

One-Dimensional 3d Electronic Bands of Monatomic Cu Chains

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The electronic structure of an array of monatomic Cu chains grown on the Pt(997) surface has been examined by angle-resolved photoemission. The monatomic wires exhibit properties associated with 3d electron confinement in one dimension. Along the wire direction, the 3d bands states display a dispersive character, with periodicity in reciprocal space defined by the wire array geometry. These observations are compared and analyzed with *ab initio* calculations based on the full-potential linearized augmented plane-wave method.

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The controlled design of the atomic geometry at surfaces opens new pathways to the physical realization of low-dimensional electronic networks with novel and tunable properties. Through nanoscale structuring and self-organization processes, metallic systems can be tailored on surfaces with given geometry, suitable periodicity, and large lateral coherence [1–3]. Although the interactions in the surface plane and with the underlying atomic layers cannot be generally neglected, these structures offer attractive ways to examine electronic properties in confined geometries. In some particular structures, artificially constructed at surfaces, the electronic states of the constituent elements can be sufficiently laterally decoupled in the surface plane to develop a one-dimensional (1D) character.

The geometry of vicinal surfaces often gives rise to a preferential 1D direction of growth of the deposited material with a high degree of order [4,5]. An exemplary case is Au atoms forming parallel chains on macroscopic areas of the Si(111) vicinal surface. In photoemission studies, they exhibit a number of exotic features [6], such as Peierls transitions, periodic lattice distortions, and charge density waves. These effects are thought to be intimately related to the perfect “nesting” of the Fermi surface in a partially filled 1D band associated with Au *sp*-electrons. One-dimensional delocalized surface states are also formed along atomic step edges of vicinal noble metal surfaces. By simply varying the spacing between step edges, acting as a barrier for electron propagation, different degrees of lateral confinement are achieved for *sp*-derived states on the terraces of metal surfaces [7,8].

While several investigations have addressed the behavior of 1D extended states formed by *sp*-derived levels, until now there has been no comparably detailed study of surface nanostructures involving *d*-electrons. The *d*-electrons have wave functions more localized near the atomic core, experience a larger correlation effect, and have much smaller energy dispersions and group velocities, exhibiting heavier electron masses. This imposes constraints on the degree of coherence to shorter length

scales, as well as on the required sensitivity of the measurements in probing smaller bandwidths. The larger Coulomb interaction and the reduction of the bandwidth profoundly influence the properties of 1D systems [9]. For instance, the *d*-electrons, which can be described in a bulk material on the basis of Landau Fermi-liquid theory, may lose their identity in one dimension and are described as Luttinger liquids, exhibiting charge and spin separation. Previous studies show that high quality monatomic arrays of Co or Cu can be grown on the vicinal Pt(997) surface, where the binding energy of the 3d states could be identified by means of photoemission [10]. However, no detailed experimental information has been available until now on the dispersion relations, i.e., the binding energy as a function of the wave vector, which describes 3d electron bands of monatomic wires in a well-defined 1D geometry.

Here, we report on an investigation of the 3d bands of a monatomic array of Cu chains, artificially constructed by self-assembling on the vicinal Pt(997) surface. Using angle-resolved photoemission spectroscopy, we examined the 3d bands of the chains as a function of the wave vector. The Cu chains are found to exhibit features of 1D character. The 1D geometry of the wires results in the localization of the Cu 3d states within the monatomic chains, with band dispersion and periodicity defined by the specific chain arrangement of the 1D superlattice. Detailed *ab initio* calculations based on the full-potential linearized augmented plane-wave (FLAPW) method closely reproduce the experimental band structure.

The experiments were performed at the VUV beam line at the ELETTRA Synchrotron Light Laboratory in Trieste. Cu monatomic chains were grown *in situ* at 250 K on the vicinal Pt(997) surface as described in Ref. [10]. This surface presents regularly arranged monatomic steps situated 20.2 ± 1.5 Å apart and separated by (111) terraces. Surface diffusion leads to step decoration by deposited Cu atoms, resulting in an array of parallel 1D chains. The geometry of the surface, decorated by monatomic Cu chains, is schematically shown in Fig. 1(a). Angle-resolved

photoemission data were collected at 165 eV photon energy, in the Pt 5*d* Cooper-minimum [11], where the $\sigma_{\text{Cu}3d}/\sigma_{\text{Pt}5d}$ cross section ratio is larger than 10. Under this condition, it is possible to achieve sufficiently high sensitivity to the 3*d* states from Cu with a low surface density, despite the overlapping emission from Pt 5*d* states. The photoemission spectra were measured at room temperature with linearly polarized radiation, incident on the sample at an angle of 45° from the surface normal. Figures 2(a) and 2(b) show photoemission spectra measured by varying the polar emission angle along the $[\bar{1}\bar{1}0]$ and $[11\bar{2}]$ directions of the Pt(997) substrate crystal which correspond to the directions parallel and perpendicular to the chains, respectively. The Cu 3*d* derived valence states are centered around 2–3 eV binding energy and constitute the main spectral feature. Along the chain direction, the Cu 3*d* states exhibit well-defined energy dispersion [Fig. 2(a)], whereas the spectra are largely independent of the polar emission angle in the direction perpendicular to the chains in Fig. 2(b).

In order to better illustrate the behavior of the chain-related states, extended measurements of the wave vector dependence are reported in Figs. 2(c) and 2(d), by a color rendering of the second derivative photoemission intensity, used here to enhance weak spectral features. Along the chain directions, the data exhibit clearly two band states; the upper states disperse to lower binding energy as the emission angle is increased, defining a bandwidth of approximately 0.8 eV, and the lower band states show a smaller dispersion with a bandwidth of 0.2 eV. In contrast, for both bands, no significant binding energy changes are observable as a function of the wave vector perpendicular to the chain axis. This qualitatively different behavior along the two directions clearly highlights the strong anisotropic character of the 3*d* electronic states reflecting the array geometry of the chains. While the Cu 3*d* states form dispersing bands along the chain axis, because of electron hopping due to overlapping *d*-wave functions at neighboring sites, they appear not to delocalize across the Pt ter-

aces. This surface electronic system, although intrinsically two-dimensional (2D), thus develops 1D features associated with the monatomic chains.

It is interesting to note that the band structure displays a periodicity along the chain axis that reflects the lateral arrangement of the Cu chains in a periodic array. The energy dispersion in Fig. 2(a) indicates that cell boundaries correspond to reciprocal vectors of $\pm 1.14 \text{ \AA}^{-1}$, as shown by the extremal values that the bands reach at these wave vectors. The cell dimension along the chain axis thus significantly differs from the one of the flat Pt(111) surface along the same crystallographic direction (1.51 \AA^{-1}). In order to understand the results, one needs to consider the proper surface unit-cell of Pt(997), defined by a parallelogram of $20.20 \times 2.77 \text{ \AA}$ [Fig. 1(a)], with high-symmetry

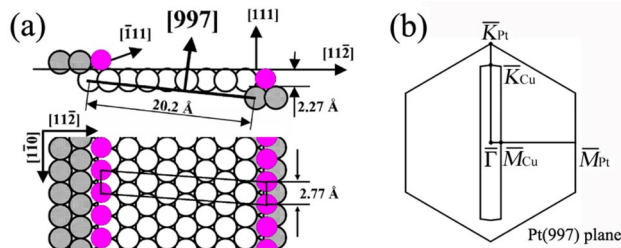


FIG. 1 (color online). (a) Geometry of the atomic structure of the Pt(997) terrace (open spheres) and one Cu chain (solid spheres) on the step edge. The parallelogram represents the surface unit cell of Cu chains on Pt(997) with $20.20 \times 2.77 \text{ \AA}$. (b) The first surface Brillouin zone (SBZ) of Cu chains and the Pt(111) terrace projected on the (997) plane. $\Gamma K_{\text{Cu}} = 1.14 \text{ \AA}^{-1}$, $\Gamma M_{\text{Cu}} = 0.156 \text{ \AA}^{-1}$, $\Gamma K_{\text{Pt}} = 1.51 \text{ \AA}^{-1}$, $\Gamma M_{\text{Pt}} = 1.30 \text{ \AA}^{-1}$.

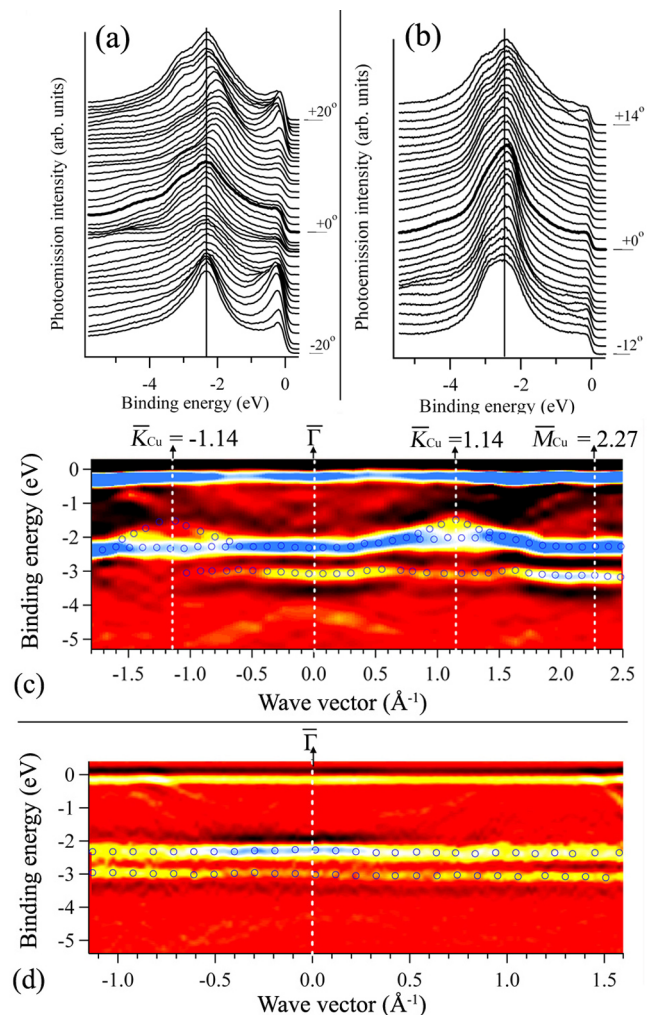


FIG. 2 (color online). Sets of angle-resolved photoemission spectra recorded for different polar angles (a) parallel and (b) perpendicular to the Cu chain direction. Corresponding second derivative photoemission intensity plots of a wide range of reciprocal lattice vectors, (c) along and (d) perpendicular to chain direction. Full circles represent band dispersions extracted from the photoemission spectra. The reciprocal lattice vectors correspond to the first SBZ of Cu chains on Pt(997).

points for the first surface Brillouin zone (SBZ) [Fig. 1(b)] at $\overline{\Gamma\bar{K}}_{\text{Cu}} = 1.14 \text{ \AA}^{-1}$ and $\overline{\Gamma\bar{M}}_{\text{Cu}} = 0.156 \text{ \AA}^{-1}$. The experimental results agree very well with the expected value for the K -point of the SBZ in the Pt(997) unit cell, which is obviously not changed for the wire decorated surface. The lateral periodicity given by the ordered sequence of decorated steps and terraces manifests itself introducing new zone boundaries along the chain axis. The experimental agreement with the expected values suggests that the Cu monatomic chains grow pseudomorphic on Pt(997), with first neighbors separated by the Pt-Pt interatomic distance of 2.77 \AA , and the wave function in the initial state is coherent in the chain and across the terrace. Along the direction perpendicular to the chains, a periodicity of 0.31 \AA^{-1} is to be expected from SBZ of Pt(997). Because of the absence of any dispersion, this can, however, not be observed in the experimental data, again pointing to very weak chain-chain interactions.

When a Cu monolayer (approximate in term of stripes of eight chains) is formed, the $3d$ states evolve from a 1D to a 2D character. Figure 3 shows second derivative photoemission intensity plots as a function of the reciprocal lattice vectors for one monolayer Cu on Pt(997). A significant band dispersion is also observed in the direction perpendicular to steps, which is absent for the monatomic chain [12]. Additionally, the bandwidth of the $3d$ states for the Cu monolayer is larger than for the case of the monatomic chain, due to the higher atomic coordination. Although the unit cell would not change for ideal row by row growth fashion, it is known that pseudomorphic growth is not maintained at full monolayer coverage in this system [13]. The extremal points of the band dispersion, $\overline{\Gamma\bar{K}}$ and $\overline{\Gamma\bar{M}}$, correspond to a wave vector of 1.50 \AA^{-1} and 1.30 \AA^{-1} , respectively. Figure 1(b) shows the first SBZ of the Pt terrace (111) surface projected on (997) plane with $\overline{\Gamma\bar{K}}_{\text{Pt}} = 1.51 \text{ \AA}^{-1}$ and $\overline{\Gamma\bar{M}}_{\text{Pt}} = 1.30 \text{ \AA}^{-1}$. The agreement of the extremal symmetry points of the wave vector indicates that the Cu atoms are hexagonally packed with the bulk Pt-Pt interatomic distance of 2.77 \AA in the case of one monolayer.

To verify and complement our interpretation of the observed 1D electronic state, we performed density functional theory (DFT) calculations based on the FLAPW method [14] as implemented in the FLEUR code [15]. A Pt(664) film as described in Ref. [16] was used as a substrate for the Cu chain: The chains were placed at positions commensurate with the substrate, separated by Pt terraces of a width of 6 atomic rows. A film of about 8 layers of fcc (111)-type was considered, resulting in a total of 45 atoms per unit cell. Figure 4(a) shows the comparison of the peaks of the spectra with the calculated band structure of Cu/Pt(664). The calculated band structure was shifted down by 1.0 eV to enhance agreement with the experimental band [17]. Open circles represent calculated states with substantial charge density on Cu chain atoms deposited on the Pt(664) vicinal surface step edge. Solid circles represent states of experimental results of Cu/Pt(997). From the picture, it can be seen that apart from the exact band position, the calculated band structure compares quite reasonably to experimental bands of Cu/Pt(997) system.

Analyzing the symmetry of the Cu $3d$ states, we find that at the $\overline{\Gamma}$ point the lower states are mainly of d_{z^2} , d_{xy} , and $d_{x^2-y^2}$ character (assuming that z runs along the chain axis), while the upper states are d_{yz} and d_{zx} orbitals. Propagating along the line $\overline{\Gamma\bar{K}}$, the d_{yz} and d_{zx} states disperse downwards, while the d_{z^2} states can be found at the top of the $3d$ band at $\overline{\bar{K}}$. At the zone boundary, d_{xy} and $d_{x^2-y^2}$ orbitals are found in between these extremes, forming “nonbonding” states. In the middle of SBZ, the d_{z^2} state hybridizes with the strongly dispersing s -band, which is not observed in the experimental spectra because the σ_s/σ_d cross section ratio at photon energy 165 eV is smaller than 10 [11]. Moreover, at the crossing of the d_{yz} and d_{zx} states (degenerate in the unsupported chain) with the d_{xy} and $d_{x^2-y^2}$ states (also degenerate in the unsupported chain), as shown in the band structure of freestanding Cu chains [Fig. 4(b)], the intensity fades out in the middle of SBZ, resulting in an apparent gap in the observed spectra, which indicates that the Cu $3d$ states hybridize here more strongly with the Pt $5d$ states than at the zone

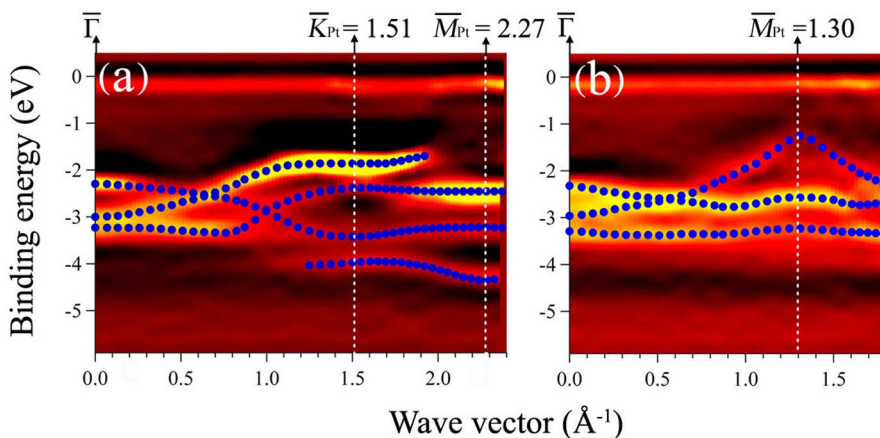


FIG. 3 (color online). Second derivative photoemission intensity plots of the dispersion of eight chains (i.e., 1 ML) of Cu on Pt(997) (a) parallel and (b) perpendicular to the chain directions, respectively. Solid spheres represent band dispersions extracted from the photoemission spectra.

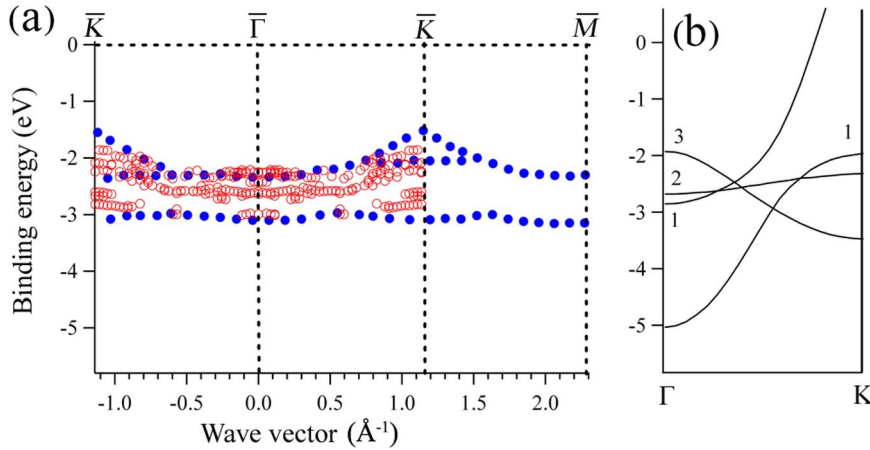


FIG. 4 (color online). (a) Comparison of the experimental data with *ab initio* calculations of the band structure of monatomic Cu chains on Pt(664). Open circles represent states with substantial charge density on Cu atoms at the step edge. Solid circles represent data from the experimental results of Cu/Pt(997). (b) *Ab initio* calculation of the band structure of freestanding Cu chain showing the d_{z^2} state (1), the degenerate d_{xy} and $d_{x^2-y^2}$ states (2), and the degenerate d_{yz} and d_{zx} states (3).

boundary. In addition, the Cu-Pt hybridization also seems to reduce the dispersion of the d_{yz} and d_{zx} states, but increases the dispersion of the d_{xy} and $d_{x^2-y^2}$ states as compared to the freestanding chains.

From prior studies, it can be concluded that the 1D confinement of the *sp*-derived electronic states on metal surfaces can mainly be attributed to two reasons: (1) the formation of step-induced states due to a vanishing interaction between the steps in the limit of large step spacing [18]; and (2) the degree of electronic decoupling from the metallic substrate due to the pseudogap of the surface projected metal bulk bands [19]. Although the Pt5*d*-Cu3*d* hybridization cannot be neglected, our experimental results demonstrate that the 1D confinement of the Cu 3*d*-derived electronic band structure for Cu chains on the Pt(997) surface is introduced by the direct wave-function overlap between next-neighbor Cu atoms in the one-dimensional chains, especially the d_{z^2} states.

In conclusion, by means of angle-resolved photoemission, we investigated the 3*d* band electronic structure of Cu chains on Pt(997). We have shown that the Cu 3*d* electronic band structure shows anisotropic 1D band dispersion. The 3*d* electrons of Cu are delocalized along the chains and localized in perpendicular directions. The photoemission spectrum can be interpreted with Fermi liquid theory on the basis of the DFT. *Ab initio* calculations based on the FLAPW method account nicely for the experimental observations.

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