Theor Chem Acc (2009) 123:85–92
DOI 10.1007/s00214-009-0536-x

REGULAR ARTICLE

Uniform linear chains of group 11 atoms: do they have a bias towards a Peierls distortion?

Pere Alemany · Miquel Llunell · Enric Canadell

Received: 10 February 2009 / Accepted: 11 February 2009 / Published online: 3 March 2009

Abstract The possible occurrence of a Peierls distortion in metallic uniform linear chains of group 11 atoms is examined on the basis of first-principles DFT calculations and orbital interaction analysis. It is found that, contrary to expectations based on the fact that these systems must possess a half-filled one-dimensional band, none of the three chains of atoms is susceptible to a Peierls dimerization. It is shown that both strong s–z^2 mixing and d^{10}–d^{10} repulsions are at the heart of this unexpected result. The relationship of these results with the presence of uniform silver chains in the recently reported $(Ca_7N_4)[Ag_{\sim 1.33}]$ phase is discussed.

Keywords Peierls distortions · Linear chains · DFT calculations · Silver · Gold · Copper

1 Introduction

Very recently, Kniep et al. [1] reported the synthesis of an interesting metallic ternary phase, $(Ca_7N_4)[Ag_{\sim 1.33}]$, in which uniform linear chains of silver atoms occur inside the channels of the three-dimensional Ca_7N_4 host. The structural analysis suggested that the silver atoms occur as neutral and that the host–guest interactions are very weak. Thus, to the best of our knowledge, $(Ca_7N_4)[Ag_{\sim 1.33}]$ is the only well characterized material containing uniform linear chains of neutral silver atoms. Silver, with a complete d-block and a single electron in the s orbital, is a textbook case of a system which should undergo a Peierls type dimerization when occurring as a linear uniform chain. Consequently, it is challenging to understand if the absence of dimerization (and thus the observed metallic behavior) in this ternary nitride is an intrinsic property of the silver chain, a consequence of strong host–guest interactions or a combination of both factors [2]. Here we would like to concentrate on the possible occurrence of a Peierls distortion in the isolated linear silver chains.

Few concepts in solid state science are as useful and ubiquitous as that of the Peierls distortion [3]. It provides a simple way to understand the origin of a plethora of structural distortions [4] as well as the correlation between the structure and conductivity of many low-dimensional solids [5, 6]. Essentially this is the solid state counterpart of the Jahn–Teller effect in molecules, i.e. the tendency for a solid with partially filled band(s) to undergo a symmetry-lowering distortion which splits the degenerate levels into filled and empty ones. For a one-dimensional (1D) system with a partially filled band it is always possible to fold the Brillouin zone so that the border of the new zone lies at the Fermi level [3]. This means that the wave functions for the two Fermi wave vectors (k_f and $-k_f$), which initially could not mix because they were associated with different k-points, in the new Brillouin zone have been translated into the same k-point and can interact through the coupling of electronic and vibrational motions. Since there are electrons to fill just one of the two states, one of the levels is stabilized

---

Dedicated to Professor Santiago Olivella on the occasion of his 65th birthday and published as part of the Olivella Festschrift Issue.

P. Alemany (✉) · M. Llunell
Departament de Química Física, Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona,
Diagonal 647, 08028 Barcelona, Spain
e-mail: p.alemany@ub.edu

E. Canadell (✉)
Institut de Ciència de Materials de Barcelona (CSIC),
Campus de la Universitat Autònoma de Barcelona,
08193 Bellaterra, Spain
e-mail: canadell@icmab.es

and becomes occupied, while the other is destabilized and becomes empty. The kind of distortion is thus completely determined by the filling of the band. For example, if the system is *half-filled*, the Brillouin zone must be folded once, i.e. the size is reduced to one-half, which means that the repeat unit in real space must be *doubled*. In general, for a 1D band which is $1/p$ filled, the Brillouin zone must be p times smaller and the unit cell must become p times larger. Thus, the Peierls distortion associated with a $1/p$-filled 1D band is a p-merization and the electronic driving force for the distortion is thus the mixing between degenerate states at the Fermi level. When there is more than one partially filled band or the system is not perfectly one-dimensional, the possibility of a Peierls instability is more conveniently discussed in terms of Fermi surface nesting [5, 6].

Systems which do not undergo a Peierls distortion, even if they apparently should do, have been known for a long time. $Na_3Cu_4S_4$ [7] and BTDMTTF–TCNQ (BTDMTTF: (bis(thiodimethylene)-tetrathiafulvalene, TCNQ: tetracyanoquino dimethane) [8] are two examples of 1D metals which remain metallic until low temperatures without undergoing any kind of structural modulation. As a matter of fact, this is not so surprising. The usual explanation for the occurrence of a Peierls distortion goes as follows. For a one-dimensional metal, a periodic lattice modulation of amplitude u and wave vector $q = 2k_f$, where k_f refers to the Fermi wave vector, opens an energy gap 2Δ at the Fermi level. The energy of the occupied states is lowered and in the case of small amplitudes of the distortion, the electronic energy gain is proportional to $-u^2 \ln u$, which is larger than the cost in elastic energy against the distortion, proportional to u^2. Consequently, the system is predicted to be unstable against the distortion at low enough temperature [9]. However, Littelwood and Heine [10] pointed out that this argument is not really correct because the electron–electron interactions have not been explicitly included in the derivation. There is an extra potential felt by the electrons due to the fact that the electron distribution suffers a deformation as a result of the distortion so that there is an extra Coulomb interaction between the electrons and such a charge distortion. In other words, there is a screening of the potential that an electron feels which, when properly included, leads to an electronic energy gain proportional to $-u^2$ [10]. Consequently, *there is no guarantee of the occurrence of the distortion*, which depends on the net balance between the two quadratic terms, the electronic energy gain ($\propto -u^2$) and the usual elastic forces ($\propto u^2$). Thus, exceptions are expected. However, since for low-dimensional systems the occurrence of the Peierls distortion, which dramatically changes the conductivity of the system, is quite often the rule, it is important to understand the reasons why some systems do not exhibit it even if they apparently fulfill the necessary conditions.

The electronic structure of silver and gold linear chains has been the object of several first-principles density functional theory (DFT) studies [11–21] stimulated by the preparation of monoatomic chains of gold atoms [22–24]. However, the situation with respect to the possibility of a Peierls distortion, especially for silver, is not yet completely clear. For instance, Springborg et al. [11, 12] mentioned that linear chains of silver atoms exhibit a bond length alternation and lose their metallic character, but no details were given. Linear chains of gold atoms are unstable towards a distortion towards a zigzag geometry [14–16] but this is not a Peierls distortion. A bond length alternation was proposed for the gold linear chains but only when they are stretched just before the wire breaks [14, 15, 19]. The apparent difference between the silver and gold chains is not obvious. In this work, we examine if isolated[1] *metallic* uniform linear chains of group 11 atoms undergo a Peierls distortion on the basis of first-principles DFT calculations and orbital interaction arguments. We also briefly comment on the nature of the silver chains in the recently reported $(Ca_7N_4)[Ag_{\sim 1.33}]$ phase.

2 Computational details

Band structure calculations were carried out using a numerical atomic orbitals DFT approach, which has been developed and designed for efficient calculations in large systems and implemented in the SIESTA code [25–27]. We have used the generalized gradient approximation to DFT and, in particular, the functional of Perdew et al. [28]. Only the valence electrons are considered in the calculation, with the core being replaced by norm-conserving scalar relativistic pseudopotentials [29] factorized in the Kleinman–Bylander form [30]. Nonlinear partial core corrections to describe the exchange and correlations in the core region were used for Cu and Ag [31]. We have used a split-valence double-ζ basis set including polarization orbitals for all atoms. The $3d$ electrons of Cu, the $4d$ electrons of Ag, and the $5d$ electrons of Au were treated also as valence electrons. These basis sets have been optimized in order to reproduce the geometry and the bulk modulus for the crystal structures of each metal. Calculations for the chains were performed by imposing periodic boundary conditions with a separation of 10 Å between neighboring chains. The energy cutoff of the real space integration mesh was 350 Ry. The Brillouin zone was sampled using a grid of 500 k-points in the direction corresponding to the metal chains [32]. Spin–orbit coupling effects were not taken into

---

[1] Here we will not consider at all the case of deposited linear chains because the interaction with the substrate modifies the charge and electronic structure of the chain.

account because previous studies showed that they are not relevant for the type of structural distortions studied in this work [11–14].

3 Results and discussion

The optimized uniform linear chains of copper, silver and gold atoms have been found to exhibit atom–atom distances of 2.25 Å (Cu), 2.60 Å (Ag) and 2.65 (Au) Å in our study.[2] These values are very similar to those obtained in previous first-principles studies for gold and silver chains [11–21]. Shown in Fig. 1 are the calculated band structures for the three uniform noble metal chains. Since the calculations have been carried out with a repeat unit of two atoms, all bands are folded. Although this is somewhat artificial, in the following we will refer to the folded bands as two different bands which touch at Z. The band structure of the silver chain (Fig. 1b) exhibits a series of five pairs of d-bands below the wide pair of s-bands. The upper and lower bands of the group of d-bands are built from the z^2 orbitals and they are nondegenerate (in our coordinate system the z axis goes along the chain). These are the wider bands because they result from σ-type interactions. The second and fifth d-bands are doubly degenerate because of the axial symmetry of the chain and are made of the xz and yz orbitals which make π-type interactions along the chain. Finally, the third and fourth d-bands are also doubly degenerate and are built from the xy and x^2–y^2 orbitals which make δ-type interactions and are thus very narrow. There is a gap of 1 eV separating the top of the d-bands and the bottom of the s-band so that there are two electrons to fill the lower s-band and the Fermi level lies at the border of the Brillouin zone (Z). Thus, the conditions to expect a Peierls dimerization are fulfilled for the silver chain.

The situation is different, however, for both the copper (Fig. 1a) and gold chains (Fig. 1c). For these chains there is no energy gap separating the s- and d-bands. This has no major consequences if the top of the d-bands overlaps only with the lower s-band, because the Fermi level will always cut the s-bands at the Z point. However, if the top of the d-bands overlaps with the upper s-band, the filling of the bands necessarily changes. The overlap between the top of the d-bands and the bottom of the upper s-band is very small according to the present calculations but we note that it has also been found in previous calculations for the gold chains [13, 15, 16]. This overlap may considerably depend of the atom–atom distance and consequently, of the computational methodology used. Although the overlap may strongly influence the possibility and nature of the Peierls distortion it is not possible at this point to safely conclude what is the real situation and we can only discuss what the different possibilities are. Essentially there are four likely possibilities. First, the d-bands are slightly lowered and the overlap with the upper s-band disappears. In that case we are in the same situation as in the silver chain and a dimerization may be expected. Second, the top z^2-band is the only band overlapping with the upper s-band. Since the two bands are nondegenerate, the Fermi wave vector associated with the top z^2-band will be k_1 (in units of the reciprocal vector c^*) and that of the upper s-band will be $0.5 - k_1$. This means that there is an interband nesting vector equal to $0.5c^*$, which will open a gap at the Fermi level for both bands and lead also to a dimerization. Third, there is an overlap between the top of the degenerate e-type xz/yz bands and the upper s-band (for instance this is the situation found for the gold linear chain in Ref. [15]). In that case, because of the different symmetry of the partially filled bands, there is no way to open a gap at the Fermi level simultaneously in the s- and e-type bands through a Peierls distortion. The only possibility would be to open a gap in either the e-bands (with nesting vector $2k_1$ in units of the reciprocal vector c^*, where k_1 is the Fermi wave vector for these bands) or in the s-band (with nesting vector $2(0.5 - k_2) = 2(0.5 - 2k_1) = 1 - 4k_1$). However, these will always be incommensurate distortions which in general have a small driving force and will not open a gap in the other type of band. Thus, it is most likely that the system will stay undistorted and metallic. Fourth, both the top of the z^2- and xz/yz-bands overlap with the upper s-band. In that case the number of holes in the z^2-band will not be the same as the number of electrons in the s-band. Thus, both the interband nesting vector allowing the opening of gaps in the s- and z^2-bands and the intraband nesting vectors will be incommensurate and will not open gaps in all the bands so that, again, the system will most likely remain undistorted and metallic. In conclusion, only if the xz/yz-bands do not overlap with the upper s-band, the expected Peierls dimerization may be observed in the copper and gold chains, provided that the cost in elastic energy does not overcome the electronic energy gain.

We then studied the possible Peierls dimerization for the silver linear chain. Thus for different values of the equilibrium distance in the uniform chain, d, we have studied the energy of the system as a function of the parameter u by allowing successive bonds to become $d + u$ and $d - u$, respectively. Some of the results obtained with different values of d are summarized in Fig. 2b. It is clear that the uniform chain does not undergo a Peierls distortion which only occurs for stretched chains. The same results have been found for the copper and gold chains (Fig. 2a and c). Slight minima for the dimerized chains start to appear for

---

[2] Note that in our study of the $(Ca_7N_4)[M_x]$ phases (M = Ga, Ag, In) [2] we have used a slightly different basis set and pseudopotential for silver.

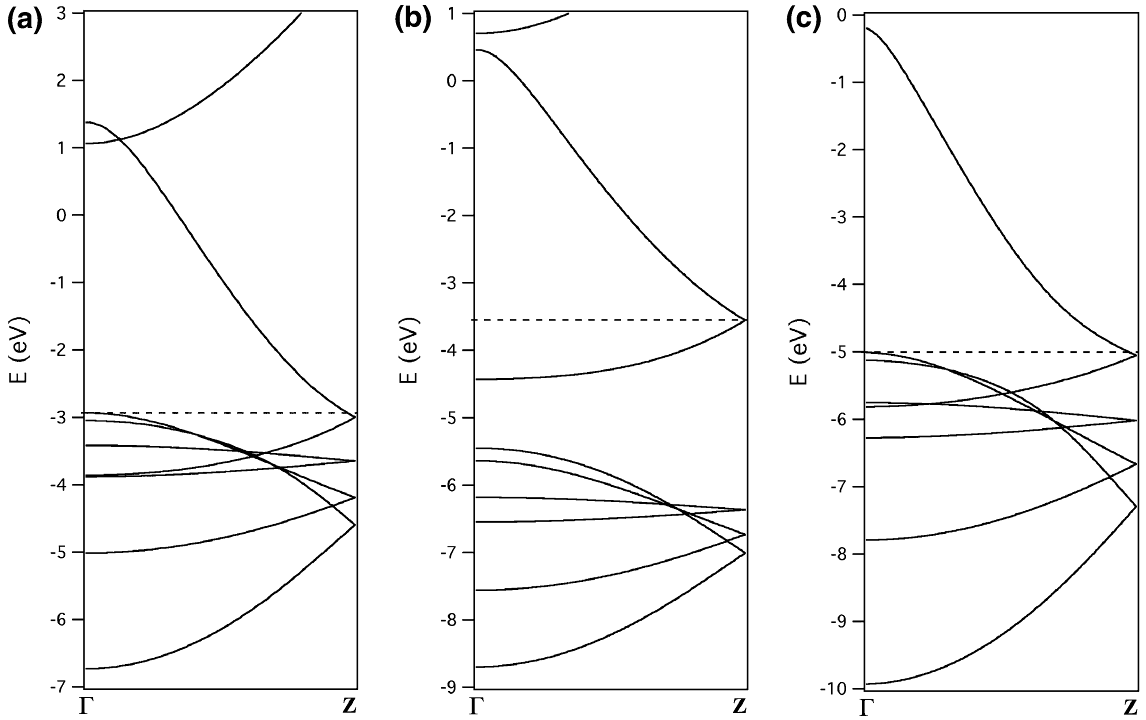

Fig. 1 Calculated band structures for the optimized uniform linear chains of: **a** copper, **b** silver and **c** gold atoms. The *dashed lines* refer to the Fermi level

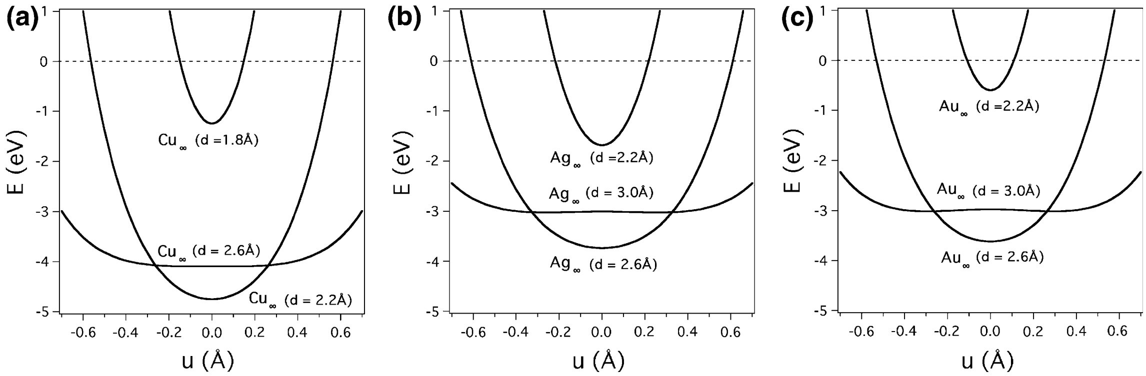

Fig. 2 Energy versus the distortion parameter *u* for different linear chains of: **a** copper, **b** silver and **c** gold. The origin of the energy scale refers to the non interacting atoms

stretched regular chains with distances of ~2.7 Å (Cu), ~2.9 Å (Ag) and ~2.9 Å (Au). Note that in the stretched chains the *d*-bands are lowered with respect to the *s* ones and the copper and gold chains recover the situation of the silver chain. However, even for these stretched chains the energy stabilization due to the dimerization is always very small, as found in previous first-principles studies of the gold chains [15, 19]. Thus, it can be concluded that the group 11 atom linear chains will stay uniform and keep the metallic character even if a Peierls dimerization could have been expected on the basis of simple electron counting arguments.

In order to find the reason underlying this observation we must come back to the band structure of the silver chain. We report in Fig. 3 the band structure for the regular and dimerized chains ($u = 0.2$), in both the optimum and somewhat stretched ($d = 3.0$ Å) geometries. The most striking observation is that the gap opened at the border of the Brillouin zone (Z) for the *s*-bands of the silver chain upon dimerization is small and does not change very much upon stretching the regular chain from 2.6 to 3.0 Å. This is not at all what is expected for a system having a clear bias towards a Peierls distortion. For instance, the hydrogen chain follows what we may consider the expected behavior,

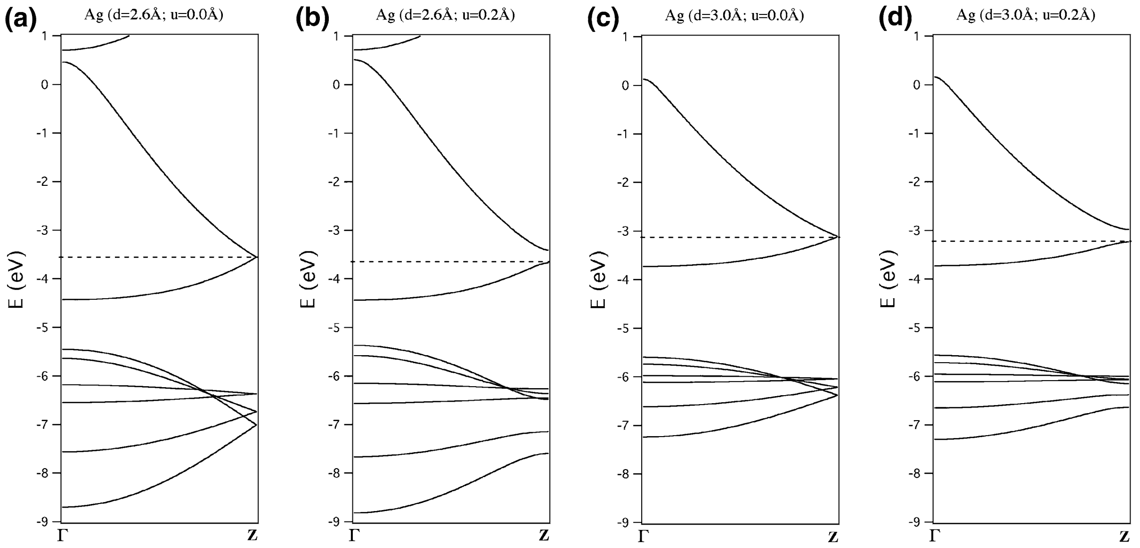

Fig. 3 Calculated band structure near the Fermi level for chains of silver atoms with: **a** $d = 2.6$ and $u = 0.0$ Å, **b** $d = 2.6$ and $u = 0.2$ Å, **c** $d = 3.0$ and $u = 0.0$ Å, and **d** $d = 3.0$ and $u = 0.2$ Å

i.e., a substantial gap opens at the Fermi level and the gap decreases with the increase of the H–H distance in the reference uniform chain. For instance the gap is 5.1 eV for the hydrogen chain with $d = 1.0$ Å, the equilibrium distance of the uniform chain, and $u = 0.2$ Å, whereas it is 2.6 eV for $d = 1.4$ Å and $u = 0.2$. It is even more surprising to realize that the dimerization in the silver chain opens considerably larger gaps at Z for the d-bands (i.e. approximately 1.2 eV for the z^2-band and 0.8 eV for the xz/yz-bands for $d = 2.6$ Å and $u = 0.2$). However, the opening of these gaps in the d-type bands cannot have any major influence in the total energy because both the stabilized and destabilized bands are occupied. This feature points towards a very small electronic driving force towards the Peierls distortion for the chain.

The reason behind this observation is easy to understand once it is realized that the s pair of bands have a very unusual shape, with a very flat lower component while the upper component is very dispersive. When unfolded, the band would be very far from the more usual cosine-like shape of the hydrogen chain. This clearly indicates that the bottom s-band must result from the hybridization with a lower lying d-type band which thus pushes up its lowest part, leading to a relatively flat band. Ultimately, this is the reason for the small gap opening by the dimerization since it means that the band is not strongly Ag–Ag bonding/antibonding and consequently the distortion cannot strongly lower/raise the degenerate bands at Z and provide a strong driving force for the Peierls distortion. Because of the symmetry properties of the chain, the lower s-band at Γ can only mix with the lower z^2-band (i.e. the lowest d-band), which is an in-phase combination of z^2 orbitals (see Fig. 4a), in a way that is stabilizing (in-phase) for the z^2-band. In contrast, the lower z^2-band at Γ mixes in a destabilizing way (out-of-phase) with the s-band, which is an in-phase combination of s orbitals (Fig. 4b). As schematically shown in Fig. 4, this hybridization strengthens the Ag–Ag bonding in the bottom z^2-band by increasing the weight of the lobes directed along the chain in the wave function (see Fig. 4c). In contrast, the out-of-phase mixing of the z^2 orbitals into the s-band deforms it in such a way that the wave function strongly decreases in the internuclear region while increasing around the planes perpendicular to the chain and containing the Ag atoms, i.e. it moves electron density from the internuclear region to the directions outside the chain (see Fig. 4d). This leads to an almost nonbonding type of wave function which is quite immune to changes in the Ag–Ag bond lengths. Inspection of the wave function shows that this kind of mixing occurs for most of the lower s-band which thus appears as quite flat and cannot lead to a significant gap opening at Z. At Z, this mixing is forbidden by symmetry and the wave function is thus a nonbonding combination of s orbitals. However, when the dimerization occurs the mixing becomes allowed, and thus it further helps in making the band gap quite small. For the upper s-band this kind of hybridization is not operative and the wave function is almost purely s in character so that the band recovers the expected antibonding behavior, rising very strongly. Using an unfolded band description we can thus conclude that s–z^2 mixing, leading to an almost nonbonding lower half of the

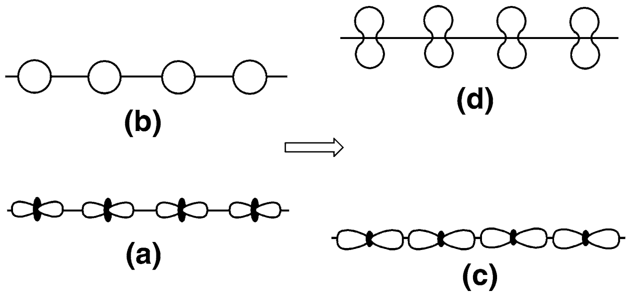

Fig. 4 Schematic diagram showing the nature of the *s*–*d* hybridization affecting the lower z^2 and *s*-bands at the Γ point: **a** and **b** are the crystal orbitals of the lower z^2 and *s*-bands before hybridization and **c** and **d** are the same crystal orbitals after hybridization

formally *s*-band, is ultimately responsible for the lack of a substantial electronic driving force for the Peierls distortion in the linear silver chain. Exactly the same conclusion applies to copper and gold chains.

We can summarize the situation saying that because of the s–z^2 hybridization, most of the σ bonding along the chain associated with the *s* orbitals is transferred to the completely filled z^2 band optimizing the stability of the uniform chain which, consequently, does not need to undergo any pairing distortion to optimize the bonding. The chains of group 11 atoms are thus quite peculiar in the sense that the gap opening does not lead to a large $-u^2$ stabilization of the electronic energy, and thus, the total energy change upon dimerization is dominated by the cost in elastic energy.

However, this scenario is still incomplete. It is a commonly accepted and well substantiated notion that an increase of the coordination around a given atom decreases the strength of the corresponding bonds. Our calculations for bulk, uniform chain and dimer of silver led to Ag–Ag distances of 2.9, 2.6 and 2.55 Å, respectively. The calculated decrease when going from bulk to the uniform chain is the expected one. However, the decrease from the uniform chain to the dimer is too small and clearly indicates that there is something opposing the tendency to shorten the Ag–Ag bond in the dimer. Not unexpectedly, given the small difference in bond lengths, the dimer is calculated to be 0.63 eV/atom less stable than the uniform chain. Similar results were found for copper and gold: the distances in the isolated dimers, 2.15 Å (Cu) and 2.55 Å (Au), were found to be only slightly shorter than those in the uniform chain, 2.25 Å (Cu) and 2.65 Å (Au), and the chain is more stable than a collection of non-interacting dimers by 0.78 (Cu) and 0.55 (Au) eV/atom. Analysis of the different contributions to the total energy of the uniform chain and the dimer showed that it is the electron repulsion term which is strongly disfavoring the dimer. These electron repulsions originate in the d^{10}–d^{10} repulsions which are substantially larger in the dimer and do not allow the two atoms to approach sufficiently to fully achieve their bonding capability.

Thus, the *d* orbitals of the group 11 atoms are responsible for the unexpected absence of Peierls dimerization in their uniform linear chain by leading to a small electronic driving force for the distortion ($\propto -u^2$) while, at the same time, providing a substantial contribution to the elastic force ($\propto u^2$) opposing the distortion. Only for elongated chains, when the electron repulsions have decreased below a certain limit, an incipient dimerization may occur (see Fig. 2). Note also that both copper and gold chains are stiffer than the silver one (see Fig. 2). According to our discussion this must, at least partially, originate from stronger d^{10}–d^{10} repulsions which, in turn, must raise the *d*-bands with respect to the *s*-bands of the uniform chains, as observed in Fig. 1. Thus, linear chains of group 11 atoms are expected to stay uniform and keep their metallic properties, except maybe when stretched to near their breaking point where a very weak Peierls distortion can be possible, something which harmonizes with the observation that gold chains (though short) are good conductors, even at very low temperatures [24].

We thus conclude that the recent finding of uniform linear chains of silver atoms inside the channels of the Ca_7N_4 framework in $(Ca_7N_4)[Ag_{\sim 1.33}]$ [1], as well as the metallic properties of this compound, do not lead to any conceptual problem, even if the host–guest interaction is very weak and the silver atoms are neutral. Let us point out that uniform linear chains of silver atoms, like those of gold, are unstable with respect to the distortion towards a zigzag chain [11–16]. This suggests that by preparing $(Ca_7N_4)[Ag_{\sim 1.33}]$, Kniep et al. [1] have nicely succeeded in creating the conditions for observing uniform chains of silver atoms for the first time, i.e. a structure containing channels of the right dimensions to accommodate silver atoms in weak interaction with the host and avoiding formation of zigzag chains. In order to check this point we have carried out calculations for $(Ca_7N_4)[Ag_{\sim 1.33}]$. We have used a unit cell containing three repeat units of the (Ca_7N_4) host and a commensurate uniform linear chain with four silver atoms as the repeat unit in the center of the channels. We have found that the Fermi level of the system cuts bands highly dispersive along the c^* direction, in agreement with the metallic character of the phase. However, analysis of the wave function shows that there is a substantial interaction between the calcium atoms of the Ca_7N_4 host and the chain of silver atoms. For instance, 33% of the calculated density of states at the Fermi level is associated with the silver atoms and 66% with the Ca_7N_4 host. There is an electron transfer from the Ca_7N_4 host to the silver chains of 0.48 electrons (in average) per silver atom, associated with the mixing of the crystal orbitals of the host and silver chain. This results in an average overlap population of 0.635 between a silver atom of the chain and the host. These results clearly show that there is a substantial interaction between the Ca_7N_4 host and the uniform linear silver chains so that, it does not seem plausible to consider that the recently prepared phase $(Ca_7N_4)[Ag_{\sim 1.33}]$ contains neutral, very weakly interacting, uniform linear silver chains. However, the fact that the linear chain keeps its uniform nature, within the limits of the experimental determination, despite different local environments for the different silver atoms is a clear indication of the intrinsic stability of the uniform chain. Although for the time being uniform linear chains of group 11 atoms have not been observed, we believe that there is no reason why it should not be possible, provided that the instability towards the zigzag chain can be avoided.

4 Concluding remarks

The present study has shown that linear chains of Cu, Ag and Au atoms are not expected to undergo a Peierls type dimerization, despite the fact that they have a complete *d*-block and a single electron in the *s* orbital. Needless to say, this observation does not cast any shadow on the usefulness of the Peierls instability concept but reminds that, as noted earlier by Littelwood and Heine [10], exceptions may and do occur. Simple electron counting arguments suggesting that a system possesses a 1/*p*-filled 1D (or pseudo-1D) band should not be taken as a warranty that the system must necessarily undergo a Peierls *p*-merization without a careful analysis of the actual electronic structure. For instance, the structure of rhombohedral phosphorous, the arsenopyrite type structure of the recently prepared IrN_2, or the dimerized structure of edge-shared NbX_4 ($X = Cl, I$) octahedral chains are some systems which were considered to result from a Peierls distortion, but the analysis of their electronic structures has shown that this is not the case [33, 34]. Although experimentally challenging, we believe that observation of metallic uniform chains of group 11 atoms may be possible if their tendency to favor zigzag chains is prevented by inserting them in narrow enough channels of an appropriate host material.

Acknowledgments We are indebted with P. Ordejón for enlightening discussions. This work was supported by the Spanish Ministerio de Educación y Ciencia (Projects FIS2006-12117-C04-01, CSD2007-00041, and CTQ2008-06670-C02-02/BQU) and Generalitat de Catalunya (Projects 2005 SGR 683 and 2005 SGR 00036). Part of the computations described in this work were carried out using the facilities of CESCA.

References

1. Höhn P, Auffermann G, Ramlau R, Rosner H, Schnelle W, Kniep R (2006) Angew Chem Int Ed 45:6681. doi:10.1002/anie.200601726
2. Alemany P, Llunell M, Canadell E (2008) Inorg Chem (in press)
3. Peierls RE (1955) Quantum theory of solids. Oxford University Press, London
4. Hoffmann R (1988) Solids and surfaces: a Chemist's view of bonding in extended structures. Wiley, New York
5. Wilson JA, Di Salvo FJ, Mahajan S (1975) Adv Phys 24:117. doi:10.1080/00018737500101391
6. Canadell E, Whangbo M-H (1991) Chem Rev 91:965. doi:10.1021/cr00005a015
7. Peplinski Z, Brown DB, Watt T, Hatfield WE, Day P (1982) Inorg Chem 21:1752. doi:10.1021/ic00135a010
8. Tarrés J, Llorca J, Molins E, Veciana J, Rovira C, Yang S, Cowan DO, Garrigou-Lagrange C, Amiell J, Delhaes P, Canadell E, Pouget JP (1995) Phys Rev B 52:8747. doi:10.1103/PhysRevB.52.8747
9. Moret R, Pouget JP (1986) In: Rouxel J (ed) Crystal chemistry and properties of materials with quasi-one-dimensional structures, Reidel, Dordrecht
10. Littlewood PB, Heine V (1981) J Phys Solid State Phys 14:2943. doi:10.1088/0022-3719/14/21/012
11. Springborg M, Sarkar P (2003) Phys Rev B 68:045430. doi:10.1103/PhysRevB.68.045430
12. Springborg M (2003) J Solid State Chem 176:311. doi:10.1016/S0022-4596(03)00209-3
13. De Maria L, Springborg M (2000) Chem Phys Lett 323:293. doi:10.1016/S0009-2614(00)00541-8
14. Asaduzzaman AM, Springborg M (2005) Phys Rev B 72:165422. doi:10.1103/PhysRevB.72.165422
15. Sanchez-Portal D, Artacho E, Junquera J, Ordejón P, García A, Soler JM (1999) Phys Rev Lett 83:3884. doi:10.1103/PhysRevLett.83.3884
16. Ribeiro FJ, Cohen ML (2003) Phys Rev B 68:035423. doi:10.1103/PhysRevB.68.035423
17. Torres JA, Tosatti E, Dal Corso A, Ercolessi F, Kohanoff JJ, Di Tolla FD, Soler JM (1999) Surf Sci 426:L441. doi:10.1016/S0039-6028(99)00333-7
18. Bahn S, Jacobsen KW (2001) Phys Rev Lett 87:266101. doi:10.1103/PhysRevLett.87.266101
19. Nakamura J, Kobayashi N, Watanabe S, Aono M (2001) Surf Sci 482–485:1266. doi:10.1016/S0039-6028(01)00865-2
20. Okamoto M, Takayanagi K (1999) Phys Rev B 60:7808. doi:10.1103/PhysRevB.60.7808
21. Häkkinen H, Barnett RN, Landman U (1999) J Phys Chem B 103:8814. doi:10.1021/jp992787p
22. Onishi H, Kondo Y, Takayanagi K (1998) Nature 395:780. doi:10.1038/27399
23. Yanson AI, Rubio Bollinger G, van den Brom HE, Agraït N, van Ruitenbeck JM (1998) Nature 395:783. doi:10.1038/27405
24. Agraït N, Levy Yeyati A, van Ruitenbeek JM (2003) Phys Rep 377:81. doi:10.1016/S0370-1573(02)00633-6
25. Soler JM, Artacho E, Gale JD, García A, Junquera J, Ordejón P, Sánchez-Portal D (2002) J Phys Condens Matter 14:2745. doi:10.1088/0953-8984/14/11/302
26. For more information on the SIESTA code visit: http://www.uam.es/siesta/
27. For a review on applications of the SIESTA approach to materials science see: Sánchez-Portal D, Ordejón P, Canadell E (2004) Struct Bonding 113:103
28. Perdew JP, Burke K, Ernzerhof M (1996) Phys Rev Lett 77:3865. doi:10.1103/PhysRevLett.77.3865

29. Trouiller N, Martins JL (1991) Phys Rev B 43:1993. doi: 10.1103/PhysRevB.43.1993
30. Kleinman L, Bylander DM (1982) Phys Rev Lett 48:1425. doi: 10.1103/PhysRevLett.48.1425
31. Louis SG, Froyen S, Cohen ML (1982) Phys Rev B 26:1738. doi: 10.1103/PhysRevB.26.1738
32. Monkhorst HJ, Park JD (1976) Phys Rev B 13:5188. doi: 10.1103/PhysRevB.13.5188
33. Seo D-K, Hoffmann R (1999) J Solid State Chem 147:26. doi: 10.1006/jssc.1999.8140
34. Hernández ER, Canadell E (2008) J Mater Chem 18:2090. doi: 10.1039/b718857a