# Domain-Wall Pinning in Uniaxial Phases of Pb Adlayers on a Cu(110) Surface

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Submonolayers of Pb adsorbed on the Cu(110) surface form a series of uniaxial commensurate phases. We report the results of synchrotron x-ray scattering studies of the global phase behavior of this chemisorption system. We observe a floating-incommensurate to soliton-glass phase transition due to domain-wall pinning. The nature of this transition and other novel features revealed in this study are discussed in the context of current theories for strong adlayer systems.

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The commensurate-incommensurate (CI) transition takes place commonly in physical systems with competing interactions.[1] Recent LEED and x-ray studies[2] of the phase diagram of Pb adlayers on the Cu(110) surface have identified a series of uniaxial commensurate (C) phases formed near monolayer coverage. These C phases undergo characteristic CI transitions as observed previously in other anisotropic systems.[3] But as we explore regions between the C phases a new transition is revealed which is different from but closely related to the CI transition. Below this transition, the phase appears to be in a frustrated state which we attribute to the pinning of domain walls to the substrate as first suggested by Bak and Pokrovsky.[4] Experimental observations of this pinning effect in physisorbed two-dimensional systems, e.g., rare gases on graphite, have not occurred. The phenomenon could take place more commonly in chemisorption systems because of the stronger adlayer-substrate interaction. Its observation is of particular relevance to catalysis and epitaxial film growth. In this Letter, we report the results of our x-ray studies of this frustrated phase in the Pb/Cu system.

The incommensurate (I) phase can be thought of as having domain walls (solitons) that experience both a repulsive interaction decaying with distance and a constant lattice pinning potential (i.e., a Peierls potential).[1] The elementary excitations in the I phase have a branch of soft Goldstone modes which are long-wavelength phonons in the soliton lattice.[5] At high temperature or in a weak potential, the sliding of the walls across the reference lattice costs little energy and the structure is a floating incommensurate (FI) phase with continuous symmetry.[1] When the system enters a state (e.g., by lowering the temperature) where the soliton-soliton repulsive interaction cannot overcome the lattice pinning potential, the soliton lattice can be broken up randomly to form a frustrated disordered state,[4,6] which we call a *soliton glass* (SG). The mean-field estimate of this phase boundary based on an axial next-nearest-neighbor Ising (ANNNI) model has been reported by Jensen and Bak.[6] They argue that near the pinning transition "the energy differences between the various stable states are vanishingly small and the chaotic states are much more abundant." Therefore, such a chaotic state is analogous to a spin-glass phase.[7]

Our experiments employed the grazing-incidence x-ray scattering technique and were performed at the National Synchrotron Light Source on Exxon beam line X10A. We used a newly constructed surface scattering spectrometer which is equipped with UHV surface preparation and characterization capabilities for LEED, Auger, sputtering, and gas handling. The Cu(110) surface was prepared using a typical procedure of $Ne^+$ sputtering, high-temperature $O_2$ treatment, and thermal annealing. The clean surface of the crystal had an in-plane mosaic width of $\sim 0.2°$. The incident x rays were focused with a bent cylindrical mirror and monochromatized with a pair of Ge(111) crystals. The scattered x rays were collimated with a pair of slits. Typical momentum-transfer resolution for our measurements was 0.0025 $Å^{-1}$ FWHM for longitudinal scans.

A schematic of the partial phase diagram of the Pb/Cu system covering the range of our x-ray studies is shown in Fig. 1. The Cu(110) surface forms a trough-like structure along [1$\bar{1}$0]. For Pb adlayers, we find[2] that the adatoms are organized into quasi-one-dimensional chains, in the troughs, whose spacing along [001] is commensurate with the substrate. Along [1$\bar{1}$0] three uniaxial commensurate ($p \times 1$) phases of Pb adlayers are observed with $p = 12$, 9, and 5 (unit-cell dimension $a = 2.556$ Å). The number of Pb atoms per unit cell ($n$) is determined to be 9, 7, and 4 for the (12×1), (9×1), and (5×1) phases, respectively. (Note in Fig. 1 that the measure of the Pb coverage is normalized to the values of $n/p$ of the corresponding C phases.) Therefore, the chains of Pb adatoms simply become more compressed along the troughs as the coverage approaches a saturated monolayer. To prepare an adlayer with a coverage in the incommensurate region, we slowly desorbed Pb at 360 °C from a higher-coverage C phase. All x-ray measurements on phase transitions were made by varying temperature at constant Pb coverage. From these measurements, the temperatures of different transitions, including CI, pinning, and melting transitions, were determined[2] (see Fig. 1). Note in the figure that the boundaries of the three C phases as defined by the Pb

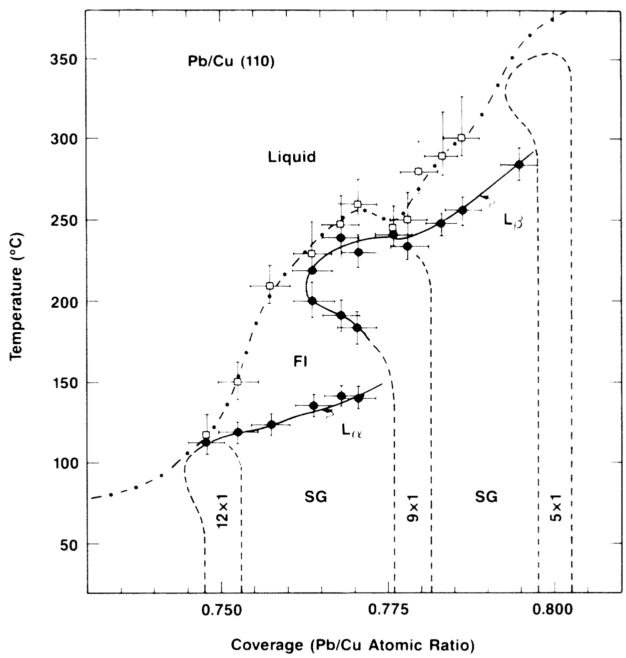


FIG. 1. The coverage-vs-temperature phase diagram of the Pb/Cu(110) system near one-monolayer coverage. Dashed lines defining the commensurate phase boundaries are speculative.

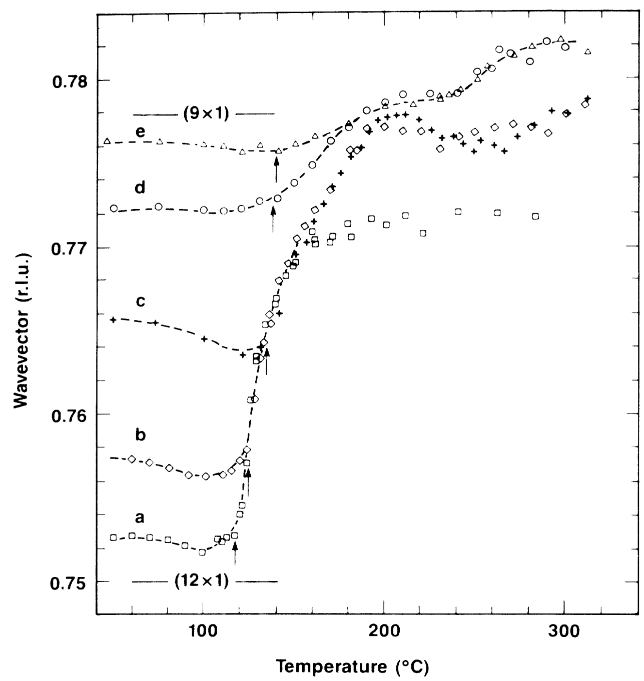


FIG. 2. The observed temperature dependence of the scattering wave vector **q** of the principal reflection from Pb adlayers with different Pb coverages between the (12×1) and the (9×1) phases. Note that the strongest reflection for the (12×1) phase is the ninth order at **q**=0.75 r.l. and that of the (9×1) phase is the seventh order at **q**=0.7778 r.l. The Pb coverages of these curves corresponding to the values in Fig. 1 are about 0.753, 0.757, 0.764, 0.768, and 0.771 for curves *a* through *e*, respectively. Note the staircase character of these curves (see text).

coverage (dashed lines) can only be regarded as rough estimates due to limited experimental accuracy in measuring coverage using Auger spectroscopy.

The phase transition of the Pb adlayers was first studied by measuring the shifts of the principal (i.e., strongest) Bragg peak as a function of temperature in the longitudinal (i.e., [1$\bar{1}$0]) direction. (No change was observed in the transverse direction for the transitions discussed in this paper.) Figure 2 shows the results of a series of such measurements taken for coverages between the (12×1) and the (9×1) phases. In a wide coverage-temperature range, these curves reveal several regions where the wave vectors are independent of temperature, suggesting that the Pb adlayer locks into a sequence of phases as the temperature is varied. Taking curve *d* of Fig. 2 (for coverage $n/p \sim 0.768$) as an example, there are three plateaus observed at ~0.7723 r.l. for $T<120\,°C$, 0.7785 r.l. for $210\,°C<T<240\,°C$, and 0.782 r.l. for $T>265\,°C$ (r.l. denotes radiation length unit). We note that most plateaus observed do not have rational **q** values which can be assigned to simple C phases. The plateaus observed for any given Pb coverage could be a general characteristic of a "devil's staircase,"[1] but we do not have a physically appealing explanation for them as in other systems (see examples in Ref. 1). Rather, we focus our study here on the *low-temperature lock-in regime* of the phase diagram (see Fig. 2, dashed lines shown as guides to the eye). Details of the FI-to-liquid transition of the Pb/Cu system[8] will be discussed in a separate paper.[2]

Let us consider curves *a*, *b*, and *c* in Fig. 2 as examples. Note the behavior of the wave vector **q** as a function of temperature for $T \lesssim 150\,°C$. The three curves overlay each other over a range from 150 to 130 °C, then each curve locks into a different wave vector. The observed gap between the lock-in **q** and the (12×1) commensurate value **q**=0.75 r.l. is found to be sensitive to coverage. The results of careful scattering studies show that the Pb adlayers in this region have special characteristics which are distinctly different from those of C phases. We designate the region as a SG phase for the reasons discussed below. Using a series of curves as shown in Fig. 2, the temperatures of the pinning transition for different coverages are determined (marked by arrows in Fig. 2) by fitting the observed transitions with the $\frac{1}{2}$-power law of the Pokrovsky-Talapov theory.[5] Jensen and Bak[6] argue that the presence of a gap between the lock-in value (e.g., the value of ~0.756 r.l. for curve *b* of Fig. 2) and the commensurate value of 0.75 r.l. is associated with a state where the adlayer is locked into an infinite number of energetically equivalent highly degenerate states.

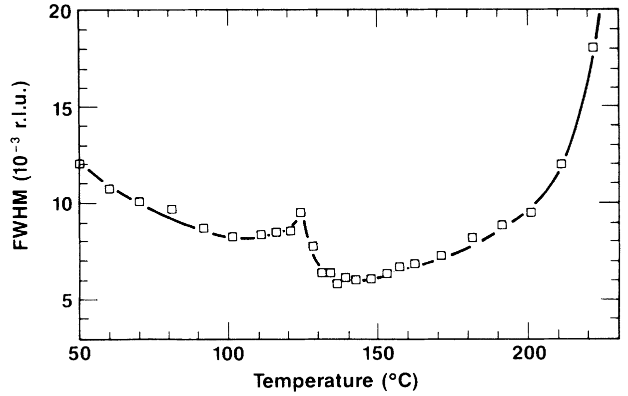


FIG. 3. The measured temperature dependence of the FWHM for curve $b$ of Fig. 2. Note the increased linewidth near and below the transition ($T_c \sim 124\,°C$).

The transition temperatures so determined are plotted as line $L_\alpha$ in Fig. 1 for the region between the $(12\times 1)$ and $(9\times 1)$ phases. Similar measurements (not shown) give line $L_\beta$ for the region between the $(9\times 1)$ and $(5\times 1)$ phases. It is interesting to note the observed steplike increase of the pinning energy by $\sim 120\,°C$ in going through the $(9\times 1)$ phase (see Fig. 1). The steplike behavior is not expected, at least from a continuum model of Villain.[1] In that model, the pinning transition is expected to be a smooth function joining the CI transitions of the C phases. Our experimental result could be due to the fact that the domain walls on two sides of the $(9\times 1)$ phase are of different types. Presumably, the walls on the low-coverage side would be the light-wall type and those on the high-coverage side the heavy-wall type.[9] Some general features in the phase diagram are worth noting. The temperature of the pinning transition seems relatively insensitive to coverage as compared to the melting temperature. Also, there appears to be a reentrant FI-to-C transition on the lower-coverage side of the $(9\times 1)$ phase. A more detailed study of this region of the phase diagram would shed further light on the possible interplay between the pinning,[6] domain-wall wetting,[9] as well as the normal CI transition.

Figure 3 shows the linewidth change with temperature due to the pinning transition shown in curve $b$ of Fig. 2. (For $T > 200\,°C$ the sharp increase of the FWHM is associated with the melting of the Pb adlayer;[2,8] details are not discussed here.) An anomaly in the value of the FWHM for $T < 135\,°C$ is seen, which is closely associated with the lock-in of the wave vector. The FWHM reaches a minimum (corresponding to a coherence length of $\sim 400$ Å) at $\sim 135\,°C$. As the temperature is lowered further, it exhibits a sharp increase with a small peak shown near $T_c$ ($\sim 124\,°C$). The increased FWHM is a direct indication that the system is going into a disordered state. Since the kinetics of the pinning transition was found to be quite slow, the equilibrium values of the

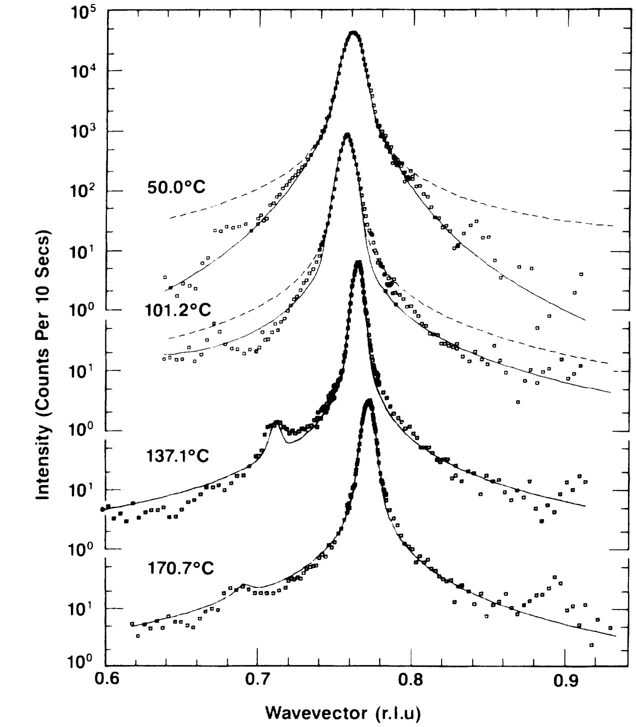


FIG. 4. Typical scattering profiles for the adlayer of curve $b$ of Fig. 2. The power-law structure factor is a good fit for the profiles measured in the FI region [above $124\,°C$; $\eta = 0.16$ ($137.1\,°C$) and 0.19 ($170.7\,°C$)], but a poor fit for the SG region (below $124\,°C$, dashed lines). The profile for the SG phase is better described by the solid lines, which are Gaussian plus Lorentzian or Gaussian plus Lorentzian squared. See text for details.

wave vector (see Fig. 2) and the linewidth (Fig. 3) were obtained by very slow cooling ($\sim 1\,°C$ per 15 min) in the experiment. However, similar equilibrium values were also obtained by fast quenching from the FI (at $130\,°C$) to the SG phase (at $100\,°C$) after a long waiting period ($\sim 2$ h), suggesting that the observed SG phase is a *stable* phase.

In a global sense, the regular CI transition, where the solitons are pinned in registry with the substrate, can be viewed as a special case of a pinning transition. However, there is a subtle difference in the elementary excitations in the two cases as observed in the changes of the scattering profile through the transition. As we discussed at the beginning, one important consequence of the pinning is the loss of the Goldstone modes in the incommensurate adlayer, which can be revealed directly in the scattering profile. Figure 4 shows representative profiles for the adlayer for curve $b$ of Fig. 2. Above $T_c$ ($\sim 124\,°C$), we show that the profiles can be fitted quite well with the structure factor of a 2D harmonic system, which is known to have the power-law decay form $S(q) \sim q^{-2+\eta}$. In our case, finite-size effects need to be taken into account so we follow the derivation of Dutta and

Sinha.[10] Typical results of the analysis are illustrated in Fig. 4. For $T > T_c$, the good power-law fit shows that the adlayer is clearly in the FI state with strong thermal fluctuations of the walls, as similarly seen in the striped phase of the $Br_2$-intercalated graphite system by Mochrie *et al.*[3] As the temperature is lowered below $T_c$, attempts to fit the scattering profiles with the same power-law structure factor generally give very poor results. As the profile is forced to fit near the peak, the observed tails fall significantly below the calculated intensity (dashed curves of Fig. 4). The results of curve fitting using different forms show that for $T < T_c$ the central portion of the profile becomes Gaussian and the tails of the profile evolve first into a Lorentzian (full curve at 101.2 °C, Fig. 4). As temperature is lowered further, the tails become Lorentzian squared (full curve at 50 °C, Fig. 4). The features of the observed profiles in the pinned state agree qualitatively with the simulation results of Jensen and Bak[6] and are similar to those observed in spin glasses.[7] For the soliton glass, the Gaussian plus Lorentzian profile is a direct indication of the loss of the Goldstone mode in the adlayer as the result of domain-wall pinning.[11]

In summary, we have presented the phase diagram of the Pb/Cu(110) system and discussed the global phase-transition behaviors in the context of current theories of chemisorption systems and soliton pinning. Based on observed lock-in behavior and analysis of the x-ray scattering line shape we have identified a floating-incommensurate to soliton-glass phase transition due to pinning of domain walls. The nature of the pinning transition is discussed. We believe that the observed pinning in the Pb/Cu system is general and should be manifested in many other chemisorption systems[12] where the soliton-substrate interaction plays a major role in the phase transitions.

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