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# Quasi-one-dimensional materials: polymers and chains

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## Abstract

Results of density-functional calculations on materials that can be considered being quasi-1D are reported. The materials include some based on carbon (fullerene nanotubes and a polyynes), chains of metal atoms (Pb, Au, and Ag), and charged chains as building blocks of crystals (PtS<sub>2</sub> chains surrounded by K atoms and NiN chains separated by Ca atoms). In many cases it is found that 2D or 3D behaviors can be recognized, but in some cases the smaller changes due to the change from true 3D or 2D to quasi-1D have profound effects.

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## 1. Introduction

One of the central issues of chemistry, physics, and materials science is that of understanding, predicting, and exploiting the relations between materials properties on the one side and their structure and composition on the other side. Most studies to this correlation have concentrated on the role of composition on the materials properties, but it is also well-known (cf. graphite vs. diamond) that the structure may have significant impact on the materials properties. In recent years, the development of various experimental methods has made it possible to also produce materials with other dimensions than those usually encountered in nature and it has been found that the properties and electronic structure of low-dimensional materials, most notably quasi-1D and quasi-0D materials, may differ markedly from the properties of truly 3D materials. Such low-dimensional materials include, for example, artificially grown semiconductor structures like quantum dots and quantum wires, 2D layers that show strong quantum behavior such as the quantum Hall effect, the high  $T_c$  superconductors, chain compounds, and fullerene nanotubes.

It is the purpose of this contribution to present results of theoretical studies of various quasi-1D materials. In particular we shall show how their properties differ from those of related 3D materials. We shall concentrate on

three classes of materials, i.e., carbon-based materials like metal-containing conjugated chains and small fullerene nanotubes, chains of metal atoms, and, finally, crystalline compounds containing charged chains.

## 2. Computational details

We have applied two computational methods that both are based on the Hohenberg–Kohn density-functional formalism [1] in the formulation of Sham and Kohn [2]. The single-particle equations

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

are solved by expanding the eigenfunctions in a set of augmented waves. These are either spherical or plane waves that inside non-overlapping, atom-centered, so-called muffin-tin spheres are augmented continuously and differentially with numerically represented functions.

For isolated, single chains that are assumed to be infinite, periodic, and helical [3,4], the waves are spherical waves, i.e., spherical Hankel functions times spherical harmonics,  $h_l^{(1)}(\kappa|\vec{r}-\vec{R}|)Y_{lm}(\mathbf{r}-\mathbf{R})$ , where  $\vec{R}$  specifies the atom where the function is centered,  $|\kappa|$  is a decay constant ( $\kappa$  is imaginary), and  $(l, m)$  describes the angular dependence of the function. On the other hand, for 3D crystalline materials we use plane waves  $e^{i\vec{k}\cdot\vec{r}}$  [5]. In both cases, the numerically represented functions inside the spheres are obtained by solving Eq. (1) when

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replacing  $V(\vec{r})$  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.

### 3. Carbon-based systems

The ability of carbon to form bonds via  $sp$ ,  $sp^2$ , and  $sp^3$  hybrids gives carbon an enormous flexibility when being part of the most different types of systems. Moreover, whereas materials based on  $sp^3$ -hybridized carbon atoms most often are large-gap insulators, those based on  $sp^2$ - or  $sp$ -hybridized atoms tend to be semiconductors or semimetals. Here, we shall explicitly concentrate on materials that are quasi-1D, and only upon passing comparing with graphite as a quasi-2D material.

#### 3.1. Small fullerene nanotubes

Carbon nanotubes were discovered in 1991 by Iijima [6]. Their structure may be considered as obtained by rolling a graphite sheet of finite width, and as long as the diameter of the nanotube is not too small, the electronic properties of the graphite sheet prevail for the nanotube. There is, however, an important difference: Whereas the graphite sheet can be considered as a 2D material, the fullerene nanotube is a quasi-1D material. Therefore, as has been discussed in detail elsewhere (see, e.g., [7]) the electronic band structures of the fullerene nanotubes can be obtained by considering only certain lines in the 2D  $\vec{k}$  space for a graphite sheet depending on the diameter and chirality of the nanotube. This means, furthermore, that only some of the nanotubes will be (semi-)metallic, depending on whether  $\vec{k} = (0, 0)$  is lying on one of those lines or not.

Within this picture the separation of the electronic orbitals into those of  $\sigma$  and those of  $\pi$  symmetry is still a good approximation. When the diameter of the nanotubes becomes smaller, this separation is no longer good, and the orbitals of  $\sigma$  and  $\pi$  symmetry start to mix. Until recently, this was merely a theoretical issue, since these small-diameter nanotubes possess a large strain and, therefore, are less stable than the larger ones. However, recently such thin nanotubes have been synthesized [8].

In one of the first theoretical studies of these thin nanotubes [9], we used the above-mentioned single-chain code in studying the structural and electronic properties of some of the absolutely thinnest ones one can think of. A main result was that the curvature-induced strain was sought released by increasing the diameter of the nanotube and simultaneously reducing

the lengths of the bonds roughly parallel to the tube axis. But we also found that for many of them more bands were crossing the Fermi level, making the nanotubes metallic and making the band structures being at variance with the simplest graphite-sheet model where the band structures can be derived from those of a graphite sheet. Other nanotubes, on the other hand, were found to be semiconducting.

As an illustration of the curvature effects, we show in Fig. 1 the frontier orbitals for some of the optimized small nanotubes. The figure shows clearly that there are strong interactions across the interior of the nanotube, also this being beyond the simplest graphite-sheet model.

Thus, the theoretical studies of these ultra-thin fullerene nanotubes reveal that these materials have unique properties that are not shared by the larger, more common fullerene nanotubes. That is, in these nanotubes the electrons are not confined to the surface but occupy also the inner parts, making these materials more homogenous than what is the case for the larger fullerene nanotubes.

#### 3.2. Pt-containing polyynes

The ultimate limit for the fullerene nanotubes is an infinite chain of carbon atoms, polyynes. This quasi-1D material is, however, not stable: finite linear carbon chains or rings do not form the stablest forms of  $C_n$  for  $n > 20$  [10]. Theoretical studies have revealed (e.g., [11]) that the hypothetical infinite polyynes would have a structure of alternating shorter (triple) and longer (single) bonds, and that the material would be a semiconductor with orbitals of  $\pi$  symmetry around the Fermi level. This makes them closely related to the conjugated polymers based on  $sp^2$ -bonded carbon atoms that have been at the center of a large research activity since more than two decades (see, e.g., the Nobel Prize lectures by MacDiarmid, Heeger, and Shirakawa [12–14]). This field has benefitted very much from carbon's ability to form different types of chemical bonds with a large number of different types of atoms, so that by modifying the structure of the polymer its properties can to some extent be varied in a controlled way. Conjugated polymers based on  $sp$ -bonded carbon atoms are much less common, but their existence would open up further possibilities for varying the materials properties.

Wittmann et al. [15] have synthesized a material whose properties resemble those of polyynes. In Fig. 2 we show a simplified material related to the one synthesized by Wittmann et al. whose material, however, had phenyl rings replacing the middle  $C_2$  units and  $C_4H_9$  groups replacing the H atoms of the  $PH_3$  groups. Nevertheless, the material of Fig. 2 has many similarities with that of the experimental study of Wittmann et al., including containing  $sp$ -bonded carbon atoms, carbon  $\pi$  electrons,

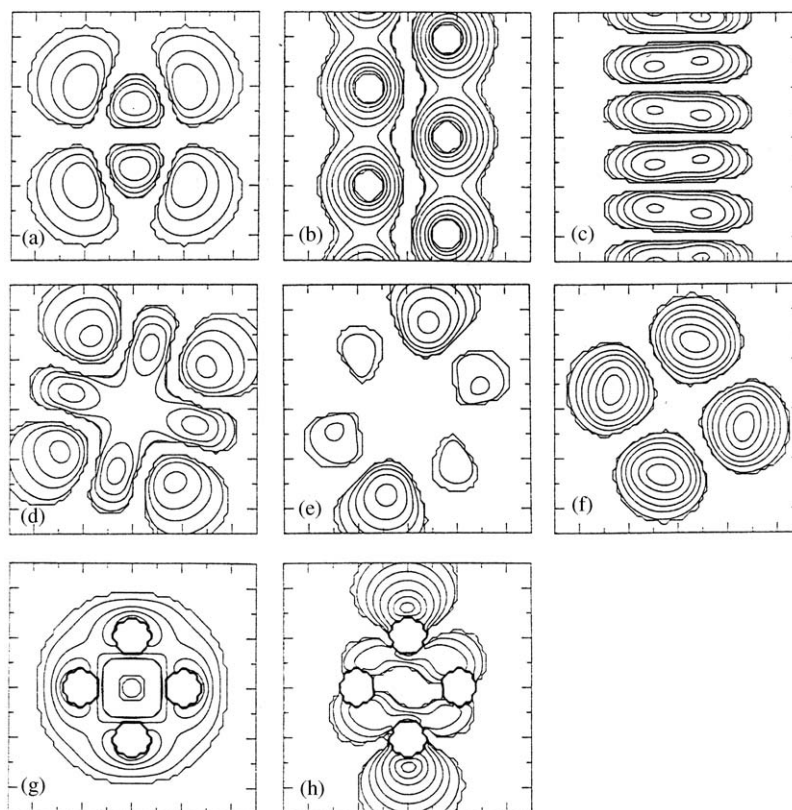


Fig. 1. The frontier orbitals for the so-called (a–c) (2,1), (d–f) (4,2), and (g,h) (2,0) fullerene nanotubes in a plane either (a,d–h) perpendicular to or (b,c) containing the tube axis.

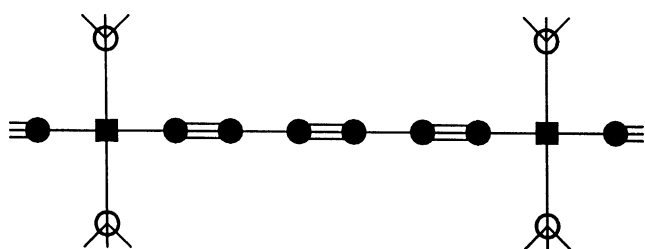


Fig. 2. Schematic representation of  $[\text{Pt}(\text{PH}_3)_2\text{C}_6]_x$  with dark squares, dark circles, and white circles marking Pt, C, and P atoms, respectively.

and  $\text{PR}_3$  groups, and, therefore, we decided to study the material of Fig. 2 [16].

One of the central questions is whether the electronic properties of pure polyynyl prevail when passing to the Pt-containing polyynyl of Fig. 2, i.e., whether the material is a semiconductor with  $\pi$  electrons around the Fermi level, and whether the electrons are delocalized over the complete backbone. In Fig. 3 we show the band structures of the compound of Fig. 2 together with those of pure polyynyl and of different segments of the material of Fig. 2. It is clear that the band structures of the Pt-containing polyynyl and of pure polyynyl resemble each other: the bands span roughly the same energy intervals, and the larger number of bands in Fig. 3(a) is

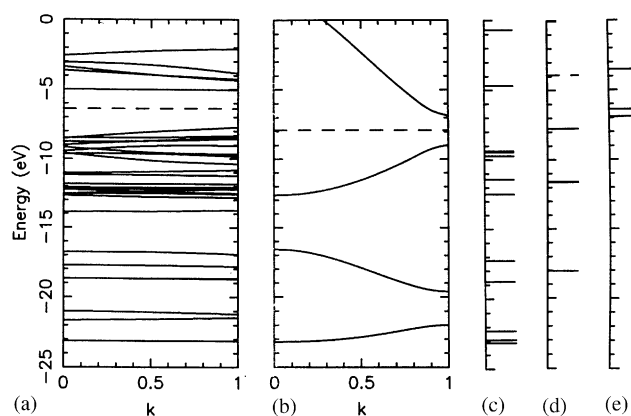


Fig. 3. Band structures of (a) the Pt-polyynyl of Fig. 2 and (b) pure polyynyl together with the energy levels of (c)  $\text{C}_6$ , (d)  $\text{PH}_3$ , and (e) a Pt atom.  $k = 0$  and  $k = 1$  mark the center and edge of the first Brillouin zone, respectively, and the dashed lines separate occupied and empty orbitals.

first of all due to the larger number of atoms per repeated unit. Moreover, from the orbital level diagrams of Fig. 3 as well as by analyzing the orbitals individually (not shown) it can be seen that at least the frontier orbitals indeed are delocalized over the complete system and are of  $\pi$  symmetry.

The theoretical study has thus confirmed that the Pt-containing polyene of Fig. 2 can be considered a member of the family of the conjugated polymers that currently are of significant scientific and technological interest. In particular, the presence of the Pt atoms does not lead to a noteworthy perturbation of the conjugation, and, instead, can lead to a stabilization of an infinite linear chain of carbon atoms.

#### 4. Metal chains

Metal atoms tend to prefer high coordination but under certain circumstances low-dimensional metallic systems can be produced. Thus, films of metal atoms are quasi-2D systems, and also quasi-1D chains of metal atoms can be formed, for instance on terraces of semiconductor surfaces or inside the channels of some host material. Also in break-junction experiments chains of metal atoms are formed at the last stages of the experiment just before breaking the junction. In some cases, these chains are remarkably stable and possess unusual properties.

##### 4.1. Pb

One example of metal chains confined to the interior of the channels of a host is chains of Bi, Pb, or Tl that were synthesized inside the channels of a zeolite by Romanov [17]. Due to the relatively small size of these channels, the types of chains that can exist inside these are limited. Some few high-symmetry ones are shown in Fig. 4.

We studied [18] the linear, zigzag, and double zigzag chain for the three elements above, but shall here concentrate on the results for Pb. It turned out that it was important to include not only scalar relativistic

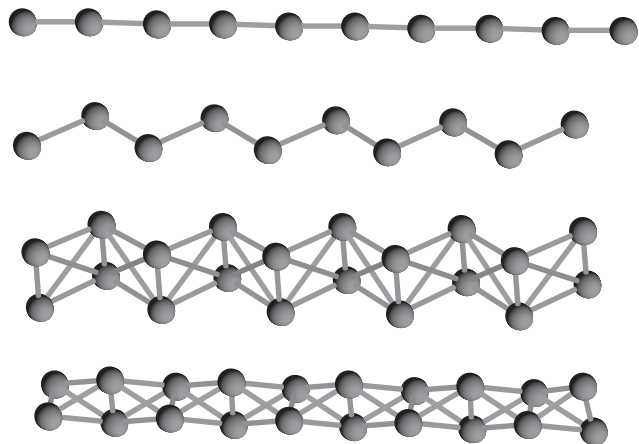


Fig. 4. Schematic representation of a linear chain, a zigzag chain, a double zigzag chain, and a tetragonal chain.

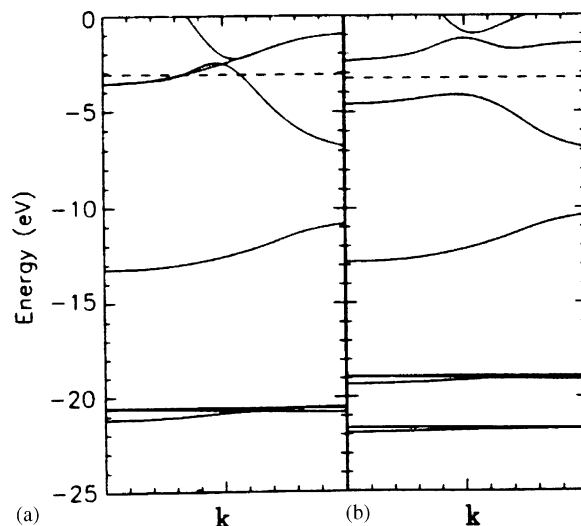


Fig. 5. Band structure of a linear chain of Pb atoms (a) without and (b) with the inclusion of spin-orbit couplings. The dashed lines mark the Fermi level. The bond length was set equal to 6 a.u.

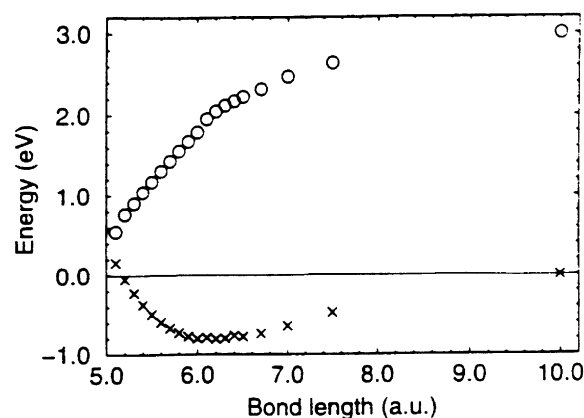


Fig. 6. Relative total energy per atom (crosses) and band gap (circles) as functions of bond length for a linear chain of Pb atoms.

effects but also the spin-orbit couplings. Actually, through these a linear lead chain was found to be semiconducting (cf. Fig. 5), whereas the two other structures were metallic. Finally, as shown in Fig. 6, the linear chain is very soft, so that it very easily can change structure, for instance in order to adapt it to that of a host, whereas the electronic properties, e.g., the band gap, depend strongly on the structure. This opens up the possibility of tailoring the electronic properties in a controlled way simply by varying the host material. That is, since the host zeolite used by Romanov is a wide-gap insulator, by using slightly different host materials, it may be possible to obtain chains with slightly different bond lengths, which are energetically very close but whose optical properties may vary significantly.

#### 4.2. Au

During the last few years there has been considerable interest in chains of Au atoms, partly as an interesting system for studying the quantum nature of resistance when a metallic wire becomes only few atoms thick. Almost simultaneously, two papers reported the observation of short Au chains with unusually long interatomic Au distances [19,20]. Later, an improved calibration of one of the works brought the bond length down to values more in agreement with chemical intuition. Our own results [21], as well as those of many other theoretical studies, gave bond lengths comparable with those of crystalline Au, and, accordingly, in agreement with one [20] but not the other [19] experimental result. This result, cf. Fig. 7, was independent of whether spin–orbit couplings were included or not. Furthermore, comparing Fig. 7 with Fig. 6 we see that the Pb chain is considerably softer than the Au chain.

A further result of this study was that for an infinite Au chain with bond lengths only slightly larger than the optimized value only one ( $\sigma$ ) band crosses the Fermi level. This suggests, similar to what is found for polyynes, that the system will lower its symmetry by doubling the unit cell and letting the bond lengths alternate, whereby a gap at the Fermi level will occur. The calculations confirmed this prediction, and we found, in addition, that the bond lengths then would take values of which one (the smaller) was very close to that of an isolated  $\text{Au}_2$  molecule.

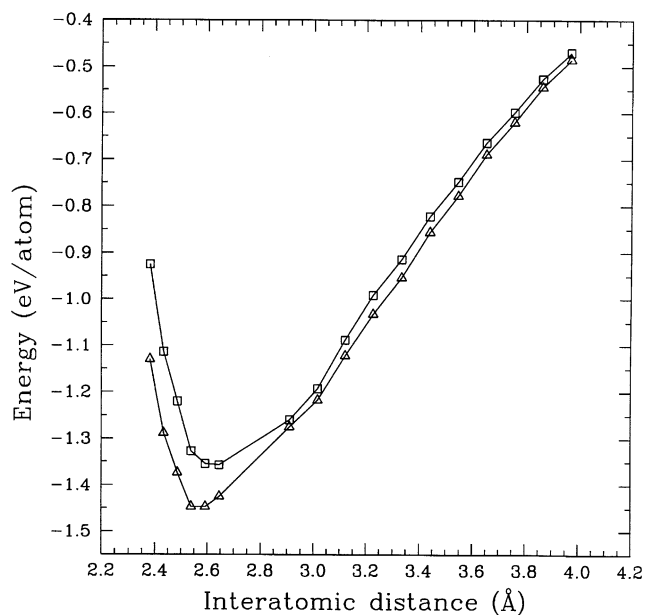


Fig. 7. Relative total energy per atom as a function of bond length for a linear chain of Au atoms with (triangles) and without (squares) inclusion of spin–orbit couplings.

Our theoretical study (as well as many others on linear chains of Au atoms; see, e.g., [22]) has confirmed the intuitive expectations, that the bond length in such chains is comparable with that of crystalline Au, and not significantly larger, in contrast to the initial experimental results. Our own study has, in addition, shown that upon distortion a chain will break into dimers.

#### 4.3. Ag

Chains of Ag atoms have been studied in two contexts. First, it is a natural and interesting extension of the studies of nanojunctions [23] where otherwise mostly Au has been considered. And second, chains of Ag atoms have been synthesized inside a host formed by self-assembled calix[4]hydroquinone nanotubes [24].

We considered isolated chains of the types of Fig. 4 [25]. As expected, in this case spin–orbit couplings are of only minor importance. e.g., the optimized structural degrees of freedom change only marginally when including spin–orbit couplings. In Fig. 8 we show the band structures for the four structures of Fig. 4. In contrast to the case of Pb, here all systems are metallic with one or two bands crossing the Fermi level. Adding spin–orbit couplings does not change this conclusion, and the only effects are smaller splittings of the bands of Fig. 8.

As a linear chain of Au atoms, the linear chain of Ag atoms has one band crossing the Fermi level, but it turns out that for Ag, a dimerized chain with alternating bond

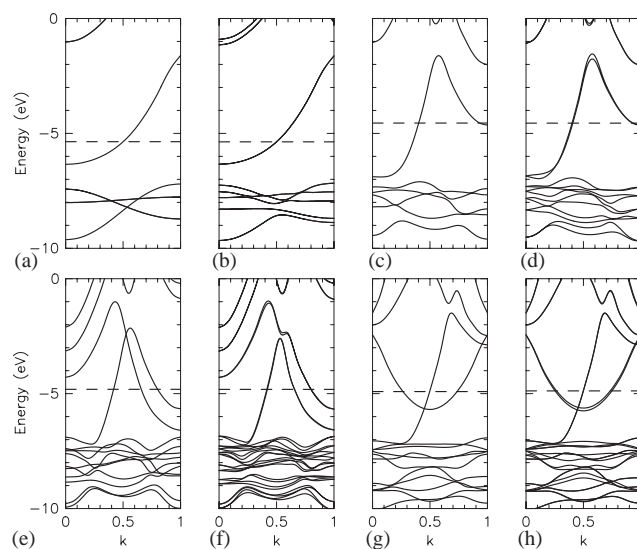


Fig. 8. Band structures for Ag chains with the structures of Fig. 4, i.e., (a,b) a linear chain, (c,d) a zigzag chain, (e,f) a double zigzag chain, and (g,h) a tetragonal chain. Spin–orbit couplings have been included in (b,d,f,h), and one unit cell contains in (a–d) one Ag atom and in (e–h) two Ag atoms.  $k = 0$  and  $k = 1$  are the center and the edge, respectively, of the first Brillouin zone, and the dashed lines show the Fermi level. The structures were all optimized; for details see [25].

lengths, whose values differ only little, is the stablest form for the linear chain, whereas for Au the chain is not stable but will split into isolated dimers. The dimerization for Ag leads to a small (less than 1 eV) gap at the Fermi level, so that Ag in this structure in fact is semiconducting. Whether this also is the case for the experimentally synthesized chains inside the organic host has, to the author's knowledge, not been explored yet.

## 5. Charged chains

Some crystalline compounds can be considered as consisting of more or less strongly interacting chains. In some cases, like crystalline Se, these chains are neutral but in other cases they are charged and are surrounded/separated by counterions. The latter case is the one we shall consider in this section.

### 5.1. $K_2PtS_2$

$K_2PtS_2$  consists of parallel, planar  $PtS_2$  chains with the structure of Fig. 9 surrounded by K atoms [26]. In the simplest picture, each K atom will donate its valence 4s electron to the chain, leaving a structure like  $[(PtS_2)^{2-}(K^+)_2]_x$ , and with essentially no electronic interaction between one chain and the other chains or the counterions.

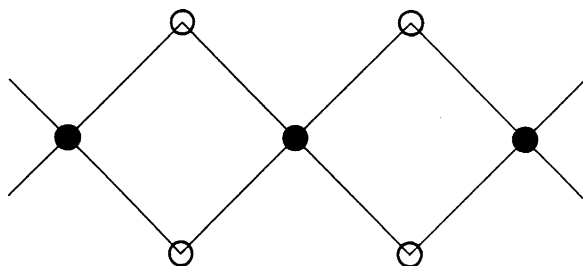


Fig. 9. Schematic representation of a  $PtS_2$  chain with dark and white circles representing Pt and S atoms, respectively.

In our theoretical study of this material [27], we first considered an isolated neutral  $PtS_2$  chain. It turned out that it was metallic (cf. Fig. 10) and that the lowest total energy was found for a non-planar structure where the angle  $\gamma$  describing the angle between neighboring  $PtS_2Pt$  rhombus was  $90^\circ$ . These conclusions were not changed when including spin-orbit couplings (cf. Fig. 10). For the planar chains (i.e.,  $\gamma = 0^\circ$ ) a rigid-band picture suggests that adding two electrons per formula unit to the chains would change them into being semiconducting, in agreement with experimental observations.

Adding 2 K atoms per formula unit so far away from the chain that there was no electronic interactions between the K atoms and the  $PtS_2$  chain gave, in contrast to experiment, a metal with orbitals both from the K atoms and from the  $PtS_2$  chain around the Fermi level. Only when going to the true 3D structure using the Wien programs we obtained a semiconductor, and, in fact, in the 3D calculations the rigid-band approximation seems to be good. On the other hand, for a hypothetical crystal structure containing neutral non-interacting  $PtS_2$  chains, we obtained results essentially identical to those of the single-chain calculations. A careful analysis of the results suggested that the electron transfer between the K atoms and the  $PtS_2$  chains leads to long-range Coulomb (Ewald) potentials that are different in the single chain and the crystal scenarios. The difference in the potentials felt by the electrons at the various atoms when going from the single chain to the crystal calculations could actually explain the different band structures. Thus, this example demonstrates the importance of including the Coulomb potentials in a proper way also when electronic interactions can be neglected, as well as suggests that dimensionality effects may have unexpected consequences.

### 5.2. $CaNiN$

Also  $CaNiN$ , Fig. 11, can be considered as being built up of (NiN) chains surrounded/separated by (Ca)

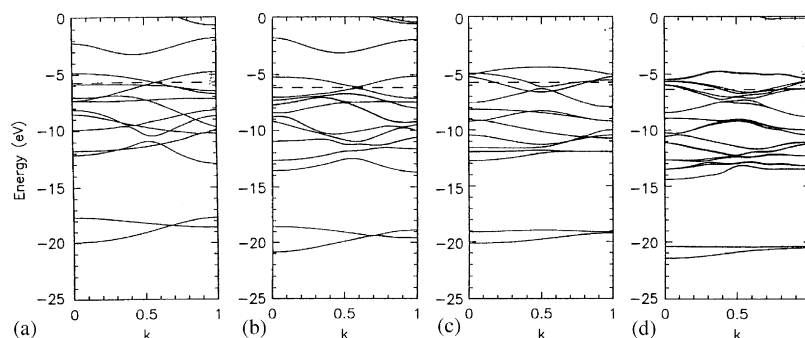


Fig. 10. Band structures of a neutral  $PtS_2$  chain calculated for (a,b) the planar structure and (c,d) the non-planar structure with  $\gamma = 90^\circ$  (a,c) without and (b,d) with the inclusion of spin-orbit couplings. The structural parameters of the chains were optimized; for details see [27].

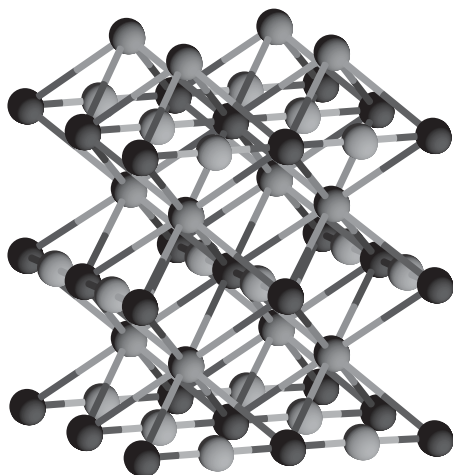


Fig. 11. Schematic representation of the crystal structure of CaNiN. The structure consists of planes of linear chains of Ni (darker atoms) and N (lighter atoms) separated by Ca atoms.

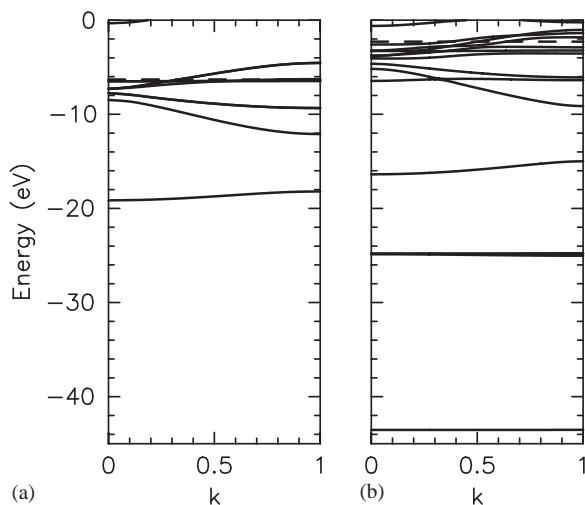


Fig. 12. Band structures for a single chain of (a) NiN and (b) CaNiN.  $k = 0$  and  $k = 1$  is the center and the edge of the first Brillouin zone, respectively, and the dashed lines mark the Fermi level. The structure was taken as that of the crystal, i.e., Ni–N bond lengths of 1.785 Å and Ni–Ca distances of 2.51 Å were used.

counterions. In this case (cf. Fig. 11), however, parallel chains form planes that in turn are separated by the counterions, and, moreover, the chains of neighboring planes are rotated by  $90^\circ$  [28].

We studied this material using both the single-chain programs and the crystal programs [29]. In this case, all calculations led to a metallic behavior, independent of which programs we used and of whether the counterions were included or not. This is exemplified in Fig. 12 which shows the band structures for the single NiN and the single CaNiN chains. As a further result of this study, we found that upon inclusion of the Ca atoms, the intra-chain bonds became slightly weaker and longer, and, in contrast to the previous case, there are

some electronic and not only electrostatic interactions between the chains and the counterions.

Through our studies we can thus conclude that although both  $K_2PtS_2$  and CaNiN consists of charged chains surrounded by counterions, the interactions are different: for the former material they are essentially electrostatic, whereas they for the latter also have an important covalent component. This difference can only with difficulties be identified in experimental studies.

## 6. Conclusions

In this contribution we have reviewed some of our results for materials that to some extent can be called quasi-1D materials. No material is, of course, truly-1D, but, as we have demonstrated, many show behaviors that have a dominating 1D component, although also contributions from other dimensionalities can be recognized.

This was clearly demonstrated for the carbon nanotubes for which the properties of an 2D graphite sheet often provide a good description, except for the absolutely smallest nanotubes considered in this work. Linear chains of carbon atoms have interesting electronic properties but are, unfortunately, not stable. By incorporating metal atoms we saw that they could be stabilized without altering the properties significantly.

Chains of metal atoms form a class of materials that currently are intensively discussed. First of all, the possibility of having a Luttinger liquid instead of a Fermi liquid is still an open fundamental question, but also since these systems form the ultimate limit of nanowires they can be of high technological relevance. We saw that the properties of these materials may change drastically when going from the conventional 3D systems to the quasi-1D systems of this work. Most dramatic, maybe, was the case of a linear chain of Pb atoms which was found to be semiconducting.

Finally, chains of atoms are often found as a building block in crystalline materials. We considered two cases here and found, most notably for  $PtS_2$ , that in some cases it is important to include 3D effects in order to get a proper description of the electronic properties, although no 3D electronic interactions are present.

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