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2007 J. Phys.: Condens. Matter 19 355006

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Fermi surface tuning in two-dimensional surface systems

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Received 29 September 2006, in final form 21 December 2006

Published 20 August 2007

Online at stacks.iop.org/JPhysCM/19/355006

Abstract

Competing electronic interactions can be used to tune materials into different phases with interesting and sometimes exotic properties, ranging from magnetic long-range order to superconductivity. Such electronic interactions are particularly pronounced in low-dimensional systems, where electronic correlation is enhanced. On surfaces, the electronic states are easily accessible for manipulation by doping, adsorption or quantum confinement. A deliberate shift of the Fermi surface of 2D or 1D electron states can have a significant influence on chemical activity, adsorbate–adsorbate interactions, surface diffusion etc. More strikingly, it may drive phase transitions and can perhaps be used to realize Peierls-distorted, magnetically ordered and even superconducting phases in two dimensions. Using the Br/Pt(110) system as a case study, the possibility and the problems of a (quasi)continuous variation of a Peierls phase by Fermi surface tuning are examined.

Synthesis of advanced materials with materials properties designed for a purpose is central to modern materials science. There are several approaches to the tailoring of materials properties. Chemistry provides the tools to design bonds and bonding networks with respect to both bonding geometry as well as bond strength. In this way supra-molecular structures, for example, can be constructed with an astonishing precision. The electronic properties of materials ranging from semiconductors to high-temperature (high- T_c) superconductors are controlled by doping. Of course there is a variety of other methods, ranging from self-organization on the atomic level to the classical methods of alloying and stress hardening, in order to improve materials properties. In the present paper we examine a particular concept of materials design which is based on a deliberate modification of the Fermi surface. We focus on surface properties, where the change of the Fermi surface may have effects on adsorbate interactions and the kinetics of film growth, as will be demonstrated below. But the concept can be developed further to gain a more general relevance: in brief, the idea is to induce comparatively small changes in the electronic structure which are then amplified by some instability, so as to give rise to a change in the macroscopic properties of the material under consideration. The change in the macroscopic properties may for instance relate to

metal–insulator, magnetic or superconducting phase transitions. Basically, the instability required for this concept is obtained by pushing the Fermi level into a peak of the density of states (DOS). Such a situation is inherently unstable, because the material tends to spontaneously break the symmetry in order to reduce the DOS at E_F . A large DOS at E_F may result from several causes: partially filled, weakly dispersing bands, as in Mott insulators; divergence of the DOS as occurs at van Hove singularities in low-dimensional materials; strong electron-mass renormalization resulting from a large electron–phonon coupling constant or other interactions of electrons with bosonic excitations (magnons, plasmons, etc). From these examples it is already clear that the concept of Fermi surface tuning is related to electronic correlation. In the following we discuss a few aspects of Fermi surface tuning, starting from weakly correlated two-dimensional (2D) metallic surface states and proceeding to quasi-1D systems on surfaces where correlation becomes increasingly important. We will, however, abstain from an in-depth discussion of electronic correlation. Instead only a few basic concepts will be introduced on a more phenomenological basis.

A specific approach to Fermi surface tuning was proposed by Plummer and co-workers [1], who coined the term ‘Fermi surface engineering’. The group proposed the production of different two-dimensional commensurate or incommensurate Peierls phases by changing the location of the Fermi surface via co-deposition of adatoms. In noble-metal bulk alloys an analogous process had been invoked previously to explain the formation of ordered phases as a function of composition, described by the Hume–Rothery rules [2]. ‘Fermi surface engineering’ used in this sense refers to $2k_F$ interactions arising from Fermi surface nesting [1]. Here, k_F designates the Fermi wavevector and the $2k_F$ interactions result from low-energy electron–hole excitations connecting different segments of the Fermi surface. Due to their particular energy–momentum relationship such excitations can hybridize with phonons and give rise to macroscopic instabilities. However, in the following we will use the term ‘Fermi surface tuning’ in a somewhat wider sense. Case studies will serve to illustrate principles, chances and also some limitations of this approach to tailor materials or surface properties.

1. Manipulating the occupancy of surface states

Due to the lowering of the symmetry, creation of a surface leads to the appearance of electronic surface states in most materials [3]. The energy position of such surface states depends critically on the details of the surface preparation and can be easily changed, e.g. by deposition of suitable adsorbates. We have to consider two main effects: an energy shift due to the associated global change of the surface potential and scattering at the adsorbate-induced local perturbation of the surface potential. The effect of defect scattering on surface states has been studied extensively, both in theory and experiment [4]. Quasi-elastic scattering gives rise to a dephasing, while inelastic scattering depopulates the excited surface states. Here we are primarily interested in ground-state properties. Hence we are concerned mainly with quasi-elastic scattering affecting electronic states within $E_F \pm k_B T$. Randomly distributed defects (adsorbates) will essentially limit the coherence length of the surface state wavefunction. Long-range ordered overlayers, in contrast, maintain the translational symmetry and therefore the phase coherence. It appears that at least for adsorbates which contribute delocalized s-like orbitals at the Fermi energy the Fourier expansion of the surface potential perturbation is dominated by long-wavelength contributions. Hence surface states are energetically shifted, but in general for such adsorbates a well-defined energy–momentum relationship is still maintained even if the adsorbate layer is disordered. This has been demonstrated for example for H, alkali metals and other adsorbates by angle-resolved inverse photoemission [5–8]. On Ni, unoccupied sp-derived Shockley surface states were observed to shift downwards by more than 1 eV as a consequence of

their interaction with the attractive hydrogen potential without losing their well-defined $E(\mathbf{k})$ relation. Generally, on transition metals, occupied sp-derived surface states are shifted below the lower edge of the bandgap. In this case strong hybridization with the bulk continuum leads to a partial loss of their surface character. The associated charge is redistributed essentially into a bonding resonance below the bottom of the d band [9–11]. By and large, the effect of H or alkali metal adsorption on surface states can be described as a delocalized contribution to the attractive surface potential, and therefore gives rise to a lowering of Shockley surface states [12]. For partially occupied surface states this results in an increase of the occupancy and hence an increase of the diffuse sp charge density in the surface layer. Other adsorbates can cause upward shifts of surface states. This has been observed for instance upon adsorption of oxygen on Ni(111) [8] and of rare gases on Ag(111) [13] and Pt(111) [14, 15]. In the case of O/Ni(111) one could argue in a semi-intuitive way that the totally symmetric Shockley state in the centre of the surface Brillouin zone (SBZ) interacts with the O p_z resonance. The resulting wavefunction possesses a node at the O site and therefore the kinetic energy is raised. Similarly, in the case of the rare gases the upshift can be attributed to the interaction of the closed p shell with the surface state and can be interpreted as Pauli repulsion [14].

Clearly the processes discussed so far lead to a significant rearrangement of charge within the surface. However, in general the charge density carried by sp-derived Shockley states is rather small. Nevertheless, if the surface is already close to an instability, the change of the surface state population can contribute significantly to the total energy balance of a surface phase transition. This is the case for some fcc(110) surfaces of transition metals, e.g. Cu(110) or Ni(110), where the adsorption of alkali metals induces a missing-row reconstruction. Figure 1 shows the alkali metal induced shift of occupied and unoccupied surface states on Cu(110) as a function of alkali metal coverage. In the case of low-temperature adsorption the alkali metal atoms adsorb in the grooves of the Cu(110) surface without changing the Cu surface atom configuration. This, however, is a metastable state. If the surface is annealed to 370 K, a missing-row reconstruction takes place with the alkali metal atoms first filling in the places of the Cu atoms, which are removed from every second row. Upon further exposure, the remaining Cu atoms in the top layer are also exchanged against alkali metal atoms. Finally, at 1 ML (here 1 monolayer (ML) refers to the close-packed alkali metal layer) coverage the surface is indistinguishable from the one prepared by low-temperature exposure. As shown in figure 1 (right panel), the replacement of Cu atoms by Na atoms leads to an upward shift of the occupied surface state. At $\Theta_{\text{Na}} = 0.25$ ML the bottom of the surface state band at \bar{Y} just straddles the Fermi level, thus the band has become almost empty. At the same coverage in the metastable, unreconstructed case the bottom of the surface state lies at about -0.6 eV. The energy cost of emptying the surface state amounts to roughly 20 meV per atom. The missing-row reconstruction requires the removal of Cu atoms from the close-packed rows of the fcc(110) surface to a kink, which is slightly larger, but of the same order of magnitude. The total energy cost is out-weighted by the energy gain from embedding the alkali metal atoms into the deep troughs of the missing-row reconstructed surface rather than the small troughs of the original one. Adopting a different point of view, the downshift of partially occupied surface states during alkali metal adsorption on the unreconstructed surface leads to an accumulation of sp charge density between the close-packed rows. This is expected to tilt the surface stress into the compressive direction [16]. On fcc(110) surfaces a compressive stress increases the driving force for missing-row reconstructions [17].

Thus, changes of the surface state occupancy play a certain role in the stress and energy balance of surfaces and may allow us to trigger reconstructions. Of course, the Fermi surface changes, as the occupancy of surface states is varied, but its exact shape and position is not critical for the mechanisms considered so far.

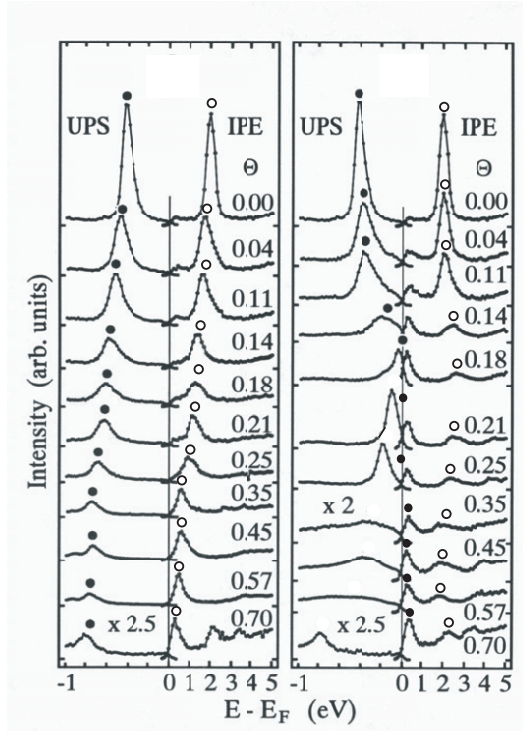


Figure 1. Shifts of occupied and unoccupied surface states on Cu(110) as a function of alkali metal coverage. The spectra are recorded by angle-resolved photoemission and angle-resolved inverse photoemission at the \bar{Y} point of the surface Brillouin zone. Spectra shown in the left panel have been recorded for Na adsorbed on Cu(110), while those in the right panel have been obtained after annealing, in which case Na is substitutionally adsorbed [14].

2. k_F dependent effects

The charge accommodated in surface states has other effects on the surface properties too. As an example we consider totally symmetric partially occupied Shockley surface states in the centre of the SBZ, as they occur on fcc(111) surfaces. Here, the charge density at and above the surface is uniformly distributed with respect to the parallel coordinates. The total kinetic energy can be divided into a parallel and a perpendicular component:

$$E_{\text{kin}} = \frac{\hbar^2 k_{\parallel}^2}{2m^*} + \frac{\hbar^2 k_{\perp}^2}{2m^*} = E_{\parallel} + E_{\perp}.$$

The evanescent probability density $|\Psi|^2$ falls off towards the vacuum side $\propto \exp(-2\kappa z)$, where $\kappa = 1/\hbar\sqrt{2m^*(V - E_{\perp})}$. As the parallel component is small for states in the centre of the SBZ, almost the entire kinetic energy enters into E_{\perp} , reducing κ and therefore increasing the attenuation length. For this reason such states contribute significantly to the vacuum tail of the electron density [18], even if the charge carried by the surface state is small in comparison to the total charge density associated with the surface atoms. The surface charge increases the Pauli repulsion for molecules [19–21], modifies the barriers for surface diffusion [22] and contributes to the adsorbate–adsorbate interaction [19, 23–27]. As we have seen above, adsorbates can be used to tune this charge density [20]. A beautiful demonstration of rare-gas induced surface

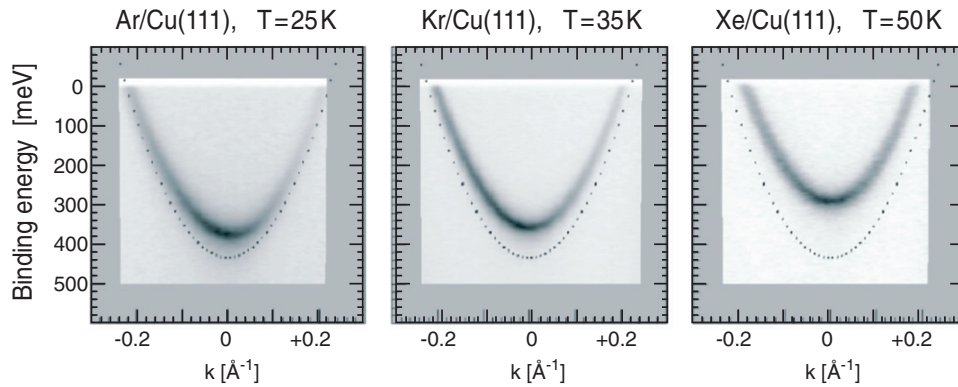


Figure 2. Shift of the surface state band caused by adsorption of a monolayer of different rare gases as measured by angle-resolved photoemission. The dotted line shows the dispersion of the Γ surface state on clean Cu(111). From [13] with permission of the authors.

state shifts and the associated changes of k_F has been carried out in a recent angle-resolved UV photoemission spectroscopy (ARUPS) study by Reinert and co-workers [13] (figure 2).

The change of the Fermi wavevector has important consequences. The scattering of the surface state by steps, impurities or the adsorbates themselves [28–30] gives rise to Friedel oscillations in the associated charge density. The functional behaviour of Friedel oscillations in (free-electron like) 2D surface states around point defects is described by

$$F(x) = \frac{x \cos x - \sin x}{x^3}$$

with $x = 2k_F r$ and r being the distance from the point defect [31].

These oscillations generate charge density modulations close to steps and around adsorbates. The wavelength of these modulations scales with k_F^{-1} and the amplitude falls off as $1/r^2$. The local reduction of charge density causes a change in the diffusion barrier [22] and has been proposed to be responsible for adsorbate clustering [19]. Lau and Kohn [31] were the first to calculate the resulting surface-state mediated adsorbate interaction potential. Triggered by the first direct experimental evidence for such an adsorbate–adsorbate interaction [24], Hyldgaard and Persson [25] refined the calculation by introducing explicitly the scattering phase shifts of the adatom. Subsequently, with the increasing availability of low-temperature scanning tunnelling microscopy, several studies of the quite subtle effect appeared in the literature [26, 27, 32]. Apart from the short-range non-asymptotic part, the potential variations caused by the charge density oscillations are of the order of \sim meV and therefore low temperatures are indispensable for experimental verification.

Making use of the long-range interaction provided by the Friedel oscillations of the surface-state charge density, Schneider and co-workers prepared a superlattice of Ce adatoms on Ag(111) [33, 34]. They also pointed out the possibility of tuning the lattice constant of the superlattice by varying the adatom or the substrate. In view of the continuous surface state shifts observed upon H or rare gas adsorption [6, 13], it would be interesting to study the effect of these co-adsorbates on the superlattice. However, all these studies have to be carried out at $T < 10$ K, because the variations in the interaction potential are so small.

In the search for more robust effects one could turn to surface states which carry a higher charge density. d-derived surface states (Tamm states) with their lower dispersion would be interesting candidates. Differential conductance maps of d-derived surface states have been

studied on NiAl(110) [35], but a study of adsorbate interactions mediated by Tamm states has not been carried out.

Strong k_F dependent effects can also be expected if singularities in the DOS occur at E_F . Generally, singular behaviour in the electronic system is the more pronounced the lower the dimensionality. It is therefore interesting to study one-dimensional systems.

3. Reducing the dimensionality

A reduction of the dimensionality has severe consequences for the properties of a material. Perhaps the simplest example is the density of states. For free-electron-like bands one obtains:

$$\begin{aligned} 3\text{D: DOS}(E) dE &= \frac{\sqrt{2}}{\pi^2} \left(\frac{m}{\hbar^2} \right)^{3/2} E^{1/2} dE \\ 2\text{D: DOS}(E) dE &= \frac{1}{\pi} \frac{m}{\hbar^2} dE \\ 1\text{D: DOS}(E) dE &= \frac{\sqrt{2}}{\pi} \left(\frac{m}{\hbar^2} \right)^{1/2} E^{-1/2} dE. \end{aligned}$$

Obviously, there is a singular DOS at the bottom of a 1D band. More generally, there are four types of critical points in 3D bands [36]: minima, maxima and two types of saddle point. In 2D one has three types of critical points: minima, maxima and one type of saddle point, while in 1D only minima and maxima occur. In 1D both extrema are associated with a divergence of the DOS of the type $(E - E_c)^{-1/2}$, while in 2D only a saddle point leads to a logarithmic divergence: $\text{DOS}(E) \propto \ln(1/|E - E_c|)$. The DOS remains finite at all critical points in 3D, as shown in figure 3 (left panel).

Another related example of singularities emerging upon dimensional reduction is the Lindhard response function (susceptibility) $\chi(\mathbf{q})$. $\chi(\mathbf{q})$ determines the response of the charge density to a static perturbing potential:

$$\rho(\mathbf{q}) = -V_{\mathbf{q}} \chi(\mathbf{q}).$$

If the perturbing potential $V_{\mathbf{q}}$ arises from a lattice distortion and $\chi(\mathbf{q})$ is large, the response of the charge density $\rho(\mathbf{q})$ may be so strong as to completely screen out the restoring force for the lattice distortion (overscreening). In this case the energy of the phonon mode \mathbf{q} goes to zero (soft phonon) and a static lattice distortion is stabilized. Such so-called Peierls transitions will be discussed in more detail below. At zero temperature, the response function diverges at $2k_F$ in 1D, but remains finite in 2D and 3D [37] (figure 3, right panel). The dependence of $\chi(\mathbf{q})$ on dimensionality may be rationalized by considering the ‘nesting’ condition for the Fermi surface. $\chi(\mathbf{q})$ can be expressed as

$$\chi(\mathbf{q}) = \int_{BZ} \frac{d\mathbf{k}}{(2\pi)^d} \frac{f(\mathbf{k} + \mathbf{q}) - f(\mathbf{k})}{E_{\mathbf{k}} - E_{\mathbf{k}+\mathbf{q}}}$$

with d being the dimensionality and $f(\mathbf{k})$ the Fermi–Dirac distribution function [38]. The integral is dominated by those areas of the Fermi surface, which can be connected with the same ‘nesting vector’ \mathbf{q} . In one dimension the Fermi surfaces can be represented by infinitely extended sheets normal to k_F , which fulfil the nesting condition perfectly. In 2D the Fermi surface of nearly free electrons is circular and the nesting condition is fulfilled by only one \mathbf{q} at a time. Therefore $\chi(\mathbf{q})$ does not even have a maximum at $2k_F$. However, if the quasi-particle dispersion in 2D is anisotropic, the circle is deformed and may develop flat sections which nest over a finite range, yielding a maximum in $\chi(\mathbf{q})$ at $\mathbf{q} = 2\mathbf{k}_F$. There is also the possibility that Fermi surfaces of different bands are connected by a nesting vector \mathbf{q} . In this case the Peierls

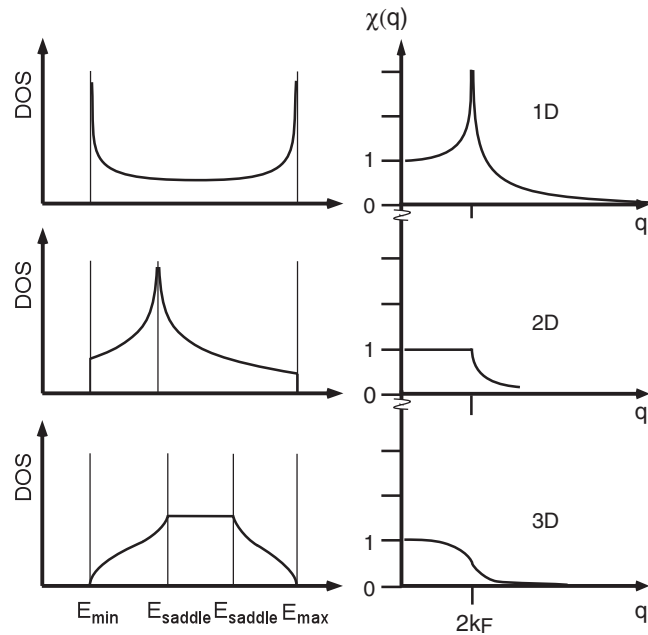


Figure 3. Dimensional dependence of the density of states (DOS) in a nearly free electron system (left panel) and of the susceptibility $\chi(\mathbf{q})$. Note, that the singular behaviour of $\chi(\mathbf{q})$ at $2k_F$ is not related to the van Hove singularities of the DOS, provided that E_F does not coincide with one of them. However, if for example in a 2D system E_F happens to fall into a saddle point of the band this will produce a divergence in $\chi(\mathbf{q})$ [39].

gap does not necessarily open at the edge of the new Brillouin zone, and the new periodicity λ introduced by the spontaneous symmetry breaking obeys the more general relation $\lambda = 2\pi/|\mathbf{q}|$. Extended nesting is not required if there are points on the Fermi surface with exceedingly large DOS. In 2D this is the case if the Fermi surface includes saddle points [39].

Generally, electron–electron correlation increases as the dimensionality is decreased and renders the systems increasingly susceptible to external perturbations and phase instabilities. This property of correlated systems can be exploited for sensing and switching applications as mentioned in the introduction. Bianconi and co-workers [40] proposed the construction of a superconducting material by means of Fermi surface tuning: If the van Hove singularities of 1D bands or the DOS divergence at the saddle point of a 2D band are pushed towards the Fermi energy, critical behaviour is expected with possible phase transitions for instance into a superconducting phase. These are only a few examples of phase transitions related to the position of the Fermi level and correlation in low-dimensional systems. Spin density waves, antiferromagnetic ordering, etc belong to this class as well.

Several strategies have been designed to achieve a dimensional reduction of electronic states at metal surfaces. Perhaps the earliest observation of quasi-1D surface states was reported by DiDio *et al* [41] for the system (2×1) -O/Cu(110). Oxygen adsorption on the Cu(110) surface leads to the self-organized formation of Cu–O chains along the [001] direction. The O(2p)–Cu(3d) antibonding orbitals are pushed above the Cu d manifold and form quasi-1D bands well discernible in ARUPS. This is a prototypical case of self-organization of 1D adsorbate chains, which can be exploited systematically to obtain 1D electronic systems.

Another route to quasi-1D surface states is one-dimensional disorder, as occurs for instance upon H adsorption on Ni(110) [42]. However, neither system qualifies for Fermi surface tuning, because in the first case the surface states are fully occupied and in the second fully unoccupied. The O/Cu(110) adsorption system, however, allows still another approach to dimensional reduction, namely the formation of 1D stress domains in the well-known striped structure [43]. At oxygen coverages $\Theta_{\text{O}} < 0.5$ ML (here a monolayer refers to the number of Cu(110) surface atoms) the Cu–O chains mentioned above self-organize into a stripe pattern with a comparatively constant periodicity of about 65 Å and a stripe width varying linearly with O coverage. The surface oxide stripes form potential barriers for the Cu(110) Shockley surface state at \bar{Y} which is therefore confined to the narrow copper channels between the oxide stripes. At small coverages there is a residual wavefunction overlap between the channels resulting in a 2D phase coherence. The 2D surface state band is then split by the lateral super-grating of the stress domains into sub-bands. Each of these sub-bands exhibits a saddle point (alternating at the edge and in the centre of the new SBZ), producing a succession of spikes in the DOS [44]. Variation of Θ_{O} changes the Cu channel width and the quantum size effect shifts the spikes relative to the Fermi level. Thus this system is a 2D realization of the strategy proposed by Valletta *et al* [40] for the construction of a superconductor. However, the charge density in the surface state is very small. The divergence in the DOS is rounded off as in every real system due to size effects and non-negligible coupling to bulk states. Therefore the DOS remains finite and in fact quite small. Furthermore the range of tunability is limited, because at larger oxide stripe widths the wavefunction overlap decreases and the system becomes increasingly susceptible to imperfect order and thermal fluctuations, both destroying the phase coherence between the individual quantum well states [45]. Thus the system allows us to study the formation of superlattice bands and van Hove singularities in quasi-1D states, as well as decoherence due to disorder or thermal fluctuations, but it probably does not support any electronically induced phase transitions.

An alternative route to 1D electronic surface states is surface state confinement between steps [46–48], self-organized formation of metallic chains on surfaces [49–52] and decoration of steps by single or multiple atom metal chains [53–55]. Tailoring of quasi-1D states can be achieved by varying the terrace width [48, 56], by doping [53, 57] and of course by choosing different adatoms for forming the chain structures.

4. Peierls phases

Whenever there is a large DOS at E_{F} , a system is prone to instability. The system will tend to rearrange in such a way that the DOS is redistributed, for instance by a spontaneous symmetry breaking, which introduces a new Brillouin zone. This may open a gap at the new zone boundary pushing the excess DOS partly above, partly below E_{F} . This so-called Peierls phase is therefore characterized by a lattice distortion associated with a corresponding charge density modulation. The distorted phase is also called a charge density wave (CDW) phase [38]. The situation is completely analogous to the Jahn–Teller effect in a single molecule, which splits partly occupied degenerate orbitals by means of a spontaneous molecular distortion reducing the symmetry. If we consider a surface layer of a 3D crystal, the situation is more complex than in a molecule: the surface lattice distortion is generally hindered by the bonding to the bulk. Thus the electronic energy gain has to compete with the extra energy needed for the elastic deformation within the selvedge. Therefore, a spontaneous symmetry breaking will only occur if the electronic energy gain exceeds the elastic deformation energy. There are two limiting cases: the opening of a small gap within small areas of k space associated with a soft phonon (weak coupling limit generating a weakly coupled CDW: WCDW) or the opening of a

larger gap over more extended regions of k space (strong coupling limit generating a strongly coupled CDW: SCDW). The first case—a small gap within a narrow region of k space—occurs typically in (quasi-)1D compounds. Here the distortion energy is usually small due to the absence (weakness) of 3D bonding and $\chi(\mathbf{q})$ (almost) diverges at k_F . The second case occurs more frequently in 2D systems. The delocalization of the energy gain over several states in k space corresponds to a localization in real space. One can therefore think about this case as a formation of localized bonds leading to a displacement reconstruction [58].

From this discussion it is clear that Peierls systems are particularly interesting objects for Fermi surface tuning. Such a tuning may either enable the system to go through a CDW phase transition or it may, by variation of k_F , allow one to deliberately change the periodicity of the system [1]. In principle, this would offer the possibility to study a succession of commensurate, higher-commensurate and incommensurate phases, i.e. to construct a ‘devil’s staircase’ [59]. Because of their sensitivity to changes in k_F , WCDW systems are more suitable for this purpose than SCDW systems. As the electronic energy gain is smaller in WCDWs, systems are required in which the deformation energy is small. For surfaces and adsorbate systems this implies either a weak bonding to the substrate or the presence of low-energy phonon modes, e.g. Rayleigh modes, which require only a moderate charge density modulation to evolve into soft modes.

Several candidates for surface CDW systems have been investigated in the literature (e.g. [1, 49, 60–63]). Some of them appear particularly suitable for exploring the concept of Fermi surface tuning. For instance, noble metal chains on stepped Si(111) [49] should be good candidates, because doping in order to shift k_F is easily possible. A problem for a continuous tuning of the periodicity is the strong substrate corrugation, as will be discussed further below. Also, quasi-1D systems on metal surfaces [60, 61, 64] should be well suited for Fermi surface tuning. In this case, the surface states can be shifted with respect to E_F by co-adsorbates or by quantum size effects, i.e. by modification of the surface potential.

One of the best investigated systems, where a Fermi surface shift almost leads to a soft phonon, is the well-studied case of W(110) [65, 66]. Here, H adsorption shifts a surface resonance into a projected bulk band gap, thus rendering it a 2D surface state. The Fermi contour of this surface state exhibits a clear nesting, which in turn is reflected in a giant Kohn anomaly. The screening falls just short of inducing a static distortion. Thus this system can be considered as a borderline case of Fermi surface engineering: inducing a surface reconstruction via a H induced Fermi surface shift. Another system where Fermi surface engineering has been tried is Br/Pt(110) [67, 68]. This will be discussed in more detail in the following.

Clean Pt(110) exhibits a (1×2) missing-row reconstruction and is therefore a strongly anisotropic system. The existence of quasi-1D surface resonances has been demonstrated by ARUPS [69]. Adsorption of 0.5 ML (coverage defined with respect to the (1×1) surface atom density of Pt(110)) of Br on this surface lifts the missing-row reconstruction and gives rise to a $c(2 \times 2)$ overstructure [70]. This is a quasi-hexagonal array of covalently bound Br atoms sitting on every second short-bridge site of the close-packed Pt atom rows. This adsorbate structure is rather unstable against additional adsorbates (Br, CO, NO, etc), which turn it into a (3×1) structure [71]. Here, the Br atoms alternately occupy every third short-bridge and long-bridge site, respectively. Ideally this would correspond to a coverage of $2/3$ ML. However, the structure already appears at coverages only slightly above $1/2$ ML. Room temperature STM measurements reveal strong fluctuations in the system. Photoemission shows that the $c(2 \times 2) \rightarrow (3 \times 1)$ transition is indeed associated with a backfolding of a band at its Fermi level crossing. In the (3×1) phase, the Pt substrate is buckled, as one would expect from a soft Rayleigh mode. We have therefore interpreted the $c(2 \times 2) \rightarrow (3 \times 1)$ transition as an adsorbate induced Peierls transition [61, 71]. The idea is that the CDW develops together with a soft Rayleigh mode in the close-packed Pt rows. Once the CDW is established, the

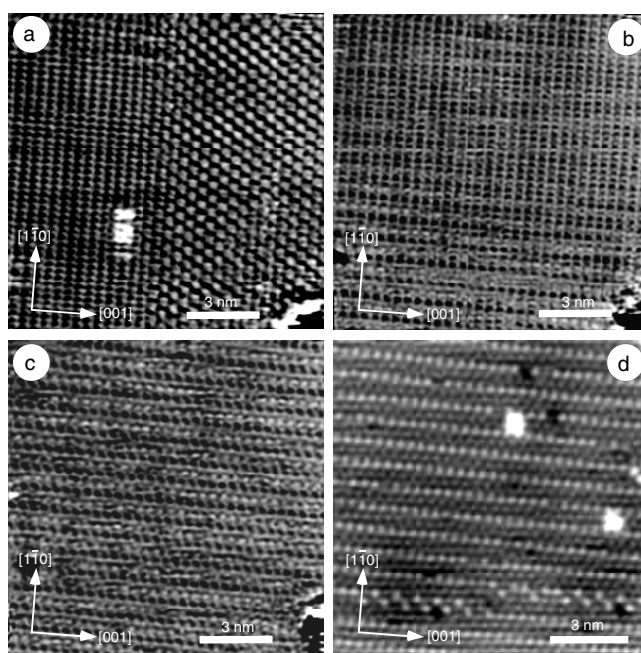


Figure 4. Scanning tunnelling microscopy images recorded during exposure of a $c(2 \times 2)$ -Br/Pt(110) surface to NO. Various stages of the transition from the $c(2 \times 2)$ to the NO induced (3×1) structure are imaged.

$c(2 \times 2)$ and (3×1) Br structures are almost degenerate and the adsorbate fluctuates between the two structures. At even higher additional coverages, the (3×1) structure is globally preferred, which might be caused by improved Fermi surface nesting. Alternatively, the additional stabilization could be due to short-range adsorbate–adsorbate repulsive interactions. Assuming that the $c(2 \times 2) \rightarrow (3 \times 1)$ transition is driven by a Peierls instability, we tested the reaction of the $c(2 \times 2)$ system on additional co-adsorbates, namely NO and CO. Preliminary photoemission results [68] indicate a Fermi surface shift caused by these adsorbates towards smaller k_F . In agreement with this observation the system goes through a succession of transitions $(3 \times 1) \rightarrow (7 \times 1) \rightarrow (4 \times 1)$. This is consistent with a shift of the surface periodicity in accordance with the gradual change of the Fermi surface. The STM images shown in figures 4 and 5 reveal characteristic properties, which are presumably generic for such quasi-continuous phase changes induced by Fermi surface shifts, namely dynamical fluctuations and soliton formation. Figure 4 shows a series of STM images illustrating the transition from the $c(2 \times 2)$ -Br/Pt(110) to the (3×1) -NO/Br/Pt(110) structure. After very small NO exposures ($\Theta_{\text{NO}} < 0.02$ ML) the $c(2 \times 2)$ domains start shrinking and transforming into an apparent (1×1) structure. The boundaries between the two domains are not abrupt, but the pattern changes in a continuous way. It is known from density-functional theory (DFT) calculations [70] that the bright spots in the STM images of the $c(2 \times 2)$ structure are due to Br atoms. Furthermore, the DFT calculations show that Br atoms cannot occupy neighbouring short-bridge sites because the mutual repulsion is too large. In contrast to these DFT results we observe in figure 4(a) (i) a continuous variation of the brightness of the Br features and (ii) a (1×1) structure, requiring occupation of nearest-neighbour sites, if it is attributed to a static configuration. The apparent conflict is resolved if one admits the possibility of fluctuations. The brightness of the Br induced

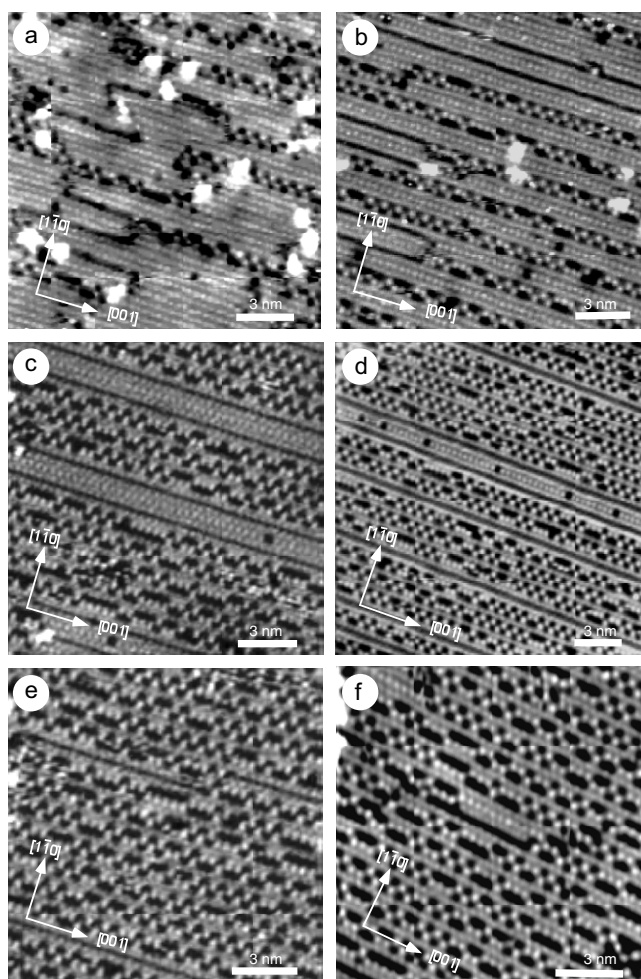


Figure 5. Scanning tunneling microscopy images recorded during exposure of a $c(2 \times 2)$ -Br/Pt(110) surface to NO. The images show the evolution of the surface structure at NO exposures beyond the formation of the (3×1) phase. Note the appearance and disappearance of straight empty domain walls during the transition from the (3×1) to the NO induced (4×1) structure.

features is then related to the mean residence time of a Br atom on that particular site and the apparent (1×1) structure simply results from an equal average occupation probability for every short-bridge site in the lattice. In figure 4(b) a new (threefold) periodicity starts to vaguely appear in the (1×1) pattern and confirms the assignment to fluctuating structures. In figure 4(c) the threefold periodicity is already well developed, but the features are still blurred indicating considerable dynamics in the adlayer. In figure 4(d), the spots are again well defined, with essentially two different intensities corresponding to Br atoms in short-bridge sites (bright) and in long-bridge sites (less bright), respectively [71]. Close to the bottom of the image, a new structural element appears in the shape of more or less regular zig-zag lines. The whole transition from the $c(2 \times 2)$ to the (3×1) structure takes place without formation of distinct static domain walls. Intermediate structures are rapidly fluctuating and seem to accommodate the misfit in mobile defects.

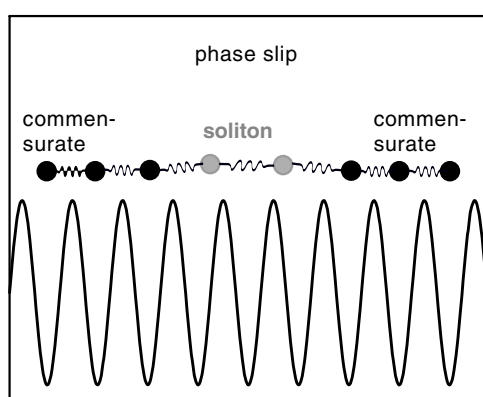


Figure 6. Basic ingredients of the 1D Frenkel–Kontorova model: periodic substrate potential, elastically coupled adsorbate layer, commensurate domains and domain walls (solitons) accommodating a phase slip in order to release the elastic energy resulting from the adsorbate–substrate mismatch.

This scenario changes in a characteristic way for the succeeding transition from the (3×1) to the (4×1) structure. Here, the distribution of Br atoms is fixed with the exception of occasional hopping between nearest-neighbour sites in the $[001]$ direction within the zig-zag rows. The hopping occurs on a timescale of several seconds, thus the structure can be considered essentially static. The transition from the threefold to the fourfold periodicity occurs via intermediate phases without long-range order, containing a succession of commensurate stripes and very localized domain walls or solitons as shown in figure 5. A peculiar phenomenon are light domain walls extending straight across whole terraces in the $[001]$ direction (see figures 5(b)–(e)). These domain walls disappear whenever a commensurate structure is possible, i.e. they are absent in the (3×1) phase (figure 4(d)), the (7×1) phase, which consists of a regular succession of (3×1) and (4×1) structural motifs (lower right part of figure 5(b)), and in the (4×1) structure (figure 5(f)). They are apparently formed in order to accommodate the misfit between the proper periodicity of the adsorbate layer and the substrate.

Generally, the observed patterns correspond well to the theoretical models developed in order to describe the properties of incommensurate CDW phases [59]. For the present case it is sufficient to briefly consider the one-dimensional Frenkel–Kontorova model, because it is simple, intuitive and reflects the qualitative features quite well. In this model, the substrate is represented by a periodic potential V (thus ignoring the elastic response of the substrate to an overlayer with different periodicity). The overlayer in turn is represented by particles moving in the substrate potential, but elastically coupled to each other by a harmonic force (with force constant k) as shown in figure 6.

In the limiting case of $V/k \rightarrow 0$ (rigid adlayer on a weakly corrugated substrate), the adlayer remains almost undistorted and the resulting structure is a moiré pattern. Here, the phase difference between substrate and adsorbate periodicity increases linearly as one proceeds along the surface. For finite V/k it turns out that the energetically preferable situation consists of stripes of commensurate domains separated by domain walls (phase discommensurations, solitons). The domain walls are inserted into the structure to release the elastic distortion energy of the adlayer or, in other words, to restore the average natural periodicity of the adlayer. Each domain wall is associated with a well-defined phase jump.

Accordingly, the phase difference between adlayer and substrate is constant within each commensurate domain, but changes by a certain amount within the domain walls. In

equilibrium, these solitons occur within equal distances [72], i.e. they form a periodic pattern of their own, the soliton lattice. The width of the solitons decreases as V/k increases. The movement of solitons is associated with the hopping of adlayer particles from one site to the next, so it is activated. Equilibration of the solitons is therefore kinetically hindered for large V/k . As a result, in many real systems the formation of a regular soliton lattice is suppressed and instead a chaotic soliton arrangement is observed such as in figure 5. Given that Peierls phases occur preferentially in quasi-1D systems, the 1D Frenkel–Kontorova model captures quite well the principal features which are to be expected as a surface CDW phase is continuously tuned through commensurate and incommensurate periodicities.

The CO(NO)–c(2 × 2)-Br/Pt(110) co-adsorbate system is apparently a physical realization of the 1D Frenkel–Kontorova model. We mention here that an additional adsorption of Br (instead of NO or CO) also yields a sequence of ($n \times 1$) structures beyond the (3 × 1) phase, i.e. (8 × 1), (6 × 1) and (4 × 1) phases have been observed [73]. Detailed structural analyses are under way in order to clarify, how these phases are related with the NO (CO) induced structures and whether they can also be interpreted as incommensurate (or higher-commensurate) Peierls phases. So far, it is not yet completely clear whether the various phases are actually driven by a Peierls instability. At present, we cannot exclude that a similar behaviour could result from more local adsorbate–adsorbate interactions. Actually, there is a continuous transition from the classical CDW model (weakly coupled CDW) to the so-called strongly coupled CDW (SCDW) case [62]. As discussed above, the former requires Fermi surface nesting or saddle points. The corresponding interaction is long-range in real space. In the SCDW case, larger parts of electron bands are lowered in energy. The energy gain is not limited to distinct k values but occurs over larger parts of the (surface) Brillouin zone. Accordingly the interaction is more localized in real space. In the extreme limit, it is essentially a nearest-neighbour interaction. Here, any correlation with the Fermi surface is lost. The charge density modulation can then be described as a local charge transfer between inequivalent neighbouring atoms. A model where only the interaction between nearest neighbours was retained has been explored, for instance, in the much disputed case of Pb/Ge(111) [74].

Characterization of a Peierls transition within the framework briefly outlined above requires a complete Fermi surface mapping, and a detailed investigation, of which portions of the band structure are affected upon the transition. Particular attention has to be paid to saddle points, because they contribute the lion’s share to the DOS in 2D, as discussed above. Saddle points at E_F are indeed present in Pt(110) [69] and the Br/Pt system, but their role is not yet clear [75]. Furthermore the transition should be investigated as a function of temperature at fixed coverage. For weak coupling CDWs, it is the thermal excitation of electrons across the gap which leads to the vanishing of the latter at the critical temperature T_c and to the restoration of the normal state. For strong coupling CDWs a local charge density modulation, and hence a (pseudo)-gap, persists above T_c , but the phase coherence is lost. Accordingly, the symmetry-broken state does not disappear at T_c but fluctuates in space and time [58]. Such fluctuations are obviously present in the Br/Pt(110) system, indicating that it is not in the pure WCDW limit. The concept of Fermi surface tuning, however, is strictly valid only for the WCDW case. It gradually loses its meaning as the symmetry-broken state is no longer strictly tied to a $2k_F$ periodicity. Thus the CO(NO)–c(2 × 2)-Br/Pt(110) system remains a possible candidate for Fermi surface tuning, but to what extent the concept is actually realized in this system will only become clear when the whole 2D electronic structure has been mapped.

A further complication in the Br/Pt(110) adsorbate system arises from the fact that the substrate is not just an inactive template on which only the adsorbate develops a CDW phase. Rather, in our model it is the substrate which exhibits the CDW, in the sense that the charge density modulation couples to a Rayleigh phonon in the Pt top layer and the relevant electronic

surface state bands are only weakly modified by the Br adsorbate [69]. The role of the adsorbate is twofold: on the one hand it modifies the surface resonances, thus driving the top substrate layer into the CDW phase, on the other hand it ‘decorates’ this phase. However, at low temperatures, hopping of the adatoms could become kinetically hindered, rendering the observation of the genuine equilibrium phases difficult. Our variable-temperature STM experiments indicate so far that even at 100 K equilibration of the structure is still possible.

In summary, while the system $\text{NO}(\text{CO})\text{-c}(2 \times 2)\text{-Br/Pt}(110)$ certainly exhibits several features which are characteristic of a continuously tunable CDW system, in particular the succession of ordered commensurate and chaotic soliton phases, robust evidence for driving the transitions via Fermi surface tuning is still lacking. Nevertheless, the experiment serves to demonstrate the rich phenomenology of phases and processes which might become accessible through Fermi surface engineering of surface CDWs. In view of the increasing number of systems discovered recently which seem to show surface Peierls transitions, one can anticipate that the concept of tailoring CDW phases by means of Fermi surface tuning will soon be put to a rigorous test.

5. Outlook

In the last section we discussed the tuning of CDW phases via Fermi surface manipulation. A look at a (schematic) phase diagram of low-dimensional systems shows immediately that this might just be the very beginning of an exciting journey. Tuning the Fermi surface might also give rise to a variety of spin-ordered phases and therefore surfaces with differing magnetic properties. It is expected that 1D electronic systems exhibit Luttinger-liquid properties, but one problem in preparing Luttinger-liquid systems is the intervention of Peierls transitions. Perhaps it is possible to suppress the formation of a CDW on a surface to some extent by tuning it into incommensurability. Furthermore, the study of surface CDWs close to T_c can give valuable insights into fluctuating and pseudo-gapped phases. As (quasi-)1D structures on surfaces can be prepared with a variety of geometric and electronic properties, it might even become feasible to engineer superconducting surface layers.

Acknowledgments

The work has been sponsored by the Austrian Science Fund and the West-Austrian Initiative for Nano-Networking (WINN). Critical reading of the manuscript by A Menzel and N Memmel is gratefully acknowledged.

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