

2.12 Doping of Cu/Cu(111) quantum wires by single magnetic atoms

Several properties of nanostructured magnetic materials — such as oscillatory magnetic coupling in layered systems — are triggered by quantum size and confinement effects. We used low-temperature scanning tunneling microscopy and spectroscopy (LT-STM/STS) to engineer and probe surface-supported magnetic/nonmagnetic atom chains, i.e., prototype structures representing the one-dimensional (1D) analogue of magnetic 2D superlattices. Suitable constituents providing structural stability of the model nanostructure correspond to single Co and Cu adatoms manipulated and assembled on a Cu(111) surface at a temperature of 7 K.

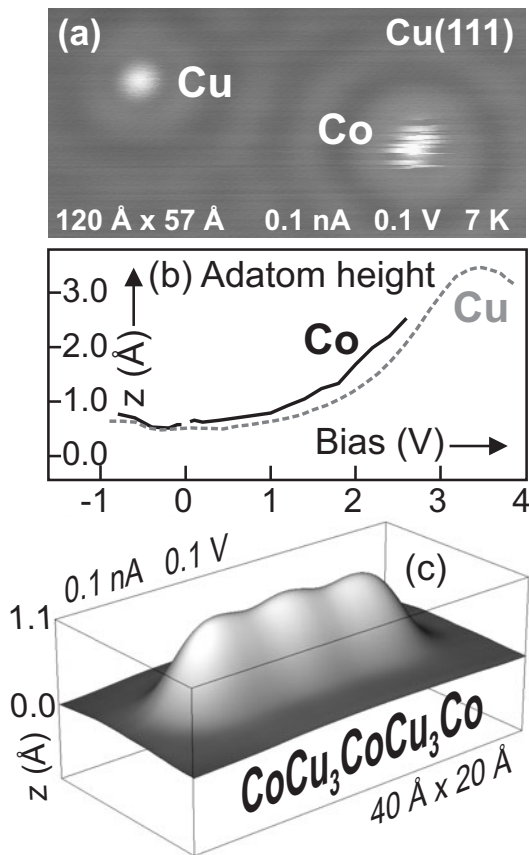


Fig. 32. (a) Constant-current STM image of a surface area of Cu(111) with a single Cu (left) and a Co adatom (right) at 7 K, (b) bias-dependent height of the two adatom species, and (c) contour plot of a monatomic $\text{CoCu}_3\text{CoCu}_3\text{Co}$ chain.

to 15 pm at the Co location when tunneling in the regime of unoccupied sample states at typically 0.1 to 1 V. This topographic signature is systematic and provides a means to determine the internal structure of composite chains. As an example, Fig. 32(c) shows the STM topograph of a monatomic chain comprised of three Co and six Cu atoms with the Co atoms located at the ends and in the center of the structure, respectively.

STS reveals Co-Cu chain quantum states with subtle downward shifts in binding energy relative to the states of pure Cu chains with the same number of atoms. For example, the

The constant-current STM image in Fig. 32(a) shows the two adatom species serving as building blocks of the composite Co-Cu chains. The Cu atom is unperturbed for the present measurement parameters, while the Co adatom is unstable due to excitations by inelastic electron tunneling, which induces hopping between adjacent adsorption sites [J. A. Stroscio *et al.*, *Science* **306**, 242 (2004)]. The height of the Co atom [(b), full line] is 20 to 30% larger than the one of Cu (dashed line) at positive sample bias, revealing "chemical resolution" in STM imaging. The steady increase in apparent Cu height is due to the unoccupied sp -derived Cu/Cu(111) adatom state 3.3 eV above the Fermi level E_F , which we found earlier by STS and density functional calculations. The observation of the same trend in height increase for both species indicates that also the Co adatom is associated with a quasi-atomic state in the relevant energy regime above E_F .

Co atoms added to close-packed Cu chains by atom manipulation lead to a height increase of 10

dI/dV spectra of a CoCu_3Co chain [cf. Figs. 33(a) and 33(b), full lines] indicate a downward shift of 80 mV for the ground state (a) and 170 mV for the first excited state (b) relative to the resonances of the Cu_5 chain (dashed curves). Data obtained for various chain lengths and compositions reveal that the energy shifts sensitively depend on the internal structure: The ground state shift is larger (smaller) compared to the shift of the first excited state when the added Co atoms are located in the center (at the end) of the chain. This systematic trend is plausible in view of the wave function of 1D confined states with $n = 1$ (single lobe) and $n = 2$ (two lobes, one node), because the perturbation imposed by the added impurity is larger for states having a large density around the impurity location. The experimental local density-of-states (LDOS) distributions (obtained by dI/dV mapping at constant tip height) show that the simple picture of a wave function with n lobes and $n - 1$ nodes is in fact adequate to describe the confinement also in Cu-Co chains.

The quantum state energies and LDOS distributions observed for composite Co-Cu chains can be well described within a tight-binding (TB) scheme considering a linear chain with N atoms of two different species, nearest-neighbor coupling, and one type of atomic orbital involved. The TB analysis shows that the orbital binding energy accounting for the Co atom is 3.0 eV (i.e., slightly below the one of the Cu atom), while the Cu-Cu and the Co-Cu nearest-neighbor coupling are the same within the accuracy of the evaluation.

Our STS data indicate in combination with the successful TB description that Co-Cu chains exhibit states delocalized along the heteroatomic chain and that the Co adatom is associated with an unoccupied state showing an orbital character similar to the one of the sp -derived quasi-atomic Cu state. Co doping of the assembled structure

enables to perform a fine tuning of the chain-localized state. This situation is contrary to the previously reported case of impurity-localized states, which are largely decoupled from the host structure [T. M. Wallis *et al.*, J. Chem. Phys. **122**, 11101 (2005)]. The present system thus provides an interesting model case, where magnetic impurities contribute to the (potentially spin-polarized) quantum states of the confining nanostructure, which can be engineered in an atom-by-atom fashion.

(J. Lagoute, C. Nacci, S. Fölsch)

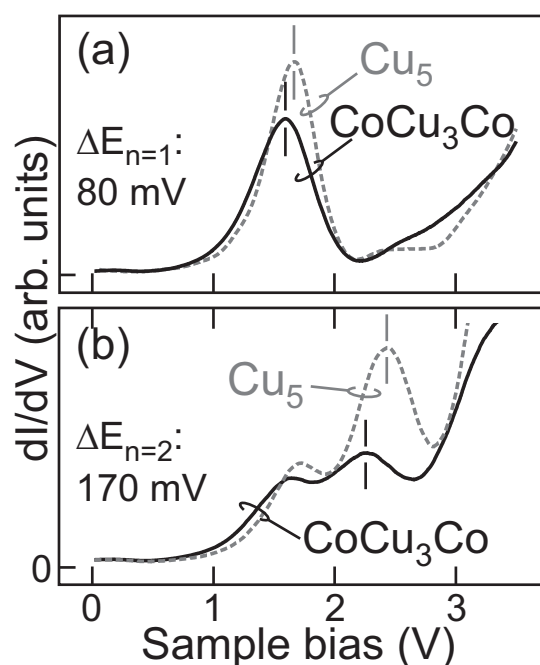


Fig. 33. dI/dV spectra of a CoCu_3Co chain on Cu(111) [full lines] detected with the tip positioned (a) over the center and (b) over the end of the chain. The dashed curves indicate the spectra of a Cu_5 chain.