Electronic surface states of crystals

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Experimental and theoretical research on the electronic structure of crystal surfaces over the past 10–15 years is reviewed. The nature of the Tamm (surface) levels of metals and semiconductors, the conditions for their existence, and their spectrum is discussed. Emphasis is placed on the role played by surface states in the reconstruction of surfaces and of the atomic structure and on how surface states affect the surface properties of magnets and work functions. Certain aspects of the formation of the chemisorption bond are discussed briefly.

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INTRODUCTION

It has now been nearly 50 years since the publication of Tamm's[1] paper with the first prediction that certain special bound electronic states might exist near crystal surfaces. These states were originally called "surface" states, and more recently they have been called "Tamm" states. This classic work by Tamm founded a distinct new direction in the physics of surfaces, and rapid advances in this direction are presently being made. The rapid progress has resulted from the demands of microelectronics, where miniaturization is being pursued to the limits, and from the practical importance of the elementary processes which occur on the surfaces of crystals (metals and semiconductors) and which are fundamental to such effects as adsorption, catalysis, and crystal growth. Reaching an understanding of the mechanisms for these processes requires study of the electronic and atomic structure of surfaces.

Already in the introduction to his work Tamm set forth the physical reasons for the confinement of an electron near a surface: On the vacuum side of the interface the motion of the electron is opposed by the potential barrier associated with the work function of the crystal, while on the crystal side the electron wave is diffracted by the crystal potential, so that, for certain values of its energy, the electron is prevented from propagating into the interior.

Mathematically, surface states arise in the solution of the wave equation for an electron in the field of a crystal bounded by a potential barrier. In contrast with an infinite crystal or a crystal with periodic boundary conditions, confinement of the wave function may also occur at energies inside the energy gap, if it is possible to join a solution which decays exponentially with distance into the crystal with a solution which decays exponentially with distance into the vacuum (Fig. 1).

Shockley[2] offered an explanation for the appearance of surface states by a slightly different approach, in terms of valence bonds. He noted that, if the valence band and the conduction band are formed as a result of a hybridization of atomic states (s and p states, say) which lead to an intersection of bands, then the splitting of the hybrid orbitals of the surface atoms, which have fewer neighbors than interior atoms, may turn out to be smaller than the width of the energy gap. These orbitals would thus produce unsaturated valence bonds or "dangling" bonds which would be confined to the surface.

For many years, until the early 1960s, the physics of surface states remained a matter of interest primarily to theoreticians. Their approach was to examine various model crystal potentials and to attempt to formulate general conditions for the existence of surface states from the particular electronic structure of the crystal itself and its particular surface geometry. This work, which led to the identification of several distinct types of surface states, has been reviewed by Davison and Levine[3] (see also the earlier review by Lifshits and Pekar[4]).

Experimental work in this field has run into the difficulty of obtaining atomically smooth and clean surfaces, i.e., surfaces free of defects and adsorbed impurities. There is the added difficulty of preserving these surfaces for a time long enough to allow experimental study. For example, a surface will remain clean for $\sim 10^4$ s at a gas pressure no higher than 10^{-10} torr ($\sim 10^{-8}$ Pa). Suitable apparatus became available in the 1960s and led to the development of new methods for studying surfaces. The method of low-energy electron diffraction (LEED) became the analog of x-ray diffraction of crystals.[5,6] The chemical composition of the surface is usually monitored by Auger-electron spectroscopy. Several methods have been proposed for studying the electronic structure (electron-emission spectroscopy in a static electric field or field emission microscopy, ion neutralization spectroscopy, electron energy loss spectroscopy, etc.; see the review by Gadzuk[7]), but the most popular method today is the method of angle-resolved ultraviolet photoemission spectroscopy (ARUPS).[8] As follows from its name, this method (which usually involves the use of intense sources of synchrotron radiation) makes it possible to analyze the energy spectra of those electrons which are emitted from the crystal at a certain angle, i.e., which have a fixed wave-vector component along the surface, $k_{\parallel}$. It is thus possible to study directly the dispersion of the surface-state band, $E_s(k_{\parallel})$.

The intense development of experimental methods over the past 10–15 years has been accompanied by substantial progress on the theoretical front. In the 1970s,
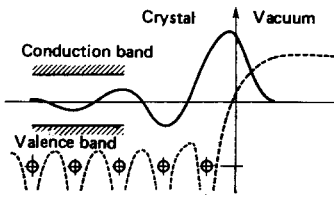
FIG. 1. Dashed curve—potential energy of an electron near a crystal surface; solid curve—wave function of a surface state in the energy gap.

new ideas in the electron theory of the solid state (the pseudopotential method, the density-functional method, and the X_α method, among others), combined with the dramatic improvements in computers, made it possible to take up calculations of the electronic structure of real crystals, particularly crystal surfaces. The results of this theoretical and experimental work have been reviewed in several recent papers.[9-11]

Let us take a brief look at certain methodological questions in the theory of Tamm states.

Strictly speaking, a semi-infinite crystal, in which the translational periodicity is disrupted in the direction normal to the surface, has only a two-dimensional zone structure, corresponding to the quasimomentum parallel to the surface, $k_{\shortparallel}$; the third quantum number $(k_\perp)$ does not represent a quasimomentum in this case. The spectrum of a macroscopic crystal is, on the whole, perturbed only slightly by the introduction of a free surface, so that surface effects can be described by mean of the "projected" two-dimensional zone structure of the infinite crystal.

This concept of projecting the zone structure can be explained with the help of a procedure for increasing the size of a selected unit cell in the direction perpendicular to the surface. The increase in the size of the unit cell leads to a corresponding contraction of the Brillouin zone in this direction, and in the limiting case the zone becomes planar. This "flattening" of the Brillouin zone obviously does not change the eigenstate spectrum; it simply projects states with a fixed value of $k_{\shortparallel}$ and different values of $k_\perp$ onto the energy axis. In the projected zone structure of the ideal crystal which is obtained in this manner, each value of $k_{\shortparallel}$ may correspond to several quasicontinuous bands of allowed states, differing in the symmetry of the wave functions.

If the crystal has no eigenstates in a certain energy interval (or gap), this gap is obviously preserved in the projected band structure. If, on the other hand, the discontinuity in the energy spectrum exists in only a certain interval of wave vectors, rather than throughout the Brillouin zone, in the three-dimensional case, then this gap may either remain or disappear upon projection, depending on the orientation of the projection plane. Specifically, if the ray of a projection with a given $k_{\shortparallel}$ and a given E does not intersect a single sheet of the $E(k)$ surface, then the gap will survive the projection. Such gaps are sometimes called "absolute" gaps. In the opposite case, the energy interval corresponding to the rupture of some branch of the spectrum

becomes occupied by states of other branches, and the corresponding gaps are called "relative." Figure 3 illustrates the situation with an absolute gap and a relative gap caused by the spin-orbit splitting of bands.

As mentioned earlier, an energy gap must be produced, by some factor or other, if surface states are to appear; consequently, in a two-dimensional projected zone structure the surface levels are grouped near absolute or relative energy gaps, although these gaps themselves are not seen directly.

Let us briefly examine the general behavior of the wave functions. A surface state inside an absolute gap is described by a wave function which decays exponentially on both sides of the surface, as mentioned above. If the energy of such a state lies in the quasicontinuum (corresponding to a relative gap), then the wave function usually has an additive increment of nondecaying "bulk" states. Such a state is called a "surface resonance." Surface resonances can exist even in the continuum, above the vacuum level. They are seen in LEED spectra and in other experiments in which electrons are scattered from surfaces. They contain useful information on the crystal potential near the surface (see the review by McRae[12]).

The model of a "slab superlattice" is frequently used in numerical calculations of the electronic structure of surfaces, so that sophisticated "three-dimensional" methods can be used. This model has a periodic array of crystalline films (10–20 atomic layers thick) separated by vacuum gaps whose width is such that the interaction between films is essentially eliminated. In order to distinguish surface states from bulk states in this model, one identifies as "surface states" those for which 70–80% of the wave function is in the first atomic layers.

At this point we must end this very brief review of the history of research on surface states and of the methods for studying them, and we will turn to some specific recent results. No claim is made that this review is comprehensive; furthermore, its content is determined by my own subjective choices, which have been made with the goal of pointing out what I believe to be the most promising problems and those of most current interest. One result of this subjectiveness is that relatively little space is devoted to the surfaces of semiconductors in comparison with metals, so that the relative weights established in the current literature are somewhat distorted.

TAMM LEVELS AT METAL SURFACES

We will begin our examination of surface states in metals with the group VI transition metals.

The first experimental observation of Tamm levels at metal surfaces was probably Swanson and Crouser's 1966 observation[13] of structure in the W(100) field emission spectrum. Until 1970, however, this structure was interpreted as "bulk" structure. Theoretical work on the surface states of metals began with the papers by Pendry and Fortsman,[14] who showed that surface states may arise in relative gaps, e.g., those associated with
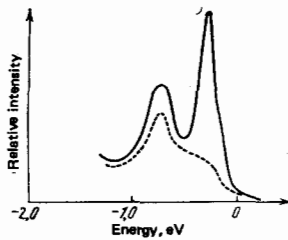
FIG. 2. Change in the ultraviolet photoemission spectrum of the W(100) surface during adsorption of an oxygen monolayer.[16] Solid curve—clear surface; dashed curve—W(100)+O_2. Normal emission ($k_\parallel = 0$), $\hbar\omega = 21.2$ eV.

a hybridization of s and d bands.

In 1970–1973 the existence of a surface electron structure at the W(100) surface was demonstrated reliably by several methods (field emission spectroscopy, ultraviolet photoemission spectroscopy, ion neutralization spectroscopy, etc.). The primary result of that work (see the review by Gadzuk and Plummer[15]) was to demonstrate that just below the Fermi level (~0.4 eV below it) there is a peak in the state density which is very sensitive to surface contamination. Figure 2 shows the typical change in the ultraviolet emission spectrum of W(100) when an O_2 monolayer is adsorbed. We see that the sharp peak below the Fermi level, which can be observed best in emission in the direction normal to the surface ("normal exit"), is greatly suppressed by adsorption. In emission at some angle from the normal, corresponding to a displacement from the point[1] $\bar{\Gamma}$ to the point $\bar{X}$ of the two-dimensional Brillouin zone, the peak approaches the Fermi level, and at $k_\parallel > 0.5$ Å^{-1} the peak becomes far broader.

Structure in the electron spectrum related to Tamm levels has also been observed at the Mo(100) surface.[17] For normal exit these structural features are at − 0.3 eV and − 3.3 eV (with respect to the Fermi level). In emission in a direction away from the normal (at the point $\bar{X}$), yet another peak appears in the surface electron structure near the Fermi level. Finally, there are also recent indications of surface states at the Cr(100) surface, about 1 eV below the Fermi level.[18]

Many theoretical papers have been devoted to finding the reasons for these surface states. Interest in this field was particularly intensified by observations of a reconstruction of the W, Mo, Cr(100) surfaces and a possible relationship between this reconstruction and surface states (more on this below). Feder and Sturm[19] have carried a non-self-consistent calculation of the W(100) surface electron structure by the LCAO method for d electrons. They noted that surface states can arise in two gaps associated with the spin–orbit splitting: a relative gap and an absolute gap one of which lies below the other (Fig. 3). Their calculated results showed that the surface band at − 0.4 eV at the point $\bar{\Gamma}$ probably corresponds to the relative, higher-lying gap,
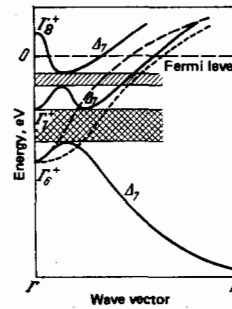

FIG. 3. Band structure of W along the $\Delta(\Gamma \to H)$ direction in the Brillouin zone with spin–orbit splitting. Dashed curves—no splitting; hatched regions—"relative" and "absolute" gaps (only three d bands are shown).

so that these states are surface resonances, rather than true localized states. Feder and Sturm's calculations also predicted surface states in the absolute gap, but these have not been observed experimentally. Recent self-consistent calculations by the augmented-plane-wave method for W(100) surface states have shown[20] that just below the Fermi level there is in fact a set of surface states, whose basic characteristics agree well with the observed ones. Figure 4 shows dispersion curves for these surface states and resonances. The surface states are noticeably grouped near the Fermi level. In addition to these states, there are some surface branches deep in the band, which are associated with sd-hybridized gaps.

Symmetry analysis of the photoemission data on W and Mo(100) has shown that there are also surface states near the Fermi level, probably due to sd gaps. Self-consistent calculations for Mo(100) predict a similar structure for the surface-state band.[21]

It can be said that, on the whole, both experiment and theory show convincingly that there is a large number of surface states lying a few tenths of an electron volt below the Fermi level. They can apparently be attributed to the known minimum in the density of bulk states of bcc group VI metals, near which surface levels are also concentrated; the exact conditions for the appearance of these states, however, have not been finally determined. Similar surface states might exist for bcc metals of group V, but in their case the Fermi
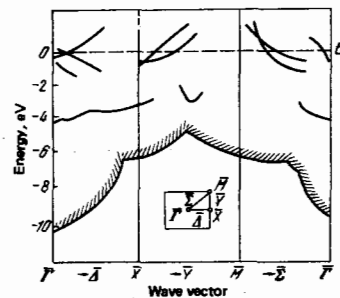

FIG. 4. Dispersion of surface states and resonances of the W(100) surface.[20] The hatching shows the lower boundary of the "bulk-state" spectrum and the two-dimensional Brillouin zone.

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[1] The symmetry points and lines of the two-dimensional Brillouin zone are denoted by capital letters with a superior bar.

levels should be vacant and much more difficult to observe.

A group led by Cohen[22] has also carried out self-consistent calculations of the dispersion of Mo(100) surface states in the presence of an adsorbed hydrogen monolayer. These investigators assumed that the hydrogen atoms occupy "bridging" positions between two nearest-neighbor molybdenum surface atoms (the adsorption occurs by a dissociation mechanism). It was found that hydrogen adsorption simply causes an energy shift of the surface states of the clean Mo(100) surface; the number of these states remains essentially the same. The adsorption does, however, cause two bands associated with hydrogen $1s$ states to "fall" below the bottom of the bulk-state band. These "hydrogen" surface states exist along the entire two-dimensional Brillouin zone and may be compared with the hydrogen bands typical of hydrides of transition metals.

Well above room temperature, according to LEED data, the Mo and W(100) surfaces have a "bulk" periodicity, basically as if the crystal had simply been sliced by the plane of the surface. [This structure is called the (1×1) structure, to indicate that both elementary translational periods are preserved at the surface.] The only deviation from this simple model is to assume that the last atomic layer is slightly displaced ("relaxed") toward the crystal (the displacement is ~5% of the interplanar spacing in the case of W and ~12% in the case of Mo). In 1971, however, Yonehara and Schmidt[23] observed that the W(100) surface undergoes a "reconstruction" or "rearrangement" as the temperature is reduced; in other words, there is a change in the symmetry of the surface unit cell, accompanied (in this case) by a doubling of both translation vectors. The quadrupled surface unit cell is a centered square. This surface structure is designated as both $c(2×2)$ and $(\sqrt{2} × \sqrt{2})R45°$. The reconstruction was observed as a second-order transition: As the surface temperature was reduced to 370 K, spots with half-integer indices appeared on the LEED pattern. The intensity of the structural spots fell off, indicating a reconstruction of the displacement type, rather than of the ordering type. The Mo(100) surface undergoes a similar transformation at 300 K, but in this case it is a first-order transition.[24] Finally, it has recently been reported[18] that a reconstruction occurs at the Cr(100) surface.

Careful studies by a battery of procedures have verified that the $c(2×2)$ reconstruction is a property of the clean W surface.[25] Furthermore, even trace amounts of adsorbed nitrogen (as little as 10^{-3} of a monolayer) completely suppress the W(100) − $c(2×2)$ reconstruction,[26] but the adsorption of hydrogen makes the W(100) superstructural spots sharper at 300 K.

To determine the atomic structure of surfaces from LEED data (by analogy with x-ray structural analysis) is a complicated problem, which has not yet been finally resolved. Most of the difficulties stem from multiple scattering of the low-energy electrons in the surface layers. The most popular method of LEED structural analysis involves choosing an atomic model for the surface through a comparison of the calculated and observed behavior of the spot intensities as functions of the electron energy.

Debe and King[27] proposed the model shown in Fig. 5 for the reconstruction of W and Mo. The atomic displacements in the surface layer reduce to longitudinal displacements of the [110] atomic rows; the displacements in adjacent rows are in opposite directions. The displacements can be described as a static surface deformation wave with a wave vector $k_{\parallel} = \pi/a(1\bar{1}0)$ (the point $\bar{M}$) and with a polarization $e = (1/\sqrt{2}, 1/\sqrt{2}, 0)$. The space group of the resulting structure, $p2mg$, is unique in that it does not have a fourfold axis, which would be allowed if we assumed that the reconstruction affected only the upper atomic layer. The magnitude of the displacement vector has been estimated[28] by the method described above to be ≈0.3 Å (at 100 K).

The nature of this instability of the Mo and W(100) surfaces and its possible relationship to surface electron states of steel have been the subject of several recent theoretical papers, in which attempts have been made to attribute the reconstruction to a surface instability similar to a Peierls instability or to the appearance of a charge-density wave. Further evidence for these mechanisms comes from the presence, near the Fermi level of surface-state bands with a relatively low dispersion and from the interesting fact that the $c(2×2)$ reconstruction of the Mo(100) surface, in contrast with the W(100) surface, has an incommensurable period; the modulation wave vector is $k_{\parallel} = 0.9\pi/a(1\bar{1}0)$, and the superstructural spots constitute a "quartet" of points on the LEED diagram.

Tosatti[29] reported the first attempt to relate the reconstruction to the electron structure; he applied his and Anderson's theory of charge-density waves at semiconductor surfaces.

Terakura[30] examined the relationship between reconstruction and surface states, considering a system of 884 atoms used to simulate a crystal with a surface. Terakura used the Hartree–Fock approximation to calculate the change in the electron energy of this system upon the introduction of static displacement waves of two types: one like that of the Debe–King model and another having the same wave vector $k_{\parallel} = \bar{M}$ but polarized normal to the surface. It was found that the first mode interacts strongly with the surface state near the
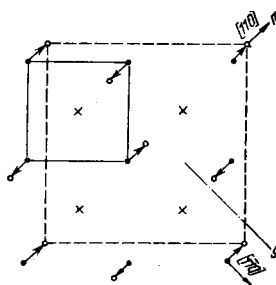

FIG. 5. Structure of the W(100)−$c(2×2)$ surface.[27] Points—"bulk" structure (1×1); open circles—$c(2×2)$ restructuring with space group $p2mg$ (m is the mirror symmetry axis and g is the grazing axis); crosses—atoms of the second layer, just below the surface layer.

Fermi surface, so that a change in structure is allowed from the energy standpoint if the bands are filled appropriately (in such a manner that the surface state turns out to lie near the Fermi level). Inglesfield[31] has also discussed an "electron" mechanism for the Mo(100) reconstruction; he showed that the static wave of the Debe–King model is stabilized by electron surface states with wave vectors $\pm \pi/a(1/2, 1/2)$, which are predominant in the surface-state density at the Fermi level (Fig. 4). Inglesfield[32] also calculated the contribution made by these states to the dielectric susceptibility of an electron gas, but this contribution turned out to lead to only a slight anomaly. From this it was concluded that the (100) surface is already unstable "by itself," because of, for example, the anharmonic nature of the effective potential, and the surface states simply "select" the deformation mode which actually occurs. The effect of surface states on the electron-reaction function has recently been studied more rigorously by Krakauer et al.,[33] who used the results of their self-consistent calculations of the electronic structure of the W(100) surface (Fig. 4). They calculated the susceptibility of an electron gas with corrections for the local field and found that these corrections lead to a sharp peak in the susceptibility at the point $\bar{M}$ (Fig. 6). They interpreted this result as confirming the interpretation of reconstruction as a charge-density wave, as proposed by Tossati.[29,34] Krakauer et al. also pointed out that the stabilizing effect of adsorbed hydrogen on the result of the reconstruction is a consequence of the pinning of a charge-density wave by mobile H atoms, which readily occupy energetically favored positions.

In connection with the adsorption of hydrogen we also note that a sharp narrowing of the infrared vibrational line of hydrogen on the W(100) surface has recently been observed for saturation coverage and for an unreconstructed structure.[35] Chabal and Sievers[35] attribute this effect to a dynamic interaction of the vibrations with W(100) surface modes.

In summary, there seems to be no doubt that surface states do exist and that they are associated with a reconstruction on the (100) surfaces of group VIA metals, although the details of this relationship remain for the present unclear. It has recently been reported, for example, that the wave of surface-atom displacements is polarized perpendicular to the surface, rather than parallel to it, as in the Debe–King model. The same
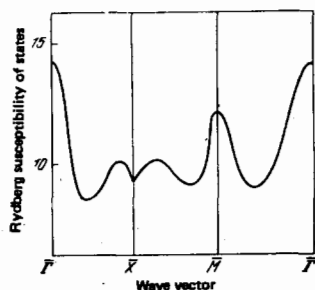
conclusion was reached by Stevens and Russell,[36] who observed the spectrum of surface resonances above the vacuum level in the scattering of low-energy electrons by the W(001) surface. Stevens and Russell also believe that, in addition to the transverse displacement wave, the surface layer undergoes a homogeneous relaxation toward the crystal.

We turn now to the electron structure of the Sc and Ti(0001) surfaces. The "bulk" band spectra of these hcp metals are isomorphic: When the valence is raised by one (as we go from Sc to Ti) the structure of the band spectrum remains essentially the same; i.e., the "rigid" band is filled up to the new Fermi level. From the standpoint of surface levels, an important feature of this band spectrum is a state-density minimum at E_F of titanium. Self-consistent calculations by Feibelman et al.[37] for an 11-layer titanium film have revealed a sharp peak in the surface states at the minimum of the "bulk" level density. The width of this peak is only a few tenths of an electron volt (Fig. 7). These surface states, which lie precisely at the Fermi level, propagate rather extensively through the two-dimensional Brillouin zone and are constructed primarily of t_{2g} and $d_{x^2-y^2}$ orbitals. Unfortunately, experimental observation of these states by the ARUPS method has been hindered by the symmetry properties of the (0001) surface, which prevent discrimination of the surface transitions from the background of bulk transitions.

Experimental data on x-ray and ultraviolet electron spectroscopy of Ti(0001) have been reported recently.[38] The pronounced capability of titanium to react makes it difficult to produce a clean surface, so that the surface-sensitive peak which has been observed (at -1.4 eV) is probably a consequence of hydrogen adsorption, as is also implied by the temperature dependence of this peak.

In direct confirmation of the theoretical results has been found from data[39] on the work functions of Ti and Sc(0001) surfaces. The scandium work function has turned out to agree qualitatively with experimental data, being only half the titanium work function (2.1 vs 3.9 eV). As Feibelman and Hamann have shown, the dif-
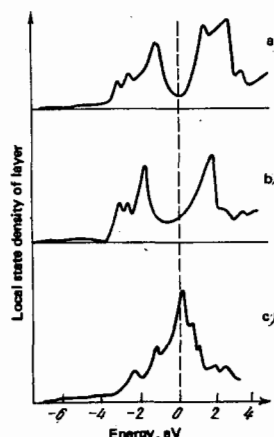

FIG. 6. Susceptibility of the electron gas as a function of the wave vector in the two-dimensional Brillouin zone of the W(100) surface.[33]

FIG. 7. Local state density of a Ti(0001) film.[37] a—The "bulk" value, corresponding to the sixth layer of an 11-atom film; b—second layer; c—first (surface) layer.

ference is due to the fact that the "rigidity" of the bulk bands extends to the surface bands, which in the case of scandium are vacant and do not contribute to the surface potential barrier, so that the work function is reduced. Feibelman and Hamann attribute this stability of the surface bands to a strong interaction of the surface atoms forming the close-packed plane with bulk atoms. This interaction is perturbed relatively slightly by the formation of a surface. We also note that the clean (0001) surface is also structurally stable: There has been no report of a reconstruction of this surface in the literature. In view of the presumed presence of surface states near the Fermi level in titanium it can probably be asserted that, by themselves, the surface states near E_F do not yet cause a surface instability if the surface structure is closely packed [in contrast with Mo and W(100)].

The noble metals are particularly attractive for a study of surface states, because of their simple band structure: The d band is completely filled, and at the Fermi surface there are only "necks" near the points L, which are consequences of the sp gap, in which we can expect to find surface states. Figure 8 shows a section along the (110) plane through the Brillouin zone of copper, along with two-dimensional zones for various surface orientations: (001), (111), (110), and (112). It can be seen from this figure that the projection of the L neck of the Fermi surface onto various planes predicts the angles (or the longitudinal wave vectors $k_{\shortparallel}$) at which the surface states should be observed. On the (111) surface, for example, the neck corresponds to the $\bar{\Gamma}$ center of the two-dimensional Brillouin zone, and emission from surface states should be observed in the direction perpendicular to the surface; for the (110) and (112) surfaces, on the other hand, the neck is projected onto a face of the two-dimensional zone, and we have $k_{\shortparallel} = 0.77$ Å^{-1} and 0.455 Å^{-1}, respectively. States with $k_{\shortparallel} = 0.77$ Å^{-1} at the (110) surface (near the point $\bar{Y}$) must be true surface states, since such values of $k_{\shortparallel}$ in the projected band structure correspond to an absolute gap. The gap at $k_{\shortparallel} = 0.455$ Å^{-1} of the (112) surface, in contrast, is a relative gap, since the projected ray intersects a sheet of the $E(\mathbf{k})$ surface, and the surface states are resonances.
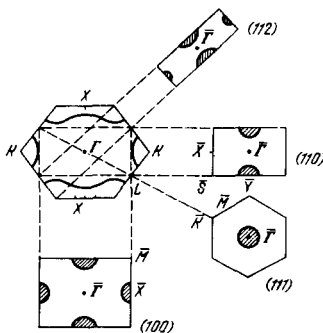
Surface states corresponding to the sp gap at the point

FIG. 8. Intersection of the Brillouin zone and the Fermi surface of Cu with the (110) plane; two-dimensional Brillouin zones of various surfaces.[40] The hatched regions contain wave vectors $k_{\shortparallel}$ corresponding to states in the necks of the Fermi surface at the points L.

L have been observed on several occasions for all noble metals and on various surfaces: Cu(111) and (110); Au(100), (111), and (112); and Ag(111) (see, for example, Ref. 40). A strong argument that the structure observed by the ARUPS method is associated with surface states comes from the excellent agreement between the experimental values of the angles at which electrons emitted from surface states should be observed and the values of these angles predicted by the projection diagram in Fig. 8 (Ref. 40). These angles are easily calculated from the longitudinal wave vector, the energy of the exciting light, and the work function.

The existence of surface states at the vertex of the d band in the sp gap of noble metals can now be accepted as firmly established. These surface states are also confirmed by self-consistent calculations of the surface electron structure. For example, the dispersion of the surface-state band near the $\bar{\Delta}(\bar{\Gamma} - \bar{Y})$ line of the two-dimensional zone of the Cu(110) surface calculated by Dempsey and Kleinmann[41] is in satisfactory qualitative agreement with experimental results. Self-consistent calculations have demonstrated a large number of surface states which are split from the vertex of the d band and which have an important effect on the surface charge density.[42]

It seems intuitively clear that a decrease in the coordination number of surface atoms should lead to a contraction of the d bands in the surface layer. In turn, this contraction should cause an increase in the center of gravity of the band if the band is nearly filled, or it should cause a decrease in the center of gravity if the band is nearly empty. This effect follows from the conservation of electrical neutrality of the layer upon a change in the extent to which its states are filled.

Although the d states of noble metals are filled, they are partially mixed with states near the Fermi surface by sd hybridization. The following question thus arose: Could this mixing lead to an effective narrowing and, as mentioned above, a rise of the d bands of noble metals, with the result that d holes would appear at the surface? The answer turned out to be negative. In a monatomic Cu(001) film, as has been shown by self-consistent calculations by Appelbaum and Hamann,[43] the edge of the d band lies only 0.1 eV below the Fermi level level, but as its thickness increases the d band becomes emptied, reaching its bulk position in a nine-atom layer. This result is closely related to the self-consistent treatment, since earlier, non-self-consistent, calculations had shown d holes at the surface.

There is particular interest in the surface structure (atomic and electronic) of the group VIII transition metals, for two very good reasons: magnetism and catalysis. We will first examine the heavy metals Pd and Pt, which are well known for their catalytic properties, and then we will discuss the ferromagnet Ni.

ARUPS spectra for the Pd(100), (110), and (111) surfaces were recorded by Lloyd et al.,[44] who found that changes in the emission angle cause important changes in the basic structure of the spectra and that the spectra are sensitive to contamination. The surface peaks

of the (111) plane are concentrated at energies 1–2 eV below the Fermi level. One of these peaks (– 2.4 eV in the case of normal emission) has been attributed by Bisi and Calandra[45] to surface states of symmetry $d_{x^2-y^2}$.

The adsorption of hydrogen on Pd is of much practical interest. Demuth[46] has measured the electron spectra before and after the adsorption of a hydrogen monolayer on Pd(111). It was found that the adsorbed hydrogen perturbs the spectrum strongly; there is a particularly marked decrease in the emission intensity near the Fermi level.

Self-consistent calculations of the electron structure for an H monolayer on Pd(111) were first carried out by Louie[47] by a pseudo-potential method. Louie calculated the surface-state spectra for both clean surfaces and surfaces with adsorbed hydrogen, for three different positions of the hydrogen atom with respect to the atoms of the surface plane. It turned out (Fig. 9) that an H monolayer strongly perturb the surface-state spectrum. The redistribution of the state density is caused primarily by the disappearance of two closely spaced plane surface bands near the point $\mathbf{k}_{\parallel} = 2\pi/a$ (0, – 2/3, 2/3) (Fig. 9), with an energy of about – 2 eV; the disappearance of the $\overline{\Gamma}$ resonance band near E_F; and the appearance of two (bonding and anti-bonding) bands of the H–Pd type. The first band drops below the d band, while the second, which is almost completely empty, lies near the point $\overline{K}$ and has a large dispersion (~4 eV). Comparison of the observed and calculated spectra has made it possible to discard one of the structural models for the adsorbed layer: The hydrogen atoms probably lie in valleys between three palladium atoms, rather than on top of a single atom. The structure found for the adsorption bond confirms the Anderson–Newns model, according to which a strong interaction of 1s(H) and 4d(Pd) orbitals leads to the formation of bonding and antibonding bands similar to molecular bands, with a width determined by the state density in the energy region occupied by these subbands.

For a long time, the Au and Pt(100) surfaces were the only examples of restructured metal surfaces.[48] Until
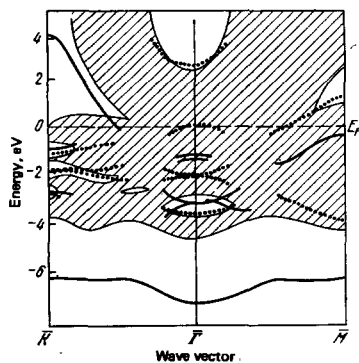

FIG. 9. Two-dimensional band structure of the Pd(111) surface.[47] Points—surface states of the clean surface; solid curves—localized states for a hydrogen monolayer on the Pd(111) surface; hatching—projected bulk bands.

the early 1970s it was assumed that the restructuring denoted by (5×1) consisted of the substitution of six rows of surface atoms for five rows of "volume" atoms, leading to a dense hexagonal structure in the surface layer. It was later found, however, that the restructuring is more complicated. In addition to the fivefold period along one axis there is a 20-fold period along the other: (5×20). This restructuring is not a consequence of adsorbed impurities but a characteristic of the cleanest of surfaces. The restructured surface is always obtained after ion bombardment and annealing, and it is preserved up to the melting point. In 1975 Bonzel et al.[49] managed to produce a metastable unrestructured structure of Pt(100) [(1×1)] and to study its electron spectrum. They first coated a platinum surface with an adsorbed layer of CO, which resulted in a (1×1) structure. Then they removed this layer with oxygen ions, O_2^+. Auger electron spectroscopy and LEED revealed that the result was a clean, unrestructured surface, which irreversibly transformed into a stable (5×20) structure upon heating above 125 C.

Figure 10 shows the electron spectra recorded for both structures. The transformation to the equilibrium structure is accompanied by a dramatic change in the spectrum near the Fermi level: The sharp peak at – 0.25 eV vanishes completely. Bonzel et al. also studied the adsorption capability of the surface in both states and found that while hydrogen and oxygen were adsorbed only poorly on the restructured surface their attachment coefficient approached unity on the metastable (1×1) surface. The thermal stability of the (1 ×1) phase increases rapidly upon the addition of even very slight amounts of carbon—amounts below the sensitivity of Auger spectroscopy. It follows that adsorbed atoms nevertheless seem to play a role in the stabilization of the (1×1) structure.

In discussing the origin of the electron surface states, Bonzel et al. concluded that it was probably a spin-orbit gap along the ⟨100⟩ direction (Γ – X). Further, indirect, evidence for a "spin–orbit genesis" of the surface states comes from the fact that the restructuring of the (100) and (110) surfaces (if this restructuring is controlled by the surface state) occurs in the case of heavy 5d metals (Ir, Pt, and Au), while it is not observed for their 4d analogs (Rh, Pd, and Ag).[2)]

A similar feature in the electron structure (at – 1.0 eV) was observed a year later on the Ir(100) surface.[51] Calculations of electron surface states by the semi-self-consistent LCAO method[52] revealed surface states at unrestructured Pt and Ir(100) surfaces near the Fermi energy, even without spin–orbit splitting.

In recent years, the interest in the electron structure of these surfaces and in its relationship to restructuring has been slightly upstaged by work on W and Mo(100).

The decrease in the coordination number of surface

[2)]A different explanation for the tendency toward a surface restructuring of 5d metals was offered in 1972 by Phillips,[50] who noted the greater polarizability of their ionic cores.

atoms should lead to a perturbation of the magnetic structure in the surface layers of magnetic materials. It was suggested a long time ago[53] that the surface of a ferromagnet may be a "dead layer," i.e., a region in which the magnetic order is disrupted. This suggestion was tested by several measurements of the spin-polarized emission from nickel, which revealed several surprising results (see the review by Feuchtwang *et al.*[54]). It first appeared that the polarization of electrons excited by photons with an energy just above the work function was positive; i.e., electrons of the completely filled majority subband were emitted preferentially. This fact contradicted the Stoner interpretation of band magnetism, according to which at low frequencies we would expect emission from the minority subband, which intersects the Fermi level. As the photon energy is increased (to about $\hbar\omega - \Phi = 0.3$ eV, corresponding to exchange splitting in nickel), the filled subband should come into play, and the polarization of the emitted electrons should change sign.

In 1976 Eib and Alvarado[55] reported that they had managed to observe a change of sign of the polarization in emission, but the change occurred at an energy only 0.05 eV above the threshold—far below the energy corresponding to exchange splitting. In an attempt to explain this contradiction, Dempsey *et al.*[56] suggested that a surface subband splits off from the majority band, and it is this subband which reduces the apparent exchange splitting. It has also been mentioned that at the center of the Brillouin zone the vertex of the ↑ subband is only 0.1 eV below the Fermi level.

To check these suggestions, Moore and Pendry[57] carried out calculations for spin-polarized emission and found that good agreement with the observed intensity curve $P(\hbar\omega - \Phi)$ can be achieved with the "ordinary" value of the splitting, 0.33 eV, adopted in band calculations; the surface states make this agreement worse in all cases.

In an effort to analyze the surface-state structure of Ni(100), Plummer and Eberhardt[58] carried out detailed measurements of the angle-resolved photoemission in various geometric arrangements, so that they were able to separately analyze the spectra of states with different spin polarizations and parities. The basic conclusion which they reached was that just below the Fermi level there are two subbands of magnetic surface states: one near the point $\bar{M}$, with spin up and one near the point $\bar{X}$, with spin down. These results were confirmed qualitatively by self-consistent calculations for surface states of a nine-atom Ni(100) film carried out by Wang and Freeman.[59,60] It was found in those calculations that a surface-state band splits off from the spin-majority subband and goes above the Fermi level; $d\uparrow$ holes are formed, and the angular momentum of the surface atoms is reduced by about 20%, but a genuine dead layer apparently does not form.

Plummer and Eberhardt pointed out that the surface states which they observed agree well with the calculations by Dempsey *et al.*[56] in terms of the positions of these states in the band and their energies; in addition to these states, however, the calculations predict sev-
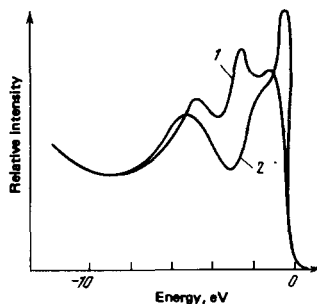

FIG. 10. Photoemission spectra of the Pt (100) surface. 1—In the stable (5×20) state; 2—in the metastable (1×1) state[49] ($\hbar\omega = 40.8$ eV).

eral other surface bands, which have not been observed experimentally. The small number of surface states in the Ni(100) case has been confirmed by recent self-consistent calculations by Arlinghaus *et al.*[61] for a nine-atom film of paramagnetic nickel. Arlinghaus *et al.* note that the close agreement between the bulk electron structures of copper and nickel (as in the case of scandium and titanium, discussed above) is greatly disrupted at the surface. Nickel has far fewer surface states, and they are spread out more over the projected band structure. (We recall that in the case of copper the surface states are concentrated primarily near the vertex of the d band.) The reason for this "disappearance" of surface electrons as we go from copper to nickel and for the decrease in E_F remains unclear; at any rate, the number of surface electrons in the Pd(100) and Ag(100) cases is apparently as great as in the Cu(100) case.

Allan[62] recently studied the conditions for the instability of the surface layers of a paramagnet with respect to the formation of magnetic order in the strong-coupling approximation. He showed that the Stoner condition can be satisfied easily at the V(100) surface. This instability is caused by a high local state density near the Fermi level, which Allan attributes to a large number of dangling bonds. A large change in the angular momentum in the surface layers can also be expected in the case of chromium; it has in fact been reported that chromium surfaces are ferromagnetic.[63]

The surfaces of the rare earth metals have some interesting electron properties. Wertheim and Crecelius[64] used x-ray photoemission to observe the presence of Sm^{2+} at the surface of trivalent samarium. Brouers *et al.*[65] have offered a model which explains this change in valence as the result of the contraction of the d band in a surface layer, which results in an emptying of d states. Electrical neutrality is then achieved by the filling of $4f$ states up to the $4f^6$ configuration, in contrast with the $4f^5 5d^1$ configuration in the volume. The possible decrease in the effective valence of rare earth metals upon a decrease in coordination number (at a surface, edge, or corner of a crystallite) has been discussed by Johansson[66] on the basis of an empirical relation between the surface tension and the bond energy. Johansson found that a valence change at the surface is energetically favorable only in the case of samarium; a valence change at an edge is favored in the case of

samarium and thulium; and a change at a corner is favored for several rare earth metals. Unfortunately, detailed calculations have not yet been carried out for the band spectra of either the surface or the volume of samarium, with its complex hexagonal lattice.

To conclude this part of the review on the surface states of metals we will take a brief look at a few other systems. Among the nontransition metals, several papers have been published on aluminum. The states at the (100), (110), and (111) surfaces were calculated by Caruthers *et al.*,[67] who found these states in all three cases. ARUPS experiments[68] confirm the presence of these surface states, which are attributed to different projections of the sp gap near the point X. The surface states at the (100) and (110) surfaces are "actual" surface states, while those at the (111) surface are resonances, because of a mixture of a second band during the projection.

Many recent papers have dealt with the surface properties of the hexaborides of rare earth elements, particularly LaB$_6$. This compound has a very low work function [2.3 eV for the (100) face and 2.5 eV for the (110) face], combined with high mechanical properties and a metallic conductivity. Interestingly, the LaB$_6$(110) surface has a $c(2 \times 2)$ restructuring; the lanthanum atoms, which are enclosed by a "sheath" of boron atoms, are displaced toward the surface and along it, forming a superlattice.[69] Surface states have been observed on the LaB$_6$(100) plane by ARUPS.[70] Aono *et al.*[70] decided that these states were "dangling-bond" states (after Shockley), but Tomašek and Pick[71] believe that these surface states are not related to the breaking of covalent bonds at the surface and are instead characteristic of heteroatomic lattices.

These results on the electron structure of metal surfaces seem to show that this branch of solid state physics, only ten years old, has already reached a state of maturity. This rapid progress can be attributed to the development of powerful experimental and computational methods. Intense work is presently being carried out along many directions, among which the most important are the study of the nature of the restructuring of the atomic structure of surfaces, the study of the special magnetic properties of surfaces, and the analysis of the mechanism for the catalytic activity of metals, in particular the electron structure of the chemisorption bond.

TAMM LEVELS OF SEMICONDUCTORS

Research on the electron structure of semiconductor surfaces has a longer history than that for metal surfaces. Surface states in the energy gap (if they exist) should cause important changes in properties. For example, if a surface band intersects the Fermi level and is partially filled, then there will be a band curvature near the surface which will keep the electron electrochemical potential constant throughout the sample. On the other hand, since a surface band may contain a rather large number of states (of the order of one state per surface atom or $\sim 10^{15}$ cm^{-2}, the filling of the surface band will determine the position of the Fermi level at the surface, as Bardeen[72] showed in 1947, while the

position of the Fermi level in the volume can easily be changed by an amount of the order of the gap width by suitable doping. The Fermi level is "pinned" at the surface.

Experimental work on the surface properties of semiconductors began back in the 1960s with measurements of the photo-emf, the photoconductivity, the work function, etc. In 1962, Allen and Gobeli[73] demonstrated through measurements of the photoelectric effect that there were apparently surface states inside the gap at the Si(111) surface. For a detailed discussion of these and other early results and also the results of a determination of the structure of surface bands, the reader is referred to the review by Davison and Levine.[3] Since the early 1970s, when more sophisticated methods were also adopted, it has turned out that in addition to the states in the main gap there are deeper surface levels.

At about the same time, the first realistic calculations of the electron structure of semiconductor surfaces began to appear. Of primary importance here was the (111) surface of silicon, which is the basic material of microelectronics.[74,75] This surface also attracted interest because of its "special" behavior; it has been known for a long time that this surface undergoes restructuring. The Si(111) surface, freshly cleaved in high vacuum, exhibits a (2×1) structure of LEED spots. After annealing, the surface undergoes an irreversible relaxation to a (7×7) structure; the same structure is produced by ion bombardment and annealing. At ~1175 K, the (7×7) superstructure "melts," changing back into the (1×1) "volume" periodicity. A similar sequence of structures is observed for the Ge(111) surface: The (2×1) structure transforms into a (2×8) structure, which then "melts" at ~600 K.

In 1975, two US groups simultaneously carried out self-consistent calculations of the surface electron spectrum of Si(111) with the (2×1) structure, in an effort to determine the reasons for the surface instability and the possible effect of the electron structure on it.[76-79] The atomic structure of the reconstructed surface was described in the Haneman model,[80] according to which the period along one of the ⟨100⟩ directions on the surface is doubled by alternate displacements of neighboring ⟨010⟩ atomic rows out of and into the crystal. Furthermore, the atoms of the second layer undergo slight longitudinal displacements, which preserve the lengths of the covalent bonds (Fig. 11). Such a structure gives a reasonable approximation of the LEED and ESR data.

To a large extent, the results obtained by the two theoretical groups agreed, but the Berkeley group used a
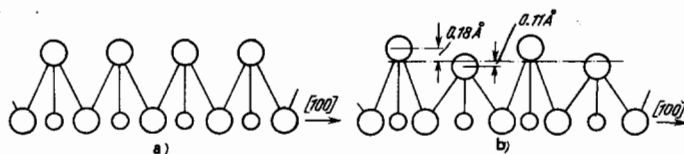

FIG. 11. a—Structure of the (111) surface of a diamond lattice in the ideal (1×1) state; b—in the (2×1) restructured state.

pseudopotential method, while the San Jose group used a bond-orbital method. Three bands can be seen in the surface-state spectrum: S_1, S_2, and S_3. Their positions with respect to the bulk state density of silicon are shown in Fig. 12. For the ideal surface there is a very narrow, precisely half-filled band of surface states inside the gap; this band is formed primarily by dangling bonds with definitely p_z orbitals, centered at surface atoms. When a relaxation of the surface layer over a distance 0.33 Å into the crystal is introduced (without restructuring), this band begins to interact with the broadening "backward-bond" band (S_2) and undergoes an asymmetric broadening. The lower part of this band, which is formed primarily by states near $\overline{K}$, retains a well-defined dangling-bond nature. A further evolution of the dangling-bond band occurs upon the introduction of a (2×1) restructuring: The band splits into two parts, separated by a rather deep pseudogap. The distribution of the electron density of these subbands is quite interesting. The lower, filled, subband corresponds to dangling-bond wave functions which are concentrated at the atoms displaced outward (Fig. 11b). The wave functions of the upper, unfilled, subband are concentrated primarily at the "lowered" atoms and are very hybridized. During the restructuring, therefore, the unsaturated valence electrons go from the lowered atoms to the raised atoms, forming paired bonds. The existence of two closely spaced surface subbands is supported by measurements of the infrared absorption spectra, and the positions of these bands agree with optical data, which show that the surface-state band lies 0.5 eV below the edge of the valence band. Another interesting feature of the calculated surface spectra is the presence of states whose wave functions are localized between the second and third atomic layers. These states correspond to point $\overline{K}$ of the Brillouin zone and lie at energies −2.0 and −9.7 eV below the edge of the valence band.

Similar results were found by Batra and Ciraci,[76,77] who also concluded that the dangling-bond band is split during the (2×1) restructuring, but the surface retains its metallic nature. In support of their conclusions, Batra and Ciraci point out that Tosatti and Anderson[81]
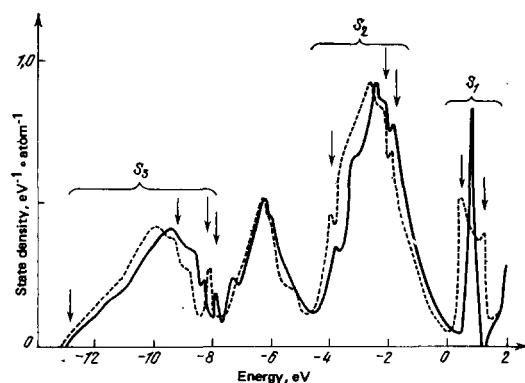
FIG. 12. Calculated state densities for a 12-atom Si(111) film. Dashed curve—in the relazed state; solid curve—in the unrelaxed state.[78] The arrows show the positions of the surface levels of various symmetries.

were not able to explain the (2×1) restructuring as the result of a metal–dielectric transition in a two-dimensional system of dangling-bond electrons.

Batra and Ciraci also calculated the spectral changes resulting from the adsorption of hydrogen on the Si(111) surface; they found that the dangling-bond peak disappears, but a peak appears in the interior of the band. This result and also the observed "restoration" of the (2×1) structure into the ideal (1×1) structure after hydrogen adsorption[82] indirectly confirm a relationship between the dangling orbitals and the restructuring of the Si(111) surface.

The changes which occur in the atomic structure upon the (2×1) → (7×7) restructuring of the Si(111) surface have stimulated a lively discussion. The large cell of the superlattice seriously complicates all theoretical calculations of both the LEED spectra and the electron structure. There are experimental data[83] which show that the state density at the Fermi level increases upon the transformation (2×1) → (7×7), in contrast with the restructuring (1×1) → (2×1). Furthermore, this surface becomes more reactive.[84] Several models have been proposed for the (7×7) restructured surface, but apparently none of them can explain all the experimental data. The model of ordered surface-layer vacancies[85] is the most popular; it succeeds in explaining both the increased adsorption capability and the "melting" of the superstructure at 1175 K. As Mark et al.[86] have mentioned, however, the oscillatory redistributions of the spot intensities as functions of the beam energy cannot be explained under the assumption that the lattice distortion involves only one surface layer. Furthermore, the changes in the electron spectrum of the surface states during the (2×1) → (7×7) restructuring are apparently still small: The observed energy-loss spectra of low-energy electrons can be described quite well by working from a surface-level distribution similar to that described above for the relaxed (1×1) surface[87] (Fig. 12).

Let us briefly discuss the electron structure of the Ge, Si, and C(100) surfaces, which have many features in common. All exhibit a "simple" (2×1) restructuring, for which at least three models have been proposed: (1) the model of "lost" atomic rows; (2) the model of surface "dimers"; (3) the chain model. Self-consistent calculations of the electron spectra have been carried out and compared with photoemission data to determine which of these models is correct.[88] It has been shown that the model of lost atomic rows and the chain model are at odds with the ARUPS spectra, while the dimer or "paired-atom" model agrees well with these spectra. Unfortunately, these conclusions contradict the results of a LEED analysis, which favor the chain model. In the competition which has arisen between "electron" and "atomic" methods of structural analysis, "electron" arguments are winning out.

Appelbaum and Hamann[89] have shown that the model of a dimerized surface can be saved if the LEED spots are explained by assuming a pronounced relaxation of layers near the surface under the influence of elastic forces. The same model easily explains why the (2×1) LEED

superstructure is suppressed by hydrogen adsorption: The hydrogen destroys the dimer bonds and eliminates the cause of the relaxation of the inner layers.

An important defect of all these models is that they predict that the surface layer will be metallic, while ARUPS experiments have indicated that the surface remains a dielectric. This contradiction was resolved by Chadi,[90] who showed that a dielectric surface can be obtained if the dimer bond is partially ionic. Figure 13 shows the intersection of the Si(100) surface with the (010) plane. The arrows show the direction of the displacement during the restructuring. A dimer is formed by atoms 1 and 1', which are displaced slightly upward and downward, respectively. By minimizing the total energy of the system, Chadi showed that there is a charge transfer of ~0.36e from the "lower" atom of the dimer to the "upper" one. This charge transfer yields a heat of reaction ~0.5 eV/dimer (~240 erg/cm^2) when the relaxation of five atomic layers near the surface is taken into account. Figure 14 shows the change in the dispersion of the surface band when the ionic nature of the dimers is taken into account. The upper band becomes much flatter, and near the vertex of the valence band a gap opens up between the filled and empty surface states.

The agreement of the calculated surface-band structure with the ARUPS results is still less than completely satisfying. The filled band which is observed is much narrower (~0.3 eV) than according to the calculations, and its position at point $\bar{\Gamma}$ is lower than the calculated position. Another important feature of the observed spectra is the existence of two filled bands at the point $\bar{J}'$ (rather than a single band, according to the calculations), 0.4 and 0.9 eV below the edge of the valence band. It may be that the first of these states is a state which "has arrived" from point $\bar{\Gamma}$ as the result of an additional splitting of the Brillouin zone.

This brief look reveals that the results obtained over two decades have put us in a position where we can carry out quantitative calculations of the electron and atomic properties of silicon surfaces. Calculations of the electron spectrum and a comparison of this spectrum with spectroscopic data will apparently give us an effective method for analyzing surface structures.

In addition to the common procedure of carrying out experiments in high vacuum, experiments have been reported in which a clean surface is prepared by cleavage in liquid helium. This method has certain advantages (chemical cleanliness of the surface is essentially guaranteed) and certain disadvantages (a surface cleaved
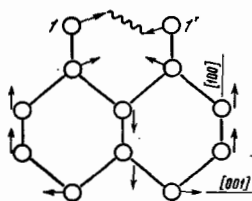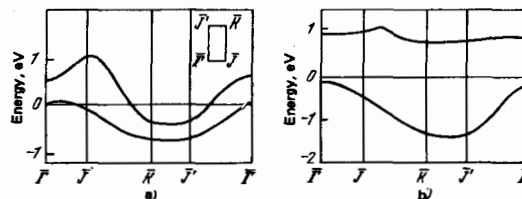

FIG. 14. Dispersion of the surface bands of the Si(100) − (2×1) surface. a—For symmetric, "covalent" dimers; b—for asymmetric, "ionic" dimers.[90] Here $E = 0$ corresponds to the top of the valence band.

at liquid-helium temperature may contain many defects which are difficult to monitor). Vul and Zavaritskaya have recently studied the kinetic properties (the conductivity and the Hall effect) of Ge(111) surfaces prepared in this manner. They have observed[91] that the initial conductivity level of the freshly cleaved surfaces is very sensitive to the surface quality, ranging from ≤10^{-9} mho (the bulk conductivity) for mirror-smooth surfaces to 10^{-5} mho for defective surfaces. After an intermediate heating in helium vapor at 35–45 K and above, however, the conductivity increases sharply and irreversibly (Fig. 15). The conductivity level reached after this heating (≈4· 10^{-4} mho) is the same for all surfaces; the surface current is five or six orders of magnitude higher than the volume current.

The Hall effect was measured in Ref. 92 in order to determine the type of conductivity of the cleaved surfaces and the number of carriers. The results showed that the surface exhibits a hole conductivity, with an effective hole concentration of (0.6–1)· 10^{13} cm^{-2} and a mobility of 400–250 cm^2/(V· s). This conductivity is nearly independent of the nature of the sample (p-type and n-type germanium samples were studied with impurity concentrations ranging from 10^{14} to 3· 10^{15} cm^{-3}). It can be seen from the kinetics of the conductivity upon heating and when the samples are held at temperatures below 35–45 K that the hole concentration remains constant, so that the change in the surface conductivity is a consequence of a change in the carrier mobility.

The overall process by which the low-temperature surface conductivity arises can be described as follows. Upon cleavage in helium, electrons from the valence band become bound by dangling bonds; their number is

FIG. 13. Atomic displacements in the first five layers during the formation of "dimerized" structure (2×1)−Si(100) (Ref. 89).
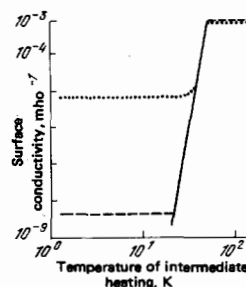

FIG. 15. Electrical conductivity of germanium single crystals cleaved in liquid helium at 4.2 K, plotted as a function of the temperature of intermediate heating.[91] Points—defective surfaces; dashed line—mirror-finish surfaces.

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determined by the balance between the energy released during the binding and the electrostatic repulsion. The holes which form in the valence band are relatively immobile at low temperatures because of the strong scattering by structural defects. Upon heating, the structural defects are partially annealed out, and the carrier mobility is increased. The high conductivity at liquid-helium temperatures and the associated effects (the Hall effect and the oscillation of the magnetoresistance) have also been observed at the contact surface of a bicrystal.[93]

The structure of the surface bands on the Ge(111) plane produced by cleavage and annealing in high vacuum has recently been studied experimentally by photoemission yield spectroscopy and by measurements of the contact potential difference.[94] It has been found, for samples with various doping levels (10^{15}–10^{18} cm^{-3}, p- and n-type), that there is a surface-state band on the cleaved surface with (2×1) structure which is centered 0.7 eV below the edge of the valence band. Measurements of the work function for various doping levels have shown that there should be an empty surface-state band above the Fermi level. After annealing at 350 °C, the structure transforms into a (2×8) structure, and the surface band shifts upward, closer to the edge of the valence band. This change in the surface spectrum is similar to that observed during the $(2 \times 1) \rightarrow (7 \times 7)$ restructuring at the Si(111) surface.

Among the surfaces of heteropolar semiconductors, that which has received the most study is the GaAs(110) surface, which is easily produced by cleavage in an atomically clean, defect-free state and which does not undergo restructuring. One of the interesting problems associated with this surface is the absence of observable surface states in the energy gap, although several calculations predict that there should be such states. Only recently has this contradiction been resolved. Chadi[95] used the strong-coupling method to calculate the surface electron spectrum for three possible models for surface relaxation and found that all the models cause the Tamm levels to move out of the gap. The calculated spectra agree satisfactorily with the photoemission spectra. Chelikowski and Cohen[96] later showed that the surface states actually disappear when the relaxation found from the LEED experiments is introduced, and only with a realistic choice of crystal potential.

Molecular-beam epitaxy has recently made it possible to synthesize the GaAs(100) surface; however, it is very unstable and undergoes several restructurings.[97] Detailed ARUPS measurements of this surface in two modifications, As(2×4) and Ga(4×2), have shown that there are well-defined surface peaks near the top of the valence band.[98] The changes in these peaks during adsorption of H_2 and O_2 and during annealing show that none of these structures is formed by atoms of a single species.

The GaAs(111) polar surfaces are again not cleavage planes, but they can be synthesized by molecular-beam epitaxy. A distinction is made between the (111) surface, which consists of gallium atoms, and the ($1\bar{1}\bar{1}$) surface, which consists of arsenic atoms. The electron properties of these surfaces should also be dif-ferent. Nishida[99] has calculated the surface states of these surfaces by the Hückel method, using the relaxation proposed previously by Harrison: an inward relaxation of Ga(111) layers and an outward relaxation of As(111) layers. The most important results of those calculations were that the band of surface states of the dangling-bond type in the gap rises during the Ga(111) relaxation and becomes broader because of an increased overlap with lower layers. Furthermore, it turns out that relaxation can even cause the appearance of new surface states of the "backward-bond" type. At the point $\bar{\Gamma}$, for example, such states are highly localized at gallium atoms and exhibit a predominantly s-type symmetry. The significant contradictions in the photoemission data make it difficult to use those data for a comparison.

To conclude this section on the surface states of semiconductors, we would like also to mention a study by Courths,[100] who used the UPS and LEED methods to study the $SrTiO_3$ and $BaTiO_3$(001) surfaces. Courths found surface states associated with oxygen orbitals at the top of the valence band.

CONCLUSION

In concluding this review of research on the electron structure of surfaces we would like to emphasize that we have selected material which we believe represents the most interesting and best-developed questions in this now extremely broad branch of solid state physics. We have attempted to show how modern concepts and the methods of traditional "bulk" band theory are applied to the problem of the electron structure of surfaces. From a different standpoint, the results found in research on surfaces may be of assistance in solving such fundamental problems as the relationship between the electron structure and the stability of crystal lattices, the magnetism of transition metals, and the nature of the interatomic bond. This hope can be based on the fact that an atom at a solid surface is, in a certain sense, in an intermediate state between the state of an isolated atom and the state of an atom in a crystal. It may prove to be the "missing link" which will be the key to the solution of the age-old problem of solid state physics: deriving the properties of a crystal from the properties of the individual atoms.

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