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Structural and electronic properties of thin chains of Ag

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Results of first-principles, density-functional, full-potential calculations on four different types of chains (linear, zig–zag, double-zig–zag, and tetragonal) of Ag are reported. In particular, structural degrees of freedom are optimized, and the band structures and electron densities reported and discussed. Some discrepancies with earlier theoretical works are found and it is suggested that the effects of an organic matrix, inside which Ag chains have been synthesized, are stronger than previously assumed. The bond lengths are found to be between those of the Ag_2 dimer and those of crystalline Ag, and for the nonlinear systems the bond angles are in all cases somewhat larger than 60°. All chains are found to be metallic, except for the linear chain where a bond-length alternation opens up a gap at the Fermi level. As expected, spin–orbit couplings have only minor effects on the results.

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I. INTRODUCTION

One of the central issues of chemistry, physics, and materials science is to control, vary, exploit, and understand the dependence of materials properties on their structure and composition. With the development of experimental techniques for artificially producing low-dimensional materials new possibilities for varying the materials properties have opened up, and in some cases also new phenomena are observed that are absent in the materials found in Nature. Quantum dots form one class of such materials, as also do the materials of the present work, quantum wires.

There are different ways of experimentally producing nanowires. In one approach, they are grown at steps on crystal surfaces, whereby the structure of the nanowires to a large extent is dictated by that of the underlying substrate. Alternatively, they may be synthesized inside some crystalline host that contains sufficiently long and wide channels for hosting the nanowires. Also in this case the host material dictates partly the structure of the nanowire. Third, in break-junction experiments nanowires of limited length form the ultimate junction just before breaking. In this case, the structure is rather an intrinsic property of the material of the nanowire, but the nanowire is often of only very limited length.

The present work was motivated by progress in the last two categories. Thus, ultrathin silver wires with a width of 0.4 nm were synthesized inside the pores of self-assembled calix[4]hydroquinone nanotubes by Hong *et al.*[1] By performing a structural analysis, Hong *et al.* found that the structure of the Ag chain is related to the tetragonal structure of Fig. 1. Moreover, recently the intense research activity in break-junctions of Au was extended to other metals, including Ag.[2,3] In this case the structure of the nanowire is rather like that of the linear chain of Fig. 1. For the case of completeness we add that slightly thicker Ag nanowires have been considered by Tosatti *et al.*[4] and by Rodrigues *et al.*[5] The materials of those studies are, however, not the topic of the present work.

Motivated by experimental work on Au nanojunctions[6,7] we have earlier studied the structural properties of a linear chain of Au atoms.[8] Moreover, in another work[9] we studied the different structures of Fig. 1 for chains of Tl, Pb, or Bi following an experimental work by Romanov[10] on the synthesis of such chains inside the channels of a zeolite. Thus, besides giving relevant and interesting information on the material of interest, Ag, the present study can be considered a very natural and relevant extension of our earlier studies on monatomic, metallic nanowires.

We have applied a density-functional method for the infinite, periodic structures of Fig. 1. This method will be briefly outlined in Sec. II. The results are presented in Sec. III, and a brief summary is offered in Sec. IV.

II. CALCULATIONAL DETAILS

The computational method[11,12] we are using is based on the Hohenberg-Kohn density-functional formalism[13] in the formulation of Sham and Kohn.[14] The single-particle equations

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

are solved by expanded the eigenfunctions in a set of augmented waves. These are spherical waves that inside non-overlapping, atom-centered, so-called muffin-tin spheres are augmented continuously and differentiably with numerically represented functions. The spherical waves are spherical Hankel functions times spherical harmonics,

$$h_l^{(1)}(\kappa|\boldsymbol{r}-\mathbf{R}|)Y_{lm}(\widehat{r-R}), \tag{2}$$

where $\mathbf{R}$ specifies the atom where the function is centered, $|\kappa|$ is a decay constant (κ is imaginary), and (l,m) describes

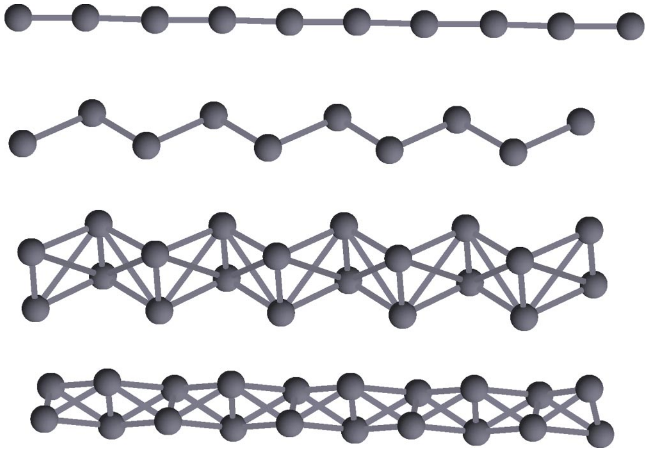

FIG. 1. Schematic representation of the chains considered in the present work. From above the structures are the linear chain, the zig–zag chain, the double-zig–zag chain, and the tetragonal chain.

the angular dependence of the function. The numerically represented functions inside the spheres are obtained by solving Eq. (1) when replacing $V(\mathbf{r})$ by its spherically symmetric component for an energy for which the resulting function has its major support, plus its energy derivative. We stress, however, that the muffin-tin approximation is used solely in the definition of the basis functions, but the full potential is used in the other parts of the calculations.

The chains are assumed being infinite, periodic, isolated, and helical. The primitive helical symmetry operation consists of a translation of h and a rotation of v. Moreover, the position of each atom inside the helical unit cell is given through three parameters (r_i, ϕ_i, z_i) so that in a global coordinate system with the z axis along the helical-chain axis the position of the ith atom in the nth unit cell is given by

$$x_{ni}=r_i\cos(u_{ni}),$$

$$y_{ni}=r_i\sin(u_{ni}),$$

$$z_{ni}=h/v\cdot u_{ni}+z_i, \tag{3}$$

with

$$u_{ni}=n\cdot v+\phi_i. \tag{4}$$

By using the helical symmetry, the linear, zig–zag, double-zig–zag, and tetragonal structure of Fig. 1 contains 1, 1, 2, and 2 atoms per unit cell, respectively, and has $v=2\pi$, π, π, and $\pi/2$, respectively.

The radius of the muffin-tin spheres was chosen equal to 2.4 a.u. Moreover, all but the $5s$ and $4d$ electrons were treated in a frozen-core approximation. In most cases we used the local-density approximation of von Barth and Hedin[15] but in some few cases (see below) the changes when using the generalized-gradient approximation of Perdew[16] were studied. Finally, we used 16 equidistant k points in half-part of the first Brillouin zone except for the linear chain where we used only 11 k point.

III. RESULTS

In Table I we have collected the optimized values of the structural parameters and in Fig. 2 we show the band structures for the optimized structures. Only for the zig–zag chain we optimized the structure both with a local-density approximation and with a generalized-gradient approximation and both without and with the inclusion of spin–orbit couplings, whereas we in the other cases used only the local-density approximation and excluded spin–orbit couplings in the optimization. Nevertheless, we show in all cases the bands both without and with spin–orbit couplings, and for the linear and zig–zag chains also those obtained with the generalized-gradient approximation.

Table I shows that the nearest-neighbor bond lengths vary only little for the different structures but show an overall increase with coordination. That the generalized-gradient approximation leads to longer bonds than the local-density approximation is consistent with general findings for all kinds of different systems. It is also seen that the spin–orbit couplings affect the structure only very little, consistent with the finding of Fig. 2 that the band splittings due to those are small. In crystalline Ag, the nearest-neighbor bond length

TABLE I. Optimized structural parameters for the different types of Ag chains of Fig. 1 (characterized by ‘‘System’’). ‘‘lda,’’ ‘‘gga,’’ and ‘‘soc’’ describes whether a local-density or a general-gradient approximation was used and whether spin–orbit couplings were included in the optimization. The two bond lengths given for the double-zig–zag chain are those within and between the two zig–zag chains, respectively, whereas those for the tetragonal chain are those between atoms at different and at the same z, respectively. Lengths are given in a.u., angles in deg, and the factor k_2 in eV per atom and bohr^2. Finally, $E_{\rm rel}$ gives the relative total-energy (in eV/atom) for the different structures as calculated with a local-density approximation and without spin–orbit couplings.

System	Method	h	r_i	ϕ_i	Bond lengths	Bond angles	k_2	$E_{\rm rel}$
Linear	lda −soc	4.98	···	···	4.98	180	2	0
Zig–zag	lda −soc	2.78	2.14	···	5.10	66	15	−0.7
	lda +soc	2.78	2.12	···	5.07	67	11	
	gga −soc	2.85	2.21	···	5.26	66	9	
	gga +soc	2.87	2.19	···	5.24	67	13	
Double zig–zag	lda −soc	2.64	3.86	±55	5.15, 6.32	63	12	−1.5
Tetragonal	lda −soc	3.09	2.97	···	5.21, 5.94	73	12	−0.9

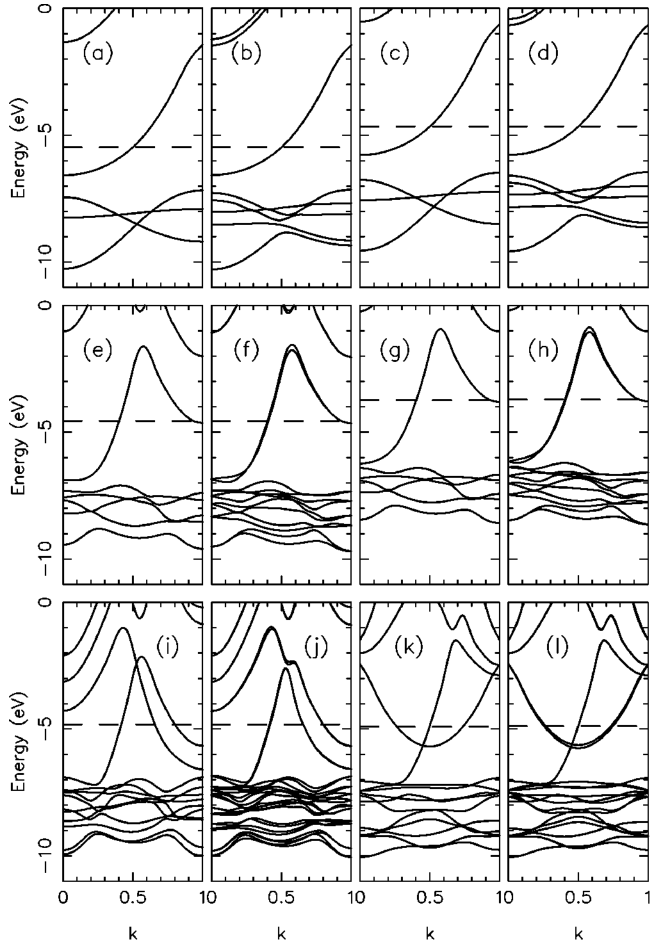

FIG. 2. Band structures for the (a)–(d) linear, (e)–(h) zig–zag, (i)–(j) double-zig–zag, and (k)–(l) tetragonal chain [(a),(c),(e),(g),(i),(k)] without or [(b),(d),(f),(h),(j),(l)] with the inclusion of spin–orbit couplings. In [(c),(d),(g),(h)] a generalized-gradient approximation was used, otherwise a local-density approximation. Except for (g)–(h), the structures were only optimized within the local-density approximation and without spin–orbit couplings. Finally, $k=0$ and $k=1$ represent the center and edge of the first Brillouin zone, and the dashed lines mark the Fermi level.

equals 5.47 a.u., so that those of Table I are seen to be somewhat smaller, which can be related to the lower coordination in the chains. This is confirmed by comparing the bond lengths for the zig–zag and the double-zig–zag chains: for the latter the bond lengths of one of the two zig–zag chains are slightly larger than for the former, although the bonds between the two zig–zag chains are quite long.

In some sense the double-zig–zag and the tetragonal chain are closely related. Both contain two infinite, linear zig–zag chains that are bonded together, but for the double-zig–zag chain the planes of the two chains are parallel and the two chains are "in phase," whereas for the tetragonal chain the two planes are not parallel and the two chains are "in antiphase." The bond lengths of Table I show then that the interchain bonds are longer for the double-zig–zag chain whereas the intrachain bonds are shorter for this. Thus, the double-zig–zag chain is more like two coupled zig–zag chains than is the tetragonal chain, which, on the other hand, more is a thicker nanowire.

The band structures for the linear chain [Figs. 2(a)–(d)] show that in all cases exactly one band crosses the Fermi level. This suggests that a bond-length alternation would open up a gap at the Fermi level, resulting in a semiconductor, as we have found earlier for linear Au chains[8] although for Au only when the chain was being stretched. Some further calculations confirmed this expectation, although the resulting bond-length alternation was very small (the two bond lengths differed by less than 0.05 a.u.) as also was the case for the band gap. For later purpose we notice that also the tetragonal structure has one band that is exactly half-filled, although also another band (which, furthermore, becomes split when spin–orbit couplings are included) crosses the Fermi level.

The structure of thin chains of Ag atoms has been studied by others, too. In one of the earliest works, McAdon and Goddard[17] used the Hartree-Fock approximation in studying Ag_n rings as finite approximations to infinite, linear chains. For a structure with constant bond lengths and $n=8$ they found the lowest total energy for bond lengths of 5.46 a.u., which is considerably longer than our value. However, they also reported that for the Ag_2 molecule the Hartree-Fock approximation leads to bond lengths of 5.14–5.25 a.u., whereas inclusion of correlation reduces the length to 4.89 a.u., and the experimental value is 4.67 a.u. This suggests that their bond length for the Ag_8 ring is overestimated. By subsequently allowing for a bond-length alternation they found bond-lengths that alternated by 0.71 a.u., i.e., considerably more than our findings.

Hong *et al.*[1] extended their experimental work on silver nanowires inside the organic matrix with density-functional pseudopotential calculations on chains with a structure related to the tetragonal structure of Fig. 1, except that they allowed the structure to have two different bond lengths in the x and y direction (with the z direction being along the chain direction). They found $h=2.63$ a.u., i.e., considerably smaller than our values but in good agreement with the experimental value of 2.60 a.u. for the nanowire inside the matrix. This is surprising since it suggests that the matrix has only little effect on the structure of the chain, although according to the experiment, the chain and the matrix have structures that are mutually commensurate. Finally, the longer bond length across the nanowire was found to be 7.46 a.u.

Table I contains also our estimated values of the force constant k_2 for the silver chains, i.e.,

$$E_{\mathrm{tot}}(h)\simeq E_{\mathrm{tot}}(h_0)+\tfrac{1}{2}\,k_2(h-h_0)^2, \tag{5}$$

where h_0 is the optimized value of h and E_{tot} is the total energy. It could be expected that the thicker chains are less flexible than the thinner ones, but the numbers in the table do not confirm this expectation. The large distances between the two zig–zag chains of the double-zig–zag chain make this structure very similar to that of the single zig–zag chain, and for the tetragonal chain the extra structural degrees of freedom make this less rigid. On the other hand, the linear chain is softer than the other structures. Notice that our value for the linear chain does not consider the bond-length alternation.

The numbers can be compared with those for the Ag_2 molecule. For these McAdon and Goddard[17] report 0.7–1.2 eV/bohr^2 within the Hartree-Fock approximation, 1.8 eV/bohr^2 when including correlation effects, and 2.1 eV/bohr^2 according to experiment. Although these numbers are per two atoms but one bond, our value for the linear chain matches well the results of McAdon and Goddard.

Bahn and Jacobsen[3] performed density-functional calculations on linear, periodic chains and found an optimized bond length of 5.01 a.u., close to our value and smaller than that of McAdon and Goddard. They did not consider the possibility of a bond-length alternation which, however, because of band-structure effects and according to our work and to that of McAdon and Goddard may be highly relevant. Their results indicate a force constant k_2 of 7.3 eV/bohr^2, i.e., larger than our results and than those of McAdon and Goddard.

The band structures, Fig. 2, show, not surprisingly, that spin–orbit splittings are small. This is in marked contrast to our results for the chains of heavier atoms [i.e., Au (Ref. 8) and Tl, Pb, and Bi (Ref. 9)], where the splittings amounted to more eV and where even in one case (a linear chain of Pb atoms) the spin–orbit couplings changed a metal into a semiconductor. From Fig. 2 we also see that the bands from the generalized-gradient approximation in general are shifted slightly less than 1 eV upwards relative to those of the local-density approximation.

The bands from the local-density calculations split into one set between -10 and -7 eV from the $4d$ orbitals and a broader set between -7 and -2 eV from the $5s$ functions. For the isolated atom numerical calculations give $4d$ orbitals at -8.45 and -7.89 eV (the splitting is due to spin–orbit couplings) and $5s$ orbitals at -5.13 eV, which matches well with the energies of the bands. Also Hong *et al.*[1] find *d*-derived bands with a width of about 3 eV and *s*-derived bands with a width of 5 eV in their theoretical study of the distorted tetragonal chain.

Although the distance between the two individual zig–zag chains constituting the double-zig–zag chain is fairly large, the interactions between the two chains are not so weak that the band structures in Figs. 2(i) and 2(j) simply can be obtained from those of Figs. 2(g) and 2(h) by doubling the number of bands and adding some smaller splittings due to the interchain interactions. In particular, the broad bands crossing the Fermi level show significant splittings (of the order of several eV) that, in addition, are *k*-dependent.

Our results for the tetragonal chain [Figs. 2(k) and 2(l)] show one band crossing the Fermi level very close to $k=0.5$, indicating that a doubling of the unit cell and a simultaneous symmetry-lowering would open up a gap for that band at the Fermi level, thus reducing the density of states at the Fermi energy and giving an explanation for the lower symmetry. Since we have imposed the helical symmetry in our calculations for the tetragonal chain, this symmetry lowering is not considered here. However, the structure considered by Hong *et al.* is markedly different from that of our study, and the just-mentioned effect is partly suppressed, i.e., the band gap opens up above the Fermi level and several bands cross the Fermi level. This result is also found by Zhao *et al.*[18] who, however, studied only the experimental structure of Hong *et al.*

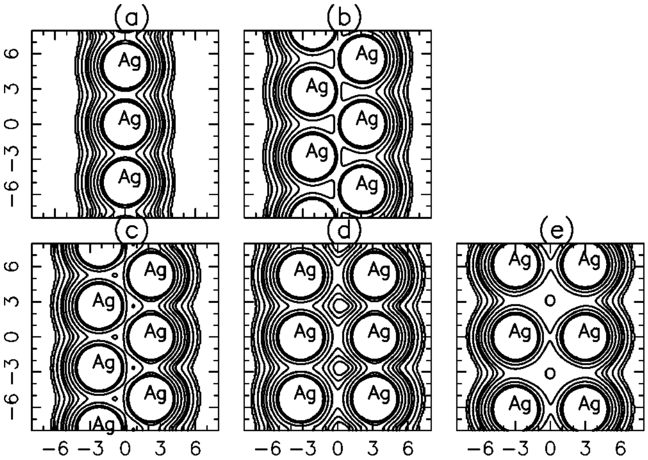

FIG. 3. Electron density for the (a) linear, (b) zig–zag, (c),(d) double-zig–zag, and (e) tetragonal chain outside the inner parts of the muffin-tin spheres. The contour values are 0.003, 0.005, 0.01, 0.02, 0.03, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 a.u.

Finally, McAdon and Goddard[17] estimate that the $5s$-derived band spans the region -9.5 to -3.8 eV, i.e., the band is both at lower energies and broader. Such a difference is common when comparing bands from density-functional and from Hartree-Fock calculations. Moreover, Hartree-Fock calculations on the isolated Ag atom give $5s$ orbitals at -5.99 eV, in fair agreement with the density-functional value, but $5d$ orbitals at -14.62 eV, i.e., significantly lower than in the density-functional calculations.

The electron density, Fig. 3, shows that the density in each zig–zag chain is very similar for the single and for the double zig–zag structure. There is some build-up of electron density between the chains in Fig. 3(d), which partly simply is due to the extension of the atomic orbitals that already for the linear chain, Fig. 3(a), gives an extended electron density. On the other hand, the tetragonal chain is so compact that on the chain axis the electron density is surprisingly homogeneous, cf. Fig. 3(e).

Finally, Table I shows that the double-zig–zag structure is the stablest structure of the ones considered here, and the linear structure the least stable one. The different numbers of nearest-neighbors is clearly one reason for this difference.

IV. CONCLUSIONS

In this work we have presented results of density-functional calculations on isolated thin chains of silver atoms with four overall different types of structures. The optimized structures were characterized by bond lengths somewhere between those of the Ag_2 molecule and of crystalline Ag. This result is in perfect agreement with standard expectations. Moreover, density-functional calculations on smaller Ag_n ($n=2–12$) clusters have given averaged bond lengths of 5.06–5.18 a.u.,[19] whereas coupled-cluster calculations on Ag_n clusters with $n=2–8$ have given bond lengths in the range 4.86–5.27 a.u.[20] Thus, our bond lengths seem to be very realistic.

Our optimized bond lengths were smaller than those of earlier Hartree-Fock studies and close to those of earlier density-functional studies. Moreover, for the nonlinear structures we found bond angles slightly above 60°, in accord with the value (60°) for crystalline Ag.

The largest discrepancies were found for the structures of the tetragonal chains, where the work of Hong *et al.* indicates a close similarity between the optimized structure of an isolated chain and the experimental structure of a chain embedded in an organic matrix. This result is surprising since it suggests that the host has only very little influence on the structure of the chain. Their structure is characterized by a significant distortion that leads to a cross section significantly different from a square. Our band structures for the optimized high-symmetry structure lead support for the occurrence of such a distortion, but in their structure the distortion is so large that the band-structure effects (i.e., a reduction of the density of states at the Fermi level) are suppressed.

The band structures indicated that all systems are metallic. This conclusion was obtained irrespective of whether spin–orbit couplings were included or not and was, accordingly, different from what we earlier have found[9] for linear Pb chains that became semiconducting when the spin–orbit couplings were included. For elongated linear Au chains we have found[8] a tendency towards bond-length alternation that opens up a gap at the Fermi level. In the present work, the same behavior was found for linear Ag chain in their equilibrium structure.

The electron density showed that the electrons are delocalized over the major parts of the chains. For the tetragonal chain, the electron density in the interior was surprisingly homogenous, which may be due to the fact that this chain can be constructed as a quasi-one-dimensional part of the crystalline structure. A similar behavior was not seen for the double-zig–zag chain.

Finally, our calculated force constants for compression/stretching along the chain axis were smallest for the linear chain (where the value, moreover, agreed well with values for the Ag_2 molecule but was smaller than that of an earlier density-functional study), suggesting that this structure is mechanically less stable than the others.

In total our study has revealed that although the different types of ultrathin Ag chains that we have considered have many similar properties (e.g., bond lengths, band structures, etc.), there are also structure-specific properties that make each type of chain unique. Therefore, synthesis approaches like the one of Hong *et al.* but extended to allowing for new types of guest chains as well as making it possible to vary the length of the repeat unit (assuming that the host–guest interactions are stronger than what is indicated in the work by Hong *et al.*) may be a very promising way of producing new nanoscaled materials with controlled properties.

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