End electronic states in Cu chains on Cu(111): *Ab initio* calculations

V. S. Stepanyuk,* A. N. Klavsyuk, L. Niebergall, and P. Bruno

Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany
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The state-of-the-art *ab initio* calculations are performed to study the effect of surface-state electrons of Cu(111) on electronic states in Cu chains. We reveal the existence of localized electronic edge states at energies close to the surface-state band edge of Cu(111). These states are shown to be similar to the bound states at single adatoms on Cu(111) recently detected by the low-temperature scanning tunneling microscopy [Limot *et al.*, Phys. Rev. Lett. **94**, 036805 (2005) and Olsson *et al.*, Phys. Rev. Lett. **93**, 206803 (2004)].

Atomic chains on surfaces exhibit many interesting properties and could be considered as possible candidates for constituent components in future electronic devices.[1–8] An advanced experimental method, such as the scanning tunneling microscope (STM), allows us to construct chains on surfaces in atom-by-atom fashion and to study their electronic properties. For example, Cu chains have been produced on Cu(111) by atomic manipulation using the STM.[6] Their electronic states have been found to exhibit the one-dimensional (1D) quantum confinement. The experiments on Au chains on NiAl(110) have revealed that the electronic properties are determined by an unoccupied electron band.[7] The development of 1D electronic structure with increasing the number of atoms in the Au chains has been demonstrated. The STM experiments of Crain and Pierce[8] on gold chains self-assembled on the vicinal Si(553) surface have given the first proof of the formation of end states in atomic chains.

The behavior of atomic chains on metal substrates supporting the 2D electron gas, for example, on (111) surfaces of noble metals, could be of particular interest. The interaction of surface-state electrons with adsorbates on metal surfaces leads to many interesting phenomena, such as the long-range adsorbate-adsorbate interactions,[9] the quantum mirage in corrals,[10,11] the standing wave pattern near steps,[12] and on islands.[13] The theory predicts the existence of a quasistationary state on single adsorbates in 2D electron gas located just below the 2D Shockley surface-state continuum.[14] The recent low-temperature scanning tunneling spectroscopy (STS) experiments on magnetic and nonmagnetic adatoms on Cu(111) and Ag(111) surfaces performed by Olsson *et al.*,[15] and Limot *et al.*,[16] have detected such states. They have found that the adatom-induced surface-state localization occurs at energies close to the surface-state low band edge.

In this Brief Report, we report on *ab initio* studies of electronic states in Cu chains on Cu(111). We reveal the localized electronic states forming over end atoms in the Cu chains. The end electronic states are found to appear at the bottom of the surface band and are caused by the interaction of surface-state electrons with end atoms of chains.

Our recent studies have demonstrated that the multiple-scattering theory is well suited for calculations of interactions of surface-state electrons with different adsorbates on metal surfaces.[9,11,13] We use the multiple-scattering approach in the framework of the Korringa-Kohn-Rostoker (KKR) Green's function method.[17] First, we perform the self-consistent calculations of the Green's function of the ideal Cu(111) surface. This function is then used as the reference Green's function to calculate the Green's function of the perturbed system with linear chains on the surface. We allow the potentials of all atoms in the chain and of all references sites adjacent to the adatoms to be perturbed. The local approximation of the density functional theory is used. The effect of bulk states on the scattering of the surface electrons is taken into account in our method. Using the Green's function of the surface with the atomic chain, the local density of electronic states (LDOS) is calculated. Atomic relaxations in Cu chains are performed using the *ab initio* based many body potentials.[18] It has been demonstrated that such potentials allow us to relax atomic-scale nanostructures in a very good agreement with the fully *ab initio* calculations. Our studies have shown that atomic relaxations in Cu chains on Cu(111)
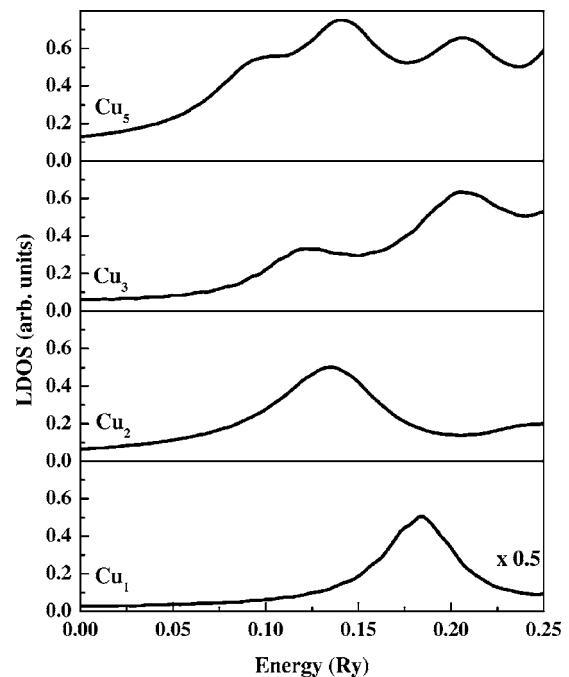

FIG. 1. The LDOS above the Fermi energy over the Cu monomer and short Cu chains on Cu(111). The calculations are performed for 2.1 Å above the chains. Mainly *sp*-components contribute to the LDOS. The Fermi energy is chosen as zero energy. The results for the monomer are scaled by a factor of 0.5.
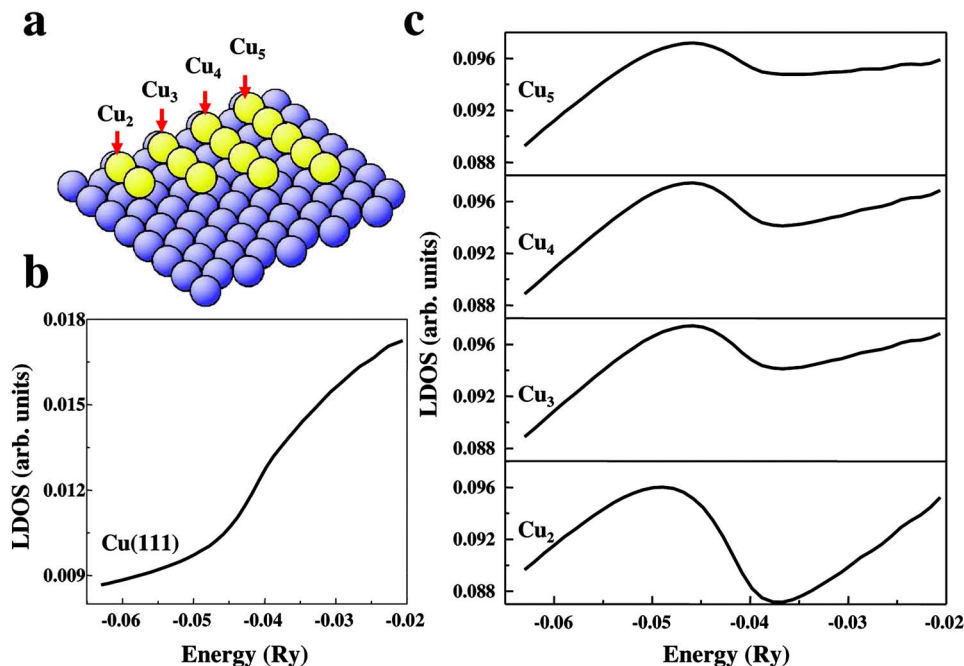
FIG. 2. (Color online) End electronic states in Cu chains on Cu(111). (a) the geometry of chains; (b) the LDOS of Cu(111); and (c) the LDOS over the edge of Cu chains on Cu(111).

are rather small (atomic positions in the relaxed geometry differ from the ideal positions only by 2–2.5%). Therefore *ab initio* calculations of the interactions of surface-state electrons with atomic chains are performed for the ideal atomic positions. Details of our method are described elsewhere.[11,13,17,18]

If the atomic chain is placed on the Cu(111), two main factors determine the electronic states in the chain. First, the quasi-1D quantum confinement of electronic states, and the second, the interaction of the atoms of the chain with surface-state electrons. The first mechanism has been studied by Fölsch *et al.*[6] They have performed the experimental and theoretical studies of the quantum confinement in 1D Cu chains on Cu(111). The main result of their work is that the confinement of unoccupied electronic states to the chain occurs. Our calculations of the local density of states (LDOS) for short Cu chains are shown in Fig. 1. In the agreement with the experiment of Fölsch *et al.*,[6] we find that the LDOS above the Fermi energy exhibits a series of resonances peaks indicating the 1D quantum confinement.[19]

Our calculations for the Cu(111) surface give a surface state band edge at $E=-0.5$ eV and surface-state Fermi-wavelength $L=29$ Å, in good agreement with experiments.[20] The LDOS on Cu(111) is shown in Fig. 2. We have calculated the LDOS for different distances above the surface ranging from 2.1 to 5 Å. The results are found to be qualitatively the same. The steplike rise of the LDOS allows one to determine the low edge of the energy band of the surface-states. The interaction of surface electrons with end atoms of the chain leads to an interesting effect. We present in Fig. 2 our calculations of the LDOS at the edge of Cu chains. One can see that the localized peak exists at the energy below the Fermi energy. The position of this peak is very close to the bottom of the surface band and practically does not change with increasing the number of atoms in the chain. Our analysis of the charge distribution shows that the localized states are mainly determined by *sp*-electrons.

To demonstrate that the electronic states predicted by our calculations are truly edge states, we calculate the LDOS over an atom's inside chains. As an example, we show in Fig. 3 our results for a seven atom Cu chain. One can see that there is clear suppression of the localized state on the interior atoms of the chain.

To gain detailed insight into the physics underlying the localized states at the edge of chains, we have performed the calculation for a single Cu adatom on Cu(111). Our results
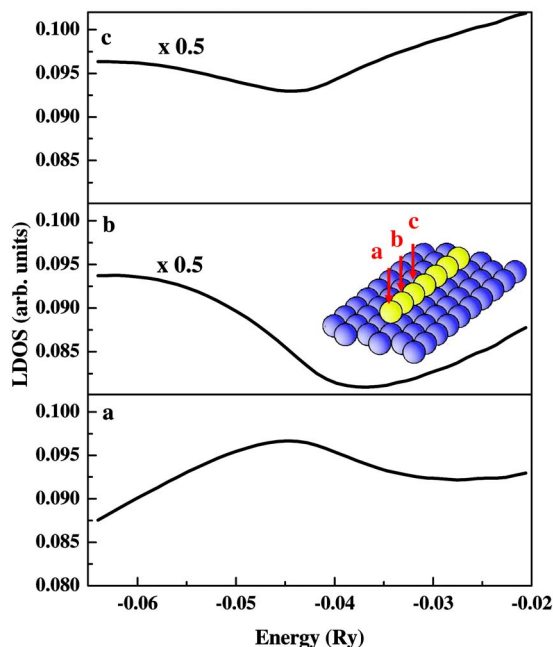

FIG. 3. (Color online) The change in the LDOS along the Cu chain. The localized state at the bottom of the surface band exists only at the edge. The calculations are performed for 2.1 Å above the chain. The LDOS over the atoms inside the chain is scaled by a factor of 0.5.
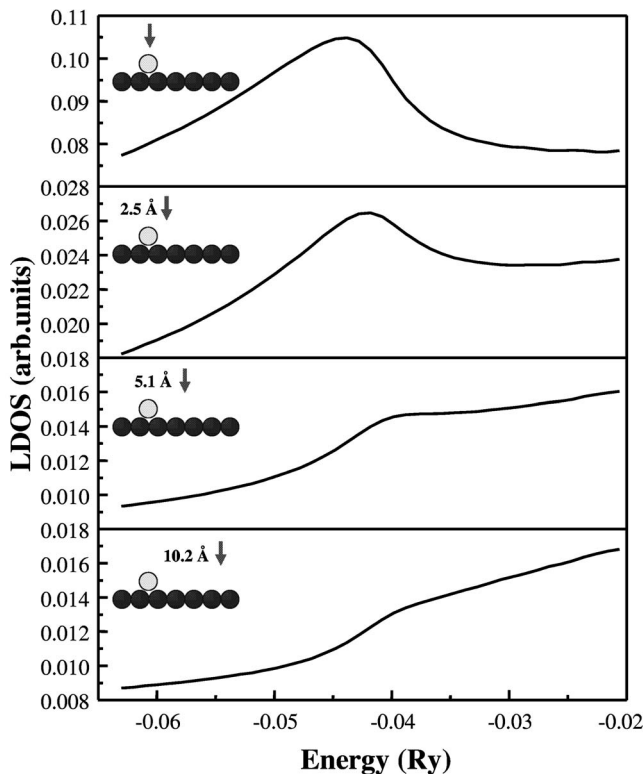
FIG. 4. The LDOS over the Cu adatom on Cu(111) at different lateral distances.

FIG. 5. (Color online) The LDOS over magnetic adatoms on Cu(111). The localized states are spin-polarized.

presented in Fig. 4 demonstrate the localization of surface-state electrons at the Cu adatom in agreement with the experiments.[15,16] This state is found below the binding energy of the surface state, i.e., similar to the edge states in Cu chains. In fact, the existence of such states is predicted by the theorem of Simon:[21] any attractive 2D potential has a bound state. One should notice that Gauyacq *et al.*[14] have shown that localized states splitting off the surface-state bottom should appear whenever the surface-state continuum is perturbed by an attractive potential. To give a clear demonstration that the interaction of surface-state electrons with adatoms leads to the localization of electrons at the surface-state bottom, we have performed calculations of the LDOS above the Cu adatom for different lateral distances. Results presented in Fig. 4 show that with increasing the distance from the adatom, the localized peak in the LDOS continuously decreases in amplitude, and at a distance of about 15–20 Å the LDOS is found to be very close to the LDOS of a clean Cu(111) surface. Similar results have been obtained for the edge states of Cu chains. However, in this case, the localized states are found to decay faster than for a single adatom. Our results predict that despite the fact that surface-state electrons have a rather small den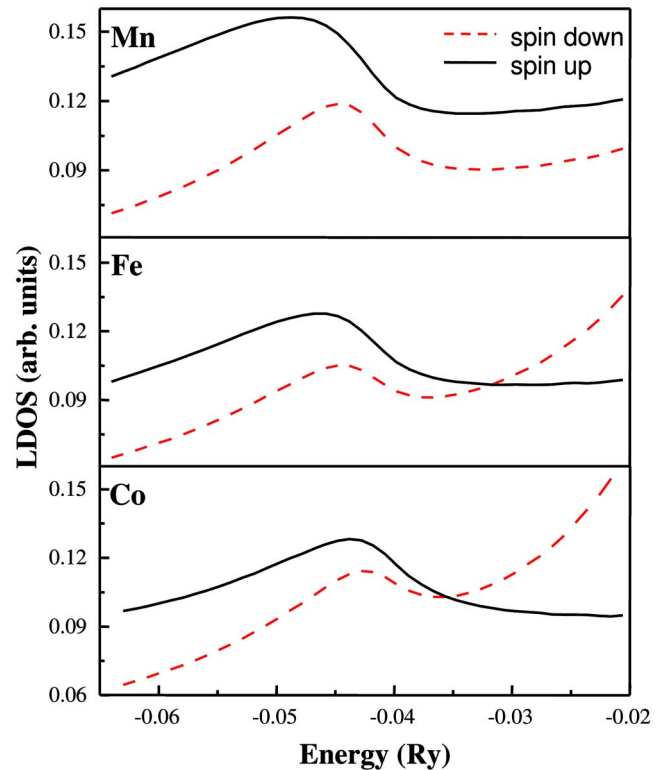sity on metal surfaces (one electron per 20 surface atoms) their impact on electronic properties of atomic chains can be significant.

Finally, we would like to note that the localized surface states should also occur near magnetic adatoms. Our calculations for Mn, Fe, and Co adatoms on Cu(111) presented in Fig. 5 reveal that the spin-polarized localized states appear at energies close to the surface state band edge. Similar results for a single adatom have been recently obtained by Lazarovits *et al.*[22] We expect that the localized surface states at edges of magnetic chains can also be spin-polarized. We are performing *ab initio* calculations for magnetic chains on different clean and stepped surfaces. The results will be presented in our future work.

In summary, we have presented the *ab initio* calculations of electronic states of Cu chains on Cu(111). The localized surface states are revealed over end atoms of chains. These states are found to occur at the bottom of the surface band. We believe that new electronic states in atomic chains predicted by our work can be detected by the STS.

*Email address: stepanyu@mpi-halle.de

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