

How Can We Make Stable Linear Monoatomic Chains? Gold-Cesium Binary Subnanowires as an Example of a Charge-Transfer-Driven Approach to Alloying

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On the basis of first-principles calculations of clusters and one dimensional infinitely long subnanowires of the binary systems, we find that alkali-noble metal alloy wires show better linearity and stability than either pure alkali metal or noble metal wires. The enhanced alternating charge buildup on atoms by charge transfer helps the atoms line up straight. The cesium doped gold wires showing significant charge transfer from cesium to gold can be stabilized as linear or circular monoatomic chains.

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The study of nanostructured materials bearing novel properties is one of the most active fields of current research. Small nanomaterials are of particular interest because the dominance of quantum effects in such small dimensions alludes to the emergence of intriguing characteristics [1–5]. Monoatomic linear chains which are the ultimate in one dimension (1D) have recently been transiently produced experimentally for Au, Ir, Pt, Co, Pd, and Ag [2–5]. Because of the quantum confinement of the electrons, these exhibit interesting behavior with respect to their mechanical, electrical, and chemical properties [2,6]. However, the 1D structures are not stable even with extreme conditions because they readily transform to the more stable 2D or 3D structures. To form longer and more stable chains, the *5d* elements seem to be better suited, because the relativistic effect plays an important role in the formation and stabilization of chains [5]. Especially a length of up to 20 Å has been observed for Au chains [3]. A systematic study of the relativistic effects shows a pronounced local maximum at Au, while equally strong relativistic contraction is not found until reaching fermium [7]. Hence, there is not much room left in the periodic table after *5d* transition metals.

On the other hand, surface reconstructions which may be regarded as indication of the chain formation [3,5], can be induced for *4d* elements Rh, Pd, and Ag by deposition of a low density of specific adsorbates which modify the balance between the *s* and *d* bonds in the metal. Furthermore, it has been noted that alkali metals can induce the surface reconstruction of Ag [8].

The above facts put together prompt one to speculate that alloying Au, a *5d* transition metal, with suitable elements could help form a linear chain. Our *ab initio* studies predict that the 1D Au chain has two energy minima, where the zigzag structure has lower energy than the linear one. However, the zigzag structure readily changes into 2D or 3D structures with more nearest neighbors towards better

stabilization by multicoordination (e.g., in the case of the bending angle of $\sim 120^\circ$, the tricoordinated 2D planar structure would be more favored than a zigzag 1D structure; for $\sim 60^\circ$ as in Au, the hexacoordinated 2D/3D structures are favored). Thus, we explored alloys of Au and alkali-earth metals, which had a local minimum for the linear structure [9]. However, this system still has a lower energy minimum for the zigzag structure. To realize a linearlike atomic chain, we need to find atomic wires having a lower energy minimum for a linear or circular chain. In this way, each atom would show dicoordination along a line.

With this in mind, we present an in-depth study on electronic orbitals and energies in binary clusters composed of Au and alkali metals (Cs and Na). The geometries and electronic structures of 1D atomic chains were explored to predict Cs-doped linear nanowires. Here, we report that alloying Au with Cs gives an energy minimum for a linear or circular structure.

To understand the structures and electronic properties of alkali-noble metal alloy clusters, we began with the density functional theory (DFT) employing the Becke three parameters with Lee Yang-Parr functionals (B3LYP), using the GAUSSIAN package [10]. The CRENB and Stuttgart relativistic effective core potentials were used for heavy metals, and the 6-311 + +G** basis set was used for alkali metals [11]. For linear chains, first-principles calculations (based on DFT) on freestanding infinite Na-Au and Cs-Au atomic chains were carried out. To serve as reference systems, the chains of pure Au, Na, Cs, and the bulk Cs-Au in CsCl structure [12,13] were also studied. Supercell geometry was used for chains taking the unit cell as a rectangular parallelepiped. To effectively remove the interchain interaction, the cross section of the unit cell, perpendicular to the chain direction, was taken to be $20 \times 20 \text{ \AA}^2$. Plane wave functions were used with the cutoff energy of 260 eV. Brillouin-zone integration was per-

TABLE I. B3LYP binding energies (BE) per atom (eV) and average bond length d (Å) of linear alkali metal and binary alkali-metal-noble metal clusters (These are compared with those of AuAg and Au_n clusters; the bond angle for Au_4/Au_6 is $128^\circ/132^\circ$.)

	AuAg	Au ₂	Au ₄	Au ₆	Cs ₂	Cs ₄	Cs ₆	Na ₂	Na ₄	Na ₆	Na-Au	(NaAu) ₂	(NaAu) ₃	Cs-Au	Au-Cs-Au	(CsAu) ₂	Au(CsAu) ₂	(CsAu) ₃	(CsAu) ₄	(CsAu) ₆
BE	0.92	0.95	1.05	1.21	0.19	0.20	0.21	0.37	0.39	0.40	1.16	1.29	1.36	1.24	1.04	1.36	1.25	1.43	1.47	1.51
d	2.58	2.57	2.61	2.62	4.71	4.96	5.00	3.05	3.27	3.30	2.62	2.75	2.77	3.22	3.37	3.41	3.43	3.44	3.45	3.46

formed within a Monkhorst-Pack scheme using $(1 \times 1 \times 25)$ k points for the wires. Ionic potentials were the Lee-Yang-Parr functionals represented by ultrasoft Vanderbilt-type pseudopotentials [14]. Fully relaxed atomic structures were obtained using the generalized gradient approximation [15]. The Vienna *ab initio* simulation package (VASP) code [16] was used to investigate the geometries and cohesive energies.

To study the formation of 1D monatomic chain at the atomic level, we studied gold-alkali metal alloys starting with the dimers. It is interesting to note that the binding energies (Table I) per atom of pure alkali metal dimers are exceptionally small, while those of binary dimers (Na/Cs-Au) are larger than those of the pure Na, Cs, or Au dimer. The Na-Au and Cs-Au dimers have larger binding energies per atom than for the gold dimer, by 0.2 and 0.3 eV, respectively, at the B3LYP level. This suggests that the binary clusters of alkali metal and noble metal atoms could offer monatomic wires with a better linearity and stability as compared to Au monatomic wires.

As a next step towards building a nanowire, we increased the size of the system by considering higher clusters starting with trimers. The linear trimer (Cs-Au-Cs, Au-Cs-Au) shows a minimum energy with a significant charge transfer from the middle atom to both end atoms. Figure 1 shows optimized 1D hexamers for each system with the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The binding energies of various clusters are in Table I. 1D pure Au_n (n : integer) shows zigzag structures, while 1D linear Cs_n , $Au(CsAu)_n$ and $Cs(AuCs)_n$ are on local energy minima and 1D linear $(CsAu)_n$ are on a flat potential surface. Since the linear Na_n were almost on a flat potential surface, the binding energies were studied for the linear structures. While circular Au_n are not stable collapsing to 2D structures, circular Na_n , Cs_n , and $AuCs_n$ are on local energy minima, which are slightly more stable than the corresponding linear structures due to an extra bond between both end atoms.

1D clusters for pure Cs, Na, and Au are less stable than the 1D binary clusters. For 1D systems, the binding energy per atom increases from the dimer to the higher cluster. Basically, this is caused by the increase in the ratio of the number of bonds to that of atoms. However, it is notable that the differences in binding energies per atom between the dimer and the hexamer for pure Na, Cs, and Au systems are 0.03 eV, 0.02 eV, and 0.16 eV, respectively, whereas those for binary systems Na-Au and Cs-Au are both

0.19 eV, which is much larger than those for the pure systems. This shows that the binary systems have a better tendency towards 1D chains than the pure systems.

It is clear that the larger binding energy of the binary systems comes from the electrostatic energy which is due to the charge transfer from alkali metal to gold. The large charge transfer from cesium to gold appears in binary clusters due to the strong electronegativity of gold and the weak ionization potential of alkali metal. The shapes of HOMO and LUMO of $(CsAu)_3$ in Fig. 1 show the results of the charge transfer, where the HOMO is contributed by the 6s orbital of the terminal gold atom which has withdrawn the electron cloud from the cesium atom and the LUMO is contributed by 6s orbital of the terminal cesium atom. It is interesting to note that the amount of transferred charge increases as the linear chain gets longer, resulting in strong polarization similar to the 1D short H-bond phenomenon [17]. This effect helps the formation of long 1D atomic chains.

On the other hand, the geometries for 1D chains of the pure Au/Na/Cs systems and Na/Cs-Au binary systems were optimized with two same (former case) or different (latter case) atoms. One atom is fixed and the other is

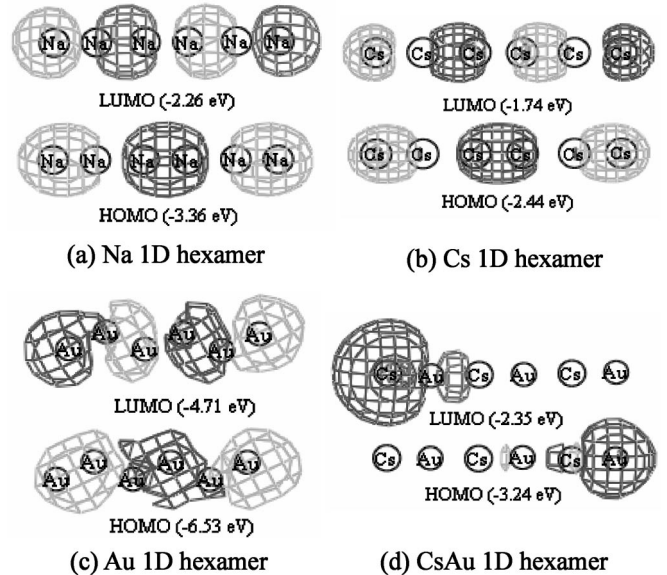


FIG. 1. HOMO and LUMO of 1D hexamer clusters: (a) Na_6 , (b) Cs_6 , (c) Au_6 , (d) $(CsAu)_3$. Charges on each atom are 0.86, -0.86 for Cs-Au (0.70, -0.70 for Na-Au), and 0.92, -0.90 , 0.91, -0.90 , 0.86, -0.88 for CsAuCsAuCsAu (0.86, -0.82 , 0.80, -0.79 , 0.70, -0.74 for NaAuNaAuNaAu).

allowed to move in the yz plane as shown in Fig. 2. The variations of the cohesive energy per atom and bond angle as a function of cell size are also shown for the pure Au/Na/Cs and binary Na/Cs-Au atomic chains.

A striking feature of the infinitely long chains in Fig. 2 is that the Cs-Au chain has only one energy minimum in the linear region (bond angle of $\sim 180^\circ$ and bond length of 3.5 \AA), while the other chains have an energy minimum in the zigzag region. Figure 2 shows that the Au chain has two energy minima, one of which lies in the zigzag region and the other in the linear region. Here, the energy minimum in the linear region is less stable, and the energy barrier from the linear to zigzag structure is $\sim 0.10 \text{ eV}$. This value is so small that the linear structure would not be stable. The pure Na atomic chain has only one energy minimum in the zigzag region, and the pure Cs atomic chain has two energy minima, but the minimum in the linear region is as shallow as 0.02 eV , which shows that the pure Na or Cs chain finds it difficult to form the linear structure. However, for the Na-Au chain the energy is lower in the linear region than the zigzag region. Thus, the linear structure is more favored. Yet, the Na-Au chain still has a minimum in the zigzag region. Therefore, the Cs-Au chain can be the best candidate for a linear atomic chain.

Analyzing the above results, we note that in the case of pure atomic chains like Na, Cs, and Au systems, no charge

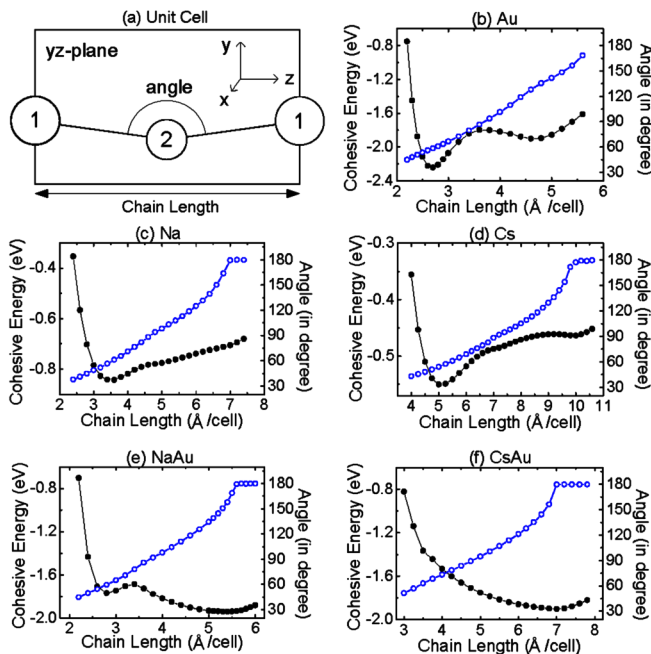


FIG. 2 (color online). Schematic diagram of a unit cell projected onto the yz plane (circles are for atoms) (a), and plots of cohesive energies and bond angles as a function of the chain length for pure Au/Na/Cs and binary Na/Cs-Au atomic chains: (b) Au, (c) Na, (d) Cs, (e) Na-Au, and (f) Cs-Au (where solid and open circles indicate cohesive energy and bond angle, respectively).

transfer occurs between atoms. Consequently, the zigzag structure is favored over the linear one. In contrast, significant charge transfer can occur for binary systems like Na/Cs-Au atomic chains. For the linear hexamer, sodium and cesium lose the charge of ~ 0.8 and ~ 0.9 a.u. to gold, respectively. Subsequently, the electrostatic interaction between negatively charged gold atoms and the neighboring positively charged alkali metal atoms in the zigzag structure forces the atoms to line up straight (Fig. 3). The binding energy effect leading to the zigzag structure competes with the electrostatic effect leading to the linear structure. The former is dominant for pure atomic chains, and the latter for binary chains. The amount of transferred charge can dictate the structure of 1D atomic chains. The more the charge transferred from one atom to the other, the more is the linear structure favored over the zigzag one. Thus, the alkali and noble metal binary chains favor the linear structure, and among them the Cs-Au chain is the most suitable. As an Au atom prefers to bind Cs atoms on both sides along a linear line, and vice versa, the self-assembling process to form a Cs-Au single atomic linear chain would be feasible when a suitable template or substrate to support the chain is provided.

We further explored the stability of the Cs-Au chain. The calculated binding energy values were fitted with the curve of the form, $a/x^{1.33} + b \exp(-cx)$, where a , b , and c are fitting parameters and x is the bond length between nearest neighbors. This bond length for Cs-Au bulk crystal (lattice structure of CsCl) [12,13] and that for linear chain are 3.89 and 3.50 \AA , respectively, and their binding energies per bond are 0.57 and 1.90 eV , respectively. Thus the bonds in the 1D structure become much shorter (towards the bond length 3.22 \AA of the dimer) and stronger. This is supported by the recent scanning tunneling microscope studies revealing that the bond strength of the Au nanowire is about twice that of a bulk metallic bond [18]. It has been shown [19] that Au and Pt exhibit a relatively large ratio of the break force of the chain to that of the bulk crystals (2.98 and 3.18 , respectively) in agreement with mechanically controlled break junction (MCBJ) experiments where atomic chains of Au and Pt were most frequently observed [5]. For the Cs-Au linear chain, we find this ratio as 3.36 , suggesting that these chains should be equally, if not more, stable as the Au and Pt atomic chains.

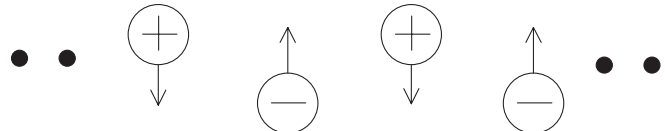


FIG. 3. Schematic diagram of electrostatic force on atoms constituting infinitely long atomic chain, disfavoring the zigzag structure. (A circle denotes an atom with positive or negative charge, and the arrow denotes the net electrostatic force on atom.)

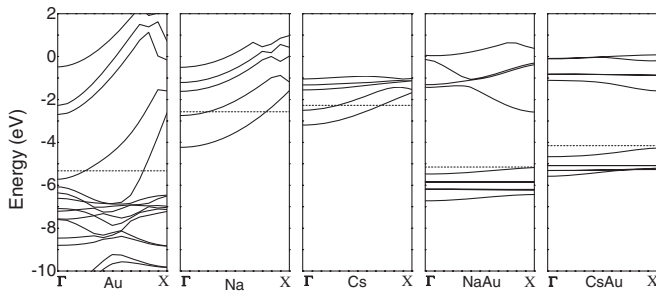


FIG. 4. Electronic band structures of pure Au/Na/Cs and binary Na/Cs-Au chains for the minimum energy structures.

Figure 4 shows the band structures of the pure Au/Na/Cs and binary Na/Cs-Au chains. It shows that the pure Au/Na/Cs chains have the typical metallic character with the s -band crossing the Fermi level. The alloying has a dramatic effect on the band structure. The electrons in s band of Na and Cs transfer considerably to the s band of Au. Unlike Au and Cs chains where intersection of s bands with the Fermi level imparts metallic nature to the respective linear chains, the s band of the Cs-Au chain stays close to the Fermi level, but does not cross it. Interestingly, the calculations without including the relativistic effects indicated that the bulk Cs-Au [12] is a conductor, emphasizing that the relativistic effects play an important role in not only geometries but also electronic structures of gold and its alloys. The Cs-Au linear chain shows a semiconducting feature with a band gap of 2.7 eV, wider than that of the bulk crystal (1.96 eV). Tuning the band gap of the linear chain by a template or substrate could be exploited for the utilization as light emitting diode as well as semiconducting devices.

To conclude, we showed the way towards linearization of nanowires by means of the significant charge transfer effect by taking the example of Cs-Au alloy system. The Cs-Au alloy would form linear atomic wires with reasonable stability by using templates or substrates. This approach is worth further investigation and would pave a way in realizing linear monatomic nanowires, which would prove crucial in development of nanoelectronic devices.

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