

Electronic states and magnetism of monatomic Co and Cu wires

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The electronic structure of monatomic Cu and Co wires grown by step decoration of the vicinal Pt(997) surface has been investigated by angle-resolved photoemission with synchrotron radiation. Sensitivity to the small amount (≈ 0.1 monolayer) of deposited material that forms the one-dimensional wires could be achieved at photon energies close to the Pt 5*d* Cooper minimum, where the photoemission cross section of the substrate valence band is strongly reduced. A single photoemission feature is associated with the 3*d* emission from the Cu monatomic wire. A double-peaked 3*d* structure is instead observed for Co wires, suggesting the presence of a one-dimensional exchange-split band and of local magnetic moments.

The electronic structure and magnetic behavior of a material can be significantly modified by reducing its dimensions along one or more directions in space. Quantum-size effects give rise to electronic and magnetic properties for low-dimensional systems that have no counterpart in the bulk. The physical realization of these systems opens up the possibility of designing new kinds of materials (“atomic engineering of materials”). Nearly two-dimensional (2D) magnetic systems, such as ultrathin films and superlattices, have recently been the aim of intensive investigations.^{1,2} However, very little is known so far about the electronic and magnetic structure of systems with still lower dimensionality because of difficulties in their preparation and characterization.

The manipulation of single atoms and their displacement on surfaces has been demonstrated by scanning tunneling microscopy (STM). However, this technique does not permit the preparation of nanostructured large-area samples, which are required by standard methods for band structure determination, such as angle-resolved photoemission. Large-area samples with a structuring on a nanometer scale, in particular samples with monatomic chains, can be obtained by molecular beam epitaxy exploiting self-organization mechanisms of adatoms on suitable substrates.³ Examples of one-dimensional systems grown by self-organization include Cu, Pd, and Fe chains on Pd(110),^{3,4} and Gd on W(110).^{5,6} During the growth of Au on Ni(110), the development of a Au dimer-trimer chain structure has been observed.⁷ In this system the one-dimensionality of the Au-induced states could also directly be derived from their dispersion behavior.⁸ However, no information about the magnetic properties of 1D systems can be deduced in this case.

1D nanostructures can also be prepared by molecular beam epitaxy on stepped single-crystal surfaces that serve as a template for growing nanowires exploiting step decoration.^{9,10} Submonolayer amounts of Fe on a W(110) surface with irregular atomic steps were found to be ferro-

magnetic down to an Fe coverage of 0.05 ML.¹¹ Smooth and coherent Fe stripes on W(110) still exhibited ferromagnetism at a coverage of 0.5 ML with an average monolayer stripe width of 20 atomic rows.¹² On a vicinal Cu(111) substrate, Fe stripes of 5–15 atom width and 1–2 atom height, with a corresponding coverage of 0.3 ML, were found to exhibit a time dependent remanent magnetization.¹³ Concerning the electronic structure of 1D systems, a pioneering inverse photoemission experiment has already been performed for Cu on W(331),¹⁴ where the authors report on an electronic state which has been interpreted as a “single-row-state.”

Here we present, to the best of our knowledge the first measurements on the electronic and the magnetic properties of a 1D system that approaches the *monatomic* limit. The ideal system for the investigation of 1D electronic and magnetic properties with valence band photoemission is a set of parallel, equidistant, straight monatomic chains consisting of a magnetic element on a nonmagnetic substrate. The distance between the chains has to be large enough to allow mostly intrachain and only weak interchain interaction, but also small enough to ensure a sufficiently large contribution from the chains to the photoemission spectra. In these respects, the vicinal Pt(997) surface represents an excellent substrate. It supports the 1D growth of various elements, in particular the growth of monatomic Co and Cu wires,¹⁵ which are arranged in an array of high regularity with a distance of 8 ± 1 atomic rows. As will be demonstrated here, the step density is high enough to observe chain-induced electronic states in the angle-resolved photoemission experiment.

The characterization of single and multiple monatomic chain growth of Co and Cu on Pt(997) has been extensively carried out at EPF-Lausanne by means of thermal energy helium atom scattering (TEAS) and STM.¹⁵ Pt(997) is a vicinal surface cut 6.5° off normal with respect to the (111) atomic plane. The angle miscut determines the average step separation which is 20.1 Å. Repulsive interactions between adjacent steps suppress step meandering, resulting in steps that run parallel to each other (see Fig. 1). In order to obtain samples with a regular step distribution, repeated cycles of

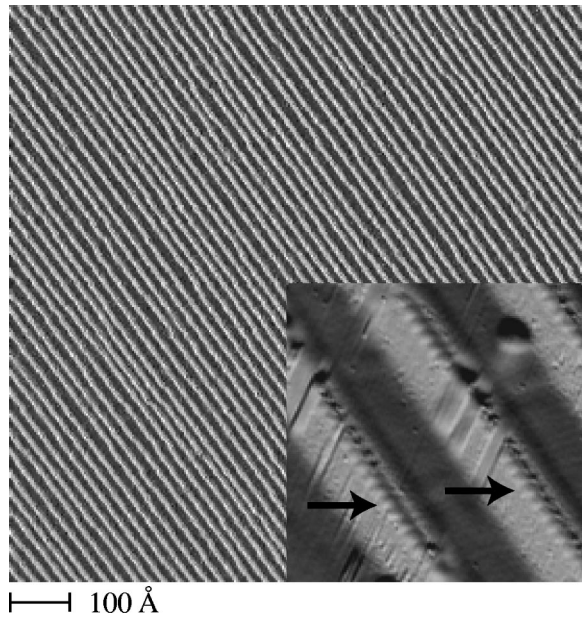


FIG. 1. STM topograph (dz/dx mode) of the clean Pt(997) surface. The terrace width distribution follows a Gaussian law with an average spacing of 20.1 Å [standard deviation $\sigma=2.9$ Å (Ref. 27)]. The step edges appear as white lines. Step down direction is from the upper right to the lower left. The inset shows the decoration of the Pt steps by single monatomic Co chains (indicated by the arrows).

sputtering and annealing to 850 K are performed in a UHV environment (base pressure 1×10^{-10} mbar), followed by a few minutes exposure to 1×10^{-7} mbar oxygen and by a flash to $T > 1000$ K to remove residual contaminants. Cooling the sample to the deposition temperature has to be done at a slow rate (< 40 K/min) to prevent step bunching effects. The quality of the periodic pattern can be routinely checked by taking TEAS diffraction spectra or by low energy electron diffraction (LEED) measurements.

The growth of Co and Cu monatomic chains along the Pt step edges can be followed in real time by TEAS measurements in grazing incidence conditions.^{10,15} TEAS results show that smooth monatomic row growth takes place above 250 K and 150 K for Co and Cu, respectively. The deposition of 0.12 ML in the allowed range of temperatures results in the decoration of each step by a single monatomic row. The inset in Fig. 1 shows Co monatomic chains decorating Pt steps after deposition at 250 K. Chains wider than one atomic row can be obtained by increasing the coverage up to 1 ML.

The angle-resolved photoemission measurements were performed at the undulator beamline TGM-5 at BESSY. The energy analysis of the photoemitted electrons was performed with a 90°-spherical electron energy analyzer with an energy and angle resolution of 250 meV and $\pm 1^\circ$, respectively. Unless specifically mentioned, all measurements have been performed at room temperature. After repeated cycles of Ne-ion sputtering and annealing, a very good LEED pattern with sharp diffraction spots and a low background intensity confirmed a high degree of structural order in the topmost surface layers. In addition to the $p(1 \times 1)$ spots we found extra spots that were induced by the step edges and stressed the high surface quality of the sample used in the photoemission

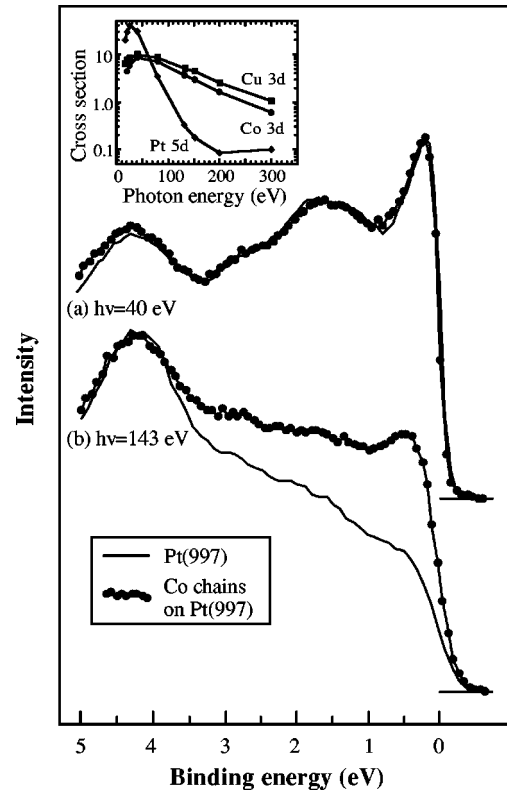


FIG. 2. Photoemission spectra of clean Pt(997) and after the deposition of 0.12 ML Co taken at photon energies of (a) 40 eV and (b) 143 eV. The inset shows the atomic photoionization cross sections for 5d transition metals (e.g., Pt) and 3d transition metals (e.g., Cu and Co) as a function of photon energy (Ref. 16).

experiment. The base pressure of 1×10^{-10} mbar rose to 4×10^{-10} mbar as Co and Cu were deposited by electron beam evaporation. The thickness calibration was done by means of a quartz crystal microbalance. A cross check with Auger spectroscopy enabled us to make a direct comparison of the absolute amounts of deposited material between the samples prepared at BESSY and the ones studied at EPF-Lausanne.

A serious problem for the determination of the electronic states of 1D monatomic chains by angle-resolved valence band photoemission is the small amount of deposited material (≈ 0.1 ML) and its weak contribution to the photoemission spectra which makes the identification of chain-induced states very difficult. It is therefore crucial to find experimental conditions that offer a high spectroscopical sensitivity for the chain-induced states. In fact, for an arbitrary choice of photon energy, nearly no changes in the photoemission spectra could be found after the preparation of Cu or Co wires. This is demonstrated in Fig. 2(a), which shows photoemission spectra of the clean Pt(997) substrate and of 0.12 ML Co on Pt(997), taken at a photon energy of 40 eV. The sensitivity for the small amount of deposited Co can be strongly enhanced, taking advantage of the Pt 5d Cooper minimum. The atomic photoionization cross sections for 3d and 5d transition metals are shown in the inset of Fig. 2. The corresponding cross section ratios in the solid state were found to be of similar magnitude.¹⁷ Photoemission spectra of the clean Pt substrate and with a coverage of 0.12 ML Co show indeed strong changes at a photon energy of 143 eV [Fig. 2(b)].

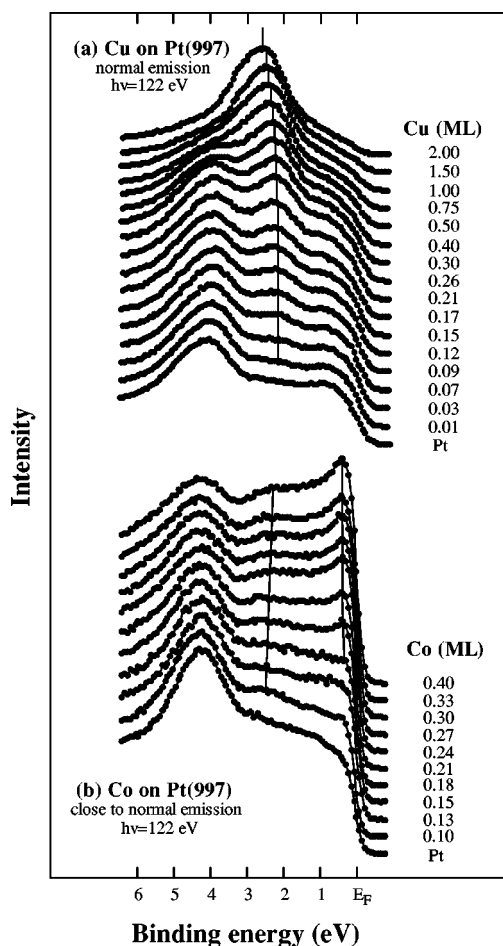


FIG. 3. (a) Photoemission spectra taken at a photon energy of 122 eV displaying the development of Cu states on Pt(997) with increasing coverage. (b) Photoemission spectra taken at a photon energy of 122 eV displaying the development of Co states on Pt(997) after deposition of up to 0.40 ML Co.

In Fig. 3(a), the changes of the electronic states with increasing Cu thickness are displayed. At coverages below 0.1 ML, the development of a single Cu $3d$ state at a binding energy of 2.3 eV already can be observed. No Cu-derived electronic states can be found close to the Fermi level because the Cu $3d$ shell is filled and the photoemission cross sections for s states are very small in this photon energy range. Above a coverage of 0.17 ML, the Cu $3d$ states shift to higher binding energy, and at 2.0 ML they have reached a value of 2.7 eV. These changes in the electronic structure are likely to reflect the changes in the dimensionality of the system. The development from a 1D to a 2D system, as it is realized for the growth of Cu and Co on Pt(997), will result in different electronic configurations, that should lead to observable changes in the electronic structure. At a coverage of 0.17 ML, where the wires are already completely formed and the growth starts to become two-dimensional,¹⁵ the shift of the Cu $3d$ states to higher binding energy begins to take place. For systems with 2D island or 3D cluster nucleation instead, almost no changes in the electronic structure can typically be observed with increasing coverage in the submonolayer regime,^{18,19} because for low coverages the average atomic coordination is already quite similar to the coordination in the monolayer or in the bulk, respectively.

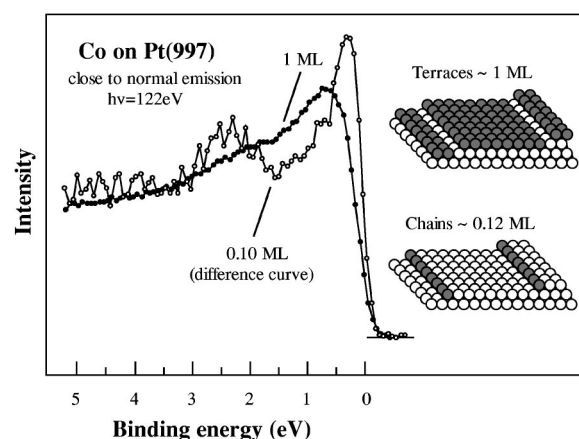


FIG. 4. Difference spectrum showing the Co chain-induced states in comparison with a photoemission spectrum of a Co monolayer (not a difference spectrum) and schematic pictures of Co chains and a Co monolayer on Pt(997).

For Co the development of the electronic states with increasing coverage also has been studied. The sequence of spectra in Fig. 3(b) was taken at a photon energy of 122 eV and close to normal emission (4° off normal). It shows that in the low-coverage region up to 0.4 ML, the changes of the electronic states related to the Co deposition clearly differ from the changes observed in the case of Cu. Here, close to the Fermi level and at a binding energy of approximately 2.4 eV, new electronic states appear in the photoemission spectra. With increasing Co deposition these structures become prominent in the spectra and their separation slightly decreases (see also Fig. 4).

In order to make the chain-induced states more clearly visible, a difference spectrum between the spectrum at 0.10 ML Co and the Pt spectrum has been formed. The normalization of the spectra has been done by equalizing the amplitude of the Pt peak at a binding energy of approximately 4 eV. The resulting spectrum is shown in Fig. 4 in comparison with a spectrum of a Co monolayer. In contrast to the single feature found for the Cu chains, we find two peaks for the Co chains located at binding energies of 0.3 eV and 2.4 eV.

We shall now discuss the presence of a single peak for the Cu chains and of two peaks for the Co chains. One could assume that one of the two Co peaks represents a Co-Pt interface state or a 1D modified surface state. Since for the same geometric arrangement, the electronic structure of Co and Cu is very similar and differs mainly in the energetic position of the bands, we could expect to observe Cu-Pt interface states or 1D Cu states, as well. This is not the case and therefore the double peak structure found for the Co chains is likely to have a *magnetic* origin. In contrast to Cu, that has a completely filled $3d$ shell, Co has a magnetic moment because its $3d$ shell is partially unoccupied. In the electronic structure, this results in an exchange splitting of the Co $3d$ bands that probably leads to the photoemission features close to the Fermi level and at a binding energy of 2.4 eV shown in Fig. 4. So the observation of a double-peaked structure for the Co wires and of a single feature for the Cu wires strongly suggests the presence of a 1D exchange-split Co band and of local magnetic moments.

The comparison of the Co chain spectrum with the Co monolayer spectrum displayed in Fig. 4 shows obvious differences for these two systems. In particular, the magnitude of the exchange splitting seems to be larger for the Co chains than for the Co monolayer, although the exchange splitting of the Co monolayer cannot be safely determined without spin analysis. The broad feature close to the Fermi level could consist of overlapping contributions from states of different spin character and symmetry. However, the positions of the Co-induced states in Fig. 4 indicate that the exchange splitting of the monatomic Co chains is large (~ 2.1 eV). This value can be compared with typical values for thin Co films (1.4–1.9 eV),^{20,21} and for bulk Co (≈ 1.4 eV).^{20,22} This large number for the Co chains suggests that the corresponding local magnetic moments also have a considerable magnitude compared to Co films and to bulk Co. This is in line with recently performed self-consistent calculations for monatomic Co chains.²³

An enhancement of the exchange splitting can be explained in terms of the lowered dimensionality of the Co system. For a magnetic system it is well known that a reduction of its dimensionality from 3D to 2D causes an enhancement of its magnetic moments. This effect is essentially a consequence of the band narrowing due to the reduced atomic coordination in the 2D system. In the electronic structure, this results in a larger exchange splitting compared to the bulk. With the same argument, even larger magnetic moments and a larger exchange splitting can be expected for a 1D system, and this is probably what we observe in the photoemission spectra of the Co wires.

No in-plane spin polarization of the chain-induced electronic states, neither parallel nor perpendicular to the chains, could be found with a high-energy Mott detector down to sample temperatures of 100 K. The absence of long-range ferromagnetic order for a 1D system is at this temperature not surprising. From the theoretical point of view, a spontaneous magnetization with a nonvanishing net moment at $T > 0$ K is not allowed for an Ising chain with nearest neighbor exchange interaction.²⁴ Even if the array of Co chains on Pt(997) behaved unlike an Ising system and showed a long-

range ferromagnetic order, its Curie temperature would possibly be lower than 100 K, because the reduction of the dimensionality of a magnetic system is followed by a reduction of its ordering temperature. It is also possible that the easy magnetization direction of the Co stripes on Pt(997) is not the in-plane direction, as in the case of Fe on stepped W(110),¹² but the out-of-plane direction, which was not accessible in our experimental setup. For submonolayer amounts of Co on a flat Pt(111) surface, the easy magnetization direction was found to be out-of-plane,²⁵ and theoretical investigations predict a change of the easy magnetization axis from in-line to out-of-plane, as a freestanding Co chain is deposited on a Pd(110) surface.²⁶ Also, Fe on a vicinal Cu(111) surface exhibits an anisotropy perpendicular to the surface plane.¹³ This system also showed a time-dependent remanent magnetization, which indicates a superparamagnetic behavior of the Fe stripes, where thermal fluctuations are strong enough to destroy a remanent magnetization. Depending on various parameters, i.e., coverage, anisotropy, and sample temperature,¹³ the time scale for this demagnetization process can change strongly. But even if the array of Co chains on Pt(997) behaved like a superparamagnet, the sample temperature of 100 K would possibly be too high to keep up a remanent magnetization for at least 10^2 – 10^3 seconds to perform the spin analysis of the photoemitted electrons.

In summary, a highly regular array of monatomic Cu and Co wires has been prepared by step-edge decoration of a vicinal Pt(997) surface. The electronic structure of these 1D systems has been investigated by angle-resolved photoemission with synchrotron radiation. A sufficiently high sensitivity for the small amounts of deposited material (≈ 0.1 ML) could be achieved by taking advantage of the Pt *5d* Cooper minimum in the photoionization cross section. While a single photoemission feature is associated with the *3d* emission of the monatomic Cu wires, a *3d* double-peak structure is instead observed for the Co wires. This finding indicates the presence of a 1D exchange-split band and of local magnetic moments.

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