PHYSICAL REVIEW B VOLUME 56, NUMBER 11 15 SEPTEMBER 1997-I

Epitaxial rotation of two-dimensional rare-gas lattices on Ag(111)

G. S. Leatherman and R. D. Diehl
Physics Department, Penn State University, University Park, Pennsylvania 16802

M. Karimi
Physics Department, Indiana University of Pennsylvania, Indiana, Pennsylvania 15705

G. Vidali
Physics Department, Syracuse University, Syracuse, New York 13244

(Received 23 January 1997)

Low-energy electron-diffraction results from rare gases adsorbed on Ag(111) are presented. On the clean surface, the rare-gas overlayer lattices are always aligned with the substrate step direction, but when a small amount of a different adsorbate is put on the surface first, the overlayer grows in a rotated orientation at a nonsymmetry angle which depends on the rare gas and its exact lattice spacing and on the preadsorbate. These lattice rotation angles are not those predicted by the Novaco-McTague (NM) theory for epitaxial rotation, nor those predicted by any other model for epitaxial rotation. Molecular statics calculations for Xe/Ag(111) produce results in agreement with the NM prediction, not the experimental results. We speculate that atoms or molecules preadsorbed at step sites play an active role in the equilibrium rotation angles, possibly by changing the corrugation of the charge density in their vicinity. [S0163-1829(97)00435-9]

INTRODUCTION

The rotational epitaxy of incommensurate rare-gas monolayers is an important and conceptually appealing example of the collective behavior of two-dimensional solids. If an incommensurate overlayer of infinite extent were completely rigid, the overlayer atoms would sample all possible sites, and it would have no preferred lattice orientation since changing its angle would have no effect on its total energy. However, an *elastic* overlayer can relax by moving some adatoms toward the minima of the corrugated potential (having the substrate periodicity) experienced by the adatoms. One possible mode for this relaxation involves only longitudinal (compression or expansion) deformations of the lattice, forming nearly commensurate domains which are separated by high- or low-density domain walls. However, another mode of relaxation involves transverse deformations which are energetically advantageous only for overlayer lattices which are rotated with respect to the substrate. Since generally transverse deformations cost less energy than longitudinal deformations,[1] the lowest-energy configuration for an incommensurate elastic overlayer is often a structure which is rotated relative to the substrate.

The theory of the rotation of an elastic overlayer on a rigid substrate was first developed by Novaco and McTague,[2] and was immediately supported by the experimentally-observed rotation of Ar/graphite.[3] Many additional experiments have been performed on the rotation of rare-gas overlayers on graphite, and the theories extended to take into account details such as the effect of nearby commensurate structures[4,5] and anharmonicity.[6] Studies of rare-gas adsorption on metal surfaces, however, have indicated very few nonsymmetry overlayer rotation angles. That is, incommensurate rare-gas overlayers on metal surfaces usually align along a substrate symmetry direction. Such directions are also the likely directions for surface steps, and so the experimental results have usually been interpreted as being due to a pinning of the overlayer by substrate steps. In other words, the collective energy gain afforded by the overlayer rotation is not sufficient to overcome the energy gained by having some adatoms in certain step sites. The reason that this step alignment does not generally occur on graphite is possibly because graphite is easily prepared with very large terraces, and the amplitude of the potential variation experienced by the rare gas compared to the step-pinning energy may be larger on graphite than on many metal surfaces.

The assertion that substrate steps are involved in the alignment of rare-gas monolayers on metal surfaces is supported by He-atom diffraction experiments for rare gases on Pt(111).[7,8] Those experiments demonstrated that the adsorption of impurity atoms at steps influenced the rotational epitaxy of the overlayers, causing it to change from 0° to 30° in the case of Ar, and from 30° to 0° in the case of Kr. It was clearly shown that adatoms at the step sites were required for the rotation to occur, and that adatoms on the terraces alone were not sufficient to cause the rotation. In many ways, however, these observations raised more questions than they answered. It is not clear in the first place why the clean-surface orientation of the overlayer is different by 30° for Ar and Kr. Also, the change of rotation angle from one symmetry direction to another (by 30°) implies that something more than just step blocking occurs. If the steps were blocked, allowing islands to nucleate and grow on terraces, the lattice would in general be expected to be rotated to a nonsymmetry direction, as observed for rare gases on graphite. The true situation however may be considerably more complicated. Scanning-tunneling-microscopy (STM) experiments on Xe/Pt(111) indicate that after filling the upper step sites on a clean Pt(111) surface, the Xe then nucleates islands on the terraces *and* at the lower step edges.[9] Therefore in this case the first atoms which adsorb at the step do *not* nucleate islands. Both the top-step site preference and the non-nucleation at the top steps are attributed to the partially covalent nature of the Xe-Pt bond.[10] The situation for Ar or Kr adsorption might be different; however, these results certainly raise questions about the role of steps and of the preadsorbed impurity atoms in the He-atom diffraction experiments described above.

EXPERIMENT AND CALCULATIONS

The low-energy electron-diffraction (LEED) experiments described here concern the adsorption of rare gases on Ag(111). The lowest crystal temperature available in these experiments is 25 K. For experiments which involve LEED measurements while heating, the heating current is chopped out of phase with the LEED optics suppressor voltage to allow viewing and acquisition of an undistorted LEED pattern while heating. Rare gases were adsorbed by backfilling the chamber, usually to a pressure of 2×10^{-8} mbar. The experiments were performed by monitoring the LEED pattern while dosing gas onto the surface. Lattice spacings and angles were obtained from the positions of diffraction spots. The average transfer width of the LEED instrument for these measurements was about 120 Å.

Supporting molecular statics calculations were performed for Xe/Ag(111). The lattice included a three-layer slab of Ag(111) over which a single circular island of Xe was placed. Each Ag layer had 1600 atoms and the Xe island had 168 atoms. Periodic boundary conditions were employed along the *x* and *y* directions parallel to the surface of the slab. The interatomic interactions between various atomic species were employed using the following models. The Xe-Xe interaction was constructed using the X2 pair potential of Barker[11] supplemented by the substrate-mediated interaction due to the presence of the substrate.[12] The Xe-Ag interaction was considered to be a Lennard-Jones (LJ) pair potential. Parameters of the LJ pair potential were determined by fitting the well depth and position of the minimum of the lateral potential to previously-determined values for a Xe atom on an Ag(111) surface.[13] The Ag-Ag potential was modeled using the embedded atom method.[14]

RESULTS

Ar, Kr, and Xe monolayers on Ag(111) are incommensurate.[15,16] Our equilibrium experiments on the adsorption of these gases onto clean Ag(111) yielded results for structural properties and heats of adsorption[17] which were in agreement with the earlier results of Unguris *et al.*[15,16] Like the incommensurate Ar and Kr overlayers on Pt(111), rare-gas overlayers on Ag(111) are always aligned along a symmetry direction of the substrate. In this case, the direction is always the 0° direction (i.e., the overlayer unit cell is aligned with the substrate unit cell) which is the direction of the most common substrate steps,[18] leading to the conclusion that the rotation angle of the rare gases is pinned by the substrate steps. Figure 1(a) shows a LEED pattern and a azimuthal intensity profile for Xe adsorption on Ag(111) at 40 K. There is considerable azimuthal smearing of the overlayer spots which is the expected result of the step meandering commonly observed by STM on metal surfaces.[18] However, when a small amount of impurity atoms is preadsorbed, the rotation angle of the subsequently adsorbed rare-gas overlayer is a well-defined (i.e., not azimuthally smeared), non-symmetry angle of the substrate.

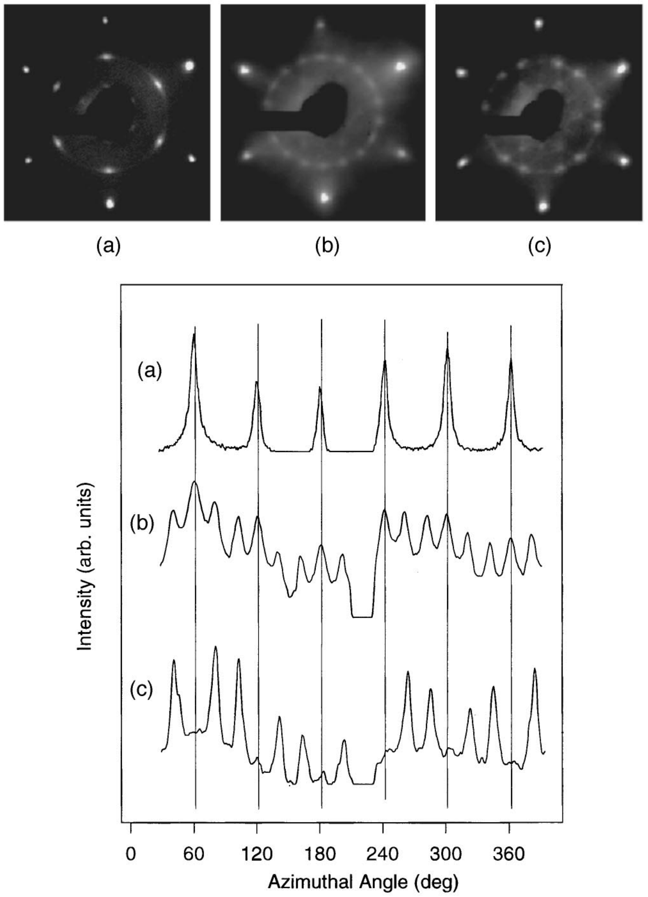

FIG. 1. LEED patterns and azimuthal intensity profiles for Xe adsorption on Ag(111). Panels (a) show Xe adsorption on clean Ag(111) at 40 K. The outer six spots are due to the Ag(111) substrate, the six inner smeared spots are due to Xe. The azimuthal profile is taken through the six Xe spots. The azimuthal smearing shows up as tails on the peaks. Panels (b) show the same thing for 0.02 precoverage of K. Panels (c) are for 0.04 precoverage of K. The monolayer saturation coverage for K is 0.40. The overexposed substrate spots and high background intensity are due to the large gain required to image the relatively weak Xe scattering.

Figures 1(a) and 1(c) show the LEED patterns obtained for Xe adsorption on Ag(111) which has a small amount of preadsorbed potassium. At a 0.02 potassium precoverage (coverage is defined as the ratio of the number of overlayer atoms to top-layer substrate atoms) there are two Xe rotated angles present, at 0° and ±19°. At 0.04 coverage, all of the Xe is rotated along the ±19° direction. Note that the diffraction spots from the rotated phase are not smeared azimuthally. Similar results were obtained for Ar or Kr adsorption on Ag(111) and K-precovered Ag(111), except that the rotation angles were different. In addition, the rotation angle was found to vary with the lattice parameter for each gas studied. The observed rotation angles of the rare-gas overlayers as a function of their lattice spacings are shown in Fig. 2. (The lattice spacings are varied by changing the sample tempera-

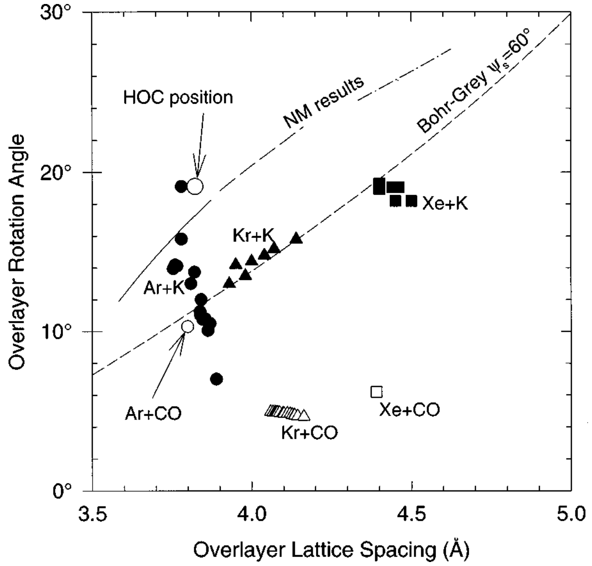

FIG. 2. Graph showing the rotation angles for Ar, Kr, and Xe on Ag(111) for small precoverages of K. The circles denote Ar, the triangles denote Kr, and the squares denote Xe. Also shown are three short curves which represent the results of Novaco-McTague calculations for each of the three gases. The dashed curve which goes generally through the experimental results is a Bohr-Grey trajectory which corresponds to fixing the overlayer domain walls at an angle of 60°. HOC denotes the location of the $(\sqrt{7}\times\sqrt{7})R19.1°$ higher-order commensurate phase. Rotation angles for CO preadsorption are also shown.

ture or the ambient pressure of the adsorbing gas.) Other properties of these overlayers such as thermal-expansion coefficients and desorption temperatures were identical to those found on the clean surface.

The molecular statics calculations indicated that the total energy of the system has two minima with respect to the rotation angle of the Xe island. One is at 0° (the aligned direction) and the other is at 25°±4°.

DISCUSSION

The results described above indicate that the preadsorption of a small amount of K causes some orienting field to overcome the step-pinning energy for the adsorbed rare gas. A simple interpretation of these results is that the K blocks the Xe adsorption at step sites, allowing the Xe to nucleate on terraces and to grow in an orientation which is determined largely by the lattice mismatch of the overlayer and substrate. Rare gases adsorbed on Ag(111) are prime candidates for the application of the Novaco-McTague (NM) theory for rotational epitaxy because the corrugation of the adsorption potential is small, and there are no nearby low-order commensurate phases.[19] We have performed NM calculations[20,21] for each of the rare gases adsorbed on Ag(111), assuming Lennard-Jones interactions between the rare-gas atoms. The calculated rotation angles as a function of lattice parameter for each rare gas are shown in Fig. 2 along with the experimental data. While the general trend in the rotation angle is similar to that predicted by the NM theory, the angles are generally about 10° different from the NM predictions. On the other hand, our molecular statics calculation results for Xe/Ag(111) which indicate a rotation angle of about 25° agree well with the NM prediction.

The discrepancy between the experimental results and the calculated NM and molecular statics results is rather large. If we assume that on the clean surface, the overlayer aligns because the step-pinning energy overrides the rotational alignment energy arising from the lattice mismatch, there seem to be only two possible solutions. One is that the first-order NM theory does not accurately describe rare-gas adsorption on Ag(111), and the other is that the preadsorbed K does more than to just block the steps sites to rare-gas adsorption.

Addressing the first, we note that the NM theory was generally reasonably accurate at predicting the rotation angles for the rare gases adsorbed on graphite, except near commensurate phases, where it is not valid because higher-order harmonic terms are more important. The first-order NM theory would be expected to be even more applicable to adsorption on Ag(111) than to adsorption on graphite since the corrugation of the substrate potential is smaller.[12] We have previously compared the first-order NM theory to the rotation of incommensurate alkali-metal overlayers on Ag(111), where the substrate is known not to satisfy the rigid substrate condition of the calculations, and we found generally better agreement than that presented here for the rare gases.[22,23] The fact that the molecular statics calculation results for Xe also agree with the NM calculations provides further evidence that NM model should be accurate for rare-gas adsorption on the flat surface. Therefore we conclude that even though the overlayers are not aligned with the steps, their rotation angles are still affected by the steps or by some other surface defects.

Figure 2 also shows a curve calculated according to the Bohr-Grey criterion that the overlayer domain walls remain pinned along a symmetry direction, in this case 60° relative to the substrate. The Bohr-Grey (BG) model[24] is a geometrical model which predicts several rotation angles (depending on the pinning direction) for each lattice misfit, but it does not predict which angle has the lowest energy; indeed, another Bohr-Grey trajectory is very close to the NM curves shown. The BG curve that we show corresponds to the domain walls aligning along a direction 60° from the substrate 0° alignment. The fact that this BG curve goes through the experimental data is suggestive that it has some relevance to the observed behavior. However for Ar and Xe the agreement appears to be accidental since thermal expansion of the overlayers leads to trajectories which are nearly perpendicular to the BG curve. In general the BG model is most applicable to systems with narrow domain walls and has been shown to be valid in the case of D_2 adsorption on graphite,[25] for instance. However, since we believe the corrugation of the substrate potential to be very weak in the case of rare gases on clean Ag(111), it would be very surprising if there were strong domain walls.

One possible explanation for the observed rotation effect with K preadsorption is that the corrugation of the substrate potential experienced by the rare gas is significantly changed by the adsorption of K. A large increase in substrate corrugation has been observed before in He-atom diffraction experiments of Pb or Bi adsorption on Cu(001).[26,27] There, a small amount of Pb or Bi atoms adsorbed on the surface led to a tenfold increase in the potential-energy corrugation experienced by the He atoms scattering from the Cu surface, and was attributed to a redistribution of charge in the top Cu layer, possibly due to a relaxation of the top layer. Alkalis are known to cause a large charge redistribution upon adsorption, and we know that K adsorption on Ag(111) causes a significant amount of relaxation of the top-layer Ag atoms, at least in the vicinity of the K atoms.[23,28] Preliminary He-atom diffraction measurements for K/Al(111) indicate that a small amount of K increases the He-atom diffraction. If the substrate corrugation were enhanced in the vicinity of the adsorbed K, then this corrugation might dominate the rotation energy of the rare gas. Molecular-dynamics simulations for small rafts of Xe on Pt(111) indicate that for the case of the compressed incommensurate Xe phase, the rotation angle is insensitive to the amplitude of corrugation.[29] (In that case, also, the molecular-dynamics calculation agreed with first-order NM predictions.) This suggests that if the overlayer rotates because the adsorbed K increases the substrate corrugation, the symmetry of the corrugation must also be changed by the adsorbed K. A change in the symmetry of the corrugation would be expected anyway, since the K atoms do not have the substrate periodicity.

These results raise the question of how alkalis interact with surface steps. Our earlier experiments involving the coadsorption of K and rare gases on Ag(111) showed that the K rare-gas interaction is repulsive at least on the terraces.[30] Experiments of Cs coadsorption with rare gases, on the other hand, indicated an attractive Cs rare-gas interaction at low Cs coverages. For an amount of preadsorbed Cs equal to the amount of K required to cause a complete rotation of the rare-gas overlayer, the rare gas was found to remain aligned. This suggests that the interaction of the rare gases with the Cs atoms adsorbed at steps is attractive, while for K atoms adsorbed at steps it is repulsive.

Calculations for Na on jellium indicate the interaction between Na and steps on jellium are repulsive at the bottom of a step and attractive at the top.[31,32] If the nucleation sites for the rare gas on the clean surface are not the same as the preferred sites for the alkali, then the first alkali on the surface may not block the nucleation of rare gases at steps. This is interesting in view of the amount of K required to cause the full rotation of the rare-gas layers. We find that the amount of preadsorbed K required to obtain full rotation of the overlayer is apparently too large to be just due to the single occupation of step sites by K. A coverage of 0.04 corresponds to about 10% of a saturated K layer. Since the average terrace width on the surface has been determined from diffraction spot profiles to be at least 200 Å, the amount of K required to saturate the steps should be less than 5% of a saturated layer, or a coverage of less than 0.02. This suggests that a significant amount of K is already on the terraces. However, if both upper and lower step sites need to be occupied before the nucleation of rare gas at steps is prevented, then twice as much K would be required. We note that if higher coverages of K were adsorbed, then the rare-gas rotation angles were often quite different, presumably because K on terraces has a different effect from that adsorbed at steps. However, in these experiments we could not determine for sure that the K adsorbs first at step sites since even at the lowest temperature attained (30 K), the K still has a relatively high mobility on the surface, evidenced by its ability to form ordered structures at higher coverages without annealing.

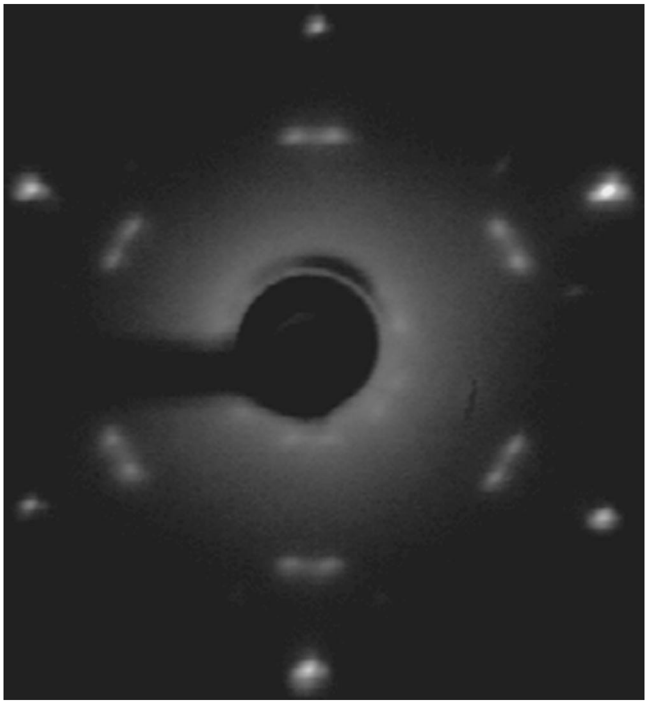

FIG. 3. LEED pattern from Kr adsorption on Ag(111) which has 0.1 L of CO preadsorbed. The outer six spots are due to the substrate. The inner ring of 12 spots is due to scattering from incommensurate Kr which has two equivalent rotational domains (±6 about 5°). The very weak spots near the center are from electrons which are scattered by both the overlayer and the substrate (multiple diffraction).

We end this highly speculative discussion by reporting additional experimental results for similar experiments using (physisorbed) CO as the preadsorbate rather than K. Small amounts of CO (less than 0.1-L exposure at 40 K; saturation corresponds to approximately 2 L) preadsorption also cause the rare-gas layer to form a rotated layer, but at different angles than those found for K preadsorption or from the NM calculation. A LEED pattern for Kr on the CO-preadsorbed surface is shown in Fig. 3. The rotation angles measured were about 12° for Ar, about 5° for Kr, and about 6.5° for Xe. [For Ar, a higher-order commensurate $(\sqrt{7}\times\sqrt{7})R19.1°$ phase was often observed to coexist with the rotated incommensurate phase.] As in the case for K preadsorption, the rotated rare-gas overlayers were identical to those formed on the clean surface aside from their angle. No evidence of mixing with the CO was observed as long as the CO precoverage was very small. In this case, however, variation of the angle with lattice spacing was very small. This suggests that the orientation of these overlayers may also be somehow pinned; however, the overlayer spots are not smeared azimuthally as they are for adsorption on the clean surface, where the overlayer aligns along the step directions.

CONCLUSION

These results provide evidence that adsorbates at steps play active roles in the determination of the equilibrium rotation angles for rare gases on Ag(111). The nature of the interactions of the adatoms with the step sites and/or impurity atoms appears to be very important since different overlayer rotation angles are observed for different preadsorbates. Step blocking appears to be one component of the role of the preadsorbate, but it alone cannot account for our observations. Adatoms on terraces may also affect the rotation angle, possibly due to reducing the overlayer island sizes or by changing the charge density in their vicinity. There are many possible mechanisms for epitaxial rotation (corrugation, size effects, edge effects, etc.) which could be tested by calculations for these systems.

ACKNOWLEDGMENTS

We acknowledge many useful conversations with J. F. Annett, L. W. Bruch, A. D. Novaco, and P. Zeppenfeld. These experiments were supported by NSF Grant Nos. DMR-9022681 and DMR-9629715.

---

[1] H. Kolsky, *Stress Waves in Solids* (Dover, New York, 1963).

[2] A. D. Novaco and J. P. McTague, Phys. Rev. Lett. **38**, 1286 (1977).

[3] C. G. Shaw, S. C. Fain, Jr., and M. D. Chinn, Phys. Rev. Lett. **41**, 955 (1978).

[4] H. Shiba, J. Phys. Soc. Jpn. **46**, 1852 (1979).

[5] H. Shiba, J. Phys. Soc. Jpn. **48**, 211 (1980).

[6] A. D. Novaco (private communication).

[7] K. Kern, P. Zeppenfeld, R. David, and G. Comsa, J. Vac. Sci. Technol. A **6**, 639 (1988).

[8] K. Kern, P. Zeppenfeld, R. David, R. L. Palmer, and G. Comsa, Phys. Rev. Lett. **57**, 3187 (1986).

[9] P. Zeppenfeld, S. Horch, and G. Comsa, Phys. Rev. Lett. **73**, 1259 (1994).

[10] J. E. Müller, Phys. Rev. Lett. **65**, 3021 (1990).

[11] J. A. Barker, R. O. Watts, J. K. Lee, T. P. Schafer, and Y. T. Lee, J. Chem. Phys. **61**, 3081 (1974).

[12] L. W. Bruch and J. M. Phillips, Surf. Sci. **91**, 1 (1980).

[13] G. Vidali, G. Ihm, H.-Y. Kim, and M. W. Cole, Surf. Sci. Rep. **12**, 133 (1991).

[14] M. S. Daw and M I. Baskes, Phys. Rev. Lett. **50**, 1285 (1983).

[15] J. Unguris, L. W. Bruch, E. R. Moog, and M. B. Webb, Surf. Sci. **109**, 522 (1981).

[16] J. Unguris, L. W. Bruch, E. R. Moog, and M. B. Webb, Surf. Sci. **87**, 415 (1979).

[17] G. S. Leatherman, Ph.D. thesis, Penn State University, 1996.

[18] E. B. Budevski, G. T. Staikov, and W. J. Lorenz, *Electrochemical Phase Formation and Growth* (VCH, New York, 1996).

[19] It is actually possible to compress Ar to the lattice parameter of the higher-order commensurate $(\sqrt{7}\times\sqrt{7})R19.1°$ phase, but, in the absence of a coadsorbate, it remains aligned and therefore incommensurate. With preadsorbed K, it will rotate into the higher-order commensurate phase.

[20] These calculations were carried out using a program adapted from one supplied by L. W. Bruch. The basis for the calculation is described in *Physical Adsorption: Forces and Phenomena* (Ref. 21).

[21] L. W. Bruch, M. W. Cole, and E. Zaremba, *Physical Adsorption: Forces and Phenomena* (Oxford University Press, Oxford, 1997).

[22] G. S. Leatherman and R. D. Diehl, Phys. Rev. B **53**, 4939 (1995).

[23] G. S. Leatherman, R. D. Diehl, P. Kaukasoina, and M. Lindroos, Phys. Rev. B **53**, 10 254 (1995).

[24] F. Grey and J. Bohr, in *Phase Transitions in Surface Films*, edited by H. Taub, G. Torzo, H. J. Lauter, and S. C. Fain (Plenum, New York, 1991), p. 83.

[25] J. Cui, S. C. Fain, Jr., H. Freimuth, H. Wiechert, H. P. Schildberg, and H. J. Lauter, Phys. Rev. Lett. **60**, 1848 (1988).

[26] W. Li and G. Vidali, Phys. Rev. B **46**, 4356 (1992).

[27] W. Li and G. Vidali, Surf. Sci. **287/288**, 336 (1993).

[28] P. Kaukasoina, M. Lindroos, G. Leatherman, and R. D. Diehl, Surf. Rev. Lett. (to be published).

[29] J. E. Black and P. Bopp, Surf. Sci. **182**, 98 (1987).

[30] G. S. Leatherman and R. D. Diehl, Surf. Sci. **380**, 455 (1997).

[31] G. Welsh and J. F. Annett, Phys. Rev. B **49**, 13 921 (1994).

[32] G. Welsh, Ph.D. thesis, Penn State University, 1994.