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On the formation of suspended noble-metal monatomic chains

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We present a tight-binding molecular-dynamics investigation of the geometrical and the electronic structure of suspended monatomic noble-metal chains. We show that linear monatomic chains are formed at temperatures equal to or smaller than 500 K for Au, 200 K for Ag, and 4 K for Cu and that they are stable for at least 10 ns. We also evidence that such stability is associated with the persisting *sd* orbital hybridization along the chains. The study highlights fundamental limitations of conductance measurement experiments to detect these chains in the breaking process of nanowires.

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Understanding physical properties such as the ubiquity of suspended monatomic chains (SMCs) is an important step to exploit their abilities to transport spontaneously spin polarized electrons[1,2] and to support high current densities.[3] In spite of different efforts,[4–13] a theoretical explanation for their relatively high stability and their characteristic linear-chain structure remains elusive.[14–18] Moreover, rationalizing the possible formation of these chains in 3*d* and 4*d* noble metals continues being a challenge to scientists mainly due to a lack of agreement between results.[19–22]

SMCs are typically generated by electron-beam irradiation of a suspended metal film[1,6,9,20,21] as well as through a stretching nanowire procedure that makes use of a scanning tunneling microscope (STM) (Refs. 4, 5, and 7) or a mechanically controllable break junction (MCBJ) technique.[5,19,22] Despite their popularity, these techniques suffer from inherent limitations that have made the unambiguous interpretation of the data a difficult task. On the one hand, SMC formation experiments with electron-beam irradiation and STM techniques are based on high-resolution transmission electron microcopy (HRTEM) observations, which are limited due to the poor time resolution (around 30 pictures/s) (Ref. 6) and uncontrollable sample contaminations.[23] On the other hand, MCBJ is based on a not totally justified interpretation of the conductance data generated during the nanowire breaking process.[19,22] Therefore, computational studies constitute an appealing complement that could pave the way for a coherent description of the experimental results.

In this paper, the formation of SMCs is investigated by stretching Au, Ag, and Cu nanowires. Using the tight-binding molecular-dynamics technique, we show that linear and stable SMCs are formed for at least 10 ns at temperatures equal to or smaller than 500 K for Au, 200 K for Ag, and 4 K for Cu and that such stability is associated with the persisting *sd*–orbital hybridization along the chains. Additionally, a good agreement is found when numerical histograms of nanowire stretching lengths are compared to experiments.

We calculated the electronic structure by considering the total-energy tight-binding method introduced by Papaconstantopoulos and Mehl.[24] These authors described the electronic structure of different metallic systems by fitting the band structures and total energies, obtained from density-functional theory (DFT) calculations, as a function of volume for face-centered, base-centered, and simple-cubic structures. Such parametrization has allowed to reproduce many static properties, such as bulk modulus, elastic constants, phonon frequencies,[24] and surface reconstruction properties[25] of noble-metal systems. Due to its computational efficiency, it has been combined with the molecular-dynamics technique and has enabled one to describe the temperature dependence of the gold lattice constant and atomic mean-square displacement.[26] Also, the transferability of gold parameters has been tested by recovering the expected liquid gold phase.[26] Furthermore, this technique has also been used to describe the formation of suspended monatomic chains,[12,13,16,27] and the results have been validated with density-functional theory calculations.[13,16]

For the molecular-dynamics simulations, we used the Verlet algorithm to integrate the equations of motion of each atom with a time step of 2 fs. The temperature T was controlled with a Langevin thermostat. The dynamical evolution of the wire under stress was simulated in the following way: for the initial configurations, we considered a metal block containing 68 atoms obtained from bulk face-centered-cubic (fcc) (111) layers oriented along the z axis and tapered to a narrowing in the middle. The atoms at the top layer were frozen and through periodic boundary conditions along the z axis, their images were considered to form also the bottom layer of the wire. These frozen layers (the real at the top and its image at the bottom) determine the bulk support of the wire during the elongation process and were used to stretch the structure along the z axis by increasing the distance between them. The atoms inside these frozen slabs remained frozen during subsequent stages of the simulation, while the other atoms between them move and rearrange into new configurations. We equilibrated the wire for about 20 ps. Then, as has been done in previous classical studies,[7,8,10,11,21,28] a stretching velocity of 5 m/s was applied. The stretching distance is defined as the increased distance between the real

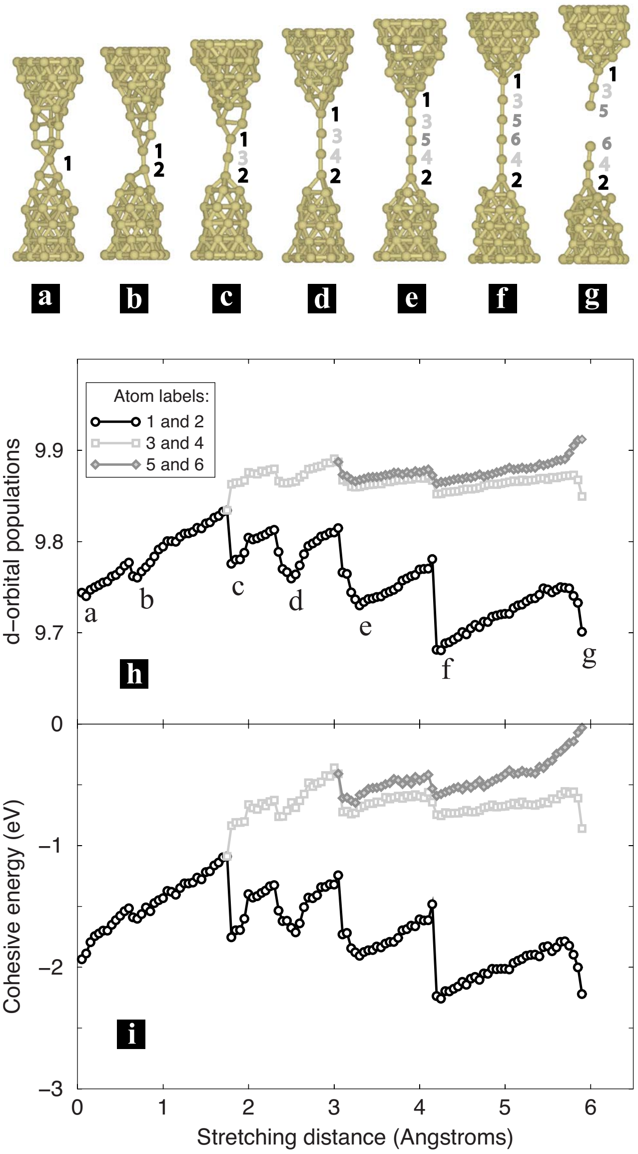

FIG. 1. (Color online) (a)–(g) Schematic representation of the formation of a chain of six atoms when a nanowire is stretched. (h) *d*-orbital populations and (i) cohesive energy as a function of the stretching distance for the different chain regions labeled in (a)–(g).

top layer and its image at the bottom with respect to the resulting nanowire configuration just before the first atom-contact appears.

Figures 1(a)–1(g) show the last stage of a nanowire stretching process when a Au SMC is formed. In all these configurations, the bond lengths between the atoms forming the chain range from 2.5 to 2.9 Å, in good agreement with experiments.[5,9] Along the chain, we computed the orbital populations based on a Mulliken population analysis, while the cohesive energy E_{coh} of an i atom was obtained by calculating $\mathrm{Tr}(\rho H)=\Sigma[\rho]_{i\alpha,j\beta}[H]_{j\beta,i\alpha}$, where ρ is the density matrix and H the Hamiltonian. The above summation is over atom labels j ($\neq i$) and state labels α,β. We found that during the nanowire stretching process, when the monatomic chain gains an extra atom [coming from the apexes of the breaking nanowire as seen in Figs. 1(a)–1(g)], the electron populations abruptly redistribute within the chain, as reflected by the jumps in the d-orbital population curves depicted in Fig. 1(h). A similar effect was found for the s-orbital populations (data not shown), in consistency with the saw-tooth-like conductance signal observed in experiments during the formation of Au SMCs.[7] Figure 1(h) also shows that depending on the monatomic chain regions, the d-orbital populations tend to decrease (increase) in the atoms located at the top and bottom (at the middle) of the chains as the stretching distance is increased. Finally, when this Au monatomic chain (consisting of six atoms) breaks, the populations abruptly increase in the central region and reach an approximate value of 9.92, a fact that is supported by the drop to zero of the corresponding E_{coh} [see Fig. 1(i)]. Such a threshold value corresponds to the typical d-orbital population for an atom located in an extreme of a Au monatomic chain. Correlatively, after some relaxation of the broken chain, E_{coh} for that atom jumps from 0 to the corresponding energy value of a single bonded Au atom (~ -1 eV).

Although the maximum number of atoms contained in a monatomic chain depends on the stretching realization (as we will discuss below), the above observed abrupt increasing behavior for the d-orbital populations in the middle of the chain seems to be independent of the chain length and realization. The latter is evidenced in Fig. 2 for two Au monatomic chains (black symbols) generated from different stretching process realizations leading to one chain of four atoms (black circles) and the other of five atoms (black triangles). As before, it is observed that E_{coh} decreases when the d-orbital populations become equal to 9.92. The results in Fig. 2 also show that Ag (filled gray circles) and Cu (open gray circles) chains of four atoms exhibit a similar behavior. In these cases, when the chains break, the d-orbital populations result equal to 9.96 and 9.98 for Ag and Cu, respectively, a fact that may reflect the weaker sd hybridization in these elements. These results also indicate that during the stretching process, the loss of the sd- orbital hybridization occurs in the lower atomic coordination region, where the atoms tend to completely fill their d orbitals.

The stability of SMCs has also been examined here by stopping the nanowire stretching process before the chains break. In the molecular-dynamics simulations, the latter is achieved by fixing to zero the stretching velocity applied to the top and the bottom of the nanowire just when each chain realization reaches its respective maximum number of atoms. To determine the "maximum" temperature where the chain continues to be stable, we have relaxed different chain samples for more than 10 ns and different temperatures (i.e., 4, 100, 200, 300 K,…, until the nanowire chain breaks). Figure 3 shows the d-orbital populations for Au (circles), Ag (squares), and Cu (triangles) at the middle of these chains as a function of time for T around values where the chains become unstable. Note that these populations fluctuate around a constant value and that the amplitude of the fluctuations depends on T and the atom type. We found that at 4 K, the structure of Au, Ag, and Cu monatomic chains remained linear and stable for at least 10 ns. When T is increased the amplitude of the fluctuations of the d-orbital populations increases, leading to an increase in the probability to break the monatomic chains by reaching the d-orbital

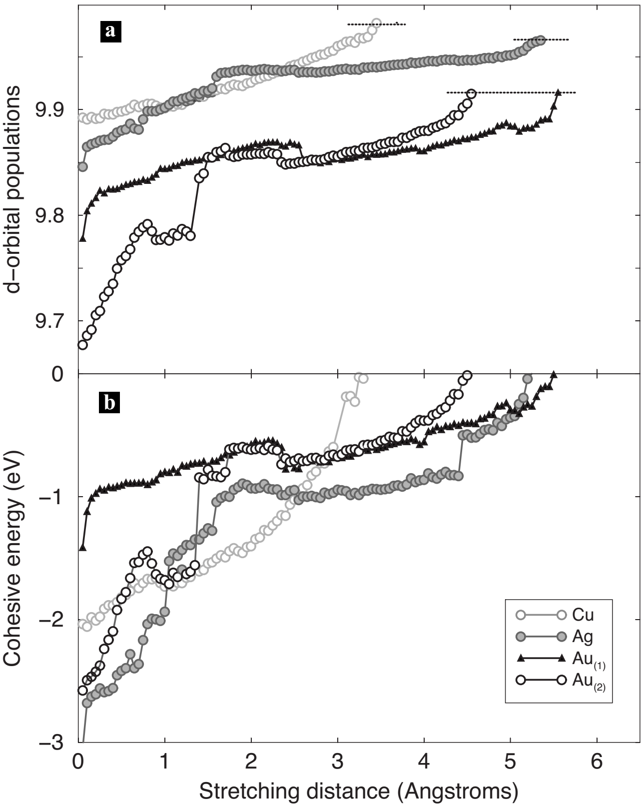

FIG. 2. (a) d-orbital populations and (b) cohesive energy as a function of the stretching distance for atoms located in the central region of Cu, Ag, and Au chains. These curves correspond to chains containing a maximum number of four atoms (circle symbols) and five atoms (triangle symbols). In (a) the dotted segments denote the threshold value for the d-orbital populations where the chains break.

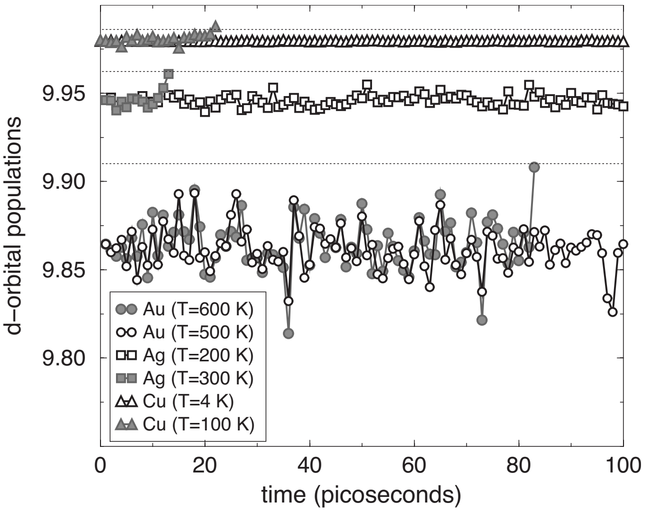

FIG. 3. Time evolution of the d-orbital populations of the atoms located in the central region of Cu, Ag, and Au chains for different T. Cu and Ag chains contain four atoms, while the Au chain contains six atoms. The dotted lines depict the typical threshold values where the chain breaks.

population threshold values. The chains break when T are increased to 600, 300, and 100 K in the case of Au, Ag, and Cu, respectively. Within the temperature variation range considered here (100 K), we have confirmed that these critical temperature values do not depend on the resulting maximum number of atoms contained in the chain (we have performed five realizations for each atom type and each temperature). In addition, for the high T considered in this study, we found that the chains tend to adopt a zigzag structure. The latter suggests that although this zigzag shape for the chain corresponds to a minimum-energy configuration (as predicted by DFT calculations[15,18]), its experimental observation is not possible because the required energy to overcome the characteristic potential barrier between the linear and zigzag chain configurations are equivalent to a temperature where these chains are unstable.

In MCBJ experiments, the conductance is monitored as a function of the stretching length, showing a steplike decrease as a nanowire is slowly broken.[5,3] Since in monovalent noble metals each atom located at the nanowire neck is expected to contribute with one quantum unit of conductance G_0 $(=2e^2/h)$,[4,6,29] the length of the last conductance plateau (where G is approximately equal to G_0) is usually associated to the chain length.[5,19,22] A large number of contact breaking cycles are typically performed in order to build histogram distributions of stretching lengths. At low T and for 5d noble metals, such histograms exhibit a series of peaks, while a single strong peak is observed in 4d metals. The difference between 5d and 4d noble-metal histogram distributions of lengths has been used to argue that only 5d noble metals exhibit SMCs,[19,22] a fact that contrasts with the stability of Ag and Cu monatomic chains for at least 10 ns reported in this study. To investigate the source of such discrepancy, numerical histogram distributions of lengths were computed by considering different chain formations generated from a hundred numerical realizations of the breaking process on Au, Ag, and Cu nanowires. A very good agreement between the resulting simulated histograms and those obtained experimentally[19,22] is deduced from Fig. 4 (solid black curves). While for $T=4$ K, Ag and Cu exhibit only a single strong peak, the Au histogram shows two strong peaks as in the experiments, with a peak-peak separation consistent with the expected bond length of the Au atoms in the chain. In addition, the vanishing second peak as T increases observed experimentally for Au (Ref. 22) is also predicted by these calculations (see Fig. 4). This agreement between the simulations and the experiments provides strong confidence on the predictive ability of the theoretical approximation considered here.

The simulation data allow a degree of a detailed analysis not possible experimentally, as is the characterization of the different contributions of chains containing different numbers of atoms in the histogram distributions of lengths. Figure 4 shows that in the case of Au, Ag, and Cu, the first peak exhibited by these histograms is due to the contributions of chains with two (dotted gray curve), three (dotted dark gray curve), and four (dotted black curve) atoms, thus indicating that a stretching length (plateau length) of 2 Å can form indistinctively short or long monatomic chains, depending on each breakage realization, i.e., the particular nanowire evo-

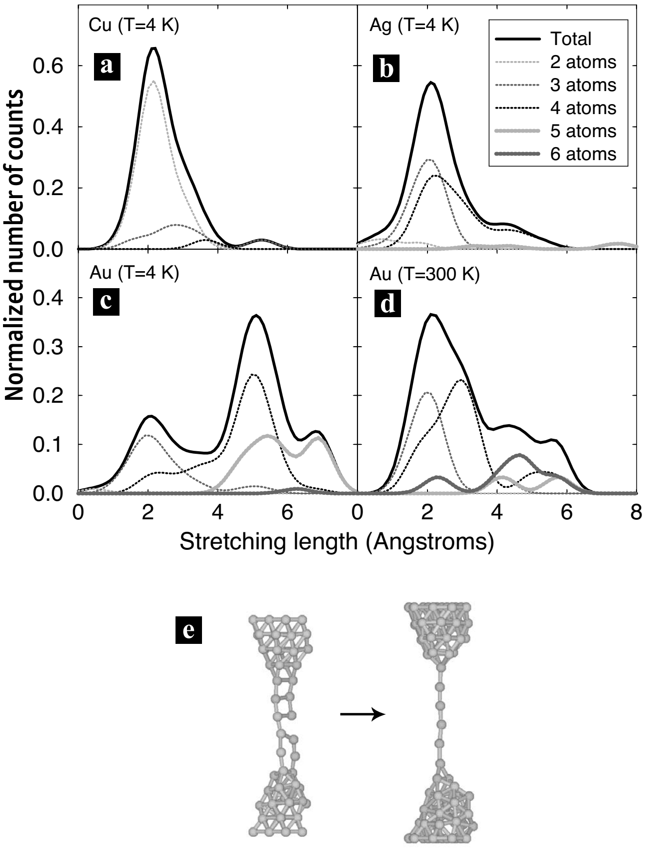

FIG. 4. (a) Cu, (b) Ag, and (c) Au histogram distribution of stretching lengths (black curves) obtained from a hundred realizations at T equal to 4 K and (d) 300 K for Au. The different contributions in these histograms of chains containing two to six atoms are depicted (see legends). (e) illustrates a situation where a stretching distance of 2.2 Å is enough to form a Au chain of six atoms.

lution process. Therefore, the stretching length required to form a diatomic suspended chain (the two columns of atoms formed just before the monatomic chain starts to appear) should serve as an indicator of what will happen in the subsequent monatomic chain formation process. Thus, in the case of Ag, we found that when the stretching length associated with the diatomic chain becomes larger than 3 Å, a monatomic chain of four Ag atoms can be formed by just stretching a length of 2 Å. However, if the stretching length corresponding to the diatomic chain formation is smaller than 1 Å, a stretching length of more than 4 Å is required to form the same monatomic chain of four atoms. This result leads to the conclusion that the presence of a single strong maximum around 2 Å in the histogram length distributions cannot be interpreted as the absence of monatomic Ag chain formation as previously claimed[19,22] and agrees with the HRTEM data that provide experimental evidence for the formation of Ag SMCs.[20] The importance of the history of the nanowire breakage process is also observed in the case of Au. Figures 4(c) and 4(d) show how the formation of monatomic chains containing four Au atoms contributes to the high intensity of the first and second maxima of these histogram length distributions. Moreover, Figs. 1(a), 1(g), and 4(e) illustrate how the chain formation process can differ from one realization to another: while the structure depicted in Fig. 1(a) requires a stretching distance of 5 Å to form a Au chain of six atoms, the configuration depicted in the left panel of Fig. 4(e) requires only 2.2 Å to form a similar Au chain of six atoms.

The chain sizes and the critical temperature where these chains lose the stability will depend on the specific electronic configuration of each chemical species. The tendency of Au to produce longer stable monatomic chains can be understood in terms of the strong sd–orbital hybridization that characterizes this metal. The strength of this hybridization can be examined by comparing the orbital populations of an isolated Au atom (one for s and ten for d orbitals), with the corresponding populations in the bulk phase (1.5 for s and 9.5 for d orbitals), a fact that can be related with the well-known strong relativistic effects in the last row noble-metal elements.[30] For other noble metals, these s-orbital (d-orbital) populations are smaller (higher) as one moves up rows in the Periodic Table. In a not clean environment or under a controlled atmosphere, there is evidence that other chemical species may participate on the bonding process of suspended noble-metal monatomic chains.[18,22] Our results are consistent with the picture that the sp character of some atoms such as O, C, or S, intercalated in monatomic metal chains, would help the hybridization of d orbitals, favoring longer chain formations, as recently suggested in an experimental study on controlled oxygen atmosphere.[22]

In summary, we show that at low T (4 K) Au, Ag, and Cu exhibit linear and stable monatomic chains and that these two last elements tend to form shorter chains. Particularly, compared to Au, the tendency of Cu to form shorter chains then agrees with a recent result.[12] Our findings show that the stability of the chains for at least 10 ns is associated with the persisting sd–orbital hybridization along the chains, which is affected when the system is heated in an amount that depends on the particular metal species. We found that among these three elements, only Au monatomic chains are highly stable at room temperature; therefore, the present study provides a coherent interpretation of the differences found in monatomic chain formations between 3d and 4d, with respect to 5d noble metals.[19–22]

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