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Electronic band gaps in one-dimensional comb structures of simple metals

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Abstract. The electronic properties of comb structures composed of one-dimensional atomic wires of alkali elements are studied. The wires and network of wires are assumed to be formed either on substrates or through networks of metal filled nanotubes. A tight-binding model is used to model the electronic structure of the wires assuming that the atoms are constrained by the substrate or nanotubes to separations exceeding their equilibrium distance. The binding between side wires and the main linear backbone in the comb network opens gaps in the density of states. The band structure of the periodic combs varies significantly with the number of atoms in the side wires as well as the periodicity of the side wires along the backbone. For some specific geometries, complete band gaps may be opened about the Fermi level. Finite combs may be designed to produce devices with electronic properties similar to those of the periodic systems and, in particular, with stop bands in their transmission spectrum.

1. Introduction

Nanowires are of great interest from an application point of view. Of particular technological and theoretical interest are nanowires composed of lines of individual atoms that may possess peculiar properties. As a result of recent progress in atom manipulation technology, it is now possible to place individual atoms on substrates by using a scanning tunnel microscope (STM) tip as tweezers. A STM permits; the fabrication of structures atom by atom such as lines of Xe on Ni substrates [1], the deposit of nanometre-size gold structures on metal substrates [2] or manipulation of individual atoms on a Si surface [3]. These advances suggest that with a STM it is becoming possible to place metal atoms along a line or a network of lines on insulating substrates for the fabrication of novel electronic devices. Such devices would behave like one-dimensional ideal chains or networks of such chains. On the other hand, the synthesis of concentric carbon nanotubes filled with metals has opened the way to the design of quasi-one-dimensional conducting nanowires with diameters larger than 100 Å [4]. The fabrication of single-wall carbon tubules with diameter of the order of 10 Å [5, 6], has opened up the possibility of producing one-dimensional metallic chains as metal atoms captured in these small tubules form an atomic linear chain. The interaction between metal atoms and carbon atoms in metal-filled carbon nanotubes is expected to be strong [7]. In contrast, the nearly insulating boron-nitride tubules [8, 9] would behave like ideal non-interacting hosts for the captured metal atom [10]. This raises the possibility

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of fabricating ideal one-dimensional metallic chains. The suggestion of carbon-nanotube connections [11] offers a means of designing networks of one-dimensional metal chains.

On the premise that this technological progress will permit the fabrication of ideal metal chains and networks of such chains, we have undertaken a theoretical investigation of the electronic properties of one-dimensional comb structures of alkali elements. These comb structures are composed of finite one-dimensional chains grafted regularly onto a backbone consisting of an infinite one-dimensional chain. With regard to the present work, we shall mention the recent theoretical investigation of a network structure constructed from a backbone with multiple dangling side branches (MDSB) [12]. The electronic properties of the MDSB structures are studied within a free-particle model and therefore rely on the assumption that the composite structure is comprised of infinitesimally thin wires. In contrast to the MDSB networks, the present paper uses a more realistic tight-binding model. With this model, we show that; (1) periodic comb structures possess gaps in their electronic band structure resulting from the periodicity of the system and from the resonance states of the grafted wires; (2) band gaps may be opened near the Fermi energy by properly tailoring the geometry of the comb; and (3) the electronic transmission spectrum of finite comb structures possesses characteristics similar to the band structure of a periodic system and in particular exhibits stop bands.

In section 2, we present the model and methods used in the calculation of band structures, density of states and transmission spectra of comb networks. Results for periodic and finite combs networks are reported and discussed in section 3.

2. Model

The s- and p-level bands of alkali elements overlap a great deal at the equilibrium inter-atomic spacing. Chains of atoms at the equilibrium spacings are, therefore, best described within the framework of a nearly free electron model. However, the separation distance between atoms in chains formed on insulating substrates or in tubules is likely to be constrained to exceed the equilibrium inter-atomic distance leading to narrower and non-overlapping s- and p-bands [13]. Furthermore, the substrate and tubule can be expected to make the alkali atom chain stable against a Peierls distortion and therefore produce a conducting chain. Under these conditions, we describe the electronic structure of the constrained chains of alkali elements with a one-dimensional s-band tight-binding model. The model is limited to interactions between first nearest neighbours. The bulk energy band is given by: $E(k) = -2\beta \cos ka$, where k is the one-dimensional propagation vector, β the hopping integral and a the lattice parameter. Since the width of the s-band varies with the separation distance between the atoms, the hopping integral will depend on that distance. For instance, at a constrained separation of 7 Å, the width of the sodium s-band amounts to approximately 1.4 eV [13] yielding a value for the hopping integral of nearly 0.35 eV. However, for a fixed distance imposed by the substrate or tubule, β will be considered as a model parameter. Here, we have chosen the atomic level as the origin of energy and we have neglected the shift integral. The bulk band extends from -2β to $+2\beta$. Using this tight-binding model and the formalism of the Green function, we construct the band structure of a comb network. The Green function of a system composed of finite chains attached along an infinite one-dimensional backbone can be constructed with the help of interface response theory (IRT) [14]. The IRT enables us to construct the Green function of the network structure in terms of its constitutive elements. These elements are the backbone and the grafted finite chains. The mathematical procedure we follow begins with the construction of the Green function of an infinite linear chain (backbone) [15]. This

lattice is divided into periodic unit cells of length Na and the Green function is expressed in one-dimensional Fourier space, namely, $\overleftrightarrow{G}_k^o$ with $k \in [0, \pi/Na]$. The Green function of a finite one-dimensional chain, $\overleftrightarrow{g}_s$, composed of L atoms has been reported in [16]. We call $\overleftrightarrow{G}_k$ the Fourier transform of the Green function of a reference system. This reference system consists of the uncoupled finite chains and infinite chain and is defined in the discrete space D of the atomic sites of the finite chains and backbone. $\overleftrightarrow{G}_k$ is therefore a block diagonal matrix with blocks $\overleftrightarrow{G}_k^o$ and $\overleftrightarrow{g}_s$. We build the network structure by linking the finite chains to the backbone with the help of a coupling operator, $\overleftrightarrow{V}$ (see figure 1). For a single finite chain linked to one atomic site on the backbone, the coupling operator is a 2×2 matrix

$$\overleftrightarrow{V} = \begin{pmatrix} 0 & \beta_I \\ \beta_I & 0 \end{pmatrix}. \tag{1}$$

In this matrix, β_I is the hopping integral between an atom at the tip of a finite chain and an atomic site on the backbone. In all cases presented in this paper, we have chosen $\beta_I = \beta$. The coupling operator is defined in the subspace, M, of D which contains all the atomic sites to be bonded. In this interface space, M, the Fourier transform of the Green function of the network structure, $\overleftrightarrow{g}_k$ is obtained from

$$\overleftrightarrow{g}_k \cdot \overleftrightarrow{\Delta}_k = \overleftrightarrow{G}_k \tag{2}$$

where

$$\overleftrightarrow{\Delta}_k = \overleftrightarrow{I} + \overleftrightarrow{V} \cdot \overleftrightarrow{G}_k. \tag{3}$$

In the preceding equation, $\overleftrightarrow{I}$ is the unit matrix.

The band structure of a periodic network of finite chains grafted onto an infinite one-dimensional backbone is then calculated by solving for zeros of

$$\det \overleftrightarrow{\Delta}_k = 0. \tag{4}$$

For this calculation, we have to consider the alignment of the Fermi levels of the finite and infinite chains. Our model is limited to alkali elements for which the bulk band is half-filled. For these elements, the Fermi energy, E_F lies in the middle of the bulk band. With our choice for the origin of energies, the Fermi level is therefore also located at zero.

To calculate the band structure of the comb network, we use the Green function of a finite chain. The finite chain is obtained by cutting a finite segment out of an infinite linear chain. These cuts introduce variations in the electronic charge in the vicinity of the tip of the finite chain. Thus, the effect of the cuts would need to be treated self-consistently. The Green function, $\overleftrightarrow{g}_s$ we use, does not include these self-consistent effects. However, it has been shown that in the case of a tight-binding model of half-filled metallic bands, the perturbing potential needed to account for self-consistency is very small [17]. Self-consistency is, therefore, likely not to be critical for our alkali elements.

To gain additional understanding into the band structure of periodic comb networks we investigate combs containing a finite number of grafted chains. In particular, we can calculate the electronic density of states of such finite combs. For this we again use the IRT. We first introduce a reference system composed of a finite number of non-grafted finite chains and of an infinite one-dimensional backbone. Using the coupling operator of equation (1), we link the finite chains to the backbone. Since this system is not periodic, the Green functions are not expressed in Fourier space anymore. The Green function of the finite combs takes on forms similar to those given in equations (2) and (3) but with real

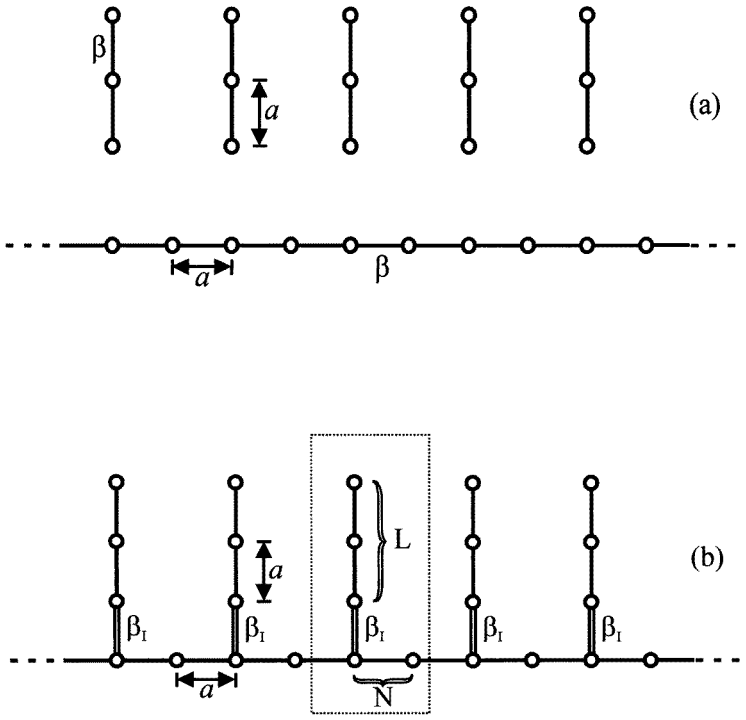

Figure 1. (a) Elementary constituents of the periodic comb. The lattice parameter, a, and the hopping integral, β are assumed identical in the backbone and in the side wires. (b) Periodic comb structure. β_I stands for the coupling hopping integral. L and N represent the number of atoms in a side wire and the number of atoms in a unit cell along the backbone, respectively.

space representations of the functions. In this case, the $\overleftrightarrow{\Delta}$ matrix is a $2n \times 2n$ matrix where n is the number of grafted finite chains. The space M encompasses the n atomic sites at the tip of the finite chains and n equally spaced atomic sites on the backbone. One can finally determine the variation in electronic density of states between the finite network and the reference system from

$$\Delta n(E) = -\frac{1}{\pi}\frac{\mathrm{d}}{\mathrm{d}E}[\mathrm{Im}\,(\ln(\det \overleftrightarrow{\Delta}))]. \tag{5}$$

The symbol Im stands for the imaginary part of the logarithm of the determinant of the matrix $\overleftrightarrow{\Delta}$. The coefficient of transmission of a comb is calculated as the ratio of the transmitted electronic wave to the incident wave. Following the IRT, the transmitted wave, u is expressed in terms of the incident one, U by the relation

$$u(D) = U(D) - U(M)\,\overleftrightarrow{\Delta}^{-1}(MM)\,\overleftrightarrow{V}(MM)\,\overleftrightarrow{G}^{0}(MD) \tag{6}$$

where the symbols D and M indicate that the quantities are expressed along the backbone chain and at the connecting points between the backbone and side chains, respectively. $\overleftrightarrow{G}^{0}$ is the Green function of the backbone in real space.

3. Results

3.1. Periodic comb structures

We have calculated the electronic band structure of periodic combs as a function of the number, L, of atoms in the side wire and the number, N, of atoms in a period along the backbone. As expected the band structure possesses $(N + L)$ bands. Combs with side wires containing an even number of atoms show a band extending across the Fermi level. On the other hand for odd values of L, the side wires open a band gap about E_F. In this case we note two different behaviours depending on the parity of N. A true band gap exists near the Fermi energy for an odd value of N. An even N leads to a gap with a flat band at the Fermi energy. We illustrate this behaviour in the following two particular cases. First, we report in figure 2 the band structure of a periodic comb network with $N = 4$ and $L = 5$ which is illustrative of an even N and odd L. Nine bands are identifiable. The upper and the lower bands originate outside the bulk band of the backbone. These bands are associated with electronic states at the interface between the finite chain and the backbone, that is, electronic states located in the space of the bonded atoms, M. More importantly, the grafted chains have opened a series of absolute gaps in the band structure of the network. The widest of these gaps is a direct band gap centred on the Fermi level; the width of which amounts to 0.7β. A flat band remains, however, at the Fermi energy. These latter states correspond to localized modes inside each grafted side wire.

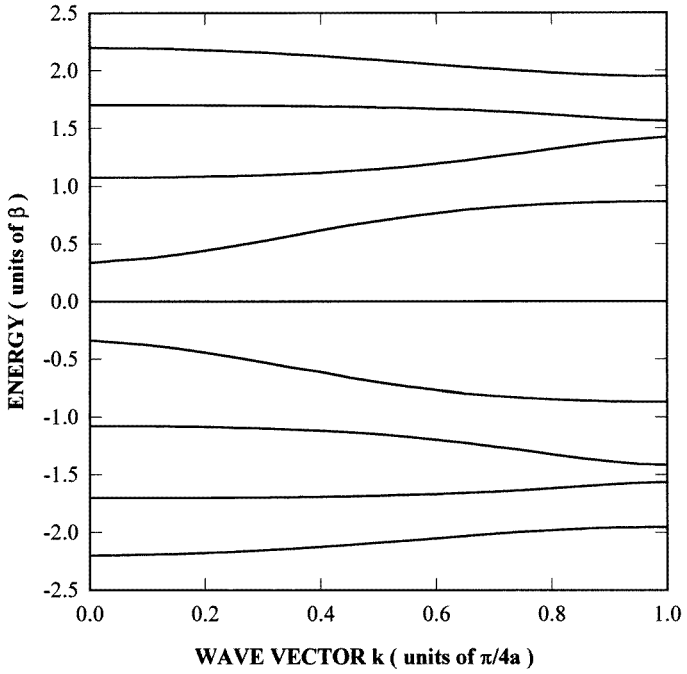

Figure 2. Electronic band structure of an infinite periodic comb structure. The side chains contain $L = 5$ atoms and are spaced every $N = 4$ lattice spacings, a of the backbone.

The band structure of figure 3 is characteristic of a comb structure with an odd N. In this case $N = L = 5$ and the band structure contains ten bands. Similar to the previous

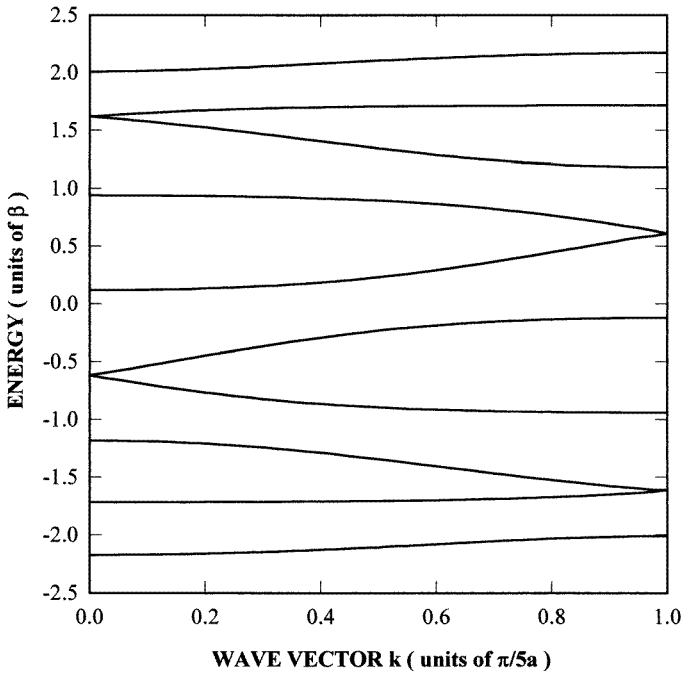

Figure 3. Electronic band structure of a periodic comb with $N = 5$ and $L = 5$.

case, one has two bands originating outside the bulk band of the backbone corresponding to the bonded atoms. The most important feature is the existence of an indirect band gap centred on the zero of energy (Fermi energy). This band gap extends over an interval of energy of approximately 0.25β.

3.2. Finite comb structures

Additional information concerning the origin of the bands in the electronic band structure of the periodic combs may be gained by investigating combs constituted of a finite number of grafted chains. For this, we study the electronic density of states as a function of the number of grafted side wires. More specifically we have calculated according to equation (5) the difference in density of states $\Delta n(E)$ defined as

$$\Delta n(E) = n_2(E) - n_1(E) \tag{7}$$

where $n_2(E)$ is the density of states of the grafted comb and, $n_1(E)$, the density of states of the reference system constituted on an infinite backbone chain and the individual unattached side wires. With this definition, $n_1(E)$ is the sum of the density of states of the backbone

$$n_0(E) = \frac{1}{2\pi\beta}\frac{1}{\sqrt{1-(E/2\beta)^2}}$$

and delta peaks corresponding to the discrete electronic states of the unattached side wires. These delta peaks are not presented in figure 4. Figures 4(a), (b) and (c) illustrate the variation in density of states for a single grafted chain ($n = 1$), $n = 2$ and $n = 10$ grafted chains, respectively. The finite chains are composed of $L = 5$ atoms spaced every $N = 4$ lattice spacings along the backbone. Since the five discrete levels of an uncoupled finite

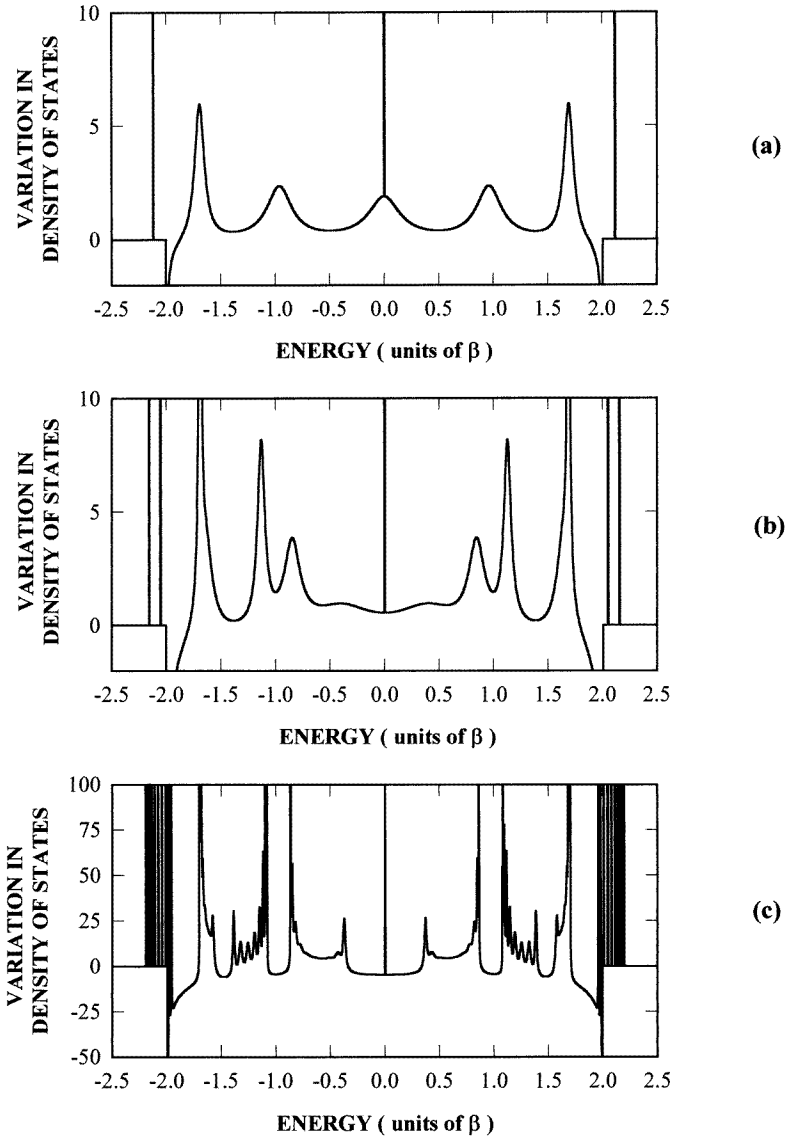

Figure 4. Difference in the density of states of a finite comb structure composed of (a) $n = 1$, (b) $n = 2$, and (c) $n = 10$ grafted chains constituted of $L = 5$ atoms and the density of states of a reference system composed of an infinite backbone with individual unattached side wires (for the sake of simplicity, the delta peaks associated with the discrete states of the unattached side wires are not represented). Negative values arise when the density of states of the reference system exceeds the density of states of the comb which is in particular the case within the band gaps. The spacing between grafted chains is $4a$.

chain fall within the bulk band of the backbone, the variation in density of states exhibits five resonances in the form of five well defined peaks. Two electronic states localized at the bonded atoms lie above and below the backbone band. Another localized state exists at the Fermi energy. Interaction between subsequently grafted chains mediated by the backbone,

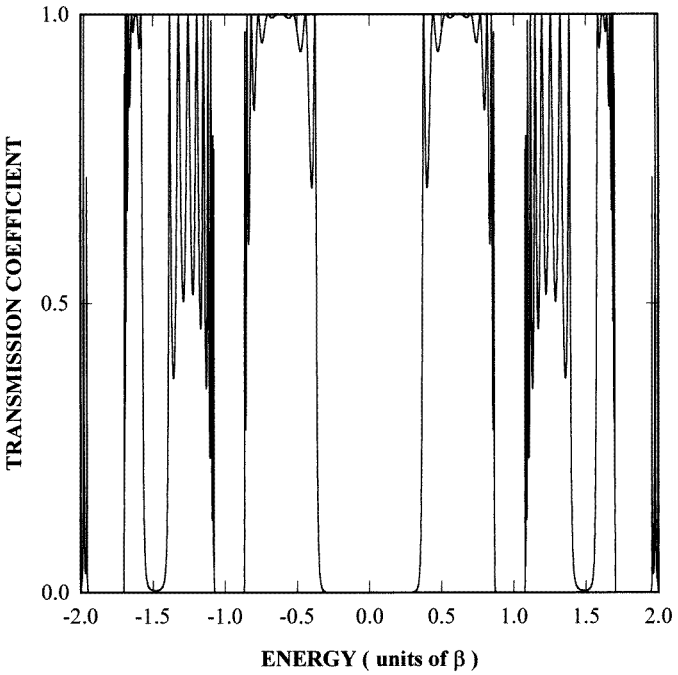

Figure 5. Transmission spectrum of the $N = 10$ finite comb structure discussed in figure 2.

leads to a splitting of the resonant peaks as well as of the localized peaks outside the bulk band. As one increases the backbone coverage further resonant peaks split in multiple narrower peaks. Anti-resonant states appear as depressions ($\Delta n < 0$) in the density of states. In the limit of a periodic system, these anti-resonances can be associated with the band gaps of figure 2. The negative values in $\Delta n(E)$ that arise at some energies result from the fact that at these energies the density of states in the grafted comb is smaller than that in the reference system, especially in the energy ranges corresponding to the band gaps of the periodic system It is known that resonating grafted chains introduce zeros of transmission in the electron transmission spectrum of an infinite backbone [18]. For instance, a single finite chain of five atoms would forbid transmission within the infinite linear chain at the energies $-\sqrt{3}, -1, 0, 1, \sqrt{3}$ in units of β.

The transmission spectrum for $N = 4$, $L = 5$ and $n = 10$ is presented in figure 5. We note that increasing the number of grafted chains to only $n = 10$, already opens up gaps in the transmission spectrum. Some of these gaps result from a broadening of the depressions around the zeros of transmission of the infinite chain containing a single grafted finite chain. Another, near 1.5β, is associated with the superlattice effect of attaching regularly finite chains along the backbone. These gaps are the precursors of those observed in the band structure. It is important to notice that although the band structure (and the variation in density of states) contains a flat band at the Fermi energy for $N = 4$ and $L = 5$, the transmission spectrum shows no indication of transmission at this energy. This energy is associated with localized modes inside each side wire which do not penetrate into the backbone. Owing to the localized character of the states corresponding to the flat band there is no contribution to the transmission at this energy.

4. Conclusion

In conclusion, we have found theoretically that network structures of linear chains of alkali elements, such as periodic comb structures, may exhibit electronic band gaps centred about the Fermi energy. Such gaps occur for an odd number of atoms in the grafted side wires independent of the parity of the number of atoms in the period along the backbone. However, in the case of an even number of atoms in the period, there exists a flat band at the Fermi energy. Further light is shed into the behaviour of periodic combs by studying the electronic properties of combs composed of a finite number of side wires. In the case of these finite combs, we show that the flat band does not contribute to the electronic transmission along the backbone. Therefore, our theoretical calculations indicate that the combs do not have to be infinitely periodic but that a reasonably small number of side chains is sufficient to produce practical devices with a behaviour characteristic of periodic ones.

Finally, we hope to motivate experimental examination of nanowires and nanowire networks of metallic elements with angstrom-scale diameters for the possibility of electronic band gaps.

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