

Structural and electronic properties of Au, Pt, and their bimetallic nanowires

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We have carried out first-principles, full-potential, density-functional calculations on different types (linear, zig-zag, double zig-zag, and tetragonal) of infinite, periodic, atomic wires of Au and Pt as well as on mixed chains containing both Au and Pt. In particular, structural degrees of freedom are optimized, and the band structures of the different types of wires are reported and discussed. The bond lengths for Au and Pt are found to be somewhere between those of the corresponding dimer and those of the corresponding crystalline phases of Au and Pt. The bond length for all three systems is progressively increased as we move from the linear to the tetragonal structure, as the number of nearest-neighbor atoms is increased. Moreover, the bond angles are around 60° as in crystalline system. The bond length for Au-Pt wire is in between the values of pure Au and Pt wires and the bond angles around 60° suggesting the possible formation of Au-Pt bimetallic materials. All wires are found to be metallic and the bands closest to the Fermi level, responsible for conduction, are analyzed and discussed.

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I. INTRODUCTION

Nanostructures, i.e., materials whose spatial extension in at least one dimension is in the nm range, have received a steadily growing interest as a result of their peculiar and fascinating properties and applications superior to their bulk counterparts. The ability to generate such one-dimensional nanostructures is essential to much of modern science and technology. It is generally accepted that quantum confinement of the electrons by the potential wells of nanometer-sized structures may provide one of the most powerful and versatile means to control the electrical, optical, magnetic, and thermoelectric properties of functional materials. Among those materials, one-dimensional (1D) nanostructures such as wires, rods, belts and tubes have become the focus of an intensive research owing to their unique properties.

There exists different experimental ways of fabricating nanowires. In one approach they are grown at steps on certain crystal surfaces and, therefore, the structures of the resulting nanowires will most likely depend critically on the substrate. In other approaches, nanowires are synthesized inside some crystalline host that has sufficiently long and wide pores to host the nanowires inside it. Also in this case, the structures of nanomaterials may partly depend on the host. Yet another approach is provided by the break-junction method. In this method, nanowires of limited length can form at the junction just before breaking. The fact that these wires are of limited length may affect the properties significantly.

In the present work we shall study chains of Au and Pt. Au has become the prototype of metallic chains¹ for which, in particular, much information on linear chains has been obtained. Two reports on experimental studies of linear, monatomic gold nanowires^{2,3} caused an intense research effort first of all devoted to characterizing their properties (e.g., structural, electronic, magnetic, etc.). Originally it was found experimentally that the bond length equals $3.5\text{--}4\text{ \AA}$, and much research was carried out theoretically to understand this exceptionally long bond length (since the bulk Au-Au

bond length is 2.88 \AA). Later it was found experimentally that the bond length in a monatomic gold nanowire is around 2.5 \AA ,⁴ in agreement with theoretical results. Of relevance to the present work is the result of Portal and co-workers⁵ who theoretically studied the stability of a gold nanowire and showed that the relaxed structure of this system corresponds to a zig-zag geometry. Recently, using scanning electron microscope, Wang *et al.*⁶ identified the formation of zig-zag chains of Au on Ge(001) surfaces. On the other hand, Kondo *et al.*⁷ synthesized gold nanowires and found that the thinnest nanowire is 4 atoms wide and that the structure is related to a tetragonal structure.

Besides Au, Pt is an important element for many quasi-one-dimensional systems. Thus, Pt has been incorporated into the backbone of conjugated polymers⁸ and it has been shown⁹ that these Pt-containing polyynes have properties as those of more well-known conjugated polymers. Also many of the quasi-one-dimensional so-called MX chain compounds^{10,11} have Pt atoms as a fundamental part. In these materials, the Pt atoms are sixfold coordinated, whereas in certain crystalline compounds like K_2PtS_2 quasi-one-dimensional wires with fourfold coordinated Pt atoms are found.^{12,13} In this case, the coordination may be either planar or tetragonal. In all these case, no Pt-Pt bonds exist, which, on the other hand, is the case for other quasi-one-dimensional Pt-containing materials like Magnus' green salt,¹⁴ where, again, the Pt atoms are sixfold coordinated.

But also pure-Pt quasi-one-dimensional systems have been produced. Thus, Oshima *et al.*¹⁵ have reported evidence for the formation of single-wall platinum nanotubes. Furthermore, using mechanically controllable break junctions Smit *et al.*¹⁶ have produced monatomic platinum nanowires. Moreover, Husain *et al.*¹⁷ have reported the fabrication of a platinum nanowire of 43 nm diameter, i.e., a rather thick nanowire, whereas Fu *et al.*¹⁸ have prepared platinum nanowires of diameter $1.5\text{--}3\text{ nm}$ by an electron-beam thinning method. Finally, fairly thick (i.e., $10\text{--}100\text{ nm}$) nanowires of Pt have been synthesized by Song *et al.*¹⁹

Bimetallic nanowires that are compositionally modulated along the axis of the nanowire can form the basis for nanowire based devices including diodes,²⁰ spin valves,²¹ and optical labels (“Nanobar codes”).²² One convenient method for preparing such a nanowire is using template synthesis which involves the electrodeposition of a metal into uniform cylindrical or prismatic pores of a host membrane. In a template synthesis experiment, layered nanowires are obtained by halting the electrodeposition of one metal, changing the plating solution for one containing a different metal ion, and resuming depositions. Walter *et al.*²³ described such a method for synthesis of bimetallic nanowire of Au, Pt, and Ag. Salem *et al.*,²⁴ on the other hand, synthesized end-to-end assembly of Au/Pt/Au multisegment nanowires using organics linkages. However, to the best of our knowledge, there is no direct theoretical studies on the structural and electronic properties of Au-Pt bimetallic nanomaterials, although few experimental studies on the synthesis of different types of bimetallic nanomaterials exist. Thus, Nakanishi *et al.*²⁵ synthesized an Au-Pt nanoparticle alloy using a sonochemistry technique. Doudna *et al.*²⁶ synthesized bimetallic Ag-Pt nanowires using a radiolytic synthesis technique. Liang *et al.*²⁷ synthesized hollow bimetallic Au-Pt tubelike one-dimensional nanomaterials. Using an electrodeposition technique, Birenbaum *et al.*²⁸ synthesized Ni-Au nanowires, Chu *et al.*²⁹ fabricated Fe-Pt nanowires, and, finally, Mallet *et al.*³⁰ synthesized Co-Pt nanowires.

Ultimately, metals prefer high coordination and closely packed structures, making the quasi-one-dimensional structures the less likely ones. In particular, the linear chains that have been the focus of most interest in the context of chains of Au or Pt, may be considered highly unstable, whereas more compact, quasi-one-dimensional chains may be more stable. Thus, as a natural and relevant extension of our earlier work on linear chains of gold³¹ and on different types of Ag nanowires³² we shall first study how the properties of the linear chains of Au or Pt change when the slightly more thick structures of Fig. 1 are considered. However, not only through variation of the dimensionality of the material it may be hoped to vary the materials properties in a controlled way, but also through the variation of the composition new possibilities for controlled variations of materials properties emerge. Despite this possibility, there exists very few studies devoted to the properties of quasi-one-dimensional chains of metals containing more types of metal atoms. In order to explore the potential of this degree of freedom we shall here address, first, the properties of different types of Au and Pt nanowires, individually and, subsequently, we will study how the properties are changed when Au and Pt form a bimetallic nanowire.

Surfaces of Au-Pt alloys are known to exhibit a phase separation, so that the surfaces are Au-rich.³³ It may be speculated that this also means that in, e.g., break-junction experiments where a nm thin junction is formed in a roughly macroscopically extended material, the junction may consist of essentially only one type of metal, say Au. Despite this speculation, we shall here assume that the bimetallic nanowires are regular.

The paper is organized as follows: After a description of our computational method, we discuss our results in detail.

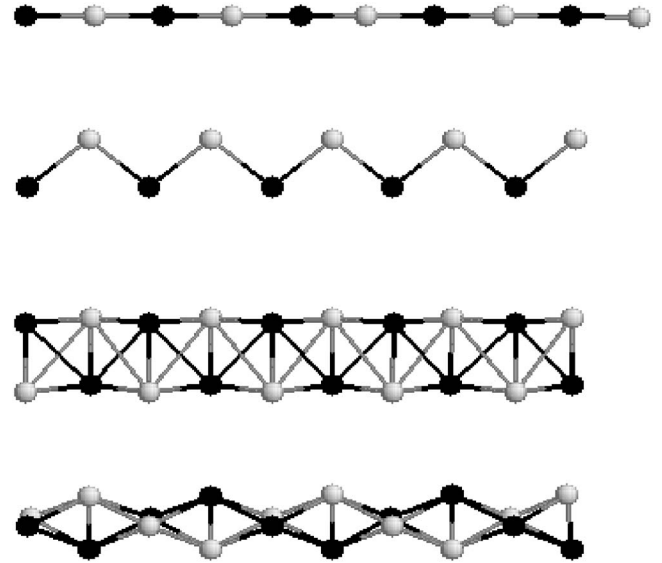


FIG. 1. Schematic representation of the wires considered in the present work. From above the structures are the linear wire, the zig-zag wire, the double zig-zag wire, and the tetragonal wire, respectively. For the pure Au and Pt wires, all atoms are identical, whereas the two types of atoms are placed as indicated in the figure for the bimetallic wires.

Finally, a brief summary of our conclusions is offered.

II. COMPUTATIONAL METHOD

For the present study, we applied a density-functional method that has been described in detail elsewhere^{34,35} and, therefore, here shall be presented only briefly. We use the Hohenberg-Kohn density-functional formalism³⁶ in the formulation of Kohn and Sham.³⁷ The resulting single-particle equations

$$\hat{h}_{\text{eff}}\psi_i(\vec{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \right] \psi_i(\vec{r}) = \epsilon_i\psi_i(\vec{r}) \quad (1)$$

are solved by expanding the eigenfunctions in a basis set of linearized muffin-tin orbitals (LMTOs)

$$\psi_i(\vec{r}) = \sum_{\vec{R}, L, \kappa} \chi_{L, \kappa}(\vec{r} - \vec{R}) c_{i, \vec{R}, L, \kappa} \quad (2)$$

A LMTO centered at an atom at \vec{R} and having an angular dependence as specified through $L \equiv (l, m)$ is defined as a spherical Hankel function times a harmonic function, $h_l^{(1)} \times (\kappa|\vec{r} - \vec{R}|) Y_L(r - R)$, in the so-called interstitial region (i.e., outside all muffin-tin spheres). Inside any atom-centered, nonoverlapping, so-called muffin-tin sphere this function is augmented continuously and differentially with numerical functions that are obtained by replacing the potential $V(\vec{r})$ in Eq. (1) with its spherically symmetric part and for an energy for which the resulting function has its major support, plus its energy derivative. This leads to a basis set that is of limited size but still provides accurate solutions to Eq. (1). It shall be stressed that the calculations consider the full poten-

TABLE I. Optimized structural parameters for different types of Au, Pt, and Au-Pt wires of Fig. 1 (characterized by “system”). “lda” and “gga” describe whether a local-density or generalized-gradient approximation was used in the optimization. The two bond lengths given for the double zig-zag wire are those within and between the two zig-zag wires, respectively, whereas those for tetragonal wire are those between atoms at different and the same z , respectively. Lengths are given in a.u., and angles are in degrees.

System	Method	Bond lengths			Bond angles		
		Au	Pt	Au-Pt	Au	Pt	Au-Pt
Linear	lda	4.86	4.50	4.93	180	180	180
	gga	4.86	4.55	4.95	180	180	180
Zig-zag	lda	5.09	5.05	5.05	62	61	60
	gga	5.09	5.09	5.08	63	62	60
Double zig-zag	lda	5.24, 5.09	4.99, 4.95	5.08, 5.03	57	60	58
	gga	5.24, 5.09	5.05, 5.00	5.15, 5.04	57	61	58
Tetragonal	lda	5.27, 6.40	4.95, 5.40	5.04, 6.30	77	78	77
	gga	5.27, 6.40	5.00, 5.50	5.10, 6.40	77	79	78

tial and the muffin-tin approximation is used solely in the construction of the basis functions.

The basis set we are using consists of two subsets of s , p , and d functions on all sites. The two sets differ in the decay constants κ of the Hankel functions, that were chosen as $0.7i$ and $1.5i$ for the two sets, respectively. Finally, the radii of the muffin-tin spheres were chosen equal to 2.2 a.u.

We assume that the wires are infinite, periodic, helical, isolated, and with a straight helical axis. The primitive symmetry operation is a combined translational (of h) and rotation (of v). Moreover, the position of each atom inside the helical unit is given through three parameters (r_i, θ_i, z_i) so that in a global coordinate system with the z axis along the helical-wire axis the position of the i th atom in the n th unit cell is given by

$$\begin{aligned} x_{ni} &= r_i \cos(u_{ni}), \\ y_{ni} &= r_i \sin(u_{ni}), \\ z_{ni} &= h/v \cdot u_{ni} + z_i, \end{aligned} \quad (3)$$

with

$$u_{ni} = n \cdot v + \theta_i. \quad (4)$$

By defining LMTOs in local atom-centered coordinate systems (i.e., right-handed coordinate systems that have z axes parallel with the wire axis) we can construct symmetry-adapted Bloch waves from the equivalent basis functions of different unit cells,

$$\chi_{L,\kappa,p}^k(\vec{r}) = \lim_{N \rightarrow \infty} \frac{1}{\sqrt{2N+1}} \sum_{n=-N}^N \chi_{L,\kappa}(\vec{r} - \vec{R}_{np}) e^{ik\pi n}, \quad (5)$$

where \vec{R}_{np} is the position of the p th atom of the n th unit cell. Then,

$$\begin{aligned} &\langle \chi_{L_1,\kappa_1,p_1}^{k_1} | \chi_{L_2,\kappa_2,p_2}^{k_2} \rangle \\ &= \delta_{k_1,k_2} \lim_{N \rightarrow \infty} \sum_{n=-N}^N \langle \chi_{L_1,\kappa_1}(\vec{r} - \vec{R}_{0p_1}) | \chi_{L_2,\kappa_2}(\vec{r} - \vec{R}_{np_2}) \rangle e^{ik_1\pi n} \end{aligned} \quad (6)$$

and

$$\begin{aligned} &\langle \chi_{L_1,\kappa_1,p_1}^{k_1} | \hat{h}_{\text{eff}} | \chi_{L_2,\kappa_2,p_2}^{k_2} \rangle \\ &= \delta_{k_1,k_2} \lim_{N \rightarrow \infty} \sum_{n=-N}^N \langle \chi_{L_1,\kappa_1}(\vec{r} - \vec{R}_{0p_1}) | \hat{h}_{\text{eff}} | \chi_{L_2,\kappa_2}(\vec{r} - \vec{R}_{np_2}) \rangle \\ &\quad \times e^{ik_1\pi n}. \end{aligned} \quad (7)$$

In the actual calculations, the n summations are carried through so far that they can be considered converged. Furthermore, the irreducible part of the first Brillouin zone corresponds to $k \in [0; 1]$, and the k -space sampling is performed using 16 equidistant k points in this interval, except for the linear wire where we used only 11 k points. Some of the calculations were numerically difficult to bring to convergence due to sharp van Hove singularities close to the Fermi level and, therefore, the energy levels were broadened slightly.

All but the $6s$ and $5d$ electrons were treated in a frozen-core approximation. In all cases, we used both the local-density approximation of von Barth and Hedin³⁸ and the generalized-gradient approximation of Perdew.³⁹ Finally, we performed both scalar-relativistic calculations and calculations where also the spin-orbit couplings were included.

III. RESULTS

A. Structures

All our optimized values of the structural degrees of freedom for the different types of wires of Au, Pt, and Au-Pt are summarized in Table I. We optimized all the structures both using the local-density and using the generalized-gradient

approximation (GGA) and both without and with the inclusion of spin-orbit couplings. With both density-functional approximations we found that the optimized structures were essentially independent on the inclusion of spin-orbit couplings.

The chemical bonding in a wire is, of course, quite different from the bonding in a bulk material where the atoms are highly coordinated. In the nanowires there are only few nearest neighbors and, therefore, as a first approximation, the bond lengths in a wire will be smaller than those of the bulk. However, many deviations from this simple rule exist, including, e.g., the average bond length in the double zig-zag and tetragonal structures of Ag.³²

Using the GGA approximation, the bond lengths for Pt and Au-Pt become slightly larger whereas a similar effect is not observed for the Au wire. Moreover, the magnitude of the bond-length difference using the two approximations for Au-Pt is less than that observed for Pt.

Bahn *et al.*⁴⁰ studied theoretically the formation of metallic wires. Using molecular-dynamic simulations they demonstrated the possible formation of a monatomic Au and Pt wire. With a generalized-gradient approximation they found an optimized bond length of the linear Pt chain of 4.55 a.u. which is in very good agreement with our value. Portal *et al.*,⁵ in their density-functional study for the linear Au wire, found bond lengths of 4.82 a.u., i.e., also in excellent agreement with our results and also with that of our previous study³¹ and slightly larger than the experimental value. On the other hand, Delin and Tosatti^{41,42} in their full-potential, density-functional, generalized-gradient study found an equilibrium bond length for linear Au and Pt wires equal to 4.94 and 4.68 a.u., respectively, slightly larger than our values.

An unexpected result is that the bond length in the linear Au-Pt chain is larger than those of the linear Au and Pt chains. However, the chains are soft and, as we shall see in the subsequent subsection, many bands cross the Fermi level, making band-structure effects important for the optimal structure.

Portal *et al.*⁵ and Ribeiro *et al.*⁴³ showed that the relaxed structure of the linear Au wire is the zig-zag structure and de la Vega⁴⁴ showed the same for the Pt wire. The zig-zag wire may be considered as being not a single wire, but rather two coupled monatomic linear wires, one displaced relative to the other by half the bond length. Then, the coordination number of the atoms in the zig-zag wire will be higher and, accordingly, the bond length will be larger. In the zig-zag wire the coordination number is 4 and the bond length for the Au wire is 5.09 a.u., for the Pt wire it is 5.05 a.u., and for the Au-Pt system it is 5.04 a.u. Ribeiro *et al.*⁴³ studied the properties of zig-zag wire of Au and showed that the minimum energy configuration of the zig-zag wire is found for bond angles around 60°. Our calculated value for the zig-zag wires for all three systems is indeed close to 60°. All bond lengths for the zig-zag Au-Pt wire are very similar to those for the pure systems.

The bond lengths of the double zig-zag and the tetragonal structures for all three systems are slightly larger than those of the zig-zag structures. The bond length is related to the coordination number which in turn equals 5 for the double zig-zag and the tetragonal structure. Our optimized bond

length for the double zig-zag and the tetragonal structure is smaller than the corresponding bulk value (where the coordination equals 12, and where the bond lengths equal 5.45 and 5.24 a.u., respectively) but longer than that of the linear structure as may be expected. Finally, the bond angle is close to the crystal bond angle.

In all higher coordinated wires (zig-zag, double zig-zag, and tetragonal) for the mixed Au-Pt system the bond length lies in between the values of the corresponding pure system, which may not surprise when considering the fact (cf. Fig. 1) that these systems contain both Pt-Pt, Au-Au, and Pt-Au nearest neighbors.

In our earlier study on Ag wires³² we found that the bond length between the atoms of the two zig-zag wires both for the double zig-zag and for the tetragonal wire is much larger than that within the single wire, and even longer than the distance between nearest neighbors in the crystal. For Pt, we find a significantly different situation, where the bond lengths between the wires are much less different from those within the wires. This result was also found for the double zig-zag structures for the Au and the Au-Pt wires, whereas the results for the tetragonal structures resemble those for Ag.

The fact that the bond lengths decrease when reducing the dimensionality is also found for even smaller Au- and Pt-based systems. For instance, Wang and co-workers,⁴⁵ in their density-functional study of small gold cluster, found a bond length of 4.81 a.u. for the dimer. On the other hand, Yang *et al.*,⁴⁶ in their density-functional study for small platinum clusters, showed that the bond length is 4.53 a.u. in Pt₂, comparable but only slightly smaller than our values for the linear wires. On the other hand, the Pt-Pt bond lengths in Magnus' green salt are around 6.15 a.u.,¹⁴ i.e., markedly different from our calculated values.

B. Electronic properties

Figure 2 shows the band structures of Au and Pt for the optimized linear structures. There are two bands crossing the Fermi level for the linear Au wire, although one band appears very close to the Fermi level. On the other hand, three bands cross the Fermi level for the linear Pt wire. Some few DFT studies^{5,43,46} have predicted that only one band crosses the Fermi level for the linear Au wire, whereas most others have found two bands crossing the Fermi level as in the present study. Our band structures for the Pt wire is in close agreement with those of Delin and Tosatti⁴¹ as well as with those of de la Vega *et al.*⁴⁴ Our result for the linear Pt wire shows that for the optimized structure, a complicated symmetry reduction is required in order to open up a gap at the Fermi level, whereas a simple bond-length alternation is sufficient to open up a band gap at the Fermi level for the linear Au chain.

Assuming that the z axis is parallel to the wire axis, we can split the bands into σ bands from the s , p_z , and d_{z^2} functions, π bands due to p_y and d_{yz} as well as p_x and d_{xz} , and, finally, δ bands due to d_{xy} and $d_{x^2-y^2}$ functions. Of those, only the σ bands are singly degenerate, whereas the others are doubly degenerate.

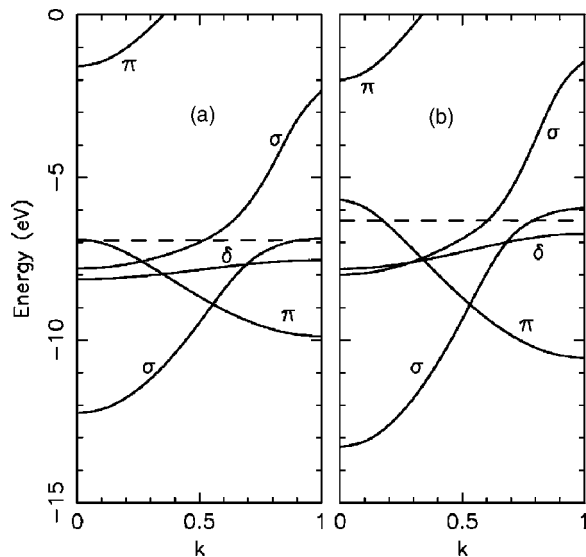


FIG. 2. Band structures for linear monatomic wires of (a) Au and (b) Pt. $k=0$ and $k=1$ is the center and the edge of the first Brillouin zone, respectively, and the dashed lines mark the Fermi energy. Spin-orbit couplings were not included, and the LDA approximation was used.

From the band structures, it can be seen that all the bands of the Au wire are narrower than those of the Pt wire. Moreover, in a break-junction experiment where the conduction through the nanojunction is measured, this will first of all depend on the number of conducting channels which in term is determined from the number of bands crossing the Fermi level. Therefore, the conductance of an Au wire is expected to be lower than that of a Pt wire.

The band widths for the linear Pt wire (7.35, 6.55, 4.86, and 1.08 eV for the bands of σ , σ , π , and δ symmetry, respectively) are in excellent agreement with the results of de la Vega *et al.*⁴⁴ (7.5, 6.90, 5.20, and 1.12 eV, respectively). When stretching the wire, the overlaps of the δ orbitals will most fast decay, whereas those of the σ orbitals will be reduced most slowly. Thus, when stretching the wire only the σ and π bands will cross the Fermi level.

Smit and co-workers^{47,48} studied in their experimental work the effect on the conductivity from the number of atoms forming an atomic wire. They have shown that for Au wire, the conductivity hardly changes with the number of atoms. In the case of Au atomic wire, the band crossing the Fermi level was found to be due to σ functions which was not changing upon increasing the number of atoms. For the Pt atomic wire, partly filled d orbitals along with half-filled s orbitals are responsible for three bands crossing the Fermi level. Smit and co-workers showed that for the Pt wire the conductivity decreases as the number of wire-forming atoms increases and, therefore, they predicted that for long wires only one or two conducting channels would survive, which is only partly in agreement with our results. We suggest, therefore, that of the three conducting channels for Pt atomic wire that we have found in our calculations, of which two are almost fully occupied, only one partially filled band may be available for conduction under the experimental conditions that, after all, are somewhat different from the idealized sys-

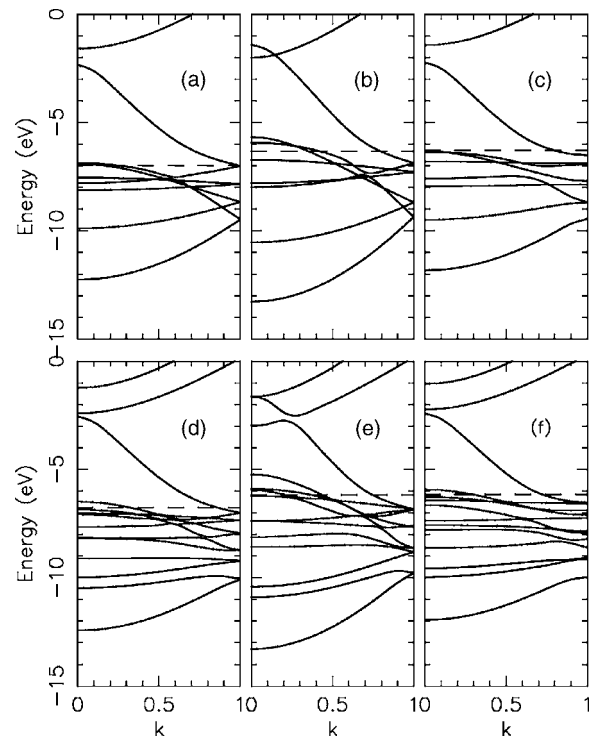


FIG. 3. Band structures of (a, d) Au, (b, e) Pt, and (c, f) Au-Pt linear wire, with two atoms per unit cell. Spin-orbit couplings have been included in (d-f), and not in (a-c). The representation is as Fig. 2.

tems we have considered. Although the band structures are slightly altered upon inclusion of spin-orbit couplings, our conclusion remains valid.

Figure 3 shows the band structures of the linear Au, Pt, and Au-Pt atomic wire. For comparison we have doubled the unit cell for Au and Pt wire. Moreover, as the only case, we show here also the band structures as obtained from calculations with the inclusion of spin-orbit couplings. These reduce the symmetry and double the number of bands. Accordingly, including the spin-orbit couplings leads to more complicated band structures although most features are recovered already without their inclusion. Therefore, we shall concentrate below on the results that we obtained without spin-orbit couplings.

There is only one band crossing the Fermi level for the Au-Pt wire. From the band structures of the Au-Pt wire, it is found that occupied σ and π bands are very close to the Fermi level. It is interesting to notice that the band structures of the Au-Pt wire do not resemble an average of those of the pure systems, but that the bands in general are narrower. The reason for this behavior may be the increase in the bond length (cf. Table I) when passing from Au or Pt to Au-Pt.

The spin-orbit couplings are around 1 eV for all three systems. This value is, however, not large enough to change any of the systems from a metal to a semiconductor as we have found earlier for Pb.⁴⁹ Finally, we mention that the bands that are obtained from the generalized-gradient approximation in general are shifted slightly less than 1 eV upwards compared to those from the local-density calculations.

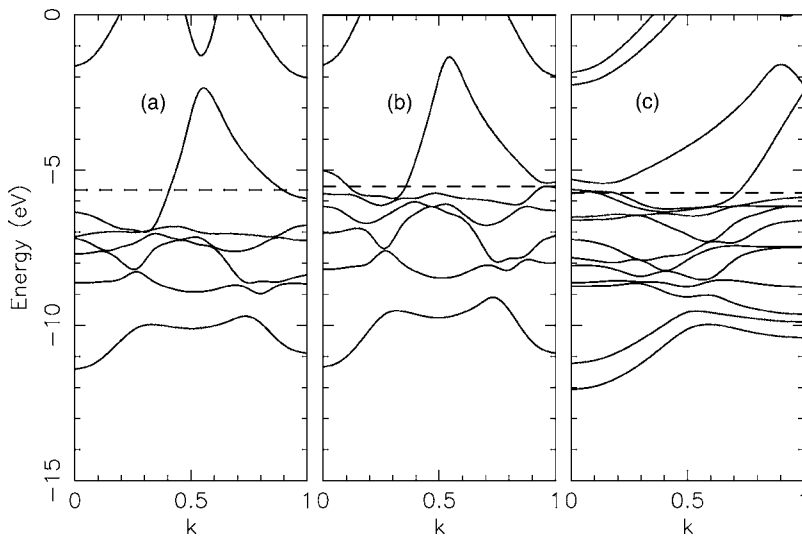


FIG. 4. Band structures of the zig-zag wires of (a) Au, (b) Pt, and (c) Au-Pt. Spin-orbit couplings were not included. The representation is as Fig. 2.

The band structures (Fig. 4) for the zig-zag wires for all three systems are more complex than those of the linear structures. For the pure system one unit cell contains one atom, whereas it contains two atoms for the Au-Pt system. This explains the larger number of bands for the Au-Pt chain. Moreover, in this case, where the structural parameters of the Au-Pt chain are similar to those of the Au and the Pt chains, the band structures of the Au-Pt wire as a first approximation can be considered an average of the other two sets. But we emphasize that there are distinct differences, e.g., in the band structures closest to the Fermi level, that could very well be significant, for instance for the conductance.

For the Pt system, the distance between the two individual zig-zag wires forming the double zig-zag wire is similar to the distance between the atoms of each zig-zag wire, the interaction between the two wires is strong so that the band structures (Fig. 5) for the double zig-zag structures are not just the doubling of the number of bands of the zig-zag structure. Though for Au the distance between the individual zig-zag wires forming the double zig-zag wire is larger than the distance between the atoms of each zig-zag wire, the interactions between the individual chains are still sufficiently strong to make the double zig-zag wire markedly different from the zig-zag wire. Finally, the double zig-zag structure of the Au-Pt system that we have considered is indeed two zig-zag Au-Pt chains, but also here the properties of the double zig-zag chain differ from those of the individual zig-zag chains. Moreover, the band structures of the Au-Pt chain are only to a first approximation a superposition of those of the Au and the Pt chains.

From the band structures for the tetragonal Pt wire we see that two bands cross the Fermi level close to $k=0.5$. This suggests that doubling the unit cell would reduce the density of states close to the Fermi level and, accordingly, stabilize this structure. A similar effect is not observed for the tetragonal Au or Au-Pt wires.

Finally, by looking at the number of valence electrons inside the muffin-tin spheres some information on the electron distribution is obtained. When comparing the pure Au and Pt systems, all but 2.5 electrons per atom are inside the Au spheres, whereas all but 2.6 electrons per atom are inside

the Pt spheres. Thus, despite the fact that Au has more valence electrons per atom, they are more localized to the atoms. For the bimetallic Au-Pt chains with the double zig-zag or the tetragonal structure the valence electrons become even more localized, so that each muffin-tin sphere contains roughly 0.2 electrons more. A similar effect is not observed for the other two structures. Thus, a small tendency towards electron localization can be identified for some of the bimetallic nanowires.

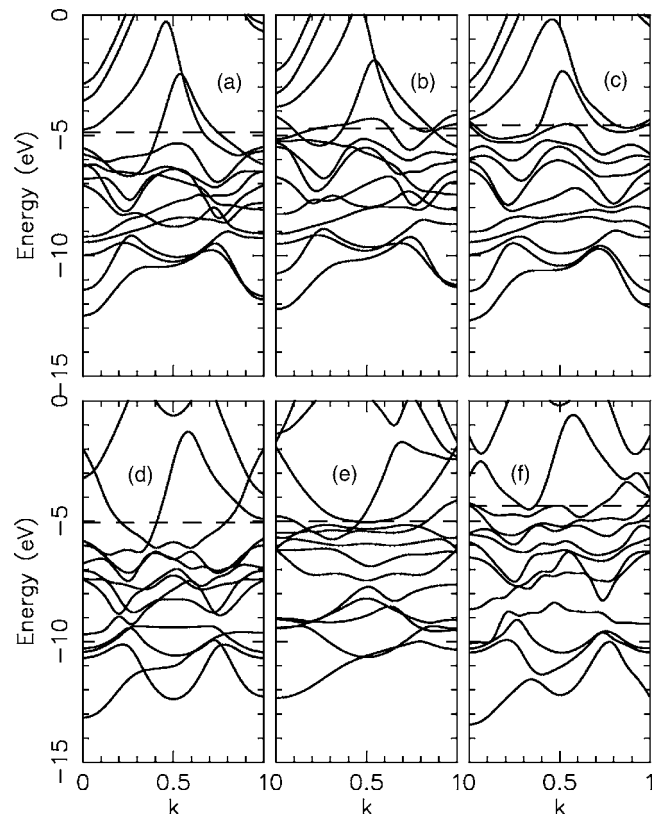


FIG. 5. Band structures of (a-c) the double zig-zag and (d-e) the tetragonal wire of (a, d) Au, (b, e) Pt and (c, f) Au-Pt. Spin-orbit couplings were not included. The representation is as Fig. 2.

IV. CONCLUSIONS

In this paper we have studied how the electronic and structural properties of metal nanowires are modified when either changing the structure of the system or changing the composition of the system. We have focused on two of the most intensively studied elements, i.e., Au and Pt, for which first of all linear chains have been at the center of a considerable research interest.

Not unexpected we found that the optimized bond lengths of the nanowires, independent of the precise structure, were lying somewhere between those of the diatomic molecules and those of the infinite crystals. In most cases, the structures of the bimetallic nanowires could be considered as intermediates between those of the pure nanowires, with the linear chain being a clear exception. This finding is interesting because it opens up the possibility of choosing materials with a predefined lattice constant that can be, e.g., produced inside channels of some host material or on the surface of a crystalline host.

Another interesting result of our study is that the band structure for the bimetallic nanowires to a good approximation can be considered averages of those of the pure nano-

wires, at least as long as no strong structural changes take place. It can be interpreted as a consequence of the electrons being quite delocalized along the chain and moving in some kind of average potential from the two metals. Following this line of thought further, it also suggests that by choosing other stoichiometries it may be possible to fine-tune the details of the band structures.

In this context we, finally, add that we also found that the details of the band structures, most notably those around the Fermi level that are responsible for conduction properties, depend critically on structure and composition, making it difficult to predict beforehand the properties of these details for a given nanowire.

In total, we hope to have presented interesting results for highly relevant nanowires and to have shown that upon changing the structure and, in particular, considering nanowires of more metals, new possibilities for controlling the properties open up.

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