Scanning Tunneling Microscopy Observation of Phase-Transition Phenomena in the Cs/Cu(110) System: Evidence for a Two-Step Disordering Mechanism of a Uniaxial (1 × 3) Phase

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The disordering of the uniaxial Cs/Cu(110) (1×3) phase was studied by scanning tunneling microscopy as a test case for the theoretical predictions of a two-step disordering mechanism. Lowering the Cs coverage first causes the formation of domain walls in the (1×3) phase, indicating a transition from a two-dimensional commensurate solid into an incommensurate floating solid. Dislocations in this wall pattern lead to progressing disordering into an incommensurate fluid. Further coverage reduction stabilizes fluctuating domains of a (1×4) phase, which signal a close by continuous solid to fluid transition.

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The study of continuous phase transitions in two dimensions is a subject of current interest. In a number of mostly physisorption systems such as Kr on graphite [1], but also a few more strongly bound adsorbate systems, e.g., Pb on Cu(110) [2], the transitions between commensurate, incommensurate, and fluid phases were studied experimentally. Theoretical progress, on the other hand, led to the development of phase diagrams and definite concepts for the structural evolution of these transitions. Simple models, e.g., the two-dimensional anisotropic next-nearest-neighbor Ising model [3], were analyzed in view of the microscopic processes involved in the phase transitions. Comparison between experiment and theory has, however, been largely restricted to macroscopic parameters such as critical exponents [4] while only few reports on the use of direct imaging techniques such as electron microscopy [5] or scanning tunneling microscopy (STM) [6,7] can be found in the literature. The latter technique offers the possibility of atomic scale observations of the structural changes involved in the respective phase transition.

In this paper we present STM observations of thermodynamic equilibrium configurations in the vicinity of a uniaxial, commensurate (1×3) phase formed on a Cu(110) surface by Cs adsorption at room temperature, which give direct insight into the mechanism of disordering in these transitions. Lowering of the Cs coverage from its ideal value for the (1×3) phase ($\theta=0.13$) [$\theta=1$ corresponds to one Cs atom per Cu atom in the topmost Cu(110) (1×1) surface layer] causes the formation of domain walls with local (1×4) periodicity. The domain walls form a phase with a very regular sequence of (1×3) domains, in which the order perpendicular to the walls is partly preserved. Such phase transitions of uniaxial $(1\times p)$ phases have been the subject of many theoretical investigations dealing with local phase diagrams and disordering mechanisms for these transitions. By use of the free fermion approximation [8] and other analytical and numerical methods [9] a two-step disordering mechanism for a uniaxial (1×3) phase has been proposed: If, for instance, in a chemisorption system the adsorbate coverage deviates from its value for the perfect (1×3) phase, the latter (which represents a commensurate solid) at first undergoes a continuous transition into an incommensurate floating solid. Domain walls develop, which separate undistorted (1×3) domains and thus form a very regularly striped pattern. The regular distribution of domain walls, formed during this Pokrovsky-Talapov transition [10] leads to an algebraically decreasing density-density correlation [11], in contrast to an exponential decrease associated with a disordered fluid phase. Incommensurate wave vectors in the density-density correlation function arise from the antiphase domain boundaries formed by the walls. Only in a second step, upon larger deviation of the coverage from its value for the commensurate phase, the regular arrangement of domain walls is destroyed by the formation of free dislocations. (Dislocations are characterized by a nonvanishing Burgers vector.) The incommensurate floating solid undergoes continuous disordering of Kosterlitz-Thouless type [12] into an incommensurate fluid with exponentially decreasing density-density correlation. This second disordering step is also indicated in the STM images: Apart from kinks in the wall pattern, also dislocations, where three walls merge, have been identified and are thought to represent low-energy excitations of the wall pattern. For the (1×3) phase, studied here, the STM observations strongly support the outlined scenario for the disordering mechanism.

The experiments were performed at room temperature with a pocket size STM, incorporated in a UHV chamber (base pressure 10^{-10} mbar) with standard facilities for sample preparation, LEED and Auger spectroscopy (AES). Experimental details are described elsewhere [13]. Cs was deposited from a commercially available SAES getter source at room temperature up to the desired coverage. The coverage was determined by AES with an accuracy of $\Delta\theta \approx \pm 0.01$ from the *MNN* transition at 563 eV of Cs, whereby calibration of the absolute coverage was achieved on the basis of $\theta=0.13$ for the (1×3) phase, in accordance with Ref. [14].

Figure 1 shows an STM image of the almost perfectly (1×3) reconstructed surface at $\theta=0.13$. The structure is of missing-row type, where every third Cu $[1\bar{1}0]$ row has been removed and where these troughs are filled with Cs atoms instead. These (Cs filled) troughs are imaged as protrusions, which show up as bright lines along $[1\bar{1}0]$. The formation of these rows was studied recently for the very similar K/Cu(110) system [7,13]. In that study it was demonstrated that the reconstruction proceeds via the formation of local nuclei, consisting of one alkali-metal atom, located in a hole, which is formed by the removal of two to three Cu atoms out of the $[1\bar{1}0]$ row of the substrate. These nuclei interact via a net attractive force in the $[1\bar{1}0]$ direction and by repulsion between neighboring adsorbate-substrate dipoles in all other directions. These anisotropic interactions lead to the stabilization of reconstructed (1×3) and (1×2) phases of missing-row type at potassium coverages of $\theta=0.13$ and $\theta=0.2$, respectively. In LEED investigations Cs was shown to exhibit quite similar behavior [14,15], as further substantiated also in this work. Only few defects are discernible in Fig. 1, where single nuclei are shifted in the [001] direction. Along $[1\bar{1}0]$, being also the slow scan direction of the STM, these defects extend mostly only one horizontal scan line, indicating short lifetimes of the order <0.25 s. The defects represent thermal excitations of the reconstruction and reflect the mobility of single nuclei in this phase on a time scale of several seconds. Hence, similar to K/Cu(110), the shown STM images represent thermal equilibrium configurations of the reconstruction pattern [7].

A slight decrease of the coverage leads to the formation of domain walls [Fig. 2(a), $\theta=0.12\pm0.01$]. The walls consist of local (1×4) units, where two Cs-filled troughs, imaged as bright strings, are separated by three $[1\bar{1}0]$ Cu rows. The walls hence separate two translational domains of the (almost perfect) (1×3) phase, which are shifted apart from each other by one lattice constant of the Cu substrate. In the $[1\bar{1}0]$ direction the walls terminate at the edges of the terrace and no influence of the steps on the walls is discernible. Also a defect, imaged as a white dot, has no considerable influence on the wall distribution. The walls exhibit sudden cutoffs in the horizontal direction indicating again the mobility of the reconstruction pattern. Apart from kinks only very few dislocations in the wall pattern are formed: A free dislocation is marked by a circle in Fig. 2(b). At this point three adjacent (1×4) walls merge and terminate amidst the terrace. Paired dislocations, as shown in Fig. 2(c), are formed, too, to a minor extent: Three adjacent (1×4) walls are visible amidst a (1×3) domain. Apart from various kinks in the walls a dislocation has evolved at each end of the wall pattern (marked by circles). On the

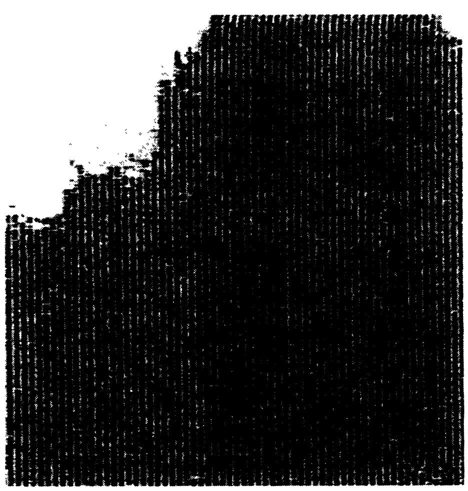

FIG. 1. STM image of the (1×3) missing-row reconstructed Cu(110) surface ($\theta=0.13$; 690×690 Å); the Cs-filled troughs are imaged as protrusions.

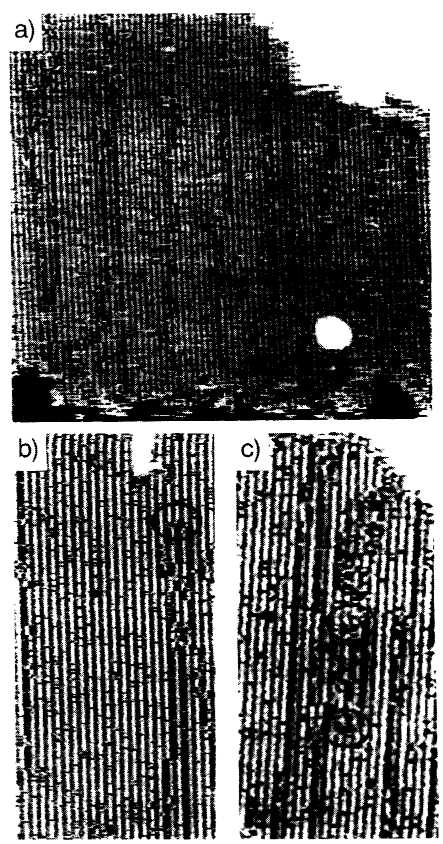

FIG. 2. (a) STM image at $\theta=0.12$ (795×800 Å); (1×3) domains are separated by walls, exhibiting local (1×4) structure (the Cs-filled troughs of the reconstruction are imaged as protrusions). The very regular sequence of domain walls supports the identification of this phase as a floating solid. (b),(c) Single and paired dislocations of the wall pattern at $\theta=0.12$; the dislocations are marked by circles.

average less than 5% of the walls are involved in such dislocations.

The existence of domain walls in Fig. 2(a) signals the location in the incommensurate region of the phase diagram: Because of the (1×4) domain walls the LEED extra spots are shifted in the (01) direction, form the $(0\,\frac{1}{3})$ positions of the perfect (1×3) phase towards the $(0\,\frac{1}{4})$ position. Indeed, LEED patterns, calculated by a two-dimensional Fourier transform of the STM image in Fig. 2(a) exhibit intensity maxima with wave vectors of $2\pi/3.2d$ (d is the lattice constant of the Cu substrate: 3.61 Å).

Figure 2(a) demonstrates that the minute deviation of the coverage from its value for the perfect (1×3) phase causes the development of domain walls. A rather regular sequence of translational domains with an average width of 54 Å (determined from the evaluation of 14 STM images with 170 walls) has evolved. This sequence extends over distances of more than 1000 Å in the [001] direction without substantial distortion. The existence of only few dislocations, as seen in Figs. 2(b) and 2(c), indicates that the striped phase is rather stable against these excitations of the wall pattern. However, from our experiments it cannot be definitely concluded whether Fig. 2(a) represents exactly the incommensurate floating solid, which is expected theoretically in the vicinity of the (1×3) phase. The finite width of the terraces, i.e., the limited maximum correlation length, prohibits a statistical evaluation of the STM images, which would be required to evaluate the decay of the correlation function. But the stability of the wall pattern gives strong evidence that the (1×3) phase is destroyed with decreasing coverage by the formation of domain walls, as expected for a commensurate-incommensurate transition of the Pokrovsky-Talapov type. It should be noted that in principle a direct transition from a commensurate solid to an incommensurate fluid cannot be excluded theoretically for a (1×3) phase with small chirality [16] and was observed recently for the (3×1) reconstruction of Si(113) [17]. The transition was observed to behave consistently with the three-state chiral Potts universality class. However, despite the rather large area, observed by STM, only (1×4) walls were found at $\theta=0.12$, which gives further support for a commensurate-incommensurate transition of Pokrovsky-Talapov type for the system investigated here. Also no indication for possible first-order transitions, i.e., phase separation or Ostwald ripening, could be found.

Upon further reduction of the coverage to $\theta=0.11\pm0.01$ more of the (1×4) periodicities form and the number of defects increases substantially. ["Defect" denotes here an imperfection amidst a (1×3) domain or a wall, where single nuclei are missing.] (1×3) and (1×4) periodicities are distributed randomly and the long-range order in [001] is definitely destroyed. Calculated LEED patterns of such structures exhibit broadened intensity maxima between $(0\,\frac{1}{4})$ and $(0\,\frac{1}{3})$ positions, as also observed experimentally. The patterns, formed at $\theta=0.11$ therefore belong to the incommensurate disordered region of the phase diagram. The distinct disordering mechanism from the floating solid into a fluid upon reduction of the coverage could not be identified. However, Figs. 2(b) and 2(c) demonstrate the significance of dislocations for the destruction of the wall pattern and its transition into a fluid phase: The spontaneous formation of free dislocations drives a transition of Kosterlitz-Thouless type from an incommensurate floating phase into an incommensurate disordered one. The unbinding of the paired dislocations, such as in Fig. 2(c), i.e., when the two dislocations move apart from each other in the direction of the terrace edges, would indeed lead to a small array of (1×4) and (1×3) periodicities. The occurrence of dislocations as the lowest excitations (after kinks) of the wall pattern is fully consistent with the theoretical ansatz of free fermions to describe the domain walls and their disordering (see, e.g., [18] for further references). In contrast to the study of the K/Cu(110) system, the Cs/Cu(100) system provides a much more convincing test case for the two-step disordering mechanism of the (1×3) phase. In particular, the occurrence of only one type of wall in Fig. 2(a), and the undistorted domain wall pattern extending over more than twenty walls, i.e., about 1500 Å, renders its identification as floating solid much more obvious than was possible with the K/Cu(110) system.

At $\theta=0.09\pm0.01$ the lowering of the coverage has led to progressive ordering of the nuclei into fairly large domains of a (1×4) phase (Fig. 3) (the Cs-filled troughs are imaged as bright protrusions). These are separated by small disordered areas, exhibiting (1×3) and (1×5) periodicities. The two images in Fig. 3 show the temporal evolution of the domain pattern over a period of 200 s. Despite considerable fluctuations of the domain boundaries, no further ordering into larger (1×4) domains was discernible during the whole period of observation of about 4 h. The average size of the domains remains constant and is about 100 Å in the [001] direction. Closer inspection shows that the disordered areas mostly represent antiphase boundaries between (1×4) domains without any decisive preference for a distinct wall type; i.e., no regular sequence of (1×4) domains can be found. Hence there is no long-range order: Figure 3 illustrates a fluid phase with no detectable dominance of one type of domain wall, indicative of very small or vanishing chirality. This, together with the rather large domain sizes and their strongly fluctuating nature, signals a nearby commensurate (1×4) phase at lower temperature. Whether the transition into this (1×4) phase occurs via a two-step mechanism as outlined above for the (1×3) phase or via a direct transition from a commensurate solid into an incommensurate fluid, which should be possible for small enough chirality [16], cannot be decided here. The occurrence of fluctuating domains, rather than the forma-

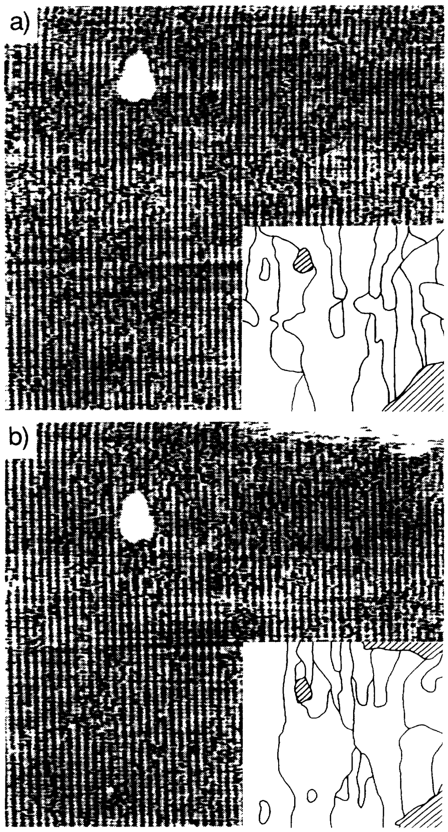

FIG. 3. STM images at $\theta=0.09$ (795×795 Å); domains of a (1×4) are revealed, separated by small disordered areas, indicating that this image belongs to the incommensurate fluid phase. The Cs-filled troughs are imaged as protrusions. The inset gives a sketch of the domain structure; defects and steps are hatched. The time interval between (a) and (b) is 200 s.

tion of islands of a (1×4) phase amidst disordered areas signals, however, a continuous transition from a (commensurate or incommensurate) solid into the liquid phase [19].

In conclusion we were able to follow the disordering mechanism in a continuous, uniaxial phase transition by direct observation. STM images recorded on Cs covered Cu(110) in the vicinity of the (1×3) phase, in the transition regime between commensurate and incommensurate regions of the phase diagram, confirm predictions of a two-step disordering mechanism derived from theoretical considerations. In particular the data strongly support the idea of a wall driven commensurate-incommensurate transition of Pokrovsky-Talapov type at the low coverage side of the (1×3) phase. They equally confirm the proposed mechanism for subsequent wall destruction via formation of free dislocations as local excitations of the wall pattern.

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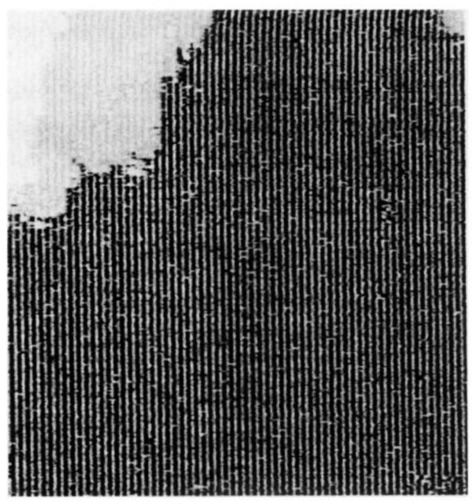

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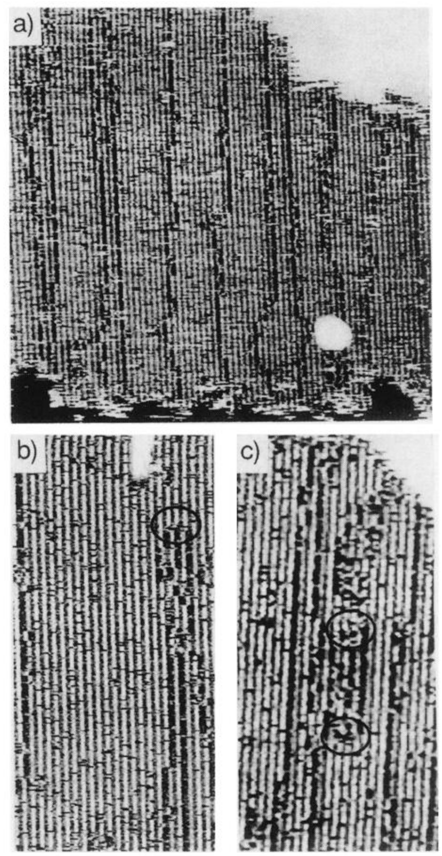
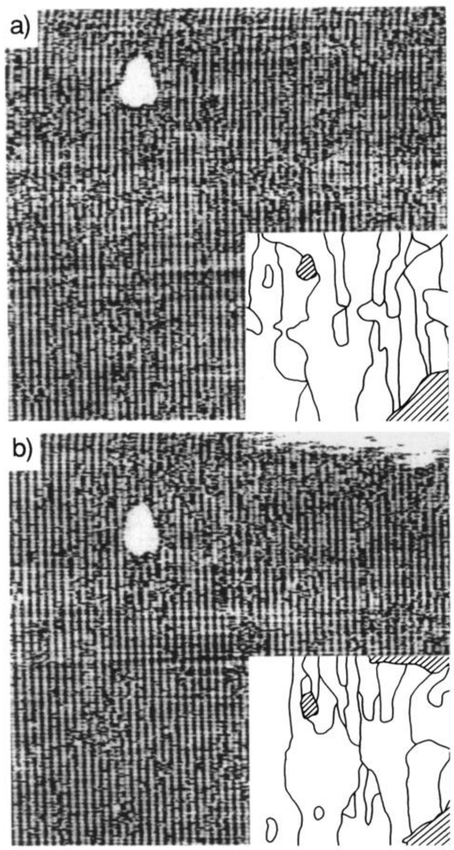


FIG. 2. (a) STM image at $\theta = 0.12$ (795×800 Å); (1×3) domains are separated by walls, exhibiting local (1×4) structure (the Cs-filled troughs of the reconstruction are imaged as protrusions). The very regular sequence of domain walls supports the identification of this phase as a floating solid. (b),(c) Single and paired dislocations of the wall pattern at $\theta = 0.12$; the dislocations are marked by circles.



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