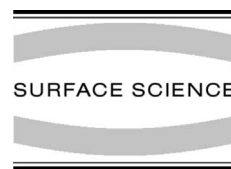




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Zigzag equilibrium structure in monatomic wires

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Abstract

We have applied first-principles density-functional calculations to the study of the energetics, and the elastic and electronic properties of monatomic wires of Au, Cu, K, and Ca in linear and a planar zigzag geometries. For Cu and Au wires, the zigzag distortion is favorable even when the linear wire is stretched, but this is not observed for K and Ca wires. In all the cases, the equilibrium structure is an equilateral zigzag (bond angle of 60°). Only in the case of Au, the zigzag geometry can also be stabilized for an intermediate bond angle of 131°. The relationship between the bond and wire lengths is qualitatively different for the metallic (Au, Cu, and K) and semiconducting (Ca) wires. © 2001 Elsevier Science B.V. All rights reserved.

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Very recently, using a combination of transmission electron microscopy (TEM) and scanning tunneling microscopy, Ohnishi et al. [1] were able to visualize the formation of monatomic gold wires. In particular, one of their images shows a wire of four gold atoms forming a bridge between two gold tips. The atoms in the wire were spaced at intervals of 3.5–4.0 Å, a distance much larger than that of nearest neighbors in bulk gold (2.88 Å). In spite of these large interatomic distances, the wire was observed for more than 2 min, showing clearly its stability. Observation of gold monatomic chains with a length of four or more atoms was independently claimed by other experimental group [2]. In this work, Yanson et al. do not

provide direct structural information, but the very long and flexible contacts formed in the last plateau of the conductance curves (with a conductance very close to one quantum, $2e^2/h$) were associated to the presence of monatomic chains. These new truly one-dimensional structures open a great number of opportunities to test our understanding of the interactions in solids. However, the very large interatomic distances found in the experiment represent by themselves a puzzle. In Ref. [3] we already addressed this issue with the aid of first-principles density-functional calculations. Our estimate of the maximum interatomic distance that the gold wires can hold before breaking was ~ 2.9 Å, in clear disagreement with the commented experimental observations. Several recently published references also report similar conclusions [4–7]. The cause for such a discrepancy between

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theory and experiment was not clear. However, in Ref. [3] we proposed a simple explanation for the puzzle posed by the TEM experiments. First, the gold wires were found to exhibit an equilibrium zigzag structure. Second, the calculated rotational energy barrier was low enough for the small zigzag wires, supported between gold tips, to be rotating at room temperature. In these conditions, only half of the atoms would be clearly visualized, the other half would produce a fuzzy image, and the apparent interatomic distance observed would correspond to that between second neighbors.

Zigzag structures for monatomic wires have already been observed and proposed by several authors. Whitman et al. [8] observed the formation of long, isolated zigzag chains when Cs was deposited over GaAs(1 1 0) and InSb(1 1 0) surfaces. March and Rubio [9] also proposed zigzag monatomic chains as the building blocks for highly expanded liquid Rb and Cs. A zigzag distortion was also predicted by Chaplik [10] for a chain of electrons held on the surface of liquid helium by the field of a charged filament.

In this paper we use first-principles density-functional calculations to study the stability and electronic properties of linear and zigzag wires, for Cu, K, and Ca, comparing the results with those of Au [3]. Our standard density functional theory (DFT) [11] calculations have been performed with the SIESTA program [12,13]. Core electrons are replaced by scalar-relativistic norm-conserving pseudopotentials [14], plus a pseudocore to account for non-linear core corrections in the exchange-correlation energy [15]. We used a double- ζ polarized basis set of numerical atomic orbitals, obtained from the solution of the atomic pseudopotentials with an excitation energy of 50 meV [16]. Real- and reciprocal-space integrations were performed with a 200 Ry-cutoff grid and with 20 inequivalent k -points, which guarantee a convergence better than 1 meV/atom. We present results obtained with the local density approximation (LDA) [17] for Au and Cu, and with the generalized gradient approximation (GGA) [18] for Ca and K. However, we stress that all the results are very similar using LDA and GGA. We have performed test calculations for the bulk phases of the studied materials, obtaining results

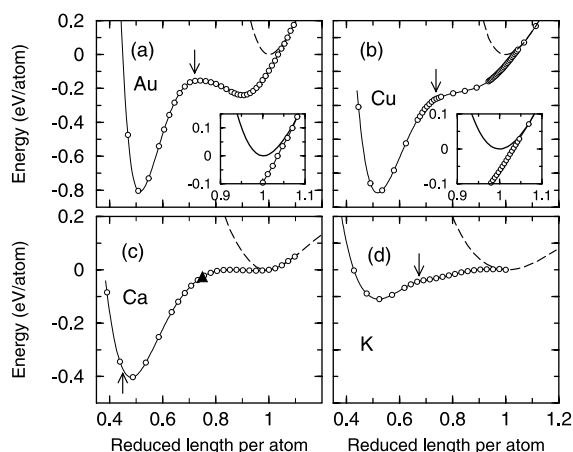


Fig. 1. Energy of monatomic wires of (a) Au, (b) Cu, (c) Ca, (d) K with a planar zigzag (○, ▲) and a linear geometry (---), as a function of the length per atom. The length x is expressed in units of the equilibrium bond length of the linear wires, and the energies are referred to the minimum of the linear wire. The arrows indicate points where a conduction band crosses the Fermi level. The triangle shows the length at which the band gap of the Ca wire moves away from the Γ point. The insets in (a) and (b) show a zoom of the energies near the equilibrium of the linear wire.

in good agreement with experiment and with previous DFT calculations.¹ In order to minimize the interactions between the wires and their periodic images, we have allowed a distance of 20 Å between wires in different cells.

Fig. 1 shows the energies of monatomic wires with a planar zigzag and linear structure, as a function of the wire length, for different elements. To facilitate the comparison, lengths are given in units of the linear-chain equilibrium length, and energies are relative to its minimum. These are: 2.56 Å and 2.09 eV/atom for Au, 2.25 Å and 2.16 eV/atom for Cu, 4.10 Å and 0.42 eV/atom for K, and 4.00 Å and 0.98 eV/atom for Ca. The evolution of the bond length in the zigzag structure can be seen in Fig. 2, where we have again used reduced units. Hereafter we will use x to refer to the

¹ The calculated equilibrium lattice parameter, bulk modulus and, cohesive energy are: 4.11 Å, 194 GPa and, 4.40 eV/atom for Au, 3.56 Å, 210 GPa and, 4.88 eV/atom for Cu, 5.51 Å, 20.3 GPa and, 2.20 eV/atom for Ca, and 5.29 Å, 4.3 GPa and, 0.94 eV/atom for K.

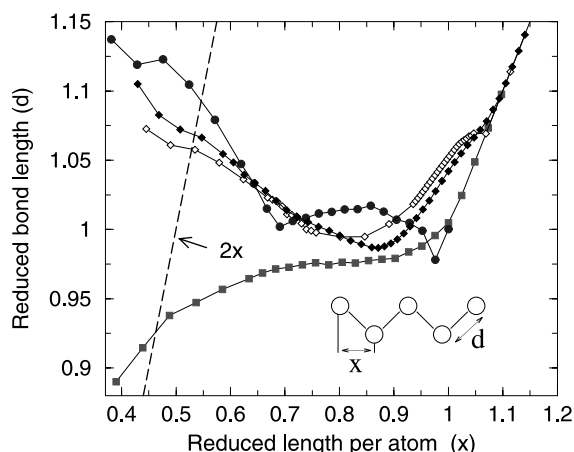


Fig. 2. Evolution of the bond length d for monatomic wires with a zigzag geometry, as a function of the length per atom x . All lengths are expressed in units of the equilibrium bond length of the linear wires. Open and solid diamonds stand for Au and Cu, respectively, circles for K, and squares for Ca. The dashed line indicates the distance $2x$ between second neighbors.

reduced length, and d for the reduced bond distance of the wires (see the inset of Fig. 2).

First, we will briefly comment on the data for Au, displayed in Fig. 1a. They present two peculiar behaviors: (i) the planar zigzag is more stable than the linear geometry, even before the latter reaches its optimum bond length, and (ii) the zigzag structure presents two energy minima as a function of the wire length. While a zigzag structure is naturally expected under compression, the first point mentioned above implies that the zigzag distortion, which increases the bond length, is favorable even when the linear wire is stretched. This is quite surprising in a metallic system like gold where, in principle, we do not expect any important bond directionality effects. Fig. 1b shows that this result also holds for Cu wires. As clearly shown in the insets of Fig. 1a and b, in both cases the linear configuration is, at its equilibrium length ($x = 1$), already ~ 0.1 eV/atom less stable than the zigzag structure. In spite of this energy gain, Fig. 2 shows that for both materials, at $x = 1$, the nearest-neighbors distance increases by $\sim 5\%$ when going from the linear to the zigzag conformation. The behavior of the energy shown in panels (c) and (d) of Fig. 1, corresponding to Ca and K, is quite

different. In those curves we do not find any sign (at least within the precision of the calculation) of the zigzag distortion until the linear chain starts to be compressed. This is what we could call a 'trivial' zigzag distortion: the energy minimum of the linear wire approximately becomes an inflection point for the energy of the zigzag configuration. This is in fact the kind of behavior predicted with, for example, a simple pairwise potential.

All the curves in Fig. 1 present a clear minimum near $x \simeq 0.5$. This minimum corresponds to a zigzag formed by equilateral triangles, where each atom has four nearest neighbors at the same distance. In Fig. 2 the equilateral configuration corresponds to the points where each curve intersects the dashed line, i.e. where $d = 2x$.

The second peculiarity of the Au wires mentioned above, i.e. the presence of two minima, is not observed for the other species studied. In Ref. [3] we explained this behavior with a simple jellium model, emphasizing the relationship between the energy vs length behavior, and the crossing of the Fermi level by different bands. For linear wires of Cu and Au with $x < 1.1$, a doubly degenerated π band (with mainly d character) rises through the Fermi level (Fig. 3a). In the case of Au linear

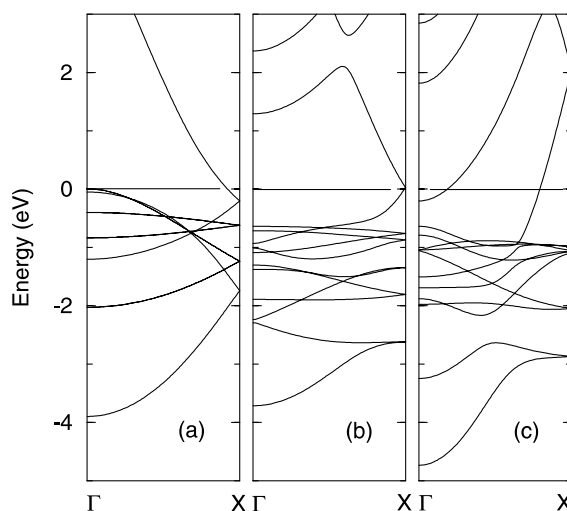


Fig. 3. Band structure of an infinite monatomic copper wire in (a) a linear geometry of length 2.20 Å/atom ($x = 0.98$), and (b) a planar zigzag geometry of 1.90 Å/atom ($x = 0.84$), and (c) 1.30 Å/atom ($x = 0.58$).

wires, this was already reported in Ref. [3], and later confirmed in Ref. [7]. The high density of states at the Fermi level, associated to this band, destabilizes the linear chain, and is the origin of the ‘anomalous’ zigzag behavior of Au and Cu (as opposed to the ‘normal’ behavior of Ca and K), which begins when the crossing occurs.

For $x > 0.7$, Au, Cu, and K zigzag wires have a single band crossing of the Fermi level (Fig. 3b), at the Brillouin zone edge. This situation might, in principle, favor a Peirls distortion. However, for the wire lengths studied here, we have not found any measurable dimerization. As the wire is contracted below $x \simeq 0.7$ (the exact positions are indicated by arrows in Fig. 1) a new conduction band crosses the Fermi level. This is shown in Fig. 3c for the Cu wire. For the three elements (Au, Cu, and K), this new band crossing precedes a change in the behavior of the energy, and may be interpreted as the beginning of a chemical bond between second neighbors.

The case of the Ca zigzag wire is different. The wire is semiconducting for most of the length interval studied here, and the bands cross the Fermi level at a much lower $x \simeq 0.45$ (below the equilibrium length) making it metallic. At $x \simeq 0.75$ its band structure suffers another qualitative change: the gap, that was direct at Γ for larger lengths, begins to move towards the edge of the two-atom Brillouin zone, still being approximately direct.

While the energy curves of K and Ca zigzag wires were relatively similar, the behavior of the bond distance, displayed in Fig. 2, is completely different for metallic and semiconducting wires. In the case of the metallic wires (Au, Cu, and K) the bond distance increases as the zigzag wire is contracted. This can be understood as a consequence of the metallic bonding: as the second-neighbor distance decreases, the first-neighbor distance must increase to maintain the optimum value of the effective atomic coordination. In fact, the calculated behavior is qualitatively reproduced by semiempirical metallic potentials like the glue model [19], or the embedded atom method [20], or even a jellium model where the volume per atom remains fixed. However, for the semiconducting wire (Ca), the nearest-neighbor distance behaves just in the opposite way, decreasing as the wire is com-

pressed. It is worth noting here that the predictions of a simple pair potential, like the Lennard-Jones [21], lie exactly in between these two regimes, i.e. the nearest-neighbors distance would remain almost constant once the wire assumes the zigzag configuration. In Fig. 2, it is also clearly visible the abrupt change in the behavior of the bond length of K wires induced by the band crossing at $x \simeq 0.7$.

In conclusion, we have applied first-principles density-functional calculations to study the energetics, and the elastic and electronic properties of monatomic wires of different elements, in a linear and a planar zigzag geometry. Surprisingly, for Cu and Au wires, a zigzag distortion is favorable even when the linear wire is stretched. This phenomenon is not observed for K and Ca wires, and might be related with the presence of d bands (with a high density of states associated) at the Fermi level for the linear conformation of Au and Cu wires. For all the studied materials, the equilibrium structure is an equilateral zigzag (bond angle of 60°). Only in the case of Au, the zigzag geometry can also be stabilized for an intermediate bond angle of 131° . The behavior of the nearest-neighbor bond length is qualitatively different in the metallic (Au, Cu, and K) and semiconducting wires (Ca).

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