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Charging mechanism for the bond elongation observed in suspended chains of gold atoms

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Abnormally large bond lengths (3.5–5.0 Å) between gold atoms forming small chains suspended between two electrodes have been observed in some experiments. Using the density functional theory we explore the possibility that the elongation could arise from the electrical charging of the chains induced in nonequilibrium by the electron beam of the transmission electron microscope used to image the nanowires in those experiments.

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Understanding the structural properties of nanostructures is essential for the atomic-scale manipulation and modification of materials, which often behave qualitatively different at the nanoscale than at larger dimensions. For instance, interesting quantum effects show up in thin nanowires.[1] Metallic nanowires can be produced by manipulation of nanocontacts:[2] Transmission electron microscopy (TEM) experiments[3,4] and mechanically controllable break junction measurements[5] have shown the formation of atomic wires and chains which consist of a few Au atoms only. A puzzling result is that the TEM experiments of Takayanagi and co-workers[3] and Rodrigues and Ugarte[6] indicate that the interatomic distances in the chain are in the range of 3.5–4.0 Å, a value substantially larger than the bond lengths of 2.47 Å in the diatomic molecule[7] and 2.9 Å in bulk gold. Kondo and Takayanagi[8] have reported even higher interatomic distances, around 5 Å.

In order to understand such elongation, several explanations based on structural or chemical effects have been proposed. One of the proposals is that the elongation of the bond lengths is not real, but an observational artifact linked to a zig-zag structure of the chain.[9] In that model, for a chain with an odd number of atoms, every second atom is at a fixed position along the chain axis, while the other atoms rotate rapidly around the axis, offering a fuzzy image that could be missed by the TEM. The formation of zigzag chains has been confirmed by different theoretical calculations.[9,10] However, a deep analysis of the high-resolution electron microscopy images has shown no evidence for the spinning Au atoms.[6,11] Insertion of chemical impurities between the Au atoms of the chain would also lead to increased Au–Au distances.[12] In fact light atoms, such as hydrogen, carbon or sulfur, would be difficult to detect in the TEM experiments.[11] However contamination appears as an unlikely possibility under the ultrahigh vacuum conditions of the experiments.[3,6] The substantial elongation of the small gold chains then remains an open question. In this paper, we explore a different explanation based on the electrical charging of the small atomic chains under the nonequilibrium induced by the electron beam.

As the starting point we have studied an infinite neutral chain of gold atoms with equal distances using density functional theory with the generalized gradient approximation (GGA) for exchange and correlation effects[13] and with ultrasoft pseudopotentials. The Vienna *ab initio* simulation package (VASP)[14] has been employed. The geometry of the chain can be considered linear near the breaking point, so we omit more complex structures. Since the VASP code uses a periodic geometry, our lattice is formed by parallel wires separated by 20 Å, with a sampling of 26 k-points in the irreducible Brioullin zone. Test calculations with a Full-Potential-Linear-Augmented-Plane-Wave (FLAPW) code[15] give mainly the same results. The total energy of a linear chain of Au atoms is given in Fig. 1 as a function of the bond length d. The minimum is found at $d=2.62$ Å. This atom separation is intermediate between the dimer bond length, 2.5 Å, and the nearest neighbor distance in bulk Au, 2.9 Å, and it is consistent with the calculated Au–Au equilibrium distances for small zig-zag chains.[9]

The elongation force for the Au chain, obtained as the

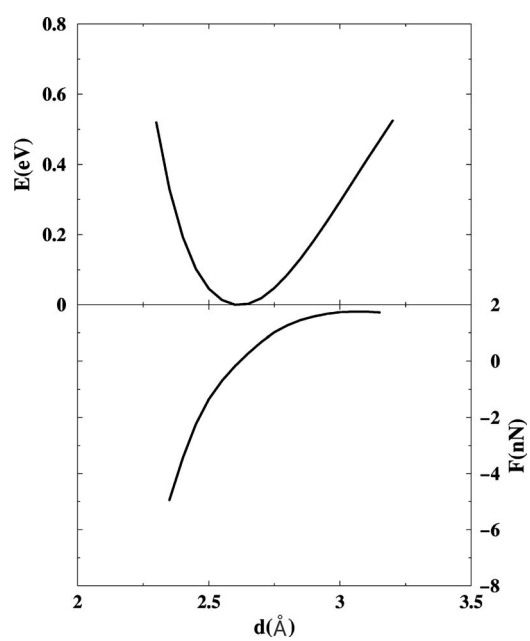

FIG. 1. Energy per atom of a linear Au chain as a function of the interatomic distance (the energy zero is taken at the minimum of the curve), and force against stretching.

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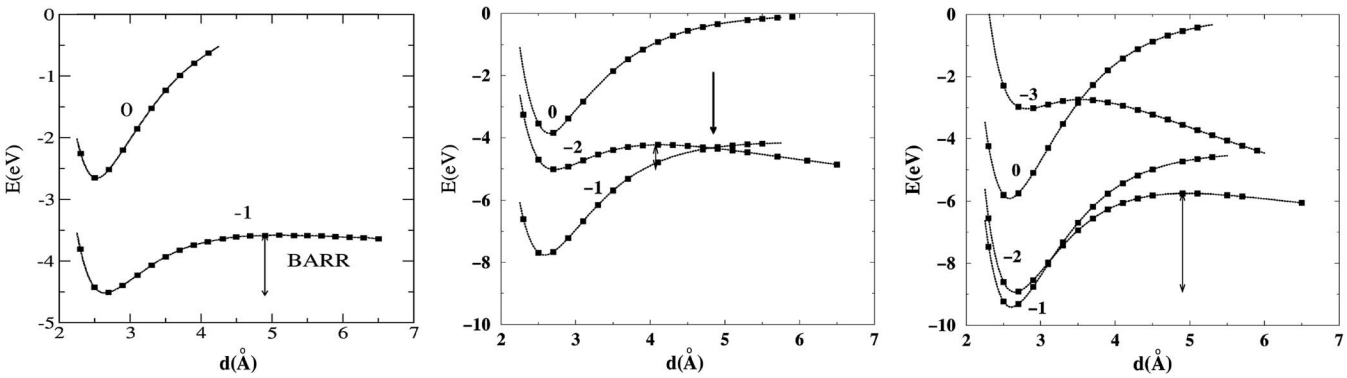

FIG. 2. Negative of the binding energy vs bond distance for neutral and charged dimer (left panel), trimer (middle panel) and tetramer (right panel) linear chains of gold atoms. The electron chemical potential coincides with the vacuum level of neutral clusters. The double arrows indicate the maximum of the barrier (BARR), and the down-pointing arrow the crossing of two relevant curves.

slope of the energy curve, is also given in Fig. 1. The elongation force has a maximum of 1.75 nN at $d=3.07$ Å. This distance can be taken as the breaking point under tension, and the value of the force agrees well with the value of about 1.5 nN measured by Rubio *et al.*[16] for the elongation force of Au nanowires just before breaking. Moreover, the experiments show that during the last stress-accumulation stage before breaking the tensile force increases in magnitude only slightly. This is in accord with the theoretical results reflecting the plateau in the force. A similar plateau was found for Pb wires by Schmidt and Springborg[17] in fully relativistic calculations. Evidently, the expanded bond lengths observed by Takayanagi and co-workers and by Rodrigues and Ugarte are not explained by the calculations presented in Fig. 1.

We now address the question concerning stability at larger distances of the gold wires when we allow for charging effects. In the context of the present investigation, charging may arise from the irradiation of the Au chain by the electron beam in the high resolution TEM used to image the chain, as pointed out by Okamoto and Takayanagi.[10] The calculated ground state structure of the free Au trimer anion Au_3^- is linear and that of the tetramer anion Au_4^- is almost linear,[18] while the structures of the neutral clusters are planar (an obtuse triangle and a rhombus for Au_3 and Au_4, respectively[19]) so one could expect a tendency for charging of linear chains of a few gold atoms stretched between two electrodes; that is, the charge would stabilize the linear chains.

In order to analyze the effect of charging on the bond lengths we have calculated the energy as a function of bond length for the Au dimers, trimers and tetramers in different charge states, assuming in all cases linear geometries. The comparison of different charge states is made by taking into account that the electron chemical potential coincides with the vacuum level for the isolated neutral clusters. The calculations were performed with the Amsterdam Density Functional (ADF) code[20] using the GGA exchange-correlation functional[13] and including relativistic effects in the Zero Order Regular Approximation (ZORA).[21] The results are given in Fig. 2, and Table I gives a summary of the binding energies for the most important energy minima, the magnitude of the barriers, and the corresponding bond lengths. As the breaking of the wire occurs between a pair of atoms, we first consider the energy as a function of the interatomic distance d in the charged Au_2^- and neutral Au_2 dimers in the left panel of Fig. 2. First of all we see that the charged dimer is more stable than the neutral by 1.9 eV. This substantial electron affinity can provide the driving force for the charging of the dimer. The energies of both the neutral and the charged dimers show an inflection point (the point where the curvature changes its sign) at $d=2.94$ and 3.10 Å, respectively. These values are similar to the corresponding inflection point for the infinite wire in Fig. 1. However, the new feature in the charged dimer is the existence of a barrier against stretching having its maximum at 4.9 Å. This Coulomb barrier provides stability and the breaking point should be associated with the top of the energy barrier as in the case of the Coulomb explosion of charged atomic clusters.[22,23] The asymptotic limits are not too relevant in this context and will be discussed in a further work.

Next we study what would happen to nanocontacts made of longer chains. The energy curves for the trimer chain in the charge states Au_3, Au_3^-, and Au_3^{2-}, are shown in the middle panel of Fig. 2. The minima of the three curves occur for values of d similar to those for the dimer. The most stable state is Au_3^-, and the stabilization of this state with respect to the neutral trimer is even stronger than for the dimer. Au_3^{2-} is

TABLE I. Summary of the binding energies E_b and barriers E_{BARR}, and the corresponding bond lenghts d_b and d_{BARR} vs the number N of atoms in the chains.

N	Charge	E_b(eV)	d_b(Å)	E_{BARR}(eV)	d_{BARR}(Å)
2	0	2.68	2.53		
	−1	4.55	2.64	0.94	4.89
3	0	3.88	2.65		
	−1	7.77	2.56		
	−2	5.03	2.71	0.80	4.09
4	0	5.90	2.58		
	−1	9.44	2.59		
	−2	8.96	2.66	3.18	4.90
	−3	3.05	2.82	0.29	3.49

less stable than Au_3^-, but still more stable than the neutral trimer. Au_3^{2-} shows an energy barrier against streching, and the maximum of the barrier occurs at 4.1 Å. This barrier has a coulombic origin, and is also present for doubly charged (2+) cluster cations.[22,23]

The tendency for charging, both in the dimer and trimer, is due to the large electron affinity of the neutrals. For normal interatomic distances (including the equilibrium bond length) the charging is restricted to one extra electron due to the Coulomb repulsion generated by additional charging. However, in Fig. 2 one observes a crossing of the curves for Au_3^- and Au_3^{2-} at a bond length d=4.8 Å (see the arrow pointing downwards). That is, the most stable charge state changes from Au_3^- to Au_3^{2-} for increasing interatomic distance in the linear trimer cluster. The reason for this transition is the following. As the interatomic distance is increased in the singly charged cluster, the overlap of the electronic clouds of neighbor atoms decreases and consequently the binding energy of the system also decreases. Then, an extra electron is able to provide additional bonding charge that stabilizes the stretched Au_3^{2-} with respect to stretched Au_3^-. The breaking point of the charged three-atom chain can then be associated with the value of d at which the singly and doubly charged energy curves cross, that is d=4.8 Å. A second possibility can be contemplated. The direct double charging of the trimer could occur, since the linear Au_3^{2-} is metastable, protected by an energy barrier. Then, under stretching, this chain will break when the barrier is surpassed, that is at d=4.1 Å.

The energy curves for neutral and charged linear Au chains of four equidistant atoms are plotted in the right panel of Fig. 2. Again the minima of all those curves occur at nearly the same value of d, and we conclude that the equilibrium interatomic distance is almost constant for these small chains, independently of the chain length and charge state. The most stable charge state of the tetramer in equilibrium is the singly negative one, as for dimers and trimers. The double-negative chain shows a Coulomb barrier against dissociation, with its maximum at d=4.9 Å. The curves for Au_4^{2-} and Au_4^- are much closer compared to the corresponding double-negative and singly negative curves for the trimer. As a consequence the crossing between the two curves occurs earlier, at d=3.2 Å. For the four-atom chain the picture of breaking is that the linear chain can become doubly charged in the presence of the electron beam and then it breaks under tensile stretching when the Coulomb barrier maximum at d=4.9 Å is surpassed. The charging with two electrons could occur almost simultaneously or in two steps during the experimental process.

We still have to comment on three aspects. First, even if in the case of Au_3^{2-} the Coulomb repulsion among the excess charge seems to make the molecule unstable with respect to the electron auto-detachment, the Coulomb barrier could provide dynamic stability with high lifetimes as in Ref. 22 for Au_2^{2+}. This indicates that the detection of highly charged states could be possible in experiments. Second, when considering a wire between electrodes we have to take into account the difference in the electron chemical potential between the wire and the electrodes.[24] This determines the relative stabilities of the different charge states instead of the chemical potential with respect to the vacuum in the case of free atomic clusters. Thus, the above results related to the changes in the charge states of the free clusters can be applied to the case of the chain between electrodes only qualitatively. In addition we now provide convincing arguments supporting the idea that the gold nanochain can sustain the excess charge gained from the electron beam. First-principles calculations by Lee *et al.*[25] for Au linear atomic chains between electrodes indicate that some electron transfer from the electrodes to the chain can occur already in the equilibrium situation. The reason is the depopulation of the antibonding d states (opening of the d band) counterbalanced by the population of the s states. This charge transfer is possible because at the low-coordinated chain atoms the s charge can spill out from the ion core regions lowering the kinetic energy. The charge spill-out in turn increases the local work function, resulting in the charge transfer from the electrodes to the atomic chain. We are convinced of the fact that the charge transfer from this mechanism is not large enough to explain the observed chain elongation, but these results indicate that the chain can easily accommodate an excess of charge. Thus, in the electron microscopy experiments it is very plausible that substantial charging of the atomic chain can occur due to the stabilization mechanism discussed above for free Au atom chains.

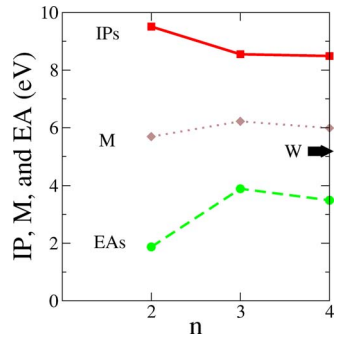

FIG. 3. (Color online) First ionization potential IP, electron affinity EA and electronegativity M as a funtion of chain size. The experimental work function (Ref. 26) of the Au (100) surface is denoted by W.

A related argument supporting the stabilization of the excess charge in the chain suspended between the electrodes arises from a comparison of the electronegativities of Au chains and the their bulk counterpart, the work function. Figure 3 gives the calculated ionization potentials (IP), electron affinities (EA) and the Mulliken electronegativities, defined as $M=(\mathrm{IP}+\mathrm{EA})/2$, for chains of 2–4 Au atoms. The electronegativity is the negative of the electrochemical potential. The electronegativities of the short Au chains are slightly higher than the work function of around 5.22 eV[26] for the Au(100) surface. Because the electronegativities of the electrodes can be assumed to be close to the bulk work function one can conclude that a small electron transfer may occur from the electrodes to the chain in contact. The Au chains behave differently from small spherical sodium clusters for which the electronegativity approaches the bulk work function from below.[27] Thus, noble metal and alkali metal nanostructures would behave differently with respect to the

charge transfer. This is in agreement with the results by Lee *et al.*[25] for the noble and alkali metal atom chains connected to electrodes. Again we stress that the only feature we use from Fig. 3 is that, once the chain is charged by the effect of the electron beam, that charge is stabilized in the chain and not collected by the electrodes, resulting in the effects discussed above with reference to Fig. 2.

In conclusion, density functional calculations show that the scission of stretched charged linear chains of two, three and four Au atoms occur for interatomic distances substantially larger than the equilibrium bond lengths in the bulk metal or in of the neutral molecule. This suggest that the electrical charging of the nanochains could provide a mechanism to understand the stability and the large interatomic distances observed by some authors[3,6,8] in suspended gold chains formed by only a few atoms just before breaking. The charging may originate from the electron beam of the transmission electron microscope used in those experiments.

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