a function of these averages. An immediate consequence of $\langle \hat{a}_{\vec{q},l}{}^\dagger \rangle$ and $\langle \hat{a}_{\vec{q},l} \rangle$ being nonzero is a static displacement of the atoms in the monolayer from their ideal-lattice sites. This static displacement is just $\langle \hat{u}_j{}^\alpha \rangle$, the average value of $\hat{u}_j{}^\alpha$. If the substrate lattice is now assumed to have an inversion symmetry about the point $\vec{r} = \vec{\Delta}$, then the Fourier coefficients can be written as $\varphi_{\vec{G}} = \bar{\varphi}_{\vec{G}} \exp(-i\vec{G}\circ\vec{\Delta})$ where $\bar{\varphi}_{\vec{G}}$ is real and symmetric in $\vec{G}$. After some simplification, the $\langle \hat{u}_j{}^\alpha \rangle$ can be written as

$$\langle \hat{u}_j{}^\alpha \rangle = \sum_{\vec{G},l} \epsilon_l{}^\alpha(\vec{G})\eta_l(\vec{G}) \sin[\vec{G}\cdot(\vec{R}_j - \vec{\Delta})], \tag{5}$$

$$\eta_l(\vec{G}) = \left[\frac{\bar{\varphi}_{\vec{G}} G^\beta \epsilon_l{}^\beta(\vec{G})}{M\omega_l{}^2(\vec{G})}\right], \tag{6}$$

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 static displacement of the atom at the jth site 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 $N\sum_{\vec{G}}\sum_{\vec{\tau}}\varphi_{\vec{G}}\delta_{\vec{G},\vec{\tau}}$ is zero for incommensurate lattices. The strain energy it costs to produce the SDW phase is $N\sum_{\vec{q},l}\hbar\omega_l(\vec{q})\times\xi_{\vec{q},l}{}^*\xi_{\vec{q},l}$, where $\xi_{\vec{q},l}=ig_{\vec{q},l}{}^*/\hbar\omega_l(\vec{q})=\xi_{-\vec{q},l}{}^*$ and the corresponding adatom-substrate potential-energy term is $\sum_j\varphi^\alpha(\vec{R}_j)\langle\hat{u}_j\rangle$. Since the second-order terms in $\varphi(\vec{r})$ 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

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

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 the two reciprocal lattices oriented at some angle, with $\theta=0$ being the $\sqrt{3}\times\sqrt{3}$ superlattice orientation. The SDW energy term has its largest negative value when the $\eta_l(\vec{G})$ are largest. At what angle this occurs 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 vector $\vec{q}=\vec{G}-\vec{\tau}$ which defines the mode. This term favors long-wavelength distortions. 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 $\omega_l{}^2(\vec{q})$ term tends to align the lattices at $\theta=0$, since that minimizes q. However, when $\theta=0$, only longitudinal modes can contribute. Thus the minimum energy is found at some nonzero value of θ, allowing contribution of transverse modes to the distortion.

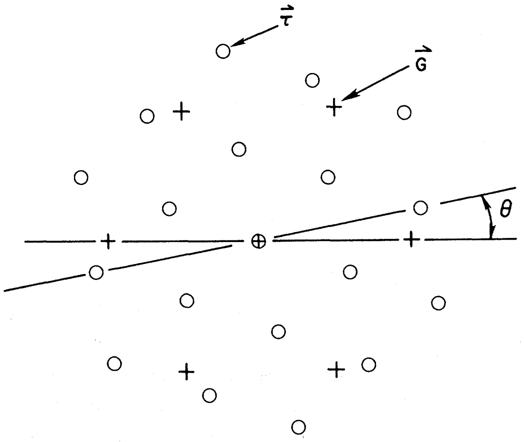

FIG. 1. The reciprocal-lattice vectors $\{\vec{\tau}\}$ for the monolayer lattice and $\{\vec{G}\}$ for the graphite lattice. The angle θ is the angle of rotation relative to the superlattice orientation.

The simplest, and most studied, experimental systems are rare-gas monolayers on the graphite (001) surface,[6] whose interactions are to a good approximation pairwise additive. 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. Argon is of particular interest since both its monolayer structure and lattice dynamics have been measured.[7] We have accordingly made calculations of the SDW phase for these systems, using the known rare-gas–rare-gas Lennard-Jones interactions, as well as the lowest-order Fourier coefficients of Steele's estimated rare-gas–substrate potential.[8] The potential parameters used for this calculation are given in Table I. It is known[7] that these potentials are a reasonable representation of rare-gas–graphite monolayers. The resultant SDW energy as a function of angle is shown in Fig. 2 for both Ne and Ar on graphite. Note that the Ar monolayer is nearly aligned with the $\sqrt{3}\times\sqrt{3}$ superlattice orientation. The minimum energy is at $\theta=3.5°$. This is due to the lattice constant of Ar being close to the superlattice value of 4.26 Å, resulting in a dominance of the $\omega_l{}^2(\vec{q})$ term in Eq. (6). For Ne on graphite, the angle for minimum energy is about 18°. The Ne lattice constant is so far from registry that the $G^\beta\epsilon_l{}^\beta$ term plays a more important role. Thus, the distortions in the Ar solid are mainly longitudinal in nature while the distortions in the Ne solid have large transverse components.

The linear-response calculation predicts orientational epitaxy for the rare-gas monolayers at zero kelvin, even for adsorbate crystallites of

TABLE I. Input parameters for strains.

Adatom	φ_{G_1} for graphite[a] (kelvin)	Atomic mass (amu)	Adatom-adatom ϵ (kelvin)	σ (Å)
Ne	− 3.75	20	35.6	2.78
Ar	− 4.62	36	120.0	3.40

[a] $\vec{G}_1=(0,1)$ is the shortest reciprocal-lattice vector.

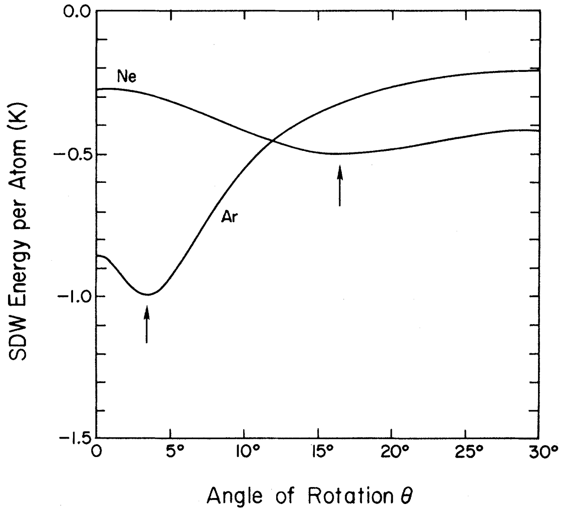

FIG. 2. The energy of the SDW state relative to the energy of the undistorted lattice with the same lattice constant. The arrows locate the angle corresponding to the energy minimum. The lattice constants for Ne and Ar are 3.12 and 3.86 Å, respectively.

infinite extent. The ground state for each of these systems is an incommensurate solid with static-distortion waves. The SDW phase can be viewed as one with periodic dislocations in the ideal-lattice position, the SDW energy terms then causing a rotational locking of one lattice relative to the other. The order parameters for this phase are the $\eta_i(\vec{G})$ terms given in Eq. (6). The total energy associated with this phase would be the energy per particule calculated via (7) multiplied by the number of particles contained in a region with linear dimensions of the order of a coherence length for the solid. Previous treatments of substrate-induced strains[9,10] have either ignored the orientational degree of freedom or have used simplifications in their treatment which cuased the energy minimum to occur invariably at zero angle.

The SDW phase would be observable through two effects. The first would be the orientation of the layer relative to the substrate for incommensurate lattice constants, with the angle of orientation being a function of the lattice constant. We believe this, in fact, has been seen in recent low-energy electron diffraction data for rare gases on homogeneous substrates.[11,12] The most direct observation would be the appearance of satellite peaks around the parent (ideal-lattice) diffraction peaks and the observation of "anomalous" anisotropic Debye-Waller factors. These effects are the clearest signature of the SDW phase and have been observed in bulk systems.[5] They have yet to be observed for monolayer systems.

The nature of the phase transitions for the SDW phase cannot be treated within the linear-response approximation. However, one can speculate on two obvious possibilities. The SDW phase could exist up to the point where the solid "melts," or it could undergo a phase transition before the melting of the solid. The second possibility implies a structural phase transition of the sort observed in bulk incommensurate systems. Because of the continuous range of possible order-parameter values, the SDW-registered transition can in principle be a continuous one. This avenue of research should be one of the more exciting ones in the study of these intriguing incommensurate solids.

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