

Fluctuations and phase separation in Br/Pt(110)

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Abstract

The quasi-one-dimensional system $c(2 \times 2)$ -Br/Pt(110) is investigated by low-energy electron diffraction (LEED) spot-profile analysis and by variable-temperature scanning tunnelling microscopy (VT-STM). An order–disorder transition is found at 375 K. For $250 \text{ K} < T < 375 \text{ K}$ a long-range ordered $c(2 \times 2)$ phase is observed, but the spot profiles reveal strong correlated fluctuations along the close-packed row direction. At $T = 50 \text{ K}$ three different phases coexist in a glassy state: $c(2 \times 2)$, (2×1) , and (3×2) . The loss of long-range order and transition into a phase-separated state is a common feature predicted for strongly correlated systems. Some inconsistencies between theory and experiment in our previous interpretation of the (3×1) -Br/Pt(110) phase as a charge density wave (CDW) are resolved by identifying it as a fluctuating (3×2) CDW phase.

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1. Introduction

The adsorbate system Br/Pt(110) exhibits a rich and very interesting phase diagram [1]. A phase transition occurring close to half monolayer coverage (here the monolayer is defined by the atom density of the bulk terminated Pt(110) surface) from a $c(2 \times 2)$ to a (3×1) structure has been argued by the present authors to be linked with the formation of a charge density wave [2]. The $c(2 \times 2)$ parent phase of the CDW was investigated more closely by spot-profile analysis LEED (low energy electron diffraction) and variable-temperature STM. The surprising result was the presence of one-dimensional fluctuations in the long-range ordered $c(2 \times 2)$ phase over a wide range of temperatures from the disordering temperature (375 K) down to $\sim 250 \text{ K}$. Below 250 K a (2×1) structure appears locally and at 50 K a third structure coexists with the previous ones, resulting in a disordered, striped pattern of $c(2 \times 2)$, (2×1) and (3×2) domains.

Disordering upon cooling seems a counter-intuitive phenomenon, but theorists have found it to be generic for systems with competing order parameters close to a quantum phase transition [3,4]. Notable examples are the high-temperature superconductors (HTSCs), where magnetic order and, depending on the doping level, charge order compete with superconductivity. This competition results in the loss of long-range order and a phase separation [5]. Br/Pt(110) is a surface system, where the competition of (at least) two order parameters leads to a strikingly similar behaviour. Lowering the temperature yields a transition from a long-range ordered phase into a strongly fluctuating and finally into an inhomogeneous state. As these transitions occur in a surface system they can be investigated by surface sensitive methods and in particular by direct imaging in scanning tunnelling microscopy (STM).

2. Experimental

The $c(2 \times 2)$ -Br/Pt(110) surface has been shown previously to be strongly anisotropic [6,7]. The $c(2 \times 2)$ phase

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is long-range ordered and well-defined at room temperature. It is obtained at a coverage $\Theta_{\text{Br}} = 0.5$ ML. The experimental procedure for the preparation of the $c(2 \times 2)$ structure has been described in detail previously [1]. Here we just mention that extreme care has to be taken in order to remove traces of carbon not visible in Auger electron spectroscopy from the Pt(110) surface before exposing to Br. This was achieved by repeated cycles of low-temperature adsorption of oxygen onto the conventionally cleaned Pt(110) surface and subsequent thermal desorption. The surface was judged to be really clean only when no traces of CO_2 nor CO could be detected in the temperature programmed desorption (TPD) spectrum after low- T O_2 adsorption. The $c(2 \times 2)$ structure was then prepared by dosing Br from a solid-state electrolysis source. The coverage calibration is described in Ref. [1]. Even a small increase in coverage beyond the 0.5 ML needed for the $c(2 \times 2)$ structure was found previously to result in fluctuations and an apparent (3×1) phase, which we attributed to the formation of a charge density wave (CDW) with three-fold periodicity [2]. The present study was intended to explore the phase diagram as a function of temperature rather than coverage. Here, an experimental difficulty arises from the fact that close to critical temperatures the system is expected to exhibit rapid fluctuations, which are not directly detectable in STM, but give rise to a time-averaged contrast. Therefore, we adopted the analysis of low-energy electron diffraction (LEED) spot profiles as a technique to extract the T dependence of the long-range order parameter and in particular to determine the presence of fluctuations and their correlation length. The procedure [8] is based on the fact that near a critical temperature the structure factor can be decomposed into three components:

$$S(q, T) = I_0(T) \delta(q - q_0) + \chi_0(T) / (1 + \xi^2(T) (q - q_0)^2) + \text{background}$$

here q refers to a reciprocal space vector, q_0 is the centre of the LEED spot, χ_0 is the generalised susceptibility and ξ is the correlation length in the system. The first component is broadened into a Gaussian in any real measurement. The height of the Gaussian describes the temperature dependence of the long-range order parameter. The second part is a Lorentzian function and characterises the fluctuations in the system. The amplitude is a measure for the generalised susceptibility, the width a measure for the correlation length. As the present system is strongly anisotropic, we investigated two orthogonal cuts through the LEED spots, namely, parallel and perpendicular to the close-packed rows.

3. Results and discussion

The result of the LEED spot-profile analysis is shown in Fig. 1. Panel a shows the Gaussian height of integer and fractional order LEED spots, respectively, whereas in panel b the Lorentzian height is displayed. Cuts through the

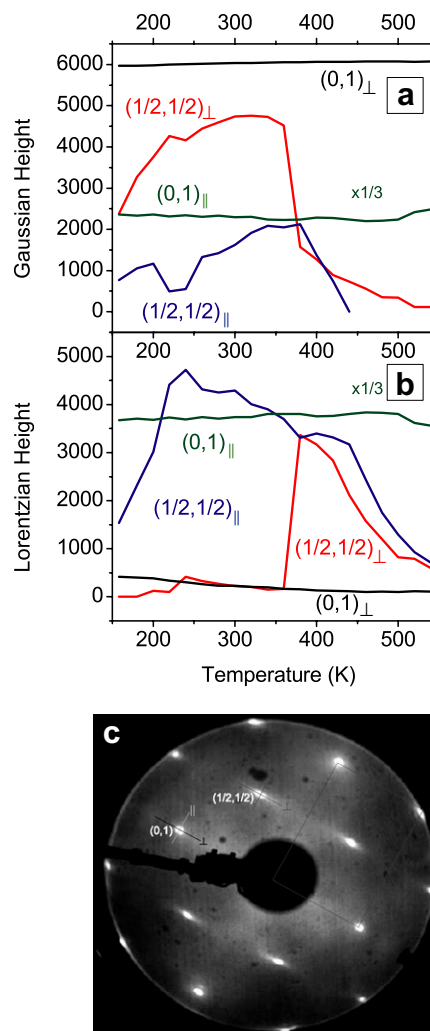


Fig. 1. LEED spot-profile analysis: (a) The height of the Gaussian peak component as a function of temperature for the (0,1) spot is shown in black for a cut perpendicular and in green for a cut parallel to the close-packed row direction. Similarly, for the (1/2,1/2) spot the red curve corresponds to the perpendicular, the blue one to the parallel direction. (b) Same as (a), but for the Lorentzian component of the spot profile. (c) LEED pattern of the $c(2 \times 2)$ -Br/Pt(110) surface obtained at 300 K ($E = 60$ eV). The (1×1) unit cell is shown as a red rectangle, the cuts through the (0,1) and (1/2,1/2) spot, respectively, along which the spot profiles were measured, are indicated.

spots parallel and perpendicular to the close-packed rows are shown. The curves have been rescaled by the Debye–Waller factor so as to remove the uniform slope. The red¹ curves are obtained from a cut through a half-order spot perpendicular to the close packed rows and show a normal order–disorder transition at 375 K with a sudden decay of long-range order (panel a) and accompanying fluctuations around the disordering temperature (panel b). The blue curves are obtained from a cut through a half-order spot parallel to the close packed rows. Although they, too, reflect the disordering temperature at 375 K, the

¹ For interpretation of color in Figs. 1–3, the reader is referred to the web version of this article.

blue curve in panel b does not drop to zero below that temperature, indicating that fluctuations parallel to the rows persist and even grow with temperature decreasing down to 250 K! Interestingly, the integer order spot has also a large Lorentzian component if measured parallel to the rows (green curve in panel b), indicating that the substrate participates in the fluctuations.

From a complete analysis we reached the following conclusions: At 375 K the $c(2 \times 2)$ structure exhibits a regular order–disorder transition featuring a sudden drop of the order parameter, the simultaneous appearance of fluctuations with a correlation length of approximately 150 Å, and a drop-off of both, the fluctuations and the correlation length towards higher temperatures. Below 375 K, LEED as well as STM shows a well developed $c(2 \times 2)$ phase, but the spot profile analysis reveals a hidden dynamics: The structure is perfectly long-range ordered perpendicular to the close-packed rows, however it fluctuates along the close-packed rows throughout the temperature range from 375 K $> T >$ 250 K with a correlation length increasing up to ~ 250 Å at $T = 250$ K. The order–disorder transition at 375 K is reflected only in the fractional-order spot profiles, while the integer-order spots are not affected. In contrast, the fluctuations along the rows appear also in the integer-order spots revealing that the substrate is involved in the fluctuations. This is consistent with the observation of a strong substrate buckling in the previously analysed (3×1) phase [2]. Surprisingly, below 250 K the propensity to form a structure with threefold periodicity does not increase. Rather, the intensity of all LEED spots drops off rather quickly indicating a loss of long-range order and rendering the spot-profile analysis less reliable.

An STM investigation of the same system yields the following result: At room temperature the $c(2 \times 2)$ structure appears perfectly ordered on defect-free terraces, as shown in Fig. 2a. In contrast, STM images from defective areas reveal the appearance of a structure with threefold periodicity (see Fig. 2b). Apparently defects pin the fluctuations and therefore they do not average out. STM images obtained at 130 K show a strongly disturbed $c(2 \times 2)$ structure and the appearance of (2×1) domains. The changing and occasionally blurred contrast is typical for STM images of fluctuating phases.

After further cooling to ~ 50 K, STM shows the coexistence of $c(2 \times 2)$, (2×1) and a (3×2) structure, all corresponding to a local Br coverage of 0.5 ML. This is shown in Fig. 3. The transitions reported above are fully reversible. After warming the system up again to 300 K, a seemingly perfect $c(2 \times 2)$ structure is observed in LEED and STM.

It appears that the three structures are essentially degenerate at 50 K. The conclusions derived from the experimental data are in partial agreement with density-functional theory (DFT) results. DFT calculations yield a near-degeneracy of the $c(2 \times 2)$, the (2×1) and the (3×2) structure [2]. Given a near degeneracy of the three structures at 0 K and

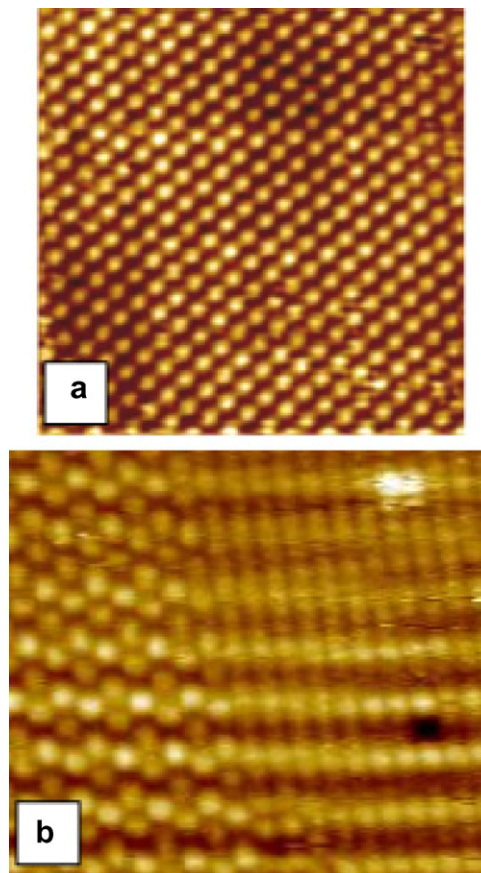


Fig. 2. (a) STM image of a $c(2 \times 2)$ preparation recorded at 300 K ($15 \times 15 \text{ \AA}^2$, 0.63 V, 1.13 nA). (b) STM image of a $c(2 \times 2)$ preparation recorded at 300 K close to a defect ($75 \times 65 \text{ \AA}^2$, 0.16 V, 1.11 nA).

no obvious entropy difference, one should assume a more or less similar share of all three phases also at higher temperatures in obvious contrast to the experiments.

The experimental observations can only be explained if one assumes temperature dependent interactions to prevail in the system. A natural candidate is a Peierls-type $2k_F$ interaction in the electronic system. At low T , such an interaction drives the system into a CDW phase, while with rising T the corresponding order parameter drops off due to thermal excitation of electrons across the Peierls gap. Thus the CDW dies out and the local adsorbate–adsorbate interactions, which are much less T -dependent, favour the global formation of the $c(2 \times 2)$ phase. However, it is important to note that the CDW is apparently not commensurate. For incommensurate CDWs it is predicted that a well-defined Peierls transition is replaced by fluctuations over a wide temperature range and phase separation into domains with different periodicities takes place [9,10]. The incommensurability is also supported by angle-resolved photoemission experiments, which yield $1/4G < k_F < 1/3G$ for the relevant surface state (G being a reciprocal surface lattice vector) [2].

We arrive at the following model: At 50 K, the $c(2 \times 2)$, the (2×1) and the (3×2) structures are degenerate, with the latter two phases being stabilised by the incommensurate

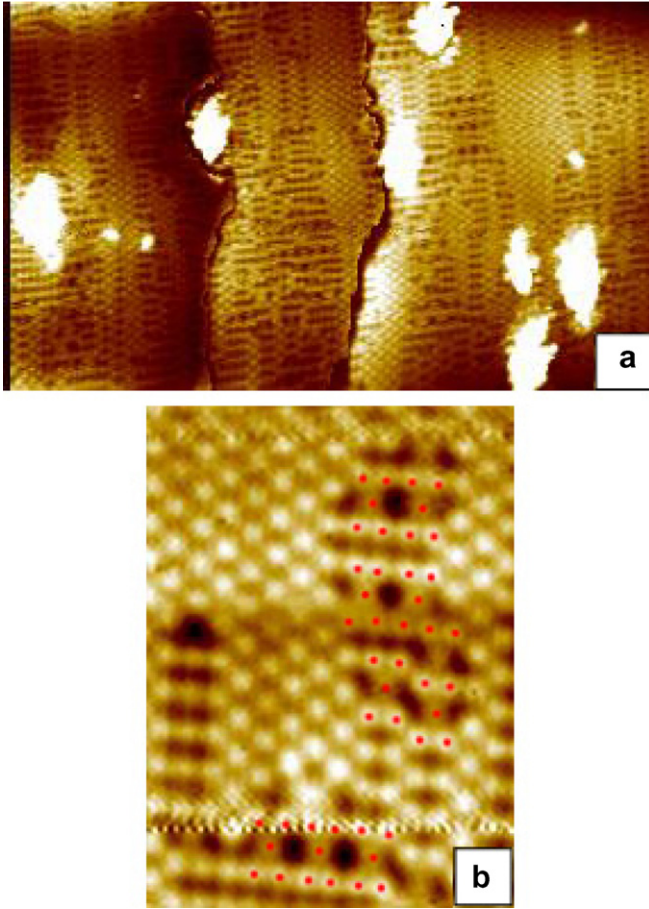


Fig. 3. (a) STM image recorded at 50 K ($415 \times 251 \text{ \AA}^2$, 0.51 V, 0.33 nA). (b) Detail of a terrace at 50 K ($78 \times 59 \text{ \AA}^2$), showing $c(2 \times 2)$, (2×1) , and (3×2) structural elements.

Peierls interaction. As T increases, the Peierls interaction is weakened, which destabilises these phases relative to the $c(2 \times 2)$ structure. Fluctuations are thermally excited, but with increasing preponderance of the $c(2 \times 2)$ phase the fluctuations drop off and an ever better $c(2 \times 2)$ order develops. Finally, at 375 K the $c(2 \times 2)$ structure is destroyed as well in a sharp order–disorder transition. The results also provide a surprising twist to our previous interpretation of the (3×1) structure as a CDW: The “ (3×1) ” domains observed at $0.50 < \Theta_{\text{Br}} < 0.55 \text{ ML}$ are fluctuating (3×2) CDW domains, whereas the proper (3×1) structure at

$\Theta_{\text{Br}} = 0.67 \text{ ML}$ is energetically indeed higher, as was predicted by DFT [2] and therefore not a true Peierls phase.

4. Conclusion

The results are related with the generic phase diagram of low-dimensional systems [11]. Phase coherence between the one-dimensional sub-units of such a system is due to a coupling parameter t_{\perp} . Raising the temperature above T_{coh} causes a loss of coherence from row to row (here: the order–disorder transition occurring at 375 K). Below T_{coh} a long-range ordered phase (the $c(2 \times 2)$ phase) is observed, but as T_{MF} (Mean-Field Peierls transition temperature) is approached fluctuations increase and finally lead below T_{MF} to the evolution of an inhomogeneous ground state (in the present case with stripes of $c(2 \times 2)$, (2×1) and (3×1) patterns). The surface system allows us to directly image the predicted phase transitions from fluctuating to inhomogeneous ground states. The results are of significant relevance for the understanding of correlated systems in general and HTSCs in particular.

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