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Noble metal surface states: deviations from parabolic dispersion

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Abstract

Dispersion relations of the s–p derived surface state on (111) surfaces of silver and copper have been measured using low-temperature scanning tunneling microscopy and spectroscopy. For silver as well as for copper we find a significant deviation from a parabolic dispersion characteristic of free-electron-like systems. A simple tight-binding model accounts for the trends in the measured dispersions. © 2000 Elsevier Science B.V. All rights reserved.

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Because of the presence of a crystal surface, bulk-forbidden electronic single-particle states may arise leading to a band in the corresponding projected bulk band gap [1,2]. These so-called surface states are highly localized perpendicular to the surface [3], and form a (quasi) two-dimensional (2D) electron gas. If present, surface states (and resonances) may contribute a considerable fraction to the local density of states (LDOS) at and in front of the surface, and hence they can play a major role in surface physics and chemistry [2].

Direct experimental access to the occupied part of surface states of metals came from angle-resolved photoemission (ARP) in the 1970s. In particular, the s–p derived Shockley surface states of noble metal (111) surfaces have been investigated extensively by high-resolution ARP [4–9]. It is found that the occupied part of the surface states is free-electron-like; i.e., it has an isotropic parabolic dispersion. However, the effective electron mass m^* is considerably smaller than m_e due to the presence of the crystal potential. Since the noble metal surface states have a band edge $E_{\bar{\Gamma}}$ lying very close to the Fermi energy E_F, the ARP studies are inherently limited to the very center of the surface Brillouin zone (SBZ), and thus they are unable to detect any deviations from the quasi free-electron picture of the surface-state band structure. The dispersion of the unoccupied part of the surface states became accessible through k-resolved inverse photoemission spectroscopy (KRIPES). Although the KRIPES dispersions available for the surface states in question show

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no significant deviation from parabolic behavior either [10–12], the values deduced for m^* depend on the energy/momentum interval used for fitting the parabolic dispersion to the experimental data. Furthermore, the values are usually larger than the corresponding ARP values and differ from one group to another [10,12]. The interval dependence was interpreted in terms of the expected flattening of the dispersion towards the SBZ boundary [11]. Altogether, it is not clear to what extent the bands of these surface states deviate from the parabolic free-electron-like behavior.

With scanning tunneling microscopy (STM), new and fascinating access to the *local* electronic structure of surfaces has emerged. Through local, spatially resolved differential conductance spectra dI/dV, STM offers direct access to the surface LDOS [13,14]. (I and V are the tunneling current and the applied bias voltage, respectively.) Furthermore, the surface Fermi contour is directly accessible [15]. The advantages of STM are the ability to easily access states both below and above E_F, the inherently well-defined position of the Fermi level, and the very good energy resolution (better than 1 meV) in scanning tunneling spectra [16]. Also, the real-space imaging properties of STM allows for easy evaluation of the amount of surface impurities (adsorbates) with a very high sensitivity. However, contrary to ARP and KRIPES, STM is not a priori sensitive to the in-plane wave vector $\mathbf{k}_\parallel$. Only via the Friedel-like LDOS oscillations around static scatterers (e.g., point defects and step edges) does $\mathbf{k}_\parallel$ manifest itself in STM measurements. STM has repeatedly been used to map the dispersion relation for s–p derived surface-state electrons on noble metals by measuring the wavelength of such LDOS oscillations at different energies [17–20]. But all these STM studies were limited to $\mathbf{k}_\parallel$ vectors in the very center of the SBZ ($k_\parallel < 0.2\overline{\Gamma\mathrm{M}}$), and thus no deviation of the dispersion relations from a parabolic behavior could be detected.

In this letter we present a high-resolution low-temperature STM study of the band structure $E(k_\parallel)$ for the Shockley surface states on Ag(111) and Cu(111). We have measured $E(k_\parallel)$ along $\overline{\Gamma\mathrm{M}}$ over an extended range of the SBZ ($0 < k_\parallel < 0.6\overline{\Gamma\mathrm{M}}$), contrary to previous STM studies. To do so we have recorded dI/dV images at descending straight step edges for different energies. From the wavelength of the Friedel-like oscillations in these images, the wave vector corresponding to every energy can be inferred. We find a significant deviation from free-electron behavior for wave vectors exceeding $0.4\overline{\Gamma\mathrm{M}}$.

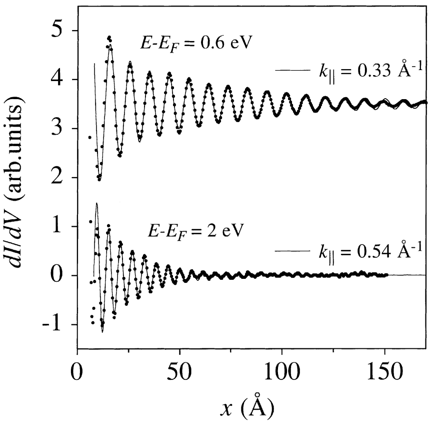

Fig. 1. Typical dI/dV data perpendicular to a straight descending Cu(111) step obtained by averaging over several line scans. The data at 0.6 eV and 2 eV were taken with a stabilizing current of 3 nA and 10 nA and a ΔV of 101 mV and 156 mV, respectively. The solid lines depict the fits with Eq. (3).

The experiments were performed with a home-built, low-temperature, ultrahigh vacuum scanning tunneling microscope (UHV-STM) described elsewhere [20]. The Ag(111) and Cu(111) surfaces were cleaned by sputter–anneal cycles, resulting in terraces several 1000 Å wide with less than 0.05% impurity atoms of unknown chemical identity. All measurements have been performed at $T = 4.9$ K, with a tungsten tip and the bias voltage V applied to the sample. The dI/dV data were acquired simultaneously with the constant-current "topography" image, under closed feedback-loop conditions and by the lock-in technique with a sinusoidal bias modulation of ΔV (peak-to-peak). With ~5.5 kHz, the frequency of the bias modulation was chosen above the band width of the feedback loop.

Fig. 1 shows dI/dV data perpendicular to $\langle 1\bar{1}0\rangle$-oriented monoatomic steps of a Cu(111) surface. x characterizes the distance from the step edge. To do the measurements we chose surface

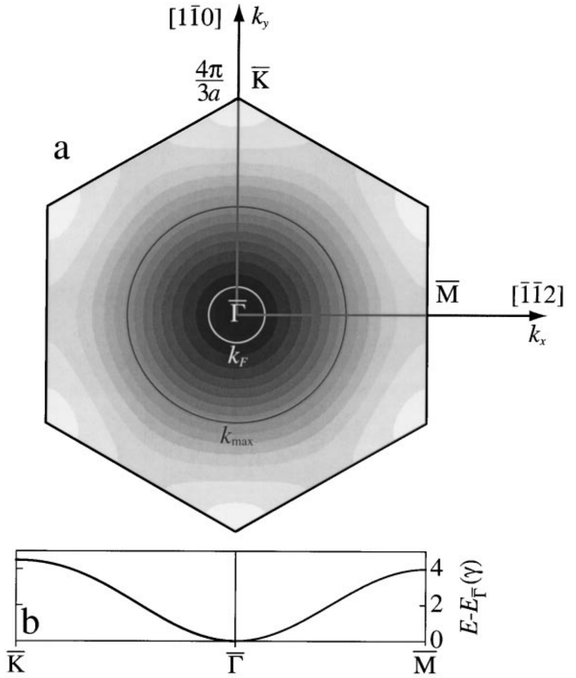

Fig. 2. (a) First SBZ of an fcc (111) surface. The tight-binding dispersion relation from Eq. (4) is plotted in gray scales. The inner white circle (k_F) depicts the surface-state Fermi contour for Cu(111). All our mesurements have been limited to the area enclosed by the black circle ($k_{\max}$), where the tight-binding dispersion can be considered isotropic. (b) Tight-binding surface-state band along high-symmetry lines of the SBZ.

spots bare of impurities. Since dI/dV is a quantity roughly proportional to the surface LDOS [14], the clearly visible spatial oscillations in Fig. 1 are a direct consequence of Friedel-like oscillations in the surface-state LDOS. We have been able to observe these oscillations over many periods, and thus our measurements are very sensitive to the wave vector. Note the different oscillation periods for different energies: the higher the energy, the shorter the wavelength.

In order to extract the dispersion relation over an extended region of the SBZ we analyzed our dI/dV line scans as outlined in the following. It is well established that, for bias voltages $V>0.3$ V and x not too close to the step edge ($x>\pi/k_{\|}$), the lateral variations in the closed feedback-loop dI/dV signal are proportional to the spatial variations in the surface LDOS, ρ_s [17,18,21]. To model the surface LDOS ρ_s at a $[1\bar{1}0]$ step let us consider a 2D electron gas with a dispersion given by $E'(q_x, q_y)$, where (q_x, q_y) characterize the 2D Bloch wave vectors. The x-axis has been chosen perpendicular to the $[1\bar{1}0]$ step direction; i.e., q_x is along $\overline{\Gamma \mathrm{M}}$ (see Fig. 2a). We assume that $E'(q_x, 0) \leq E'(q_x, q_y)$ for all (q_x, q_y), which is certainly fulfilled for our systems and the SBZ region of interest [4–12]. The step is modeled as an electron reflector of reflectivity $r^2(q_x)$ and phase shift $-\pi$ [22]. Since the bulk electrons efficiently screen the mutual Coulomb interaction between these surface-state electrons [21,23], the latter can be treated as uncharged particles. ρ_s in the presence of a step edge is then readily calculated to yield

$$\rho_s(E, x) = \rho_b + \int_0^{k_x} \mathrm{d}q_x [1 - r(q_x) \times \cos(2q_x x)] w(q_x, k_x), \tag{1}$$

where ρ_b is the bulk contribution to the surface LDOS, k_x is given by $E'(k_x, 0)=E$, and $w(q_x, k_x)$ is a weight function depending on the exact form of the crystal potential [i.e., the dispersion relation $E'(q_x, q_y)$]. For normal 2D electron gases and k_x not too close to the SBZ boundary, $w(q_x, k_x)$ is strongly peaked at $q_x = k_x$; e.g., for free-like electrons $w^0(q_x, k_x) = 2m^*/(\pi^2\hbar^2\sqrt{k_x^2 - q_x^2})$. Thus, as a consequence of this property of $w(q_x, k_x)$, $\rho_s(x)|_E$ from Eq. (1) is oscillatory with period π/k_x independent of the exact form of $w(q_x, k_x)$. Since we are only interested in the oscillation period (i.e., wave vector), we therefore can also choose the free-like $w^0(q_x, k_x)$ to interpret our data. The fact that deviations of the dispersion relation from free-electron-like behavior turn out to be rather small further justifies this (see below). With the free-like $w^0(q_x, k_x)$ and a reasonable q_x dependence of r, Eq. (1) simplifies to [21]

$$\rho_s(E, x) = \rho_b + L_0[1 - r(k_x) J_0(2k_x x)], \tag{2}$$

where J_0 is the zero-order Bessel function, and $L_0 = m^*/(\pi\hbar^2)$ is the density of states of the free-like 2D gas. Under the conditions of our experiment dI/dV is directly proportional to ρ_s [21], and therefore dI/dV results directly from Eq. (2),

$$\mathrm{d}I/\mathrm{d}V(V, x) = A - B \exp(-|x|/l) J_0(2k_x x), \tag{3}$$

where A and B are constants, l is an effective mean

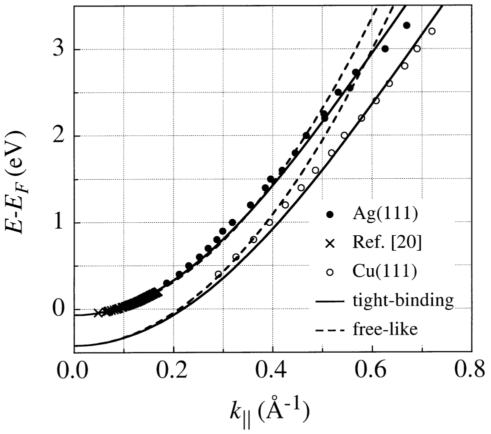

Fig. 3. Dispersion relation of the s–p derived surfaces states on Ag(111) and Cu(111) along the $\overline{\Gamma\mathrm{M}}$ direction.

free path, and k_x is related to V by $E'(k_x, 0) = eV$. The term $\exp(-|x|/l)$ term accounts for inelastic processes and the bias modulation ΔV, both of which damp the oscillations away from the step [21]. Neither the bias modulation nor inelastic processes alters the oscillation period (i.e., k_x)!

Fig. 1 depicts fits of our $\mathrm{d}I/\mathrm{d}V$ data with Eq. (3). By fitting similar $\mathrm{d}I/\mathrm{d}V$ data for silver and copper taken at different energies we obtain $k_x(E)$, and thus the dispersion relation along $\overline{\Gamma\mathrm{M}}$ shown in Fig. 3. The data points in Fig. 3 are averaged over several independent data sets measured at different $\langle 1\bar{1}0\rangle$-oriented steps, with different tips and different tunneling impedances. The absence of an influence of the latter on our measurement has been checked by measuring $k_\parallel$ at fixed bias and a stabilizing current that has been varied by a factor of 100 around the usual values. Thus, the presence of the tip — i.e., the tip-induced electric field or tip–surface interactions — does not influence the measured wave vectors. By far the largest contribution to the error in $k_\parallel$ (not shown in Fig. 3) comes from the uncertainty in the STM piezo calibration of about 5%. We have not been able to measure the dispersion relation beyond energies of about 3.5 eV since the decrease in the step reflection amplitude with increasing energy leads to a decrease in the LDOS oscillation amplitudes. Anyway, tunneling experiments are limited to energies smaller than the work function of typically 3.5–5 eV, since the tunneling barrier breaks down when eV approaches the value of the work function.

It becomes clear from Fig. 3 that the measured dispersion relations for the silver as well as for the copper surface state (resonance) deviate considerably from free-electron-like behavior. The dashed lines depict the parabola corresponding to low-temperature values of the band-edge energies $E_{\bar{\Gamma}}$ and effective masses m^* determined previously with ARP and STM measurements in the SBZ center: $E_{\bar{\Gamma}} = -65$ meV, $m^* = 0.40 m_\mathrm{e}$ and $E_{\bar{\Gamma}} = -420$ meV, $m^* = 0.40 m_\mathrm{e}$ for silver and copper, respectively [4,6,8,9,17,19,20]. With increasing wave vector the dispersion bends away from the free-electron-like parabola and flattens when getting closer to the $\bar{M}$-point, as expected. In the case of silver we can detect an inflexion point.

There exists some theoretical work on the band structure of noble metal (111) surfaces [24–26]. But we are not aware of any such calculation giving results over the extended $k_\parallel$ range studied here. Therefore, we discuss our data with simple general models. First of all, the nearly free-electron approximation, i.e., electrons in a weak periodic 2D potential, cannot explain effective masses smaller than m_e, and thus has to be discarded. On the contrary, since our m^* are considerably smaller than m_e we expect the crystal potential to be rather strong. Therefore, we compare the measurements with a simple tight-binding model [27,28]. This model considers a single s-band in an infinite lattice cleaved along some crystallographic direction. We have adopted the formalism given in Ref. [27] to a (111) surface of an fcc crystal, leading to the following surface-state dispersion:

$$E(k_x, k_y) = E_{\bar{\Gamma}} + \gamma\left[3 - \cos(k_y a) - 2\cos\left(\frac{k_y a}{2}\right)\cos\left(\frac{\sqrt{3}k_x a}{2}\right)\right], \qquad (4)$$

where a is the next-nearest-neighbor distance (2.89 Å and 2.56 Å for silver and copper, respectively), $E_{\bar{\Gamma}} = E_0 + U_0 + 3E_1(2 + 3E_1/U_0)$ and $\gamma = -2E_1(1 + E_1/U_0)$. Here E_0 and E_1 are the one-center and the nearest-neighbor matrix elements, respectively, and U_0 is the one-center surface perturbation matrix element as defined in Ref. [27].

In Fig. 2 we have plotted the dispersion relation from Eq. (4) in the first SBZ. [The white and the black levels are separated by $(9/2)\gamma$.] It is evident that this dispersion can be considered isotropic for the wave vectors accessible to our measurements. The surface-state band width of our model is $(9/2)\gamma$ and the corresponding surface DOS shows a logarithmic van Hove singularity at $E=E_{\bar{\Gamma}}+4\gamma$, where the dispersion goes through the saddle points at $\bar{M}$.

Since the band-edge energy $E_{\bar{\Gamma}}$ is known precisely (−65 meV and −420 meV for silver and copper, respectively), we are left with a single unknown parameter, namely γ. The full lines in Fig. 3 depict the least-squares fits with Eq. (4). We find γ values of 1.6 eV and 1.8 eV for silver and copper, respectively. The surface-state band widths can thus be estimated to be 7 eV and 8 eV, implying that possible van Hove singularities would lie outside the STM-accessible range. The tight-binding fits are satisfactory, and obviously reproduce the flattening of the dispersion. In addition, the Taylor expansion of these fits around the $\bar{\Gamma}$-point yields effective masses of $m^*=0.37m_e$ and $m^*=0.42m_e$ for silver and copper, respectively, in agreement with previous results.

In conclusion, using scanning tunneling microscopy and spectroscopy, we have for the first time experimentally quantified the deviation of noble metal surface-state bands from free-electron parabola.

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References

[1] S.G. Davison, M. Stęślicka, Basic Theory of Surface States, Oxford University Press, New York, 1992.

[2] E. Bertel, M. Donath, Electronic Surface and Interface States on Metallic Systems, World Scientific Publishing, Singapore, 1995.

[3] T.C. Hsieh, T. Miller, T.-C. Chiang, Phys. Rev. Lett. 55 (1985) 2483.

[4] P.O. Gartland, B.J. Slagsvold, Phys. Rev. B 12 (1975) 4047.

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

[6] S.D. Kevan, R.H. Gaylord, Phys. Rev. B 36 (1987) 5809.

[7] Z. Qu, L. Ye, A. Goonewardene, N. Mainkar, K. Subramanian, J. Karunamuni, R.L. Stockbauer, R.L. Kurtz, J. Vac. Sci. Technol. A 12 (4) (1994) 2187.

[8] R. Paniago, R. Matzdorf, G. Meister, A. Goldmann, Surf. Sci. 336 (1995) 113.

[9] B.A. McDougall, T. Balasubramanian, E. Jensen, Phys. Rev. B 51 (1995) 13891.

[10] S.L. Hulbert, P.D. Johnson, N.G. Stoffel, W.A. Royer, N.V. Smith, Phys. Rev. B 31 (1985) 6815.

[11] S.L. Hulbert, P.D. Johnson, N.G. Stoffel, N.V. Smith, Phys. Rev. B 32 (1985) 3451.

[12] A. Goldmann, V. Dose, G. Borstel, Phys. Rev. B 32 (1985) 1971.

[13] L.C. Davis, M.P. Everson, R.C. Jaklevic, W. Shen, Phys. Rev. B 43 (1991) 3821.

[14] G. Hörmandinger, Phys. Rev. B 49 (1994) 13897.

[15] L. Petersen, P.T. Sprunger, P. Hofmann, E. Lægsgaard, B.G. Briner, M. Doering, H.-P. Rust, A.M. Bradshaw, F. Besenbacher, E.W. Plummer, Phys. Rev. B 57 (1998) R6858.

[16] A. Yazdani, B.A. Jones, C.P. Lutz, M.F. Crommie, D.M. Eigler, Science 275 (1997) 1767.

[17] M.F. Crommie, C.P. Lutz, D.M. Eigler, Nature 363 (1993) 524.

[18] Y. Hasegawa, P. Avouris, Phys. Rev. Lett. 71 (1993) 1071.

[19] J. Li, W.-D. Schneider, R. Berndt, Phys. Rev. B 56 (1997) 7656.

[20] O. Jeandupeux, L. Bürgi, A. Hirstein, H. Brune, K. Kern, Phys. Rev. B 59 (1999) 15926.

[21] L. Bürgi, O. Jeandupeux, H. Brune, K. Kern, Phys. Rev. Lett. 82 (1999) 4516.

[22] L. Bürgi, O. Jeandupeux, A. Hirstein, H. Brune, K. Kern, Phys. Rev. Lett. 81 (1998) 5370.

[23] F. Stern, Phys. Rev. Lett. 18 (1967) 546.

[24] J.A. Vergés, E. Louis, Solid State Commun. 22 (1977) 663.

[25] J.A. Appelbaum, D.R. Hamann, Solid State Commun. 27 (1978) 881.

[26] P.M. Echenique, J.B. Pendry, Progr. Surf. Sci. 32 (1989) 111.

[27] D. Kalkstein, P. Soven, Surf. Sci. 26 (1971) 85.

[28] L. Dobrzynski, Handbook of Surfaces and Interfaces, Garland STPM Press, New York, 1978.