

Species Fractionation in Atomic Chains from Mechanically Stretched Alloys

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Bettini *et al.* [Nature Nanotech **1**, 182 (2006)] reported the first experimental realization of linear atomic chains (LACs) composed of different atoms (Au and Ag). Different contents of Au and Ag were observed in the chains from what found in the bulk alloys, which rises the question of what is the wire composition if in equilibrium with a bulk alloy. In this work we address the thermodynamic driving force for species fractionation in LACs under tension, and we present density-functional theory results for Ag-Au chain alloys. A pronounced stabilization of wires with an alternating Ag-Au sequence is observed, which could be behind the experimentally observed Au enrichment in LACs from alloys of high Ag content.

I. INTRODUCTION

Metal nanowires have attracted great interest with the increasing miniaturization of electronic and mechanical devices¹, given their very interesting properties related to quantum transport². From the experimental point of view, two techniques have been mostly used in nanowires research: mechanically controllable break junctions (MCBJ)³⁻⁵ and *in situ* high-resolution transmission electron microscopy (HRTEM)⁵⁻¹¹. While MCBJ is used to obtain electronic properties of nanowires, HRTEM gives structural information, providing atomic resolution with real-time image acquisition. A combination of both techniques is frequently used in order to establish a correlation between atomic arrangement and quantum conductance¹². Since 1997 these techniques have revealed the existence of some quite unexpected structures, such as, extremely thin metal nanotubes with a square cross-section¹³, helical multishell gold nanowires¹⁴, single-walled metal nanotubes^{15,16}, and the ultimate nanowires, linear atomic chains (LACs)^{10,17}. The stability of these structures has been inferred using statistics over large number of observed structures (in HRTEM) and on conductance histograms for a large number of contact-breaking events (in MCJB). These experimental analyses have shown the remarkable existence of stable (or metastable) nanowires for alkali³ and noble metals.⁴

There have been many theoretical studies of these structures, mostly using classical atomistic models, as well as first principles ones^{13,18-20}. Of particular importance is the work of Tosatti *et al.*²¹, that investigated the stability of these nanostructures considering the metal wires connected to atomic reservoirs at both ends, determining the local minima (different metastable structures) as a function of the tension of the wire. Using this approach the authors were able to predict the stability of magic sizes for Au nanowires.

Although metal nanowires have been the object of intense theoretical and experimental investigations, most of these studies were carried out for pure metals. The first LAC experimental realization using metallic alloys was reported only in 2006²². They reported the observation of LACs of different lengths composed of Ag and Au atoms from Ag-Au nanoalloys of different compositions. They observed that when the nanowires are rich in Ag²², in the final states of the stretching leading to LAC formation, the observed behavior was similar to the ones for Au rich nanowires²². From classical molecular dynamics²² it was concluded that this unusual behavior is consequence of the Au enrichment at the region where the LACs were formed. The concentration of these nanoalloys changes significantly in time from the nominal initial values. They basically behave as if they had a much high Au content than in their nominal composition. This behavior was addressed by Fao²³ by considering the enthalpy as defining the stability of these atomic chains under tension, in line with what pioneered by Tosatti²¹. A grand canonical perspective, however, which is the ad-

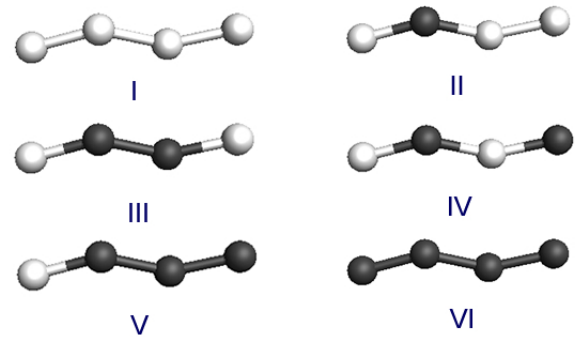


FIG. 1. Structural motifs for the atomic-wire compositions considered in this work. Dark (light) balls indicate Ag (Au) atoms. See text for discussions.

equate framework to study the thermodynamical trends in these systems, has not been done until this date and will be the focus of this work.

The main objective of this paper is to determine the relative concentrations of two species (Ag and Au in this case) in LAC when in equilibrium with bulk alloys of given composition. For the purpose the relevant free energy is defined and calculated from first principles, analogously to what was done in ref.²¹ for single-species wires and tubes, which is now generalized to a grand-canonical setting. The observed capability of the wires to change composition with respect to the bulk reservoir demands such grand canonical treatment, beyond what was presented in ref.²³.

In this way, with our approach we should be able to predict for specific bulk alloy concentrations what would be the corresponding likely concentrations for LACs formed by stretching a nanowire. It is important to remember, however, that this method takes an equilibrium viewpoint, which assumes atom exchange between reservoirs and wire, and should only be taken as a determination of equilibrium trends. The kinetics of the formation process will very probably originate deviations from this limiting behavior. It is however important to know what the thermodynamical trends are, which is what we address here.

II. METHODOLOGY

Density-functional theory (DFT) calculations were carried out for free-standing infinite nanowires by preparing arrays of sufficiently separated LACs in periodic boundary conditions. Tetragonal supercells are used with the wires aligned along the x -axis, with four atoms of Au or Ag and binary alloys of them. The considered geometries are presented in Fig. 1. The LAC geometries are relaxed for fixed supercell size, keeping the y and z sizes such that the minimum distance among wires is 15.0 Å, while the x direction was varied in increments of 0.05 Å, from 6.00 Å until the wire snapped. We have considered LAC lengths between 7 Å and 11 Å.

The DFT calculations were performed with the SIESTA method^{24,25}, using the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) for exchange and correlation²⁶. Norm-conserving scalar-relativistic pseudopotentials²⁷ replaced nuclei and core electrons, considering the normal core-valence separation for Ag and Au. Double- ζ polarized bases were used for valence electrons²⁸. Integrals in real space were performed on a mesh of 250 Ry cutoff²⁵. The integration over the first Brillouin zone was carried out using the special k -points method²⁹ with k -meshes of $1 \times 1 \times 30$ and $10 \times 10 \times 10$ for wire and bulk structures, respectively.

In order to calculate the nanowire stability for an alloy we have generalized the string tension analysis to different atomic species. The free energy Λ we will seek to

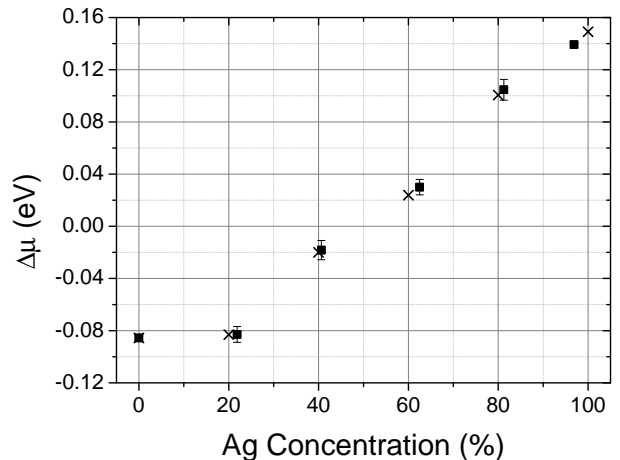


FIG. 2. Chemical potential difference $\Delta\mu = (\mu_{\text{Au}} - \mu_{\text{Ag}})/2$ calculated for a bulk AgAu alloy. Squares indicate $\Delta\mu$ values at bulk concentrations 0, 7/32, 13/32, 20/32, 26/32 and 1; crosses show the interpolated estimates for concentrations 0, 0.2, 0.4, 0.6, 0.8 and 1.

minimize is

$$\Lambda = E_{\text{LAC}} - n_{\text{Au}}\mu_{\text{Au}} - n_{\text{Ag}}\mu_{\text{Ag}} \quad (1)$$

where n_{Au} and n_{Ag} represent the number of Au and Ag atoms in the LAC (for the case of AgAu alloys), and μ_{Au} and μ_{Ag} , are the corresponding chemical potentials. It is the zero-temperature grand-canonical free energy (per unit cell) that gives the stability for a wire of unit-cell length L (length of cell along x). The analysis can also be done as a function of F , the force pulling the wire, in which case the relevant free energy would be²¹

$$\Theta = \Lambda - FL. \quad (2)$$

Here we will restrict ourselves to L -dependence and thus Λ . We will consider the low temperature limit, disregarding entropy effects. The generalization of the present scheme to finite temperature is costly but conceptually straightforward, either by including the entropy of harmonic vibrations³⁰ (for a fully quantum albeit harmonic treatment), or thermodynamic integration for the free energy³¹, using molecular dynamics for classical nuclei, or with path-integral Monte-Carlo or molecular dynamics for quantum nuclei.

If we define

$$n = n_{\text{Au}} + n_{\text{Ag}}; \Delta n = n_{\text{Au}} - n_{\text{Ag}} \quad (3)$$

we can write

$$\Lambda = E_{\text{LAC}} - n\bar{\mu} - \Delta n\Delta\mu \quad (4)$$

where

$$\bar{\mu} = (\mu_{\text{Au}} + \mu_{\text{Ag}})/2 \text{ and } \Delta\mu = (\mu_{\text{Au}} - \mu_{\text{Ag}})/2. \quad (5)$$

The $n\bar{\mu}$ term controls the energetics related to their having more or less atoms in the chain, regardless of species,

while the $\Delta n \Delta \mu$ term controls the energetics related to swapping atoms of different species in a wire with a given number of atoms. We will confine ourselves here mainly to the latter behavior considering wires with a constant n , and will consider the free energy

$$\Omega = E_{\text{LAC}} - \Delta n \Delta \mu = \Lambda + n \bar{\mu}. \quad (6)$$

The chemical potentials are defined by the bulk alloy out of which the wire forms, which constitute the effective reservoirs. In particular, the relative chemical potential can be calculated as the statistical average energy change when swapping any Au atom in the alloy into a Ag atom,

$$\Delta \mu = \langle \Delta E(\text{Au} \rightarrow \text{Ag}) \rangle. \quad (7)$$

This has been obtained by making random substitutions of Au by Ag in disordered bulk alloy samples of different relative concentrations, relaxing the structures before and after the swap, and computing the energy difference. Face-centered cubic supercell structures with 32 atoms were used for the purpose. The original concentrations of Ag in Au were 0, 7/32, 13/32, 20/32, 26/32, and 1. The results are shown in Fig. 2. Both for μ_{Au} and μ_{Ag} the zero is defined for their respective pure bulk crystals.³² The curve shows a quite linear behaviour except at very low Ag concentrations.

III. RESULTS

Fig. 3 shows the free energy Ω as a function of cell length L , for the six atomic-wire configurations shown in Fig. 1, and for the different bulk composition of the lead alloys specified on the figure. Starting from the left, the regime up to ~ 7.7 Å corresponds to zigzag wires in which three consecutive atoms define quite an equilateral triangle, i.e., essentially a band with two rows of atoms and edge-sharing triangles. The regime at larger distances corresponds to the zigzag structures shown in Fig. 1, agreeing with what known for Au wires¹⁹, which gradually stretch with growing L , until they snap at L -values slightly above what displayed. The transitions between regimes, which involve “bond” breaking, are discontinuous and hysteretic, and thus will be quite dependent on quantum and thermal fluctuations.³⁰ The experimentally observed LACs correspond to the intermediate regime.

Fig. 3 shows that for most alloy concentrations the structure IV of Fig. 1, with Ag-Au alternation is most stable in the LAC regime, with higher stabilization for higher Ag content in the bulk alloy. This implies that Ag-rich bulk alloys tend to produce wires with [Ag] tending towards 50%, i.e. the wires will be Au enriched. These results agree with the mixed and Au enriched wires seen in the experimental atomically resolved micrographs.²² Reducing the Ag concentration in the alloy there is a transition to a situation in which the wire could change equilibrium concentration with stretching, as seen for 20%. For $L \sim 9.5$ Å, the wire would tend to pure Au, thus

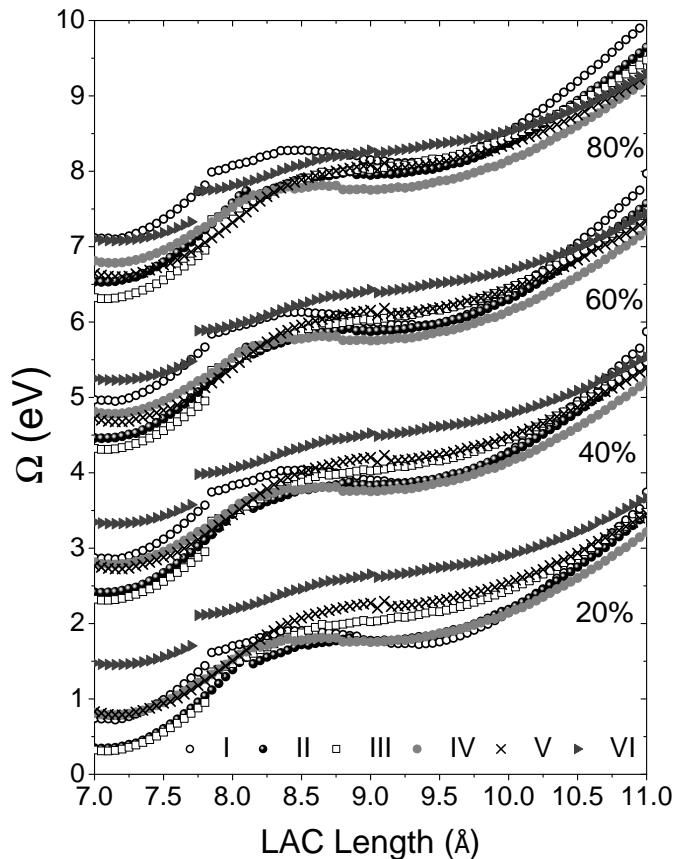


FIG. 3. Free energy Ω versus length L for atomic chains of different compositions, for different bulk compositions. Each group of curves correspond to different bulk alloy composition, as specified with the percentages on the right, and contains six curves, for the wire configurations I to VI (see Fig. 1), as specified in the legend. The curves for different bulk compositions have been shifted upwards by 85.55 eV for convenience.

depleting Ag (although the configuration II with 25% Ag is close in energy, and indeed lower for mechanically unstable shorter L). Upon stretching, though, the AgAu alternating wire dominates again, thus replenishing Ag.

In summary, we have defined and calculated from first-principles the grand-canonical zero-temperature free energy governing the fractionation of two species between an alloyed atomic chain and the bulk alloy. We have applied this to Ag/Au alloy chains and explained the tendency for Au enrichment in LACs observed experimentally for Ag rich alloys.

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