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Band Structures of Atomic Chains of Group IV, III–V, and II–VI Elements

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Abstract—The relativistic band structures of A^N and $A^N B^{8-N}$ chains have been calculated by the linear augmented-cylindrical-wave method, which is an extension of the augmented-plane-wave method for cylindrical polyatomic systems. The band structures of covalent monatomic chains of Group IV elements are characterized by $\sigma(s)$, π^+ , and π^- , and $\sigma(p_z)^*$ bands. The C, Si, Ge, and Sn chains are metallic. There is a considerable difference between the relativistic and nonrelativistic band structures. Because of the cylindrical symmetry of chains in the nonrelativistic model, the π bands crossing the Fermi level are orbitally doubly degenerate (i.e., the π^+ and π^- band energies are exactly the same). The spin and orbital motion of electrons are coupled in the chains to split π bands, but each π^+ and π^- band is doubly spin-degenerate. The spin-orbit splitting energy for C and Sn chains varies from 1.7 meV to 0.67 eV. The mass-velocity correction reduces all valence band levels: the level shifts are 2–5 meV for C and up to 2.2 eV for Sn. The Darwin corrections are several-fold lower than the mass-velocity contributions. A sharp change in the band structure is observed in going from covalent to partially ionic chains. The carbon chain has a metallic band structure with a zero gap in the center of the Brillouin zone, and a boron nitride chain is an insulator with an optical gap of 8 eV and optical transitions between the occupied π and vacant π^* states at the edge of the Brillouin zone (this is explained by the existence of the antisymmetric component of the electron potential in the BN wire, which mixes even bonding and odd antibonding π states). Going from the BN chain to the AlP, GaAs, and InSb chains is accompanied by a decrease in the chemical bond ionicity, which leads to a gradual decrease in the π - π^* gaps.

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The trends toward miniaturization of electronic devices and challenges of integrating nanodevices have caused considerable interest in stability, band structure, and conductivity of nanowires [1–3]. The thinnest possible nanowires are chains with a one-atom cross-section. The structures and properties of atomic wires differ from those of bulk materials, and they are perfect objects for studying the quantum and size effects. Currently, there is considerable progress in producing stable atomic wires. First, formation of gold atomic chains with a length of up to 10 atoms has been observed by electron microscopy during tensile deformation of nanometer gold contacts [4–6]. The structure of the nanowires and their stress-strain curves and electric properties experimentally determined on an atomic scale point to the ballistic electron transport in the wires [7]. Straight platinum atomic wires have been produced by the retraction of a Pt nanotip from the contact with a Pt plate at room temperature inside a transmission electron microscope. It has been demonstrated that the conductance of the wire depends on its length [7–9]. Binary atomic chains of composition $Au_{1-x}Ag_x$ have been generated by mechanical stretching of nanowires [10]. Organic ligand-supported linear chains of transition metal atoms have been reported

[11]. Linear carbon chains of 44 C atoms have been detected in the $Tr-C_{44}-Tr$ compound with bulky terminal groups $Tr = \text{tris}(3,5\text{-di-}tert\text{-butylphenyl)methyl}$ [9, 12]. Analogous short chains connecting two graphene flakes have been experimentally realized [13, 14]. Carbon nanotubes can be used as shells for stabilization of atomic chains promising for practical application but unstable in the free state. For example, La atoms form a linear chain of 10 nm in length inside a nanotube of appropriate diameter [15]. The introduction of molten iodine into single-walled carbon nanotubes of ~1 nm in diameter generates chains >10 nm in length [16]. A carbon chain 20 nm in length containing more than 100 atoms inserted inside a multiwalled carbon nanotube has been revealed [17]. Inorganic structures, for example, indium [18–21], lead [22], bismuth [23], and rare earth metals [24], tend to self-assemble into one-dimensional structures on the Si(001) surface.

There are a lot of first-principles calculations of the electronic structure of such systems (band structures and magnetic properties). For all 3d transition metals, the band structures and magnetic properties of infinite periodic linear and dimerized linear chains have been

studied using pseudopotential plane-wave calculations with inclusion of spin-orbit coupling [1]. Nearly the same properties of the chains of 4*d* metals have been studied by the linear augmented-plane-wave method with inclusion of spin-orbit coupling [2]. For some transition metal atoms, the character of the change in bond energy as a function of lattice constant is evidence that infinite linear structures have an energy minimum for ferro- and antiferromagnetic phases, which opens up prospects for obtaining spin-dependent ballistic conductance in atomic chains [1–3, 25, 26].

As distinct from transition metal chains and carbon atomic wires (carbynes) [21–24], little is known about atomic chains of Group IV (Si, Ge, Sn), Group A^{III}–B^V (BN, AlP, GaAs, InSb, etc.), and Group A^{II}–B^{VI} (ZnSe, CdTe, etc.) elements. We have found only two works dealing with the structure and electronic properties of these linear chains [27–29] where it has been demonstrated using pseudopotential plane-wave calculations that all chains are stable and their bond energies are close to the corresponding energies of bulk materials. Ab initio molecular dynamics shows that chain structures remain stable at temperatures to 800 K. Band structure calculations of a dozen of monatomic A^NB^{8–N} chains have been performed using only the nonrelativistic approximation [27, 28]. Because of the axial symmetry of linear A^NB^{8–N} chains, relativistic corrections for the band structure can be rather significant. For example, spin-orbit gaps in the Fermi region in planar graphene and in carbon chains are 1 μeV and 2 meV, respectively [30, 31]. In the present work, we calculated, for the first time, the relativistic band structures of A^NB^{8–N} chains by the linear augmented-cylindrical-wave (LACW) method [32–34]. The LACW method can be treated as an extension of the Slater augmented-plane wave method to cylindrical polyatomic systems. The LACW method was extended to include relativistic terms by analogy with the relativistic APW method [35].

COMPUTATIONAL DETAILS

Two-Component Relativistic Hamiltonian

We start from a two-component Hamiltonian (in Rydberg atomic units) [35–37]

$$H = -\Delta + V + \frac{1}{c^2} \boldsymbol{\sigma} \cdot [(\nabla V) \times \mathbf{p}] + \frac{1}{2c^2} \nabla^2 V - \frac{1}{c^2} p^4, \quad (1)$$

which is derived from the Dirac Hamiltonian by applying the Foldy–Wouthuysen transformation. The first two terms are the kinetic energy operator $-\Delta$ and the potential energy operator V and correspond to the nonrelativistic Hamiltonian $H_0 = -\Delta + V$. The last three terms are relativistic corrections. Here, c is the speed of light, p is the momentum operator, and $\boldsymbol{\sigma}$ are the Pauli matrices:

$$\boldsymbol{\sigma}_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \boldsymbol{\sigma}_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \boldsymbol{\sigma}_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (2)$$

In Eq. (1), the third term is the spin-orbit operator H_{S-O} , which is responsible for the splitting of degenerate levels and the level shift leading to the change in band pattern. The fourth and fifth terms (Darwin interaction H_{Dar} and mass-velocity correction H_{m-v}) do not split degenerate levels but can mix and shift the levels of the same symmetry.

The nonrelativistic part of the Hamiltonian makes the major contribution to the energy; therefore, we can use the following procedure. First, we find eigenfunctions $\Psi_{n,k}^0(\mathbf{r})$ and eigenvalues $E_n^0(k)$ of the nonrelativistic Hamiltonian, using the previously developed nonrelativistic version of the LACW method [32–34]. Then, we double the basis set by introducing spin $\Psi_{n,k}^0(r, \chi) = \Psi_{n,k}^0(\mathbf{r})\chi$ (here, $\chi = \alpha$ or β are pure spin functions). Finally, we calculate the matrix elements H_{S-O} , H_{Dar} , and H_{m-v} , using the spinor basis $\Psi_{n,k}^0(\mathbf{r})\chi$

$$\begin{aligned} \langle \Psi_{n_2,k}^0(\mathbf{r})\chi_2 | H | \Psi_{n_1,k}^0(\mathbf{r})\chi_1 \rangle &= E_{n_1,k}^0 \delta_{n_2,n_1} \delta_{\chi_2,\chi_1} \\ &+ \delta_{\chi_2,\chi_1} \langle \Psi_{n_2,k}^0(\mathbf{r}) | H_{Dar} | \Psi_{n_1,k}^0(\mathbf{r}) \rangle \\ &+ \delta_{\chi_2,\chi_1} \langle \Psi_{n_2,k}^0(\mathbf{r}) | H_{m-v} | \Psi_{n_1,k}^0(\mathbf{r}) \rangle \\ &+ \langle \Psi_{n_2,k}^0(\mathbf{r})\chi_2 | H_{S-O} | \Psi_{n_1,k}^0(\mathbf{r})\chi_1 \rangle. \end{aligned} \quad (3)$$

The relativistic energies and wave functions are calculated by diagonalization of this matrix. Analytical expressions for the matrix elements are derived in the following sections.

Cylindrical Muffin-Tin Potential

In the LACW method, structural information is used as input parameters, and the muffin-tin (MT) approximation and density functional theory with Slater exchange are used for potentials. As a starting electron density of the system, a superposition of atomic densities is used, and the electron potential is constructed to be constant in the interspherical space Ω_{II} and spherically symmetric in the MT spheres Ω_I . As usually, the MT sphere radii were selected so that the atomic spheres touched each other but did not overlap. In addition, the atoms of nanowires are surrounded by an impenetrable cylindrical potential barrier since there is vacuum on the outside of the wires and electron motion is evidently confined by the size and cylindrical shape of wires. Thus, in the LACW method, the MT approximation requires the introduction of a free parameter, namely, the barrier radius a such that the space confined by the barrier accommodates an essential portion of the electron density of the system. This radius should be larger than the covalent radius (r_{cov}) but smaller than the van der Waals radius (r_{vdw}) of atoms. For the chains of Group IV ele-

ments, a was taken to be the half-sum of these radii: $a = (r_{\text{cov}} + r_{\text{vdv}})/2$. For partially ionic chains, the a values were taken to be the same as for isoelectronic covalent analogues.

Basis Functions

We describe the procedure for calculation of eigenfunctions $\Psi_{n,k}^0(\mathbf{r})$ of the nonrelativistic LACW method. The basis functions are solutions of the Schrödinger equation for the intersphere and MT regions. In the intersphere region, the basis functions $\Psi_{PMN}^k(\mathbf{r})$ are the solutions of the Schrödinger equation for free electron motion in a cylindrical potential well in cylindrical coordinates (Z, Φ, R) and are written in the form

$$\left\{ -\left[\frac{1}{R} \frac{\partial}{\partial R} \left(R \frac{\partial}{\partial R} \right) + \frac{1}{R^2} \frac{\partial^2}{\partial \Phi^2} + \frac{\partial^2}{\partial Z^2} \right] + V(R) \right\} \times \Psi(Z, \Phi, R) = E\Psi(Z, \Phi, R) \quad (4)$$

with $V(R) = 0$ for $R \leq a$ and $V(R) = \infty$ at $R > a$.

Solutions (4) in such a potential well are referred to as cylindrical waves. Because of the cylindrical symmetry of the $V(R)$ potential, cylindrical waves are written as $\Psi(Z, \Phi, R) = \Psi_p^k(Z) \Psi_M(\Phi) \Psi_{MN}(R)$. Here, the Bloch function $\Psi_p^k(Z)$ describes the free motion of an electron along the Z axis in the system with translational period d :

$$\Psi_p^k(Z) = (1/\sqrt{d}) \exp[i(k + k_p)Z], \quad 0 \leq k \leq \pi/d, \quad (5)$$

$$k_p = (2\pi/d)P \quad \text{with } P = 0, \pm 1, \pm 2, \dots$$

Functions $\Psi_M(\Phi) = e^{iM\Phi}/\sqrt{2\pi}$, where $M = 0, \pm 1, \pm 2, \dots$, correspond to rotation of an electron about the Z axis. Functions $\Psi_{MN}(R)$ describe the radial motion of an electron in the intersphere space. They are the solutions of the equation

$$\left[-\frac{1}{R} \frac{d}{dR} R \frac{d}{dR} + \frac{M^2}{R^2} + V(R) \right] \Psi_{MN}(R) = E_{|M|,N} \Psi_{MN}(R). \quad (6)$$

The cylindrical wave energies are $E = (k + k_p)^2 + E_{|M|,N}$. For $R \leq a$, Eq. (6) takes the form of the Bessel equation

$$\left[\frac{d^2}{dR^2} + \frac{1}{R} \frac{d}{dR} + \kappa_{|M|,N}^2 - \frac{M^2}{R^2} \right] \Psi_{MN}(R) = 0, \quad (7)$$

with $\kappa_{|M|,N} = (E_{|M|,N})^{1/2}$.

The solutions of Eq. (7) are Bessel functions of the first kind J_M . These functions are zeroed at the impenetrable barrier $\Psi_{MN}(a) = J(\kappa_{|M|,N}a) = 0$, which determines the spectrum $E_{|M|,N} = (\alpha_{|M|,N})^2/a^2$. Here, $\alpha_{|M|,N}$ is the root of N th degree of the Bessel function of the M th order ($N = 1, 2, \dots$). The constant $C_{M,N} =$

$\sqrt{2}/\left\{ a \left| J'_M(\kappa_{|M|,N}a) \right| \right\}$, where J'_M is the derivative of the Bessel function, is determined from normalization of $\Psi_{MN}(R)$. Finally, in the general cylindrical coordinate system (Z, R, Φ) and in the local spherical coordinate system (r, θ, φ) with the center at atom $\alpha_{\text{MT}}(Z_{\alpha_{\text{MT}}}, 0, 0)$, the cylindrical wave takes the form

$$\Psi_{\text{II}}^{PMN,k}(Z, \Phi, R) = \left\{ \sqrt{\Omega} \left| J'_M(\kappa_{|M|,N}a) \right| \right\}^{-1} \times \exp\{i[(k + k_p)Z + M\Phi]\} J_M(\kappa_{|M|,N}R), \quad (8)$$

$$\Psi_{\text{II},\alpha_{\text{MT}}}^{PMN,k}(r, \theta, \varphi) = \left\{ \sqrt{\Omega} \left| J'_M(\kappa_{|M|,N}a) \right| \right\}^{-1} \times \exp\{i[(k + k_p)Z_{\alpha_{\text{MT}}}] \exp\{i[(k + k_p)r \cos \theta]\} \times J_M(\kappa_{|M|,N}r \sin \theta) e^{iM\varphi}, \quad (9)$$

where $\Omega = \pi a^2 d$.

Inside the MT sphere α_{MT} in the local spherical coordinate system, the basis function is expanded in spherical harmonics $Y_{lm}(\theta, \varphi)$:

$$\Psi_{\alpha_{\text{MT}}}^{PMN,k}(r, \theta, \varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l \left[A_{lm,\alpha_{\text{MT}}}^{PMN,k} u_{l,\alpha_{\text{MT}}}(r, E_{l,\alpha_{\text{MT}}}) + B_{lm,\alpha_{\text{MT}}}^{PMN,k} \dot{u}_{l,\alpha_{\text{MT}}}(r, E_{l,\alpha_{\text{MT}}}) \right] Y_{lm}(\theta, \varphi). \quad (10)$$

Here, $u_{l,\alpha_{\text{MT}}}$ are the solutions of the radial Schrödinger equation for spherically symmetric potential $V_{\alpha_{\text{MT}}}$ and energy $E_{l,\alpha_{\text{MT}}}$

$$\frac{1}{r} \frac{d^2 r u_{l,\alpha_{\text{MT}}}(r)}{dr^2} + \left(E_{l,\alpha_{\text{MT}}} - V_{\alpha_{\text{MT}}}(r) - \frac{l(l+1)}{r^2} \right) u_{l,\alpha_{\text{MT}}}(r) = 0, \quad (11)$$

and $\dot{u}_{l,\alpha_{\text{MT}}} = [\partial u_{l,\alpha_{\text{MT}}}/\partial E]_{E_{l,\alpha_{\text{MT}}}}$.

By equating the values of functions $\Psi_{\text{II},\alpha_{\text{MT}}}^{PMN,k}(r, \theta, \varphi)|_{r=r_{\alpha_{\text{MT}}}}$ (9) and $\Psi_{\alpha_{\text{MT}}}^{PMN,k}(r, \theta, \varphi)|_{r=r_{\alpha_{\text{MT}}}}$ (10), as well as their derivatives $\partial[\Psi_{\alpha_{\text{MT}}}^{PMN,k}(r, \theta, \varphi)]/\partial r|_{r=r_{\alpha_{\text{MT}}}}$ and $\partial[\Psi_{\text{II},\alpha_{\text{MT}}}^{PMN,k}(r, \theta, \varphi)]/\partial r|_{r=r_{\alpha_{\text{MT}}}}$ with respect to radius, constants $A_{lm,\alpha_{\text{MT}}}^{PMN,k}$ and $B_{lm,\alpha_{\text{MT}}}^{PMN,k}$ are selected so that basis functions $\Psi_{PMN}^k(\mathbf{r})$ (referred to as linear augmented cylindrical waves) and their first derivatives are continuous everywhere, including the boundaries of the MT spheres.

For monatomic wires, nonzero $A_{lm,\alpha_{\text{MT}}}^{PMN,k}$ and $B_{lm,\alpha_{\text{MT}}}^{PMN,k}$ values correspond to $m = M$; therefore,

$$\Psi_{\alpha_{MT}}^{PMN,k}(r, \theta, \varphi) = \sum_{l=|M|}^{\infty} \left[A_{lM, \alpha_{MT}}^{PMN,k} u_{l, \alpha_{MT}}(r, E_{l, \alpha_{MT}}) + B_{lM, \alpha_{MT}}^{PMN,k} \dot{u}_{l, \alpha_{MT}}(r, E_{l, \alpha_{MT}}) \right] Y_{lM}(\theta, \varphi), \quad (12)$$

where

$$\begin{aligned} A_{lM, \alpha_{MT}}^{PMN,k} &= r_{\alpha_{MT}}^2 D_{lM, \alpha_{MT}}^{PMN,k} a_{lM, \alpha_{MT}}^{PMN,k}, \\ B_{lM, \alpha_{MT}}^{PMN,k} &= r_{\alpha_{MT}}^2 D_{lM, \alpha_{MT}}^{PMN,k} b_{lM, \alpha_{MT}}^{PMN,k}, \end{aligned} \quad (13)$$

$$D_{lM, \alpha_{MT}}^{PMN,k} = \sqrt{\pi} \left\{ \sqrt{\Omega} \left| J'_M(\kappa_{|M|, N} a) \right| \right\}^{-1} (-1)^{\frac{M+|M|+l}{2}} \times i^l \left[\frac{(2l+1)(l-|M|)!}{(l+|M|)!} \right]^{1/2} \exp\{i(k+k_p)Z_{\alpha_{MT}}\}, \quad (14)$$

$$\begin{aligned} & a_{lM, \alpha_{MT}}^{PMN,k}(r_{\alpha_{MT}}) \\ &= I_{2, lM, \alpha_{MT}}^{PMN,k} \dot{u}_{l, \alpha_{MT}}(r_{\alpha_{MT}}) - I_{1, lM, \alpha_{MT}}^{PMN,k} \dot{u}'_{l, \alpha_{MT}}(r_{\alpha_{MT}}), \\ & b_{lM, \alpha_{MT}}^{PMN,k}(r_{\alpha_{MT}}) \\ &= I_{1, lM, \alpha_{MT}}^{PMN,k} u'_{l, \alpha_{MT}}(r_{\alpha_{MT}}) - I_{2, lM, \alpha_{MT}}^{PMN,k} u_{l, \alpha_{MT}}(r_{\alpha_{MT}}). \end{aligned} \quad (15)$$

Here, the prime denotes the radial derivative of the $u_{l, \alpha_{MT}}$ and $\dot{u}_{l, \alpha_{MT}}$ functions, and I_1 and I_2 are the integrals of augmented Legendre polynomials $P_l^{|M|}$:

$$I_{1, lM, \alpha_{MT}}^{PMN,k} = 2 \int_0^{\pi/2} \exp\{i(k+k_p)r_{\alpha_{MT}} \cos \theta\} \times J_M(\kappa_{|M|, N} r_{\alpha_{MT}} \sin \theta) P_l^{|M|}(\cos \theta) \sin \theta d\theta, \quad (16)$$

$$\begin{aligned} I_{2, lM, \alpha_{MT}}^{PMN,k} &= 2 \int_0^{\pi/2} \exp\{i(k+k_p)r_{\alpha_{MT}} \cos \theta\} \{i(k+k_p) \\ & \times \cos \theta J_M(k_{|M|, N} r_{\alpha_{MT}} \sin \theta) + (1/2)k_{|M|, N} \sin \theta\} \\ & \times [J_{M-1}(k_{|M|, N} r_{\alpha_{MT}} \sin \theta) \\ & - J_{M+1}(k_{|M|, N} r_{\alpha_{MT}} \sin \theta)] P_l^{|M|}(\cos \theta) \sin \theta d\theta. \end{aligned} \quad (17)$$

Methods of solution of the nonrelativistic Schrödinger equation with the use of the linear augmented cylindrical wave basis have been described elsewhere [32–34]. The results of this calculation are nonrelativistic energies $E_n^0(k)$ of different bands n at different points of the Brillouin zone and spin-independent wave functions $\Psi_{n,k}^0(\mathbf{r})$, presented as a linear combination of basis functions

$$\Psi_{n,k}^0(\mathbf{r}) = \sum_{PMN} a_{PMN}^{kn} \Psi_{PMN}^k(\mathbf{r}). \quad (18)$$

Matrix Elements H_{m-v}

Operator p^4 is Hermitian; hence,

$$\begin{aligned} \langle \Psi_{n_2, k}^0(\mathbf{r}) | H_{m-v} | \Psi_{n_1, k}^0(\mathbf{r}) \rangle &= -\frac{1}{c^2} \langle \Psi_{n_2, k}^0(\mathbf{r}) | p^4 | \Psi_{n_1, k}^0(\mathbf{r}) \rangle \\ &= -\frac{1}{c^2} \langle p^2 \Psi_{n_2, k}^0(\mathbf{r}) | p^2 \Psi_{n_1, k}^0(\mathbf{r}) \rangle \\ &= -\frac{1}{c^2} \langle [H_0 - V(\mathbf{r})] \Psi_{n_2, k}^0(\mathbf{r}) | [H_0 - V(\mathbf{r})] \Psi_{n_1, k}^0(\mathbf{r}) \rangle \\ &= -\frac{1}{c^2} \langle [E_{n_2, k}^0 - V(\mathbf{r})] \Psi_{n_2, k}^0(\mathbf{r}) | [E_{n_1, k}^0 - V(\mathbf{r})] \Psi_{n_1, k}^0(\mathbf{r}) \rangle. \end{aligned} \quad (19)$$

Since $V(\mathbf{r}) = 0$, outside the MT spheres, taking into account Eq. (18), we have

$$\begin{aligned} \langle \Psi_{n_2, k}^0(\mathbf{r}) | H_{m-v} | \Psi_{n_1, k}^0(\mathbf{r}) \rangle &= -\frac{1}{c^2} \left\{ E_{n_2, k} E_{n_1, k} \delta_{n_2, n_1} \right. \\ & \left. + \sum_{\alpha_{MT}} \int_{\Omega_{\alpha_{MT}}} F_{n_2, n_1, k}^{\alpha_{MT}}(\mathbf{r}) \bar{\Psi}_{n_2, k}^0(\mathbf{r}) \Psi_{n_1, k}^0(\mathbf{r}) d\mathbf{r} \right\} \\ &= -\frac{1}{c^2} \left\{ E_{n_2, k} E_{n_1, k} \delta_{n_2, n_1} + \sum_{P_2 M_2 N_2} \sum_{P_1 M_1 N_1} \bar{a}_{P_2 M_2 N_2}^{kn_2} a_{P_1 M_1 N_1}^{kn_1} \right. \\ & \left. \times \sum_{\alpha_{MT}} \int_{\Omega_{\alpha_{MT}}} F_{n_2, n_1, k}^{\alpha_{MT}}(\mathbf{r}) \bar{\Psi}_{\alpha_{MT}}^{P_2 M_2 N_2, k}(\mathbf{r}) \Psi_{\alpha_{MT}}^{P_1 M_1 N_1, k}(\mathbf{r}) d\mathbf{r} \right\}, \end{aligned} \quad (20)$$

where

$$F_{n_2, n_1, k}^{\alpha_{MT}}(\mathbf{r}) \equiv [E_{n_2, k} - V_{\alpha_{MT}}(\mathbf{r})][E_{n_1, k} - V_{\alpha_{MT}}(\mathbf{r})] - E_{n_2, k} E_{n_1, k}.$$

Substituting Eqs. (12)–(15), we obtain

$$\begin{aligned} \langle \Psi_{n_2, k}^0(\mathbf{r}) | H_{m-v} | \Psi_{n_1, k}^0(\mathbf{r}) \rangle &= -\frac{1}{c^2} \left\{ E_{n_2, k} E_{n_1, k} \delta_{n_2, n_1} + \frac{\pi}{\Omega} \right. \\ & \times \sum_{P_2 M_2 N_2} \sum_{P_1 M_1 N_1} \delta_{M_2, M_1} \bar{a}_{P_2 M_1 N_2}^{kn_2} a_{P_1 M_1 N_1}^{kn_1} \\ & \times \left\{ J'_{M_1}(\kappa_{|M_1|, N_2} a) J'_{M_1}(\kappa_{|M_1|, N_1} a) \right\}^{-1} \\ & \times \sum_{\alpha_{MT}} r_{\alpha_{MT}}^4 \exp[i(k_{p_1} - k_{p_2})Z_{\alpha_{MT}}] \end{aligned} \quad (21)$$

$$\begin{aligned} & \times \sum_{l=|M_1|}^{\infty} (2l+1) \frac{(l-|M_1|)!}{(l+|M_1|)!} \left\{ \mu_{n_2, n_1, k, l, \alpha_{MT}} \bar{a}_{lM_1, \alpha_{MT}}^{P_2 M_1 N_2, k} a_{lM_1, \alpha_{MT}}^{P_1 M_1 N_1, k} \right. \\ & \left. + \ddot{\mu}_{n_2, n_1, k, l, \alpha_{MT}} \bar{b}_{lM_1, \alpha_{MT}}^{P_2 M_1 N_2, k} b_{lM_1, \alpha_{MT}}^{P_1 M_1 N_1, k} + \dot{\mu}_{n_2, n_1, k, l, \alpha_{MT}} \right. \\ & \left. \times \left[a_{lM_1, \alpha_{MT}}^{P_2 M_1 N_2, k} b_{lM_1, \alpha_{MT}}^{P_1 M_1 N_1, k} + b_{lM_1, \alpha_{MT}}^{P_2 M_1 N_2, k} a_{lM_1, \alpha_{MT}}^{P_1 M_1 N_1, k} \right] \right\}. \end{aligned}$$

Here,

$$\mu_{n_2, n_1, k, l, \alpha_{MT}} = \int_0^{r_{\alpha}^{\text{MT}}} F_{n_2, n_1, k}^{\alpha_{MT}}(\mathbf{r}) u_{l, \alpha_{MT}}^2(\mathbf{r}) r^2 dr,$$

$$\dot{\mu}_{n_2, n_1, k, l, \alpha_{MT}} = \int_0^{r_{\alpha}^{\text{MT}}} F_{n_2, n_1, k}^{\alpha_{MT}}(\mathbf{r}) u_{l, \alpha_{MT}}(\mathbf{r}) \dot{u}_{l, \alpha_{MT}}(\mathbf{r}) r^2 dr,$$

$$\ddot{u}_{n_2, n_1, k, l, \alpha_{MT}} = \int_0^{r_{\alpha}^{MT}} F_{n_2, n_1, k}^{\alpha_{MT}}(r) \dot{u}_{l, \alpha_{MT}}^2(r) r^2 dr.$$

Matrix Elements H_{Dir}

The Darwin interaction can be rewritten in a more convenient form, using relations reported in [35] (where integrals are taken over the volume determined from the periodic boundary conditions):

$$\int \nabla[\bar{\Phi}\Phi'(\nabla V)] dv = \int_{\text{encl.surf}} (\bar{\Phi}\Phi'\nabla V) d\sigma, \quad (22)$$

$$\begin{aligned} & \nabla[\bar{\Phi}\Phi'(\nabla V)] \\ &= \bar{\Phi}\Phi'(\nabla^2 V) + (\nabla V)(\nabla\bar{\Phi})\Phi' + (\nabla V)(\nabla\Phi')\bar{\Phi}. \end{aligned} \quad (23)$$

Combining these equations with $\Phi = \Psi_{n_2, k}^0(\mathbf{r})$ and $\Phi' = \Psi_{n_1, k}^0(\mathbf{r})$, we find

$$\begin{aligned} & \frac{1}{2c^2} \langle \Psi_{n_2, k}^0(\mathbf{r}) | \nabla^2 V(\mathbf{r}) | \Psi_{n_1, k}^0(\mathbf{r}) \rangle \\ &= -\frac{1}{2c^2} \sum_{\alpha_{MT}} \int_{\Omega_{\alpha_{MT}}} \{ \bar{\Psi}_{n_2, k}^0(\mathbf{r}) [\nabla V_{\alpha_{MT}}(\mathbf{r})] [\nabla \Psi_{n_1, k}^0(\mathbf{r})] d\mathbf{r} \\ & \quad + [\nabla \bar{\Psi}_{n_2, k}^0(\mathbf{r})] [\nabla V_{\alpha_{MT}}(\mathbf{r})] \Psi_{n_1, k}^0(\mathbf{r}) d\mathbf{r} \} \\ &= -\frac{1}{2c^2} \sum_{P_2 M_2 N_2} \sum_{P_1 M_1 N_1} \bar{a}_{P_2 M_2 N_2}^{kn_2} a_{P_1 M_1 N_1}^{kn_1} \\ & \times \sum_{\alpha_{MT}} \int_{\Omega_{\alpha_{MT}}} \{ \bar{\Psi}_{\alpha_{MT}}^{P_2 M_2 N_2, k}(\mathbf{r}) [\nabla V_{\alpha_{MT}}(\mathbf{r})] [\nabla \Psi_{\alpha_{MT}}^{P_1 M_1 N_1, k}(\mathbf{r})] \\ & \quad + [\nabla \bar{\Psi}_{\alpha_{MT}}^{P_2 M_2 N_2, k}(\mathbf{r})] [\nabla V_{\alpha_{MT}}(\mathbf{r})] \Psi_{\alpha_{MT}}^{P_1 M_1 N_1, k}(\mathbf{r}) \} d\mathbf{r}. \end{aligned}$$

Substituting Eqs. (12)–(15), we obtain

$$\begin{aligned} & \langle \Psi_{n_2, k}^0(\mathbf{r}) | H_{Dir} | \Psi_{n_1, k}^0(\mathbf{r}) \rangle = -\frac{1}{2c^2} \frac{\pi}{\Omega} \\ & \times \sum_{P_2 M_2 N_2} \sum_{P_1 M_1 N_1} \delta_{M_2 M_1} \bar{a}_{P_2 M_2 N_2}^{kn_2} a_{P_1 M_1 N_1}^{kn_1} \\ & \times \left\{ J'_{M_2}(\kappa_{|M_2|, N_2} a) J'_{M_1}(\kappa_{|M_1|, N_1} a) \right\}^{-1} \sum_{\alpha_{MT}} r_{\alpha_{MT}}^4 \\ & \times \exp\{i[(k_{p_1} - k_{p_2})Z_{\alpha_{MT}}]\} \sum_{l=|M_1|}^{\infty} (2l+1) \frac{(l-|M_1|)!}{(l+|M_1|)!} \\ & \times \left\{ 2\zeta_{l, \alpha_{MT}}(u, u') \bar{a}_{l M_1, \alpha_{MT}}^{P_2 M_2 N_2, k} a_{l M_1, \alpha_{MT}}^{P_1 M_1 N_1, k} + 2\zeta_{l, \alpha_{MT}}(\dot{u}, \dot{u}') \right. \\ & \times \bar{b}_{l M_1, \alpha_{MT}}^{P_2 M_2 N_2, k} b_{l M_1, \alpha_{MT}}^{P_1 M_1 N_1, k} + [\zeta_{l, \alpha_{MT}}(u, \dot{u}') + \zeta_{l, \alpha_{MT}}(\dot{u}, u')] \\ & \left. \times \left[\bar{a}_{l M_1, \alpha_{MT}}^{P_2 M_2 N_2, k} b_{l M_1, \alpha_{MT}}^{P_1 M_1 N_1, k} + \bar{b}_{l M_1, \alpha_{MT}}^{P_2 M_2 N_2, k} a_{l M_1, \alpha_{MT}}^{P_1 M_1 N_1, k} \right] \right\}. \end{aligned}$$

Here,

$$\begin{aligned} \zeta_{l, \alpha_{MT}}(u, u') &= \int_0^{r_{\alpha_{MT}}} u_{l, \alpha_{MT}}(r, E_{l, \alpha_{MT}}) \\ & \times \frac{dV_{\alpha_{MT}}(r)}{dr} u'_{l, \alpha_{MT}}(r, E_{l, \alpha_{MT}}) r^2 dr, \\ \zeta_{l, \alpha_{MT}}(\dot{u}, \dot{u}') &= \int_0^{r_{\alpha_{MT}}} \dot{u}_{l, \alpha_{MT}}(r, E_{l, \alpha_{MT}}) \\ & \times \frac{dV_{\alpha_{MT}}(r)}{dr} \dot{u}'_{l, \alpha_{MT}}(r, E_{l, \alpha_{MT}}) r^2 dr, \\ \zeta_{l, \alpha_{MT}}(u, \dot{u}') &= \int_0^{r_{\alpha_{MT}}} u_{l, \alpha_{MT}}(r, E_{l, \alpha_{MT}}) \\ & \times \frac{dV_{\alpha_{MT}}(r)}{dr} \dot{u}'_{l, \alpha_{MT}}(r, E_{l, \alpha_{MT}}) r^2 dr, \\ \zeta_{l, \alpha_{MT}}(\dot{u}, u') &= \int_0^{r_{\alpha_{MT}}} \dot{u}_{l, \alpha_{MT}}(r, E_{l, \alpha_{MT}}) \\ & \times \frac{dV_{\alpha_{MT}}(r)}{dr} u'_{l, \alpha_{MT}}(r, E_{l, \alpha_{MT}}) r^2 dr. \end{aligned}$$

Matrix Elements H_{S-O}

Now, we can use the spin-dependent basis $\Psi_{PMN}^k(\mathbf{r}, \alpha) = \Psi_{PMN}^k(\mathbf{r}, \alpha)$, $\Psi_{PMN}^k(\mathbf{r}, \beta) = \Psi_{PMN}^k(\mathbf{r}, \beta)$ for calculating the spin-orbit matrix elements. For the spherically symmetric potential of each MT sphere, this operator can be presented with the use of the angular momentum operator [35]:

$$\begin{aligned} H_{S-O} &= \sum_{\alpha_{MT}} \frac{1}{c^2} \sigma \cdot [(\nabla V_{\alpha_{MT}}) \times \mathbf{p}] = \sum_{\alpha_{MT}} \frac{1}{c^2} \frac{1}{r} \frac{dV}{dr} \sigma \mathbf{L} \\ &= \sum_{\alpha_{MT}} \frac{1}{c^2} \frac{1}{r} \frac{dV_{\alpha_{MT}}}{dr} \left(\frac{1}{2} \sigma_+ L_- + \frac{1}{2} \sigma_- L_+ + \sigma_z L_z \right). \end{aligned} \quad (24)$$

The effect of spin operator on functions α and β is described by the equations

$$\begin{aligned} \sigma_+ \alpha &= 0, \quad \sigma_- \alpha = 2\beta, \quad \sigma_z \alpha = \alpha, \\ \sigma_+ \beta &= 2\alpha, \quad \sigma_- \beta = 0, \quad \sigma_z \beta = -\beta. \end{aligned} \quad (25)$$

The action of the angular momentum operator on spherical harmonics does not disturb the radial part of the wave function:

$$\begin{aligned} L_z Y_{lm}(\theta, \varphi) &= m Y_{lm}(\theta, \varphi), \\ L_{\pm} Y_{lm}(\theta, \varphi) &= [l(l+1) - m(m \pm 1)]^{1/2} Y_{lm \pm 1}(\theta, \varphi). \end{aligned} \quad (26)$$

As a result, integrals $\langle \Psi_{n_2, k}^0(\mathbf{r}, \chi_2) | H_{S-O} | \Psi_{n_1, k}^0(\mathbf{r}, \chi_1) \rangle$ are presented as the products of integrals over radial and angular variables. Equations (18)–(20), along with orthogonality and normalization of spin functions α and β and spherical harmonics, make it possi-

ble to perform analytical integration over angular variables, which finally gives

$$\begin{aligned} & \langle \Psi_{n_2,k}^0(\mathbf{r}, \alpha) | H_{S-O} | \Psi_{n_1,k}^0(\mathbf{r}, \alpha) \rangle \\ &= \frac{\pi}{c^2 \Omega} \sum_{P_2 M_2 N_2} \sum_{P_1 M_1 N_1} \bar{a}_{P_2 M_2 N_2}^{kn_2} a_{P_1 M_1 N_1}^{kn_1} \delta_{M_2, M_1} \\ & \times \left\{ J'_{M_1}(\kappa_{|M_1|, N_2} a) J'_{M_1}(\kappa_{|M_1|, N_1} a) \right\}^{-1} \sum_{\alpha_{MT}} r_{\alpha_{MT}}^4 \end{aligned} \quad (27)$$

$$\begin{aligned} & \times \sum_{l=|M_1|}^{\infty} (2l+1) M_1 \frac{(l-|M_1|)!}{(l+|M_1|)!} \exp\{i(k_{p_2} - k_{p_1}) Z_{\alpha_{MT}}\} \\ & \times \left\{ \zeta_{l, \alpha_{MT}} (u^2) \bar{a}_{l, M_1, \alpha_{MT}}^{P_2, M_1, N_2} a_{l, M_1, \alpha_{MT}}^{P_1, M_1, N_1} + \zeta_{l, \alpha_{MT}} (\dot{u}^2) \bar{b}_{l, M_1, \alpha_{MT}}^{P_2, M_1, N_2} b_{l, M_1, \alpha_{MT}}^{P_1, M_1, N_1} \right. \\ & \left. + \zeta_{l, \alpha_{MT}} (u, \dot{u}) \left[\bar{a}_{l, M_1, \alpha_{MT}}^{P_2, M_1, N_2} b_{l, M_1, \alpha_{MT}}^{P_1, M_1, N_1} + \bar{b}_{l, M_1, \alpha_{MT}}^{P_2, M_1, N_2} a_{l, M_1, \alpha_{MT}}^{P_1, M_1, N_1} \right] \right\}, \end{aligned}$$

$$\begin{aligned} & \langle \Psi_{n_2,k}^0(\mathbf{r}, \beta) | H_{S-O} | \Psi_{n_1,k}^0(\mathbf{r}, \beta) \rangle \\ &= -\langle \Psi_{n_2,k}^0(\mathbf{r}, \alpha) | H_{S-O} | \Psi_{n_1,k}^0(\mathbf{r}, \alpha) \rangle, \end{aligned} \quad (28)$$

$$\begin{aligned} & \langle \Psi_{n_2,k}^0(\mathbf{r}, \beta) | H_{S-O} | \Psi_{n_1,k}^0(\mathbf{r}, \alpha) \rangle = \frac{\pi}{c^2 \Omega} \\ & \times \sum_{P_2 M_2 N_2} \sum_{P_1 M_1 N_1} \text{sign}(M_1) \delta_{M_2-1, M_1} \bar{a}_{P_2 M_2 N_2}^{kn_2} a_{P_1 M_1 N_1}^{kn_1} \\ & \times \left\{ J'_{M_1+1}(\kappa_{|M_1+1|, N_2} a) J'_{M_1}(\kappa_{|M_1|, N_1} a) \right\}^{-1} \sum_{\alpha_{MT}} r_{\alpha_{MT}}^4 \end{aligned}$$

$$\times \sum_{l=|M_1|}^{\infty} [l(l+1) - M_1(M_1+1)]^{1/2} \quad (29)$$

$$\begin{aligned} & \times \left[\frac{(l-|M_1|)! (l-|M_1+1|)!}{(l+|M_1|)! (l+|M_1+1|)!} \right]^{1/2} \exp\{i(k_{p_2} - k_{p_1}) Z_{\alpha_{MT}}\} \\ & \left\{ \zeta_{l, \alpha_{MT}} (u^2) \bar{a}_{l, M_1+1, \alpha_{MT}}^{P_2, M_1+1, N_2} a_{l, M_1, \alpha_{MT}}^{P_1, M_1, N_1} + \zeta_{l, \alpha_{MT}} (\dot{u}^2) \bar{b}_{l, M_1+1, \alpha_{MT}}^{P_2, M_1+1, N_2} b_{l, M_1, \alpha_{MT}}^{P_1, M_1, N_1} \right. \\ & \left. + \zeta_{l, \alpha_{MT}} (u, \dot{u}) \left[\bar{a}_{l, M_1+1, \alpha_{MT}}^{P_2, M_1+1, N_2} b_{l, M_1, \alpha_{MT}}^{P_1, M_1, N_1} + \bar{b}_{l, M_1+1, \alpha_{MT}}^{P_2, M_1+1, N_2} a_{l, M_1, \alpha_{MT}}^{P_1, M_1, N_1} \right] \right\}, \end{aligned}$$

$$\begin{aligned} & \langle \Psi_{n_2,k}^0(\mathbf{r}, \alpha) | H_{S-O} | \Psi_{n_1,k}^0(\mathbf{r}, \beta) \rangle \\ &= \langle \Psi_{n_2,k}^0(\mathbf{r}, \beta) | H_{S-O} | \Psi_{n_1,k}^0(\mathbf{r}, \alpha) \rangle^*, \end{aligned} \quad (30)$$

where

$$\zeta_{l, \alpha_{MT}} (u^2) = \int_0^{r_{\alpha_{MT}}} [u_{l, \alpha_{MT}}(r)]^2 \frac{dV_{\alpha_{MT}}(r)}{dr} r dr, \quad (31)$$

$$\dot{\zeta}_{l, \alpha_{MT}} (u, \dot{u}) = \int_0^{r_{\alpha_{MT}}} u_{l, \alpha_{MT}}(r) \dot{u}_{l, \alpha_{MT}}(r) \frac{dV_{\alpha_{MT}}(r)}{dr} r dr, \quad (32)$$

$$\ddot{\zeta}_{l, \alpha_{MT}} (\dot{u}^2) = \int_0^{r_{\alpha_{MT}}} [\dot{u}_{l, \alpha_{MT}}(r)]^2 \frac{dV_{\alpha_{MT}}(r)}{dr} r dr. \quad (33)$$

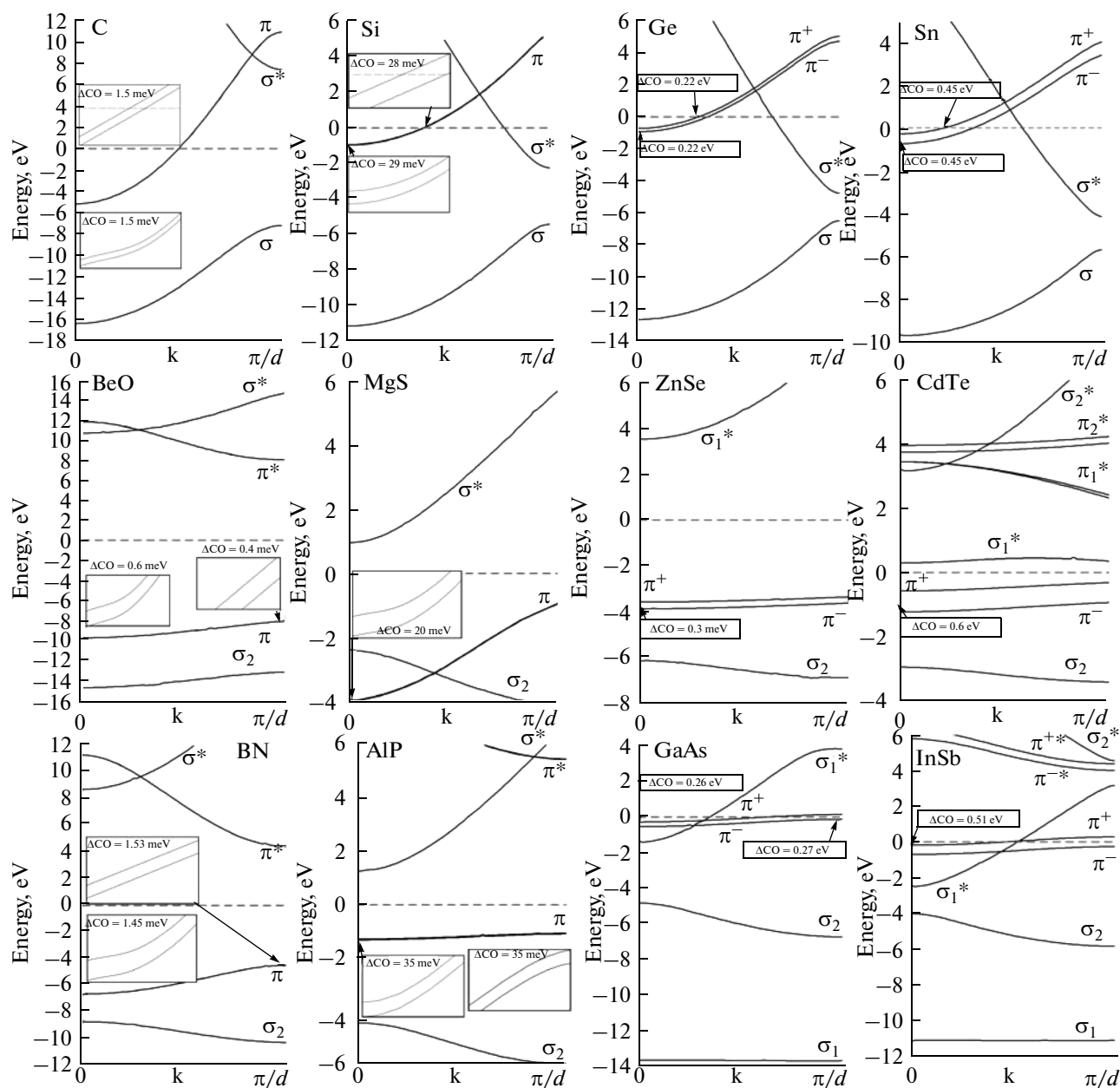
Sums over atoms α_{MT} of the unit cell include one and two atoms for covalent and partially ionic chains of Group IV and $A^N B^{8-N}$ elements, respectively.

CALCULATION RESULTS

The figure shows the calculated band structures of covalent monatomic chains of Group IV elements; points Γ and k correspond to the center ($k=0$) and the edge ($k=\pi/d$) of the Brillouin zone. The electronic structure of wires is composed of $\sigma(s)$, two π^+ and π^- , and $\sigma(p_z)^*$ bands. Like in nonrelativistic pseudopotential plane-wave calculation [27, 28], the \bar{N} , Si, Ge, and Sn chains are metallic; however, there is a great difference between the relativistic and nonrelativistic band structures. In the nonrelativistic model, because of the cylindrical symmetry of the chains, the π bands crossing the Fermi level are orbitally doubly degenerate; i.e., the π^+ and π^- band energies are exactly the same. Double orbital degeneracy of the π band corresponds to semiclassical clockwise and counterclockwise rotational motion of an electron about the symmetry axis of the wire. In the absence of spin-orbit coupling and with allowance of two possible spin directions, the π bands must be fourfold degenerate. LACW calculations show that the spin and orbital motion of electrons are coupled in the chains, thus splitting the fourfold degeneracy into the π^+ and π^- bands, as shown in the figure. Each π^+ and π^- band remains doubly spin-degenerate. The Kramers theorem for systems with time-reversal symmetry and the existence of inversion symmetry in linear chains lead to that the π^+ and π^- bands remain spin-degenerate, spin polarization directions in each of them being opposite. The spin-orbit splitting energy $\Delta_{S-O} = E(\pi^+) - E(\pi^-)$ depends on wave vector k , increasing in going from point Γ to point K of the Brillouin zone. The spin-orbit splitting energy Δ_{S-O} for C and Sn chains varies from 1.7 meV to 0.67 eV, respectively. Such spin-orbit gaps can be detected experimentally and can have an effect on the electrical properties of wires. For example, in a carbon nanotube, spin-orbit splitting, being only 0.37 and 0.21 meV for electrons and holes, is detected by the change in the magnetic field dependence of the differential conductivity and by means of tunneling spectroscopy [38]. It is evident that the spin-orbit splitting of orbitally non-degenerate σ bands is absent.

Mass-velocity corrections lead to the lowering of all valence band levels. In the carbon and silicon chains, the level shifts are 2–5 and 10–30 meV, respectively, and, possibly, they can be neglected; however, in the chains of germanium and tin atoms, this level lowering is already as large as 0.6 and 2.2 eV, respectively. The Darwin corrections are several-fold lower than the mass-velocity contributions.

Like nonrelativistic calculations [27, 28], relativistic calculations demonstrate an important difference between the band structure of carbon chains and those



Band structure of covalent and partially ionic chains. The origin is at the Fermi level.

of the chains of other Group IV elements near the Fermi level. For carbon, only the π band crosses the Fermi level at the center of the Brillouin zone at $k = \pi/2d$, which must lead to the Peierls distortion of the chain. Another situation is observed for the Si, Ge, and Sn chains: here, in addition to the π^+ and π^- bands, the σ^* band crosses the Fermi level, which must prevent the Peierls dimerization of these chains. It is worth noting that spin-orbit splitting lifts the orbital degeneracy; thus, formation of large spin-orbit gaps in the chains of heavy elements also prevents the Peierls dimerization, stabilizing chains with equal lengths of all bonds.

Going from covalent to partially ionic chains is accompanied by a sharp change in the band structure. For example, the carbon chain with all equal bond lengths has a metallic electronic structure with the zero band gap in the center of the Brillouin zone, whereas the boron nitride chain is an insulator with an optical gap of 8 eV and transitions between the occupied π^- and vacant π^* states at the edge of the Brillouin zone. Qualitatively, these differences are explained by the existence of the antisymmetric component of the electron potential in the BN wire, which mixes even bonding and odd antibonding π states. This is also responsible for the analogous splitting of the σ and σ^*

bands in going from the carbon chain to the boron nitride one.

Transition from the BN chain to the AlP, GaAs, and InSb chains is accompanied by a decrease in the chemical bond ionicity, which leads to a gradual decrease in the $\pi-\pi^*$ and $\sigma_1-\sigma_2$ gap widths. In addition, the low-energy shift of σ_1^* is observed. These effects lead to that the AlP chain turns out to be a semiconductor with an indirect band gap of 2 eV corresponding to the $\pi(K) \rightarrow \sigma(\Gamma)$ transition, whereas the GaAs and InSb chains are metals due to the crossing of the π^+ , π^- , and σ_1^* -bands. Transition from the $A^{III}B^V$ to $A^{II}B^{VI}$ chains is accompanied by an increase in the ionicity and optical gap.

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