Surface States, Surface Metal-Insulator, and Surface Insulator-Metal Transitions

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Abstract

I present an informal discussion of various cases where two-dimensional surface metal-insulator structural and charge-density-wave instabilities driven by partly filled surface states have been advocated. These include reconstructions of clean semiconductor surfaces and of W(100) and Mo(100), as well as anomalies on the hydrogen-covered surfaces H/W(110) and H/Mo(110), and possibly alkali-covered surfaces such as K/Cu(111). In addition I will also discuss the opposite type of phenomena, namely surface insulator-metal transitions, which can be argued to occur on α-Ga(001), high-temperature Ge(111), and probably Be(0001).

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I. INTRODUCTION

Mainly because they historically involved different people and different techniques, but probably also because each field had developed its own ad hoc theory, the subjects of surface structure and structural transitions, surface electronic states, and surface lattice vibrations are generally treated as disconnected.

As I see it, the main scope of this book, and of the hearty Bad Honnef discussions which the book summarizes, is precisely to remind all of us of how much these areas are, on the contrary, very much connected and intimately tangled with one another. I will discuss here, more specifically, two different instances, pertinent to crystal surfaces, where this tangling becomes of dramatic importance.

The first instance, is that whenever there are partly filled electronic surface states on a solid surface, then this sort of 2D metallic situation may be unstable. The surface structure develops a tendency to rearrange – in most cases it will reconstruct, giving rise to a new surface periodicity – in such a way as to become a 2D insulator. My shorthand reference to this class of systems will be to speak of a Surface Metal-Insulator (SMI) transition. After general remarks, and qualifications on charge-density waves, I shall devote Section 2 to a bird’s eye view over some of the most popular SMI cases. From these specific examples I shall also try to draw more general wisdom, in some cases related to other contributions in the present volume.

The second instance, is that there are now also examples (identified at least in theory), of what may be seen, in an imprecise sense, as the opposite phenomenon to SMI taking place. In systems where the bulk balance between metal and insulator (or semimetal, or very covalent metal) is only weakly tilted in favor of the latter, the balance will generally change at the surface. Here, the fully metallic state has a chance to prevail, even if only locally. Interestingly, in the cases where it does prevail, at least at low temperatures, the final metallic coating at the surface of the bulk nonmetal can be argued to have a function which is related to surface states, in this case to non-existing ones. The function is in
fact that of removing the 2D metallic Fermi surface of the half-filled surface states which the nonmetal surface would otherwise inevitably have if it did not transform into a metal. In this sense, the surface metallization transition is also driven by half-filled surface states, although in reverse. I will call these cases Surface Insulator-Metal (SIM) transitions, to be discussed in Section 3.

In the spirit of a series of introductive remarks to the more technical subject matter of this book, this paper will be quite informal, and totally devoid of either rigor or completeness. The accent will rather fall on a variety of controversial points, in an attempt to stimulate progress, whenever possible, through discussion.

II. SURFACE METAL-INSULATOR (SMI) TRANSITIONS

A. General remarks

It is obvious that a crystal surface, or more precisely a semi-infinite 3D crystal, cannot generally be treated as simply a 2D system. However, it is also true that atoms at a surface possess a lower coordination, sort of half-way between 3D and 2D, which automatically requires a reassessment of chemical bonding at a surface relative to that of a bulk. Furthermore in some cases, like that of narrow well-defined surface electron and phonon states, it is possible to map a surface onto a straight 2D problem.

If one glances at the periodic table of the (3D!) elements, one finds that a majority of them are metals, under ordinary conditions. If instead of three-dimensional, however, our world was only two- or one-dimensional, one of the ways in which it would look different would be a dramatic decrease of elemental metals. In lower dimensions, lower atomic coordination reduces the bandwidth and therefore the electron kinetic energy gain which stabilizes metals, while both electron-electron and electron-lattice interactions have no smaller role, favoring an insulating state.

Electron-electron repulsion generally leads to magnetism, Mott insulators, and the like.
While there is no reason of principle why that should not be relevant to surfaces, I am not aware well-established cases of surface magnetic instability or reconstruction, at least for bulk nonmagnetic sp-bonded elements. I will thus not discuss this possibility any further.

Apart from the additional exciting possibility of surface superconductivity in a metal whose bulk is normal, of which again I do not know a proven case, electron-lattice coupling tends to lead to a surface insulating state too, of the regular band type. Starting from an ideal surface, the SMI transition generally coincides with a structural, reconstruction, phase transition. In analogy with other structural phase transitions, the SMI transition may be gentle, or as one says displacive, or it may be dramatic, or reconstructive. The former type involves a small periodic distortion of the lattice at and near the surface, similar to a frozen-in surface phonon, with a corresponding gapping of the electronic surface states. The latter implies instead some kind of drastic rearrangement of atomic populations and positions, including creation of vacancies, adatoms, missing rows, etc., and a variety of rebonding possibilities, with the only common end result of a large insulating gap between filled and empty surface states.

The displacive SMI’s can be generally classified as charge-density waves (CDW’s) [1], to be discussed below. The reconstructive SMI’s are less universal, more system-specific in their mechanism. I will briefly allude, very incompletely, to some of them in the subsection devoted to semiconductor surfaces.

B. Charge-density waves: weak and strong-coupling

Consider a surfaces which does, in its ideal bulk-like geometry, possess well-defined partly filled electronic surface states, forming a 2D Fermi sea. The density response function of this 2D Fermi sea is peaked at the spanning, or nesting, vector 2k_F. The peak may be strongly enhanced by two separate factors. The first, is the presence of large portions of the Fermi surface, separated side by side by the same 2k_F vector (nesting [2]). The second, is a large electron-electron exchange interaction [3] [4] [5]. When the density response peak
at \(2k_F\) diverges, this signals a CDW. The 2D Fermi surface response influences also surface vibrations, so that Kohn anomalies are also generated at momentum \(2k_F\). When the CDW sets in, the Kohn anomaly is automatically large enough to drive a soft surface phonon, and there will be a displacive change of structure. The surface lattice undergoes a periodic distortion, of spatial periodicity close to \(2\pi/2k_F\), and amplitude proportional to the CDW order parameter \(\Delta\). The outcome of the CDW and its periodic lattice distortion is to eliminate as much of the original 2D Fermi surface as possible, tending to pair electrons into new completely filled states, separated by a band gap \(2\Delta\) from new completely empty states. Due to the lattice involvement, a large electron-phonon coupling at \(2k_F\) will clearly favor CDW’s, besides the purely electronic factors such as nesting, and exchange.

The general ideas behind this kind of displacive SMI transitions (under various names: excitonic insulator [4], [5], charge-density waves [1], band Jahn-Teller effect [6], [7], Peierls instability [8], etc) go back to the fifties and sixties. The possibility of their occurrence on surfaces was raised in the seventies [9], [10], [11], [12], and need not be discussed in great detail here. However, in view of the quite common confusion and controversy, often purely semantic, which these different terms and names appear to generate, it may be useful to remind ourselves about CDW’s in general.

At the general level, before entering a discussion specific to surfaces, an important distinction must be made, between weak-coupling CDW’s, (WCDW) which include Overhauser’s original state [1], and strong-coupling CDW’s, (SCDW), far more common in nature. In both WCDW and SCDW the energy gain is electronic: the gap order parameter \(2\Delta\) implies a reduction of electron kinetic energy, which in 1D is of order \(\Delta^2 |\ln \Delta|\) in the former, and of order \(\Delta\) (asymptotically) in the latter [12]. The size of the electronic gap relative to the phonon energies is the dividing line between the two.

The small gap of WCDW’s generally make them nonadiabatic phenomena, while SCDW’s can be essentially adiabatic, due to their large gap. Due to nonadiabaticity, WCDW’s ought to be sensitive to isotopic substitution, a test which, as far as I know, has never been tried. What drives thermal disordering, and the eventual phase transition to an undistorted state
above a critical temperature $T_c$, is also different in the two cases. In a WCDW, thermal disordering takes place largely due to electronic entropy. When $k_B T \sim \Delta$, electron-hole pairs are excited across the gap, which gradually loses its reason for stability, and disappears at $T_c$, alongside with the periodic lattice distortion. The lattice plays a minor role in disordering, it simply accompanies the electronic distortion. The latter could in fact even take place, driven by exchange, in the absence of a lattice distortion, as in spin-density-waves (SDW) [3].

SCDW’s represent the opposite limit. Here, electron pairs are very strongly bound. They constitute a kind of ordered superlattice of weak chemical bonds, since here the relative size of the pair is comparable with the lattice spacing, $\xi/a \sim \Delta/E_F \sim 1$. There is a strong tendency of the distortion to abandon the exact $2k_F$ periodicity, in favor of some level of commensurability with the original lattice. The electronic energy gain is entirely spread over the Brillouin Zone, (one ought to keep in mind, however, that even in the WCDW, the energy gain does not strictly originate near $k_F$! The gain would only be $\Delta^2$ in that case, not $\Delta^2 |\ln \Delta|$ as it actually is. The $|\ln \Delta|$ factor is due to electrons in the rest of the BZ, away from $k_F$ ). In strong coupling, the electronic gap is always much larger than $k_B T$, electron entropy is irrelevant, and lattice entropy is instead what drives the order-disorder transition [13]. At very high temperature, in fact, the undistorted lattice is favored, as its higher symmetry implies a larger entropy. At the critical point $T_c$, electron pairing is not undone, as was the case in the WCDW. Pairs remain bound, but simply become incoherent with one another. In other words, the lattice remains locally distorted most of the time. However, the distortion fluctuates in space and time, and true long-range order is lost.

It must be stressed that only at some higher temperature $T_o$, way above $T_c$, will the short-range distortion gradually dissolve, and a final crossover take place to a truly undistorted, ordered state. Above this crossover, fast thermal lattice fluctuations restore an ungapped band structure, through a process which has not been studied in sufficient detail, but which must be akin to motional narrowing [14].

Why is the above clarification useful for surface SMI practitioners? Essentially, it should
help us avoid unnecessary controversy, especially between groups who emphasize different aspects, claiming to have altogether different phenomena. For example band Jahn-Teller, or local bonding, which are just other names for SCDWs, are sometimes quoted as plainly alternative to CDW’s, while, as discussed, they do not represent fundamentally different physics from WCDW’s (except for adiabaticity, of course). Similarly, surface order-disorder behavior close to a deconstruction $T_c$ does not speak against a displacive mechanism. It is the rule, on the contrary, close enough to $T_c$, for all continuous, lattice-entropy driven structural phase transitions \[15\], which as mentioned above, include SCDW’s.

C. SMI transitions at semiconductor surfaces: mostly reconstructive

In surface physics, semiconductors are unique, in that essentially all of their surfaces are reconstructed. This can be traced back to the strong covalency of their bulk band structure. As is well-known, covalency requires electronic states to hybridize, and then to overlap, so that filled states correspond to bonds, empty states to antibonds, with a large energy gap in between. At the surface, hybrid orbitals pointing outwards remain as dangling bonds, with energy at mid-gap, as appropriate for a collapse between bonds and antibonds. The dangling bonds constitute therefore sharp surface states (they fall in the bulk energy gap), and are only half-filled (they are crossed by the Fermi level).

The uniqueness of covalent systems as opposed to, for example, regular metals, is that bulk covalent bonding is so directional and inflexible, that it will generally cost too much energy to locally readjust wavefunctions at the surface, without some major lattice rearrangement. In other words, it is not possible to fully rehybridize away the very costly half-filled dangling bonds. Radical rehybridization in fact would cause too much energetic disruption, particularly to the "back bonds" between first and second atomic layer. Orbital readjustment is, on the contrary, generally possible and very easy on the surface of a good metal, which has no bulk energy gap, and where covalency is unimportant. Semiconductor surfaces are thus stuck with half-filled dangling bonds, which constitute a nearly ideal 2D
metallic system, prone to SMI instabilities of one kind or another. They are so unstable, that the strict necessity for the surface to passivate itself, and become a 2D insulator, is the key to understanding in essence all microscopic semiconductor surface physics, including structure, vibrations, and electronic states.

As a consequence, the tendency towards an SMI instability, and the associated energy gain, are very large on semiconductor surfaces. A typical order of magnitude is $0.2 \div 0.3$ eV/surface atom, calculated for clean (111) surfaces of diamond-structure group IV semiconductors. Due to that, there seems to be on semiconductors, contrary to my original suggestions [9] [10] [11], relatively little room for weaker displacive reconstructions such as WCDW’s. I will return to this point, however, at the end of this section.

The majority of stable semiconductor surfaces instead undergo large reconstructive SMI-driven rearrangements. A well-known example is Pandey’s $\pi$-bonded chain model, [16] which explains the (2×1) state of the cleaved (111) surfaces of diamond [17], Si [18] Ge [19], and α-Sn (111) [20], which are free of adatoms. Another example is that of the adatom reconstructions, with the DAS model by Takayanagi et al [21] for Si(111)7×7, and the simpler but related adatom model for Ge(111) c(2×8) [22]. In the (2×1) $\pi$-bonded chain model, one back bond per surface cell is broken and shifted, so that a good resonant overlap of dangling bonds becomes possible along polyacetylene-like surface chains. On diamond (111), there appears even to be a weak dimerization of the chain [17], which is then totally similar to polyacetylene [23]. In adatom reconstructions instead, strikingly, the reconstruction-induced real-space electron pairing is ionic. Here, concerted and opposite relaxations (inwards for adatoms, outwards for free first-layer atoms, called restatoms) lead to transfer of an electron from the adatom, whose dangling bond remains empty, to the restatom, whose dangling bond becomes doubly occupied. This is an example of Anderson’s ”negative U” [24], not the only one in semiconductors and semiconductor surfaces [23] [29]. Finally, besides adatoms, also surface vacancies are predicted to have an interesting interplay with reconstructions of semiconductors. One example is the strong $\sqrt{3} \times \sqrt{3}$ buckling distortion which has been predicted to decorate the neighborhood of a vacancy on ideal Ge(111) [27].
Are there then any CDW’s on semiconductor surfaces? Actually, the answer is affirmative: but they are all very strong coupling SCDW’s, so strong that they hardly ever deconstruct at a reasonably low temperature. The dimer reconstruction of Si and Ge(100)\cite{28} \cite{29} can be seen as a very large amplitude SCDW. The up-down buckling which stabilizes the $\pi$-bonded chain (2 \times 1) reconstruction of Si, Ge, and $\alpha$–Sn (111)\cite{18} \cite{19} \cite{20}, and the dimerization which stabilizes that of diamond (111)\cite{17} are also examples of SCDWs, since the chain would be a 1D metal without them.

Finally, detailed calculations show that even on the ideal clean Ge(111) surfaces a simple alternative SCDW-type state, which consists of a regular up-down buckling (leading to a (2\times1) ionic reconstruction) does in fact exist. It is an energy extremum, only slightly higher than either the $\pi$-bonded chain or the adatom-restatom states. Hence the SCDW is in this case only a local minimum, or perhaps a saddle point. Interestingly though, even if it never makes it to the ground state, this state may still not be completely irrelevant. As revealed by recent \textit{ab-initio} simulations, it appears to play the role of a transition state in the evolution between the ideal surface and the final $\pi$-bonded chain state\cite{19}.

D. W(001), Mo(001): good examples of SCDW’s

The bcc group VA and VIA metals are those, among all transition metals which bear the closest resemblance to semiconductors. There is in their bulk electronic structure a certain degree of covalent bonding involving the d-states, which shows up clearly, even if indirectly, in the electronic density of states\cite{30}. It shows, as a function of energy, two rather well separated groups of states. Between them, a region of relatively low density of states, or pseudogap. The two large groups of electronic states are, again, superpositions of directional d-state hybrids, of bonding and antibonding character respectively\cite{31}. In the refractory metals, Mo and W, the bonding states are totally filled, and the Fermi level falls in the pseudogap, below the antibonding ones. This qualitatively explains their high stability, hardness, and melting point. On the other hand, the Fermi level cuts to some degree into
the bonding bands in the case of V, Nb, Ta (which have one electron less) and also in Cr, where s states are comparably deeper than in Mo, W. The incomplete filling of the bonding d-states is clearly connected with bulk anomalies, including the antiferromagnetism of Cr, and the superconductivity of V, Nb, and Ta.

Amusingly, the behavior of the (001) surfaces of these bcc metals is just reversed (at least for the nonmagnetic ones) with respect to their bulk. On these faces, it turns out, there are dangling-bond-like surface states, analogous to the case of semiconductors, and here too, they fall at mid (pseudo-) gap. Moreover, the ideal surface electronic structure is quite similar for pairs of bcc transition metals which differ by just one electron, like Ta vs. W, and Nb vs. Mo. Because of that one electron difference, however, the surface states are partly filled in W and in Mo(001), but totally empty in Ta and Nb(001). Electron counting, the very reason for bulk instability of Nb and Ta, has now become a reason for surface stability. Exactly the opposite is true for Mo and W: on the (001) surfaces of these very stable metals, one now expects electronic instabilities, and surface phonon anomalies, possibly leading to some kind of surface-state driven SMI transition. The reconstructions which Estrup et al. and King et al. found in the 70’s have unmistakeably that origin, and are due to those partly filled surface states, as later confirmed by many experiments (rather well summarized in Hulpke’s paper) and also by microscopic calculations.

Still, to this date, lingering questions seem to have remained around. Are these actually CDW’s or are they not? For example, is the reconstruction periodicity (exactly c(2×2) for W(001), and close but slightly different from c(2×2) for Mo(001)) dictated by the 2D Fermi surface, as originally proposed and as appropriate for WCDW’s, or is it more related to coupling with the underlying bulk lattice and its surface phonons, as expected in a SCDW? Is the finding of critical fluctuations at an apparently incommensurate wavevector, seen by elastic He-scattering on W(001) near (1/2,1/2) π/a just above Tc, an evidence for 2D Fermi surface effects, or could it again be a purely lattice effect? Finally, a basic question sometimes raised is, is the deconstruction of W(001) order-disorder like, or order-order like?
I believe it has been made very clear during the past decade, that the SCDW scenario is the correct one. The key role of the half-filled surface states is unquestionable, as shown in particular by the absence of anomalies for Nb(001) [47] [48], in agreement with predictions [36] and by their disappearance from Mo and W(001) upon H adsorption [16]. A large phenomenology (also in agreement with later electronic structure calculations) suggests in addition that coupling is relatively large, and the electron pair correlations length is correspondingly short. Under these circumstances, the effect of electronic forces may be mimicked in a first approximation by an additional short-range force between surface atoms. In other words, the net effect of half-filled states onto ionic motion can be cast into a pure, unretarded classical potential, much in the same way that an electronic bond in a solid or a molecule can often be replaced by a classical spring [42] [43]. If this picture is admittedly crude, it not outrageously so in strong coupling, and has the enormous advantage to allow an accurate treatment of everything else, related specifically with the position, dynamics, and statistical mechanics of the ions. In fact, for everything except electronic structure, which obviously it does not treat, it is found that this model works quantitatively, correctly describing how the distortions is largely, but not entirely in the first layer [43], the surface phonons, including a very elusive mode at k=0 [49] [50], the thermal deconstruction behavior, which exhibits both displacive and order-disorder features [51], the soft phonon behavior with temperature [52] [53] [54] [46]. It also predicts a large difference between a deconstruction $T_c$ around 280 K, and a much higher crossover $T_o$, expected around 800 K on W(001) [55].

For Mo(001), the classical force model suggests that lack of exact c(2×2) commensurability (formerly described as incommensurate [34], and subsequently found to be higher order c(7√2 × √2)R45° commensurate [56] [57]) need not be strictly due to a Fermi surface surface effect [36], but may also arise due to competition between in-plane and bulk-mediated purely lattice forces, giving rise to soft phonon modes away from, but close to, high-symmetry k-points [42] [58] [59]. It is in fact possible, by modifying slightly the interaction parameters [60] from the somewhat arbitrary values adopted in an earlier study [59], to reproduce rather closely the c(7√2 × √2)R45°structure recently reported for Mo(001) [61]. Very reasonable
geometries are also obtained [62], using the phenomenological potentials developed by Carls-
son [63].

As for electronic states, their accurate description at \( T = 0 \), and their thermal evolution at and across the transition, the situation is less clear. Local density calculations, at the best of their accuracy, confirm that a displacive reconstruction lowers the energy, and suggest a rather large gain in the order of 0.1 eV per surface atom at \( T = 0 \) [41] (against the 0.03 eV which realistically explain the observed transition temperature [51] [52] and distortion magnitudes [43]). Photoelectron spectroscopy has been contradictory, with papers first suggesting the irrelevance [64], and more recently the relevance of the 2D Fermi surface and its gapping across \( T_c \) both on W(001) [65], and Mo(001) [66].

In this connection, I would like to call attention to the fact, often overlooked (but not al-
ways: see Ernst et al. [46]), that the nature of the SCDW phase transition, even if displacive, implies a disorder-order crossover regime between \( T_c \) and \( T_o \), with \( T_o \gg T_c \). Thermal evol-
ution of the electronic states should begin with sharp, gapped surface bands well below \( T_c \) and end again with relatively sharp ungapped bands, \textit{not above} \( T_c \), \textit{but above} \( T_o \)! Only above \( T_o \) (\( \approx 800 \) K for W(001)), does in fact short-range reconstructive order disappear, the motional narrowing of electronic bands become complete, and the surface behave as truly undistorted. It is therefore not a surprise that photoemission evidence should appear messy, and confusing, anywhere between 100 K and 800 K for W(001), or, rescaling down a factor of roughly two, between 50 and 400 K for Mo(001).

Nobody has unfortunately given a useful theory yet, or a simulation, of what to expect of surface electronic states and their spectral function inside the crossover temperature range. However, it is unlikely that experimental results in this range should be amenable to a simple interpretation based on a mean-field picture, which is what has been tried so far. On the other hand, a mean field-like picture should work better when comparing data between, say, 50 K and 1000K, since both temperatures should fall outside of the crossover range. Should this comparison be possible in the future, we would get a clearer message about the reconstruction of W(001) and Mo(001) from electron spectroscopy.
Related comments apply to He-scattering results, discussed in great depth by Hulpke and his collaborators for W(001) [46] [38]. Here, I would like to take up a relatively controversial aspect, namely the apparently incommensurate He scattering peak just above \( T_c \) [44] [46], which is invisible in LEED, and is attributed to purely electronic incipient CDW scattering. Much as their overall viewpoint is attractive, I would be considerably less certain about the actual 2D Femi surface origin of their observed incommensurate scattering peak, than they seem to be. In their support, it must be admitted that He scattering is nearly uniquely and exquisitely sensitive to the Fermi surface (simply measuring a particular surface electronic correlation function). The evidence that Fermi level surface electron correlations becomes incommensurate above \( T_c \) must therefore be accepted as a fact. If other surface tools miss that, it must be because they are less sensitive to surface electrons near the Fermi level, not because the He results are artifacts. However, it must also be considered that if surface electrons appear incommensurate, that means something about the ions too, since electrons are in the end not really free to do what they will. Surface electrons are, adiabatically or not, tightly connected with surface ions, which in turn we know to be, at these temperatures between 300 and 400 K, barely deconstructed out of the c(2\( \times\)2) state, still strongly short-range ordered, slowly fluctuating, and very much in the crossover region. There is no such thing as a clean, free 2D Fermi surface, in this regime.

My inclination is to believe, without a definite proof for the time being, that the He-scattering incommensurability could in the end be traced back to the surface ionic distortions. In very different surfaces, namely (1\( \times\)2) reconstructed Au(110) and Pt(110), there is a very similar shift of the half-order spot remnants, towards an apparent incommensurability, which develops linearly just above \( T_c \) [67] [68] [69] [70]. The reason for that can be understood via SOS models [71], which show that due to proliferation above \( T_c \) of an excess of one type of steps (antiphase domain walls), say 1\( \times\)3 steps, over the opposite type, say 1\( \times\)1 steps, leads a shift of the 1/2 order spot towards smaller k-vector above deconstruction [72]. This feature is sometimes referred to as ”chirality” [73].

Also on the c(2\( \times\)2) distorted surface of W(001), one can consider the role of antiphase
domain walls. Chirality is expected here too, because of the obvious inequivalence of "heavy" and "light" walls. For example, the current model for the $c(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstruction of Mo(001), as determined from X-ray data consists of a regular array of strictly light walls (in fact, one every three zig-zag chains). Therefore, if domain wall proliferation is, as is likely, an important process in surface deconstruction of W(001) just above $T_c$, then the explanation of incommensurability could be, mutatis mutandis, just the same as on $(1 \times 2)$ reconstructed Au(110) and Pt(110). The main difference being that while on Au(110) the domain walls are actual surface steps, on W(001) and Mo(001) they are phase slips of a small in-plane periodic lattice distortion.

On the experimental side, if this speculation is correct, I would expect that a surface scattering tool, sensitive to ions instead of electrons, but still sensitive enough to short-range order effects, should be able to pick up again the same incommensurability above $T_c$, as the He scattering probe does.

Another point I would like to make is that it can be argued, interestingly, that a wall will necessarily involve a local vertical displacement too. This can be understood equivalently in terms of (a) the lattice dynamics of the flat, unreconstructed surface, implying mixing of the so-called $M_5$ (in-plane) and $M_1$ (vertical) modes; (b) the soliton lattice model, where the phase quadrature between $M_5$ and $M_1$ modes implies a local $M_1$ distortion creeping in between two antiphase $M_5$ regions; (c) local strain relief at the wall, which is the easiest to explain. Basically, a surface atom in the center of an antiphase wall, has a displacement whose in-plane component is zero by symmetry, but whose vertical component can generally be finite. At a light wall, all four neighboring surface atoms have moved away, creating an effective potential trough, into which the center atom must fall. Hence, I expect a downward displacement in the center of a light wall, and conversely an upward displacement at a heavy wall center. If light walls proliferate, and also move, they should carry with them this downwards surface buckling.

It would be interesting to try to pick up these vertical displacements, either in the reconstructed state of Mo(001), or on the just-deconstructed state of W(001) slightly above $T_c$. 

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As it turns out, unfortunately, X-ray data are relatively insensitive to vertical displacements, so much that the amount of buckling on Mo(001) is unknown, at least so far \[75\]. The large sensitivity of He scattering, conversely, may offer an additional clue as to why a wall proliferation should be revealed so effectively in that experiment.

On the theory side, this idea could in principle be pursued quantitatively via simulations based on classical hamiltonians (\textit{ab initio} ones being far too time-consuming, at this stage). The required simulations would need considerably larger sizes than those employed in our earlier studies \[51\] \[52\]. Some evidence for incommensurability, had in fact occasionally been seen at short times in those earlier simulations, even with their very limited cell sizes. \[76\].

A final question pertinent to that scenario is: what happens to the surface state at an antiphase domain wall? The standard soliton picture \[23\] would suggest a mid-gap state, localized at the wall. In this case, it would correspond more or less directly, to the dangling bonds of the center atom in the wall. It would possess a dispersion parallel, but not perpendicular to the wall. Moreover, the vertical displacement of the center atom would control its energy, and therefore its electron filling. Altogether, it would seem exciting to pursue this concept, and attempt a detection of such a domain wall surface state.

### E. Clean Cu(111) : incipient CDW’s on noble metals?

The (111) face of noble metals: Cu, Ag, Au, possesses an s-like surface state, with a good, roughly free-electron like, parabolic dispersion near the $\Gamma$- point \[77\]. The state is partly filled, with a modest 2D electron density, corresponding to Fermi energies $E_F$ of 0.44, 0.12, and 0.5 eV for Cu, Ag and Au(111) respectively. The 2D Fermi surface is correspondingly spanned by a rather small $2k_F$ ($\sim 0.4\text{Å}^{-1}$ for Cu(111)), very close in fact to the diameter of the famous (111) “neck” of the 3D noble metal Fermi surface \[78\]. Physical effects connected with this his surface state are further addressed by Inglesfield and his collaborators \[79\].

Probably due to a strong screening of exchange by the underlying bulk, to the insufficient nesting which provided by the approximately circular shape, and to depth mismatch, the
2D Fermi surface is unable to drive a CDW (or an SDW) on these surfaces, which remain undistorted and metallic. The surface phonons at $2k_F$ decay as $\exp(-z/z_{2k_F})$ below the surface plane ($z = 0$) with a penetration depth $z_{2k_F}$ which is large, since $2k_F$ is small. The corresponding penetration depth of the surface electronic state at $\pm k_F$ is not the same. On Cu(111) it is possibly smaller, in other cases it might be larger. Quite generally, the mismatch between penetration depths of surface electron and phonon states is a likely factor to reduce the coupling between the two, and suppress or limit the occurrence of surface CDW’s. A relative paucity of CDW examples has been noted by Kevan [80]. Depth mismatch is likely to be one important factor behind it.

On Cu(111), where there is no stable CDW, and moreover no strong Kohn anomaly has been found in the surface phonon spectrum, there is nonetheless a direct evidence that the surface response is high at $2k_F$. Recent low-temperature STM topographs have shown spatial oscillations, with the right periodicity $2\pi/2k_F \approx 15\,\text{Å}$, decorating the neighborhood of Fe surface impurities. [81]. In the light of these results, SDW’s or CDW’s might perhaps be suspected to be incipient on this and similar surfaces.

In reality, however, CDW’s are probably still far from incipient. It should be again stressed in this regard that STM and He scattering are two tools which greatly overemphasize the Fermi surface, since they couple directly to it. The underlying overall energetics associated with these surface oscillations, including for example the resulting indirect interaction between surface impurities via bulk electronic states [82] [83], and via surface states [84] [85], is in fact likely to be small in this case [80]. A well-defined Kohn anomaly, i.e. a dip in the surface phonons at $2k_F$, remains a mandatory piece of evidence, for CDW’s incipiency.

F. Alkali-covered noble-metal surfaces :K/Cu(111)

Hirschmugl et al have recently uncovered an unexpected anomaly in the IR spectrum of the alkali-covered noble metal surface K/Cu(111) [80] [87]. They find, for K coverages
sufficient for the alkali to begin forming metal islands, $\theta_K \geq 0.4$ monolayers in this case, a sharp IR *antiabsorption* peak, at a photon energy of about 0.1 eV. The antiabsorption nature of the peak signifies, as shown by Persson [88] [87] that the mode involves an in-plane charge oscillation, of a type conventionally believed to be totally invisible in IR. What is to be explained, is *what charge is oscillating*. At such a high frequency, it cannot be a lattice mode, and the oscillation must therefore be electronic. Formation of a CDW has been invoked, favored by the dense metallized alkali layer. The CDW is pinned by some mechanism, such as disorder or roughness, so that its hindered translation acquires a finite frequency, of just 0.1 eV.

At first, the proposition looks attractive. After all, there was already a surface state on clean Cu(111), with a possibly incipient CDW (see above), before the alkali was deposited. Maybe the surface state can get a little flatter, or it can get better coupled, or else maybe the metallic alkali monolayer may screen out the electric field [86], tilting the balance a little towards CDW’s. Maybe; but a few extra facts make it all a little less simple, to say the least.

One fact is that the effect is absent for good quality surfaces, and shows up only after a dose of scratching and crude roughening. Another fact is the remarkable reproducibility of the narrow antiabsorption frequency, which ought to show at least inhomogeneous broadening if due to CDW pinning. Yet another, is that there is experimental proof that alkali coverage alters the surface state picture very substantially.

The behavior of noble metal (111) surface states with alkali adsorption has been recently quite well characterized [89] [90]. For very small coverage $\theta \leq 0.1$, the clean-surface state described in Section 2.4 survives, although slightly pushed down in energy, closer to bulk states. In this regime, one might perhaps imagine a tendency for the alkali adatom density to become modulated in some interesting relationship with the $2k_F$ charge oscillation they generate in the surface. As coverage increases, however, the surface state is pushed right into the bulk continuum, *and it disappears altogether*. At the same time, the work function decreases, and an image state, initially several eV’s above $E_F$, is descending. At the met-
allization coverage, the alkali metal condenses into islands of coverage one, and this state suddenly drops below the Fermi level, forming a new partly filled surface state. It has about the same $2k_F$ of around 0.4 Å$^{-1}$ as for the clean surface, but with a mass perhaps 4 times larger, whence $E_F$ is correspondingly smaller, 0.11 eV instead of 0.44 [91]. The character of this state is now partly alkali, and partly Cu, and its penetration depth is at least a factor 2 smaller than the clean surface state.

This new surface state could now drive a CDW, and it could do that effectively, since the factor 4 in the mass will also multiply the response at $2k_F$. But why should this CDW require roughness, or disorder, or possibly impurities, and refuse to show up on clean, smooth surfaces? And why should an inhomogeneously pinned CDW yield nonetheless a single, well-defined pinning frequency? Is there perhaps a reason why the new Fermi energy and the antiabsorption peak frequency are so close? Shouldn’t a diffraction study pick up signs of at least some, even blurred, CDW scattering, anyway, before we believe it?

To an outside spectator, the 0.1 eV feature actually looks more like a 2D plasmon, localized and made accessible to optical detection by disorder and imperfections. Being determined by the full coverage 2D electron density the (wavevector integrated) plasma frequency is sharp, and independent of mean coverage, disorder, etc. Is this a true alternative explanation?

The answer to these questions and speculations is unknown, and must be postponed to the future.

G. One-dimensional Kohn anomalies on surfaces: H/W(110) and H/Mo(110)

If I must quote two surfaces where a textbook-clear fingerprint of surface-state induced giant Kohn anomaly and/or CDW is clearly visible, then those surfaces are to my mind H/Mo(110), and H/W(110).

The evidence, first found by Hulpke et al. [92] [38] is of an extremely sharp, one-dimensional-like dip in the surface phonon spectrum. Comparison with e.g., the phonons
of the quasi-one-dimensional chain compound KCP is striking: it is hard to tell the two apart. Similarly striking is a comparison with the calculated phonon/phason/ampliton spectrum of a single 1D chain, carried out long ago within mean-field theory, and reproduced in Fig. 1. The extremely large slope $|d\omega/dk|$ of the lower surface mode near the anomaly at $k = Q$ simply demands an electronic explanation (a Fermi velocity is typically $10\div100$ times larger than a sound velocity), and disfavors at the outset the alternative (and otherwise attractive) non-electronic interpretations for the anomaly. A substantial embarrassment to the surface state community comes from the fact that there was, prior to the discovery of this anomaly, no compelling reason, as to why of all surfaces, precisely H/W(110) should suddenly develop, at full coverage and only there, such a strong Kohn anomaly, and a one-dimensional one on top of that! There are in fact partly filled surface states on this surface, and their 2D Fermi surface, as extracted from photoemission data, had been previously reported. But the nesting suggested by that data, was neither strong, nor did it possess a k-vector strikingly close to the observed phonon anomaly.

Recent calculations on H/Mo(110) by the Berlin group are more illuminating, showing a 2D Fermi surface with a nesting vector in better agreement with the phonon anomaly, which is therefore likely to be indeed a giant Kohn anomaly. These calculations suggest the following overall picture. The partly filled surface electronic states and their 2D Fermi surfaces are already present on clean Mo(110). There, however they are still too close in energy to the bulk states, their penetration depth too large, to be important for surface phonons. Upon H-adsorption, the H orbitals hybridize and mix covalently with the surface states, and push them down in energy as a consequence, right into the middle of the surface gap for projected bulk states. The surface state character is thus greatly enhanced, the penetration depth now comparable with the lattice spacing, and the nesting vector closer to the observed phonon anomaly, with fairly good parallel portions. All in all, the calculation results come way closer to explaining the phonon anomaly, than the photoemission-derived 2D Fermi surface does.

Why should we trust a calculation more than a piece of data, when it comes to ar-
guing about the 2D Fermi surface? I believe we should indeed do that. The key lies in the strong possibility, which I advance, that while the surface used for the calculation is truly undistorted, that used for experiment is only undistorted on average, must be very distorted, instantaneously and locally. That this should be the case, follows from the strong, slow fluctuations which necessarily accompany the soft phonon branch, whose experimental energy takes a plunge from the 20 meV or so of the Rayleigh wave, down to a dip of 1 or 2 meV only, at $Q = 0.93 \text{ Å}^{-1}$. Also the correlation length implied by this dip is very large, of order 100 Å or so, and is probably terrace-size limited, as suggested by the overall temperature-independence of the anomaly.

Now, if in actual fact the surface is distorted, pieces of the 2D Fermi surface originally connected by the distortion wavevector $Q$ must disappear due to Bragg scattering. Their remnants are modified, and generally shifted elsewhere in k-space. Hence, the apparent 2D Fermi surface in presence of a distortion, even if local and fluctuating, differs maximally from the ideal one precisely where nesting k-vectors are closest to that of the local distortion periodicity. This means, that precisely due to the anomaly, we should not expect to see apparent nesting for $k = Q$, which is what photoemission finds! Future calculations, experiments, and simulations, should be able to enlighten further this aspect, which seems crucial in order to make contact with photoemission.

What about hydrogen? Do the adsorbed hydrogens play any additional role, other than just conveniently shifting pre-existing surface states so that they yield an anomaly? EELS data suggest an affirmative answer, with an unusual continuum of H-related modes puzzlingly terminating at 850 cm$^{-1}$, and a coalescence of higher frequency modes when the coverage approaches one monolayer, where the anomalous continuum also appears. Balden et al. [98] noted this, and suggested a 2D hydrogen fluid, as the explanation. This is however puzzling, in view of the apparent independence of all phenomenology from either temperature, or isotopic substitution of D in place of H. This aspect of the phenomenon therefore remains open to further investigations.
III. SURFACE INSULATOR-METAL TRANSITION

So far, we have seen how a 2D metallic character may become unstable on surfaces. In this section, I want to present cases where, somewhat to the contrary, the metallic character may be the one eventually preferred at the surface of a nonmetal, or of a poor metal. There is in the literature no general discussion, or basic theory, of the SIM transition, and I am not going to produce one here. I shall simply illustrate the notion by discussing a few cases where I believe a SIM is taking place. This phenomenon, in any event, is far less established than that of SMI. The most urgent effort in this area should be experimental, for my examples are, as I said, vastly (although not totally) derived from calculations.  

A. Alpha-gallium(001)

α-Ga is an unusual metal in many ways. It consists of covalently bonded Ga$_2$ molecules or dimers, which have enough overlap to metallize, along (buckled) planes. Parallel to these planes, the metallic conductivity is reasonably high. Between the planes, however, there is mostly covalent Ga$_2$ bonding, and the conductivity is poorer, semi-metallic. In the bulk Ga phase diagram, semi-metallic α-Ga has the lowest energy under ordinary conditions. However, other phases, such as Ga III, compete closely with α-Ga. In these phases, molecular bonds and covalency are absent, and metallicity is unmitigated, as in Al. At sufficiently high pressure and temperature, the fully metallic phases eventually prevail.

What should the stable structure of a close-packed surface of α-Ga, such as the (001) face, look like? On the ideal α-Ga(001) face, the Ga$_2$ dimers stick out at an angle, giving rise to an unrealistically high charge corrugation, and, in correspondence, an unacceptably high surface energy. Alternatively, the surface can be smoothed by breaking surface dimers, and removing one Ga atom from each of them. However, the surface energy is again unexpectedly high. As it turns out, the reason now is that dangling bond surface states are formed...
Eventually, calculations suggest that both the unrealistic corrugation, and the costly dangling bonds, can be eliminated, and a substantially lower energy state reached, by a simple kind of "1×1" reconstruction. Here, remarkably, the two outermost surface layers have become Ga III-like (with an in-plane expansion, as required by epitaxy on α−Ga), and fully metallic.

While it can be argued that an atomically thin metallic overlayer will quite generally contribute to lower the surface exchange-correlation energy of a bulk nonmetal, it is also clear that the surface metallization which is predicted to take place on α−Ga(001) would not have had a chance, had the dangling bond surface states not been there on the ideal surface, in the first place! In this sense, this SIM transition has a point in common with the SMI’s discussed in the previous section. Both of them take place, in order to eliminate half-filled surface states.

As this might be quite an interesting SIM test case, I would like to take this chance to remind the experimental community that, with the notable exception of very careful STM studies, there is as yet no experimental study addressing specifically either structure, both atomic and electronic, or excitations, of α−Ga(001).

B. Be(0001)

Hcp beryllium is another interesting semimetal, which has in common with α−Ga a clear pseudogap in the bulk electron density of states, constituting a signature of covalent bonding. Unlike α−Ga, however, it is not so easy here to connect bands with bonds, and in fact no pairwise bulk covalent bond have been identified. Boron is another element where the same "problem" arises. There, three-center bonds have been discussed, as the way to understand covalency in real space, and maybe three-center bonds should be invoked in Be as well. As discussed by Stumpf at this meeting, in the case of Be, the covalent semimetallic state is connected with a shorter c/a ratio, meaning that covalent bonds for an atom in a (0001) plane have to do with the six neighbors, three in the plane below and
three in the plane above. As a purely heuristic device, we could therefore think of these as six "hole bonds". What this means is that with only two electrons, or six holes, in the (2s,2p) shell, each Be atom could covalently share a hole with each of its out-of-plane first neighbors.

Let us now come to the Be surfaces. Stumpf has described, quite convincingly, how at the (0001) surface, Be gives up its covalency, locally recovering a fully metallic behavior. This is another example of SIM, somewhat similar to that just discussed for $\alpha$-Ga(001). About the physical reasons which drive this SIM, we can at best speculate, in the lack of a good chemical understanding of even the bulk Be bonding.

At the speculative level, I find the hole bonding picture rather useful in this connection. In particular, the reason for the SIM at Be(0001) can be seen as due to the necessity to eliminate the three "hole dangling bonds" which the covalent structure would retain per each surface atom. Unlike $\alpha$-Ga, where a major reconstruction is necessary to eliminate the surface states, here the close-packed structure of Be makes the transition possible by a simple outwards relaxation, a kind of displacive SIM.

Based on this picture, I can further speculate about the possible role of temperature in this system. As T grows, lattice entropy should favor a propagation of the more metallic state deeper into the bulk, while electronic forces which oppose that should act as a limiting factor. As a result, the fully metallic state could remain confined to the first layer, or to a small set of layers (a sort of incomplete wetting of semimetallic Be by a fully metallic phase), or it could instead move into the bulk, and trigger other transformations as well. It would be interesting to pursue experimentally the question of which of the various possible scenarios is realized.

C. Ge(111) at high temperature

Another example of fine balance between bulk covalency and metallicity is offered by the group IV elements Si, Ge, Sn. Semiconducting Si and Ge, in particular, turn into good metals
above their melting point. From the point of view of electronic structure, metallization has to do with the fact the fourfold tetrahedral atom coordination is lost, in the liquid state.

What should we expect of a semiconductor surface at high temperature? At the experimental level, we know that surface disorder begins to appear, even if only at the level of adatoms, at deconstruction. For instance on Si (111), $7 \times 7 \rightarrow 1 \times 1$ deconstruction takes place 70% of the melting temperature $T_m$. On Ge(111), the $c(2 \times 8) \rightarrow 1 \times 1$ deconstruction occurs at even lower temperature, around 40% of $T_m$. In both cases, it can be argued that adatoms become mobile, and diffuse on the surface. Therefore, a germ of disorder and atom diffusivity is already present at relatively low temperatures. This might suggest a gradual and continuous surface melting as $T_m$ is approached, a route which is common to most crystal surfaces. This would imply the growth, in full equilibrium, of a liquid metallic film on the semiconducting bulk, with thickness diverging as $T \rightarrow T_m$. On the other hand, we know from phenomenology that dispersion forces, surprisingly important in the surface melting problem, are going to make such a continuous melting impossible on a semiconductor surface. In this case, due to a ”negative Hamaker constant” [109], nucleation of a metallic film is welcome, but its thickness is confined to remain microscopically small. This behavior, when realized, goes under the name of ”incomplete surface melting”.

Ge(111) is perhaps the best studied case of semiconductor surface at high temperature. Although there still is some controversy [110] (once again centered around He scattering data!), several groups have reported incomplete melting transition of this surface near 1050 K [111] [112]. Recent ab initio simulations also favor incomplete melting, and predict that it should go hand in hand with surface metallization [102], for which there is now clear EELS evidence [99]. Generalizing (which may not be fully authorized!), I would venture to say that this example shows that SIM transitions are to be expected on semiconductor surfaces close enough to the melting point.

Unlike the $T = 0$ cases discussed above, the present case of a high-temperature SIM transition is not apparently related to eliminating surface states of the semiconductor. On the contrary, we do predict a very metallic density of states in the first bilayer, after the
SIM has taken place. From the point of view of local symmetry, an atom in the first bilayer should fluctuate rapidly between a diamond, and an hexagonal diamond configuration [102]. Photoemission from these first-bilayer states, if feasible, should prove extremely revealing as to the real nature and symmetry of these atoms, and of the surface metallization phase transition altogether.

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REFERENCES

[1] A.W. Overhauser, Phys. Rev. 167 (1968) 691; Adv. Phys. 27 (1978) 343.

[2] W. M. Lomer, Proc. Phys. Soc. 80 (1962) 489.

[3] A.W. Overhauser, Phys. Rev. 128 (1962) 1437.

[4] W. Kohn, in Many Body Physics, ed. C. DeWitt and R. Balian (Gordon and Breach, New York, 1968) p. 353.

[5] B.I. Halperin and T.M. Rice, Solid State Physics 21 (1968) 115.

[6] H.C. Longuet-Higgins and L. Salem, Proc. Roy. Soc. A251 (1958) 172.

[7] R. Englman, The Jahn-Teller Effect in Molecules and Crystals (Wiley, New York, 1972).

[8] R.E. Peierls, Quantum Theory of Solids (Clarendon, Oxford, 1955) Ch. 5.

[9] E. Tosatti and P. W. Anderson, Sol. State Comm. 14 (1974) 713.

[10] E. Tosatti and P. W. Anderson, Proceedings of the 2nd Int. Conf. on Solid Surfaces, Kyoto 1974, Jap. J. Appl. Phys., Suppl. 2, Pt. 2 (1974) 381.

[11] E. Tosatti, Festkörperprobleme 15 (1975) 113.

[12] E. Tosatti, in Modern Trends in the Theory of Condensed Matter, ed. A. Pekalski and J. Przystawa (Springer-Verlag, Berlin, 1980) p. 501.

[13] J. E. Inglesfield, J. Phys. C 12 (1979) 149.

[14] see, e.g., C. Kittel, Introduction to Solid State Physics, (Wiley, New York, 1971) Ch. 17.

[15] see, e.g., A. D. Bruce and R. A. Cowley, Structural Phase Transitions (Taylor and Francis, London, 1981).
[16] K.C. Pandey, *Phys. Rev. Lett.* **47** (1981) 1913; **49** (1982) 223.

[17] S. Iarlori, G. Galli, F. Gygi, M. Parrinello, and E. Tosatti, *Phys. Rev. Lett.* **69** (1992) 2947.

[18] F.J. Himpsel, P.M. Marcus, R.M. Tromp, I.P. Batra, M.R. Cook, F. Jona, and H. Liu, *Phys. Rev. B* **30** (1984) 2257.

[19] N. Takeuchi, A. Selloni and E. Tosatti, *Phys. Rev. B* **44** (1991) 13611.

[20] Z.Y. Lu, G.L. Chiarotti, S. Scandolo, and E. Tosatti, to be published.

[21] K. Takayanagi and Y. Tanishiro, *Phys. Rev. B* **34** (1986) 1034.

[22] D. J. Chadi and C. Chiang, *Phys. Rev. B* **23** (1981) 1843.

[23] see., e.g., W.P. Su, J.R. Schrieffer and A. J. Heeger, *Phys. Rev. B* **22** (1980) 2099.

[24] P. W. Anderson, *Phys. Rev. Lett.* **34** (1975) 953.

[25] F. Ancilotto, A. Selloni and E. Tosatti, *Phys. Rev. B* **43** (RC) (1991) 5180.

[26] E. Tosatti, in *Highlights of Condensed Matter Physics and Future Prospects*, ed. L. Esaki (Plenum, New York, 1991) p. 631.

[27] F. Ancilotto, A. Selloni and E. Tosatti, *Phys. Rev. B* **43** (RC) (1991) 14726.

[28] R.M. Tromp, R.G. Smeenk, F.W. Saris, and D. J. Chadi, *Surf. Sci.* **133** (1983) 137.

[29] J.C. Fernandez, W.S. Yang, H.D. Shih. F. Jona, D.W Jepsen, and P.M. Marcus, *J. Phys. C* **14** (1981) L55.

[30] see, e.g., D.A. Papaconstantopoulos, *The Band Structure of Elemental Solids*, (Plenum, New York, 1986).

[31] see, e.g., W.A. Harrison, *Electronic Structure and the Properties of Solids*, (Freeman, S. Francisco, 1980).
[32] S.L.Weng, T. Gustafsson, and E.W.Plummer, *Phys. Rev. Lett.* **39** (1977) 822.

[33] S. L.Louie, K.M.Ho, J.R.Chelikowsky, and M.L. Cohen, *Phys. Rev. B* **15** (1977) 5627.

[34] T.E.Felter, R.A.Barker, and P.J. Estrup, *Phys. Rev. Lett.* **38** (1977) 1138.

[35] M.K.Debe and D. A. King, *J. Phys. C* **10** (1977) L303; *Phys. Rev. Lett.* **39** (1977) 708.

[36] E. Tosatti, Sol. State Comm. **25** (1978) 637.

[37] J.E. Inglesfield, *J. Phys. C* **11** (1978) L69.

[38] E. Hulpke, this volume.

[39] H. Krakauer, M. Posternak and A.J.Freeman, *Phys. Rev. Lett.* **43** (1979) 1885.

[40] X.W.Wang, C.T. Chan, K.M.Ho and W. Weber, *Phys. Rev. Lett.* **60** (1988) 2066.

[41] D. Singh and H. Krakauer, *Phys. Rev. B* **37** (1988) 3999.

[42] A. Fasolino, G. Santoro and E. Tosatti, *Phys. Rev. Lett.* **44** (1980) 1684.

[43] A. Fasolino and E. Tosatti, *Phys. Rev. B* **35** (1987) 4264.

[44] H.J.Ernst, E. Hulpke and P.J.Toennies, *Phys. Rev. Lett.* **58** (1987) 1941.

[45] D.A.King, *Physica Scr.* **T4** (1983) 34.

[46] H.J.Ernst, E. Hulpke, and P.J.Toennies, *Phys. Rev.B* **46** (1992) 16081, and references therein.

[47] A.J. Melmed, S.T. Ceyer, R.T.Tung, and W.R. Graham, *Surf. Sci.* **111** (1981) 1701.

[48] E. Hulpke, M. Hüppauf, D.-M. Smilgies, A.D. Kulkarni, and F.W. deWette, *Phys. Rev. B* **45** (1992) 1820.

[49] J.P.Woods and J.L.Erskine, *J. Vac. Sci. Technol.* **A4** (1986) 1414.

[50] C.Z.Wang, A. Fasolino and E. Tosatti, *Phys. Rev. Lett.* **59** (1987) 1845.
[51] C.Z. Wang, M. Parrinello, A. Fasolino and E. Tosatti, Europhys. Lett. 6 (1988) 43.

[52] C.Z. Wang, A. Fasolino and E. Tosatti, Phys. Rev. B37 (1988) 2216.

[53] C.Z. Wang, A. Fasolino and E. Tosatti, Europhys. Lett. 7 (1988) 263; Surf. Sci. 211/212 (1989) 323.

[54] W.H. Han, S.C. Ying and D. Sahu, Phys. Rev. B41 (1990) 4403.

[55] A. Fasolino and E. Tosatti, unpublished; E. Tosatti, results presented at the Cambridge Meeting, March 1991.

[56] E. Hulpke and D.-M. Smilgies, Phys. Rev. B43 (1991) 1260.

[57] M.L. Hildner, R.S. Daley, T.E. Felter and P.J. Estrup, J. Vac. Sci. Technol. A9 (1991) 1604.

[58] A. Fasolino, G. Santoro and E. Tosatti, J. Phys. (Paris) 42, C6 (1981) 846.

[59] C.Z. Wang, A. Fasolino and E. Tosatti, Phys. Rev. Lett. 60 (1988) 2661.

[60] C.Z. Wang, private communication (1995).

[61] D.-M. Smilgies, P.J. Eng, and I.K. Robinson, Phys. Rev. Lett. 70 (1993) 1291.

[62] L.D. Roelofs and S.M. Foiles, Phys. Rev. B48 (1993) 11287.

[63] A.E. Carlsson, Phys. Rev. B44 (1991) 6590.

[64] J.C. Campuzano, D.A. King, C. Somerton, and J.E. Inglesfield, Phys. Rev. Lett. 45 (1980) 1649.

[65] K. Smith, G. Elliott, and S. Kevan, Phys. Rev. B42 (1990) 5385.

[66] J.W. Chung, this volume, and references therein.

[67] J. Sprösser, B. Salanon, and J, Lapujoulade, Europhys. Lett. 16 (1991) 283.

[68] D. Cvetko, A. Lausi, A. Morgante, F. Tommasini and K.C. Prince, Surf. Sci 269/270
(1991) 68.

[69] I.K. Robinson, E. Vlieg, and K. Kern, Phys. Rev. Lett. 63 (1989) 2578.

[70] M. Krzyzowsky, P. Zeppenfeld, and K. Kern, preprint (1994).

[71] see, e.g., M. Bernasconi and E. Tosatti, Surf. Sci. Repts. 17 (1993) 363.

[72] G. Mazzeo, G. Jug, A. C. Levi, and E. Tosatti, Surf. Sci 273 (1992) 237.

[73] M. Den Nijs, Phys. Rev. Lett. 66 (1991) 907.

[74] V. Heine and J.J.A. Shaw, Surf. Sci . 193 (1988) 153.

[75] I.K. Robinson, private communication (1993).

[76] C.Z. Wang, PhD Thesis, SISSA, Trieste, November 1987.

[77] S.D. Kevan, Phys. Rev. Lett. 50 (1983) 526.

[78] D. Shoenberg and D.J. Roaf, Phil. Trans. Roy. Soc. 255 (1962) 85 .

[79] S. Crampin, M.H. Boon, and J.E. Inglesfield, Phys. Rev. Lett.73 (1994) 1015; and, this volume.

[80] S.D. Kevan, this volume.

[81] M.F. Crommie, C.P. Lutz, and D.M. Eigler, Nature 363 (1993) 524; M.F. Crommie, C.P. Lutz, D.M. Eigler and E.J. Heller, this volume.

[82] T.B. Einstein and J.R. Schrieffer, Phys. Rev. B7 (1973) 3629.

[83] J.R. Schrieffer and P. Soven, Physics Today 28 (1975) 24.

[84] E. Tosatti, in Proceedings of the 13th Int. Conf. on the Physics of Semiconductors, ed. F.G. Fumi (North Holland, 1976) p. 21.

[85] K.H. Lau and W. Kohn, Surf. Sci . 75 (1978) 79.
[86] F.M.Hoffmann, B.N.J.Persson, W. Walter, D.A. King, C.J Hirschmugl, and G.P. Williams, Phys. Rev. Lett. 72 (1994) 1256.

[87] B.N.J.Persson, F.M Hoffmann and G.P. Williams, this volume.

[88] B.N.J.Persson and A.I. Volokitin, Surface Sci. 310 (1994) 314.

[89] N.Fischer, S. Schuppler, R. Fischer, Th. Fauster, and W. Steinmann, Phys. Rev. B47 (1993) 4705.

[90] N.Fischer, S. Schuppler, Th. Fauster, and W. Steinmann, Surf. Sci. 314 (1994) 89.

[91] N.Fischer, S. Schuppler, R. Fischer, Th. Fauster, and W. Steinmann, Phys. Rev. B(RC) 43 (1991) 14722.

[92] E.Hulpke and J. Lüdecke, Phys. Rev. Lett. 68 (1992) 2846; J. Electron Spectr. Rel. Phenom. 64/65 (1993) 641.

[93] K. Carneiro, G. Shirane, S.A.Werner, and S. Kaiser, Phys. Rev. B 13 (1976) 4258.

[94] G.Giuliani and E. Tosatti, Il Nuovo Cimento 47 B (1978) 135.

[95] G.Giuliani and E. Tosatti, in Quasi One-Dimensional Conductors I, ed S. Barisic, A. Bjelis, J.R. Cooper, and B. Leontic (Springer-Verlag, Berlin, 1979) p. 191.

[96] R.H. Gaylord, K.H.Jeon, and S.D.Kevan, Phys. Rev. Lett. 62 (1989) 2036.

[97] B. Kohler, P. Ruggerone, S. Wilke, and M. Scheffler, Phys. Rev. Lett. 74 (1995) 1387; P. Ruggerone, B. Kohler, S. Wilke, and M. Scheffler, this volume.

[98] M. Balden, S. Lehwald, H. Ibach, and D.L. Mills, Phys. Rev. Lett. 73 (1994) 855.

[99] S. Modesti, V.R. Dhanak, M. Sancrotti, A. Santoni, B.N.J. Persson, and E. Tosatti, Phys. Rev. Lett. 73 (1994) 1951.

[100] M. Bernasconi, G.L. Chiarotti, and E. Tosatti, Phys. Rev. Lett. 70 (1993) 3295.
[101] R. Stumpf, J.B.Hannon, and E.W.Plummer, this volume, and references therein.

[102] N.Takeuchi, A. Selloni, and E. Tosatti, Phys. Rev. Lett. 72 (1994) 2227.

[103] M. Bernasconi, G.L.Chiarotti, and E. Tosatti, Phys. Rev.B, to appear, and references therein.

[104] M. Bernasconi, G.L.Chiarotti, and E. Tosatti, Phys. Rev.B, to appear.

[105] O. Züger and U.Dürig, Phys. Rev.B46 (1992) 7319.

[106] O. Züger, PhD Thesis, ETH Zurich No. 9658 (1992).

[107] D. Emin, Physics Today 40 (1987) 55.

[108] If unoccupied atomic shells like 3s, 3p, etc. were sufficiently high in energy, a hole representation within the (2s, 2p) shell would be rigorously equivalent to the electron representation. Hole charge density maps, obtained by subtracting the actual electron density from a fictitious ”parent” density obtained by completely filling the (2s, 2p) shell with 8 electrons/atom, could reveal possible pairwise hole bonds, invisible in the electron maps. However, due to the closeness in energy of the higher shells, it is not obvious that in practice a hole representation can be given a quantitative meaning in Be. It is therefore used here merely as a heuristic device.

[109] X.J. Chen, A.C. Levi, and E. Tosatti, Il Nuovo Cimento D13 (1992) 919.

[110] C.A.Meli, E.F. Greene, G. Lange, and P.J.Toennies, Phys. Rev. Lett. 74 (1995) 2054.

[111] A.W.Denier van der Gon et al., Surf. Sci. 241 (1991) 335.

[112] T.T. Tran et al., Surf. Sci. 281 (1993) 270.
FIGURES

FIG. 1. Mean-field dynamical structure factor of a one-dimensional WCDW. The acoustical phonon, of initially linear dispersion, is coupled to the electron CDW. The resulting coupled modes are the phonon $\omega_o (q \leq k_F)$, the phason $\omega_- (k_F \leq q \leq 2k_F)$, and the ampliton $\omega_+ (q \geq 2k_F)$. For visual illustration of spectral weight, thick lines represent a "strong" mode. (after Giuliani and Tosatti [95]) Note the resemblance with the H/W(110), and H/Mo(110) surface modes of Hulpke and Lüdecke [38 92].