Augmented Cylindrical Wave Method in the Theory of Electronic Structure of Quantum Nanowires

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SUMMARY: A computational method for the band structure of nanowires having approximately cylindrical symmetry is developed. The effective one-electron potential is supposed to have spherical symmetry in the region of the atomic centres and is assumed to be constant in the interstitial region. The corresponding electronic density is supposed to be localised inside the region of cylindrical shape. The base wave functions are obtained by sewing together solutions of the Schrödinger equation for an electron in the empty cylinder (cylindrical waves) with spherically symmetrical solutions for the muffin-tin spheres. Under the condition of the continuity of the base functions and their first derivatives overlap integrals and Hamiltonian matrix elements are obtained. Dispersion curves and electronic densities of states for chains of transition metals and those of nanowires from metals from K to Zn are calculated.

Introduction

Preparation of the fullerene carbon nanotubes[1-7] offers strong possibilities of manufacturing the nanowires with intriguing mechanical, electronic, and magnetic properties[4, 8-13]. The inner cavity of these tubules can be filled with a variety of substances including the transition metals [2-8]. We are now being confronted with a problem of predicting structural properties of nanotubes intercalated with transition metals. Recently, a linear augmented plane-wave formalism and computer program for the quasi one-dimensional systems having a translation symmetry in one direction has been developed (bar LAPW method[14-16]) and used for calculations of the electronic structures of the nanotubes $\{M@C_{20}\}_n$ doped with 3*d*-metals. There, it is assumed that four perpendicular planes confine the essential part of the electronic density inside a bar region with a *square* cross section, although many interesting quasi one-dimensional structures like nanotubes have cross sections with approximately *cylindrical* symmetry. Here we present a principal generalisation of the previous approach, the linear augmented cylindrical wave (LACW) method, which is more adequate in description of the symmetry of the electronic structure of nanowires. The method will be used to study the ultrathin wires composed of the third period metals from the K to Zn. In addition to the carbon

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nanotubes, the metal atomic chains are available experimentally as the guests inside zeolite and deposited on crystal surfaces[17].

Formalism

As usually in the muffin-tin (MT) approximation, we suggest that the effective one-electron potential is spherically symmetric inside MT spheres and is constant in the interstitial region. In nanowires the infinite motion of electrons is possible in one direction (along the z axis) giving rise to electronic bands. We suggest that a system is confined between the impenetrable cylindrical potential barrier for the other two dimensions, so that the wave functions reduce to zero on the boundary of the cylinder and in the region beyond it. A radius a of the cylinder is chosen in such a way that the essential part of the electronic is located inside the cylinder with the πa^2 cross section.

In order to obtain the basis, one has to augment eigenfunctions (cylindrical waves) in the interstitial region with functions constructed from the solutions inside the MT-spheres. The resulting base functions (LACWs) should be continuous with continuous first derivatives on the MT-spheres. In the interstitial region the base functions are solutions of the wave equation for a free electron in the cylinder. The base function is a product $\psi_P(\boldsymbol{Z})\psi_M(\Phi)\psi_{|M|,N}(R)$[18]. The $\psi_P(\boldsymbol{Z})$ function corresponds to a free electron movement along z axis

$$\psi_P(\boldsymbol{Z})=(1/\sqrt{c})\exp[i(\boldsymbol{k}+\boldsymbol{k}_P)\boldsymbol{Z}],\ k_P = (2\pi/c)P,\ P=0, \pm1, \pm2, \ldots \quad (1)$$

here c is the lattice constant for z direction, $-\pi/c \le \boldsymbol{k} \le \pi/c$. The function ψ_M is:

$$\psi_M(\Phi)=(1/\sqrt{2\pi})\exp(iM\Phi),\ M= 0, \pm1, \pm2, \ldots \quad (2)$$

Finally, the function $\psi_{M,N}(R)$ is the radial part of the Schrödinger equation:

$$[-\frac{1}{R}\frac{d}{dR}R\frac{d}{dR}+\frac{M^2}{R^2}]\psi_{M,N}(R)+U(R)\psi_{M,N}(R)=E_{|M|,N}\psi_{M,N}(R) \quad (3)$$

Here $U(R)=U$ for $R<a$ and $U(R)=0$ for $R>a$; $E_{|M|,N}$ is the energy spectrum which depends on two quantum numbers N and M. The electronic energy corresponding to cylindrical wave $\Psi(\boldsymbol{Z},\Phi,R)$ is:

$$E = (k+k_P)^2 + E_{|M|,N}. \quad (4)$$

For $R \le a$ Eq (3) has the form:

$$[\frac{d^2}{dR^2}+\frac{1}{R}\frac{d}{dR}+\kappa^2_{|M|N}-\frac{M^2}{R^2}]\psi_{M,N}(R)=0, \quad (5)$$

where $\kappa_{|M_b N} = \{E_{|M_b N}\}^{1/2}$. This is the well known Bessel equation[19-20]. The solution is $\psi_{M,N}(R) = CJ_M(\kappa_{|M_b N} R)$, where J_M is the cylindrical Bessel function of the order M and C is a constant.

The wave function equals to zero on the impenetrable barrier $\psi_{M,N}(a) = J_M(\kappa_{|M_b N} a) = 0$; thus, the energy spectrum $E_{|M_b N}$ is determined by the roots of Bessel function as

$$E_{|M_b N} = (\alpha_{|M_b N})^2 / a^2. \tag{6}$$

Here $\alpha_{|M_b N}$ is the root number N (N=1, 2, ...) of the cylindrical Bessel function of the order M. The constant C is obtained from the normalisation condition for $\psi_{M,N}(R)$[20]:

$$C = \sqrt{2} / \{a\, |J'_M(\kappa_{|M_b N} a)|\}, \tag{7}$$

where J'_M is the derivative of the Bessel function. Finally, in the cylindrical coordinate system the base wave function in the interstitial region Ω_{II} is:

$$\Psi_{II}(Z, \Phi, R | k, P, M, N) = \{\sqrt{\Omega}\, |J'_M(\kappa_{|M_b N} a)|\}^{-1} \exp\{i(\boldsymbol{K}_P \boldsymbol{Z} + M\Phi)\}\, J_M(\kappa_{|M_b N} R). \tag{8}$$

Here $\Omega = \pi c a^2$ is the unit cell volume and $\boldsymbol{K}_P = \boldsymbol{k} + \boldsymbol{k}_P$.

Inside the α-th MT-sphere, the base function is expanded in terms of spherical harmonics[21, 22]:

$$\Psi_{I\alpha}(r, \theta, \varphi | k, P, M, N) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \{A_{lm} u_l(r, E_l) + B_{lm} \dot{u}_l(r, E_l)\}\, Y_{lm}(\theta, \varphi), \tag{9}$$

where $u_{l\alpha}$ is the solution of the radial Schrödinger equation in the α-th MT sphere for the energy E_l, $\dot{u}_{l\alpha} = [\partial u / \partial E]_{E_l}$, and r, θ, φ are the polar coordinates of the vector ρ_α of the local coordinate system of the MT sphere α. The coefficients A_{lm} and B_{lm} are obtained under the condition that the wave function (8), (9) is continuous with the first continuous derivative. These coefficients are readily calculated taking into account the addition theorem for the cylindrical Bessel functions[19, 20]:

$$\Psi_{II}(r, \theta, \varphi | k, P, M, N) = \{\sqrt{\Omega}\, |J'_{|M|}(\kappa_{|M_b N} a)|\}^{-1} \exp\{i(\boldsymbol{K}_P \boldsymbol{Z}_\alpha + M\Phi_\alpha)\} \times$$

$$\exp\{i[(k + k_P) r \cos\theta]\}\, (-1)^M \sum_{m=-\infty}^{\infty} J_m(\kappa_{|M_b N} r \sin\theta)\, J_{m-M}(\kappa_{|M_b N} R_\alpha)\, e^{im\varphi}, \tag{10}$$

where $\boldsymbol{Z}_\alpha$, Φ_α, and R_α are the cylindrical coordinates of a MT sphere α centre. We obtain:

$$\begin{aligned} A_{lm} &= (r_\alpha^{MT})^2\, D\, \{I_2 \dot{u}_l(r_\alpha^{MT}, E_l) - I_1 \dot{u}'_l(r_\alpha^{MT}, E_l)\} \\ B_{lm} &= (r_\alpha^{MT})^2\, D\, \{I_1 u'_l(r_\alpha^{MT}, E_l) - I_2 u_l(r_\alpha^{MT}, E_l)\} \end{aligned} \tag{11}$$

$$D = \sqrt{\pi}\, \{\sqrt{\Omega}\, |J'_{|M|}(\kappa_{|M_b N} a)|\}^{-1} \left\{\frac{(2l+1)[(l-|m|)!]}{[(l+|m|)!]}\right\}^{1/2} (-1)^{[0.5(m+|m|)+l]} i^l \times$$

$$\times \exp\{i(\boldsymbol{K}_P \boldsymbol{Z}_\alpha + M\Phi_\alpha)\}\, (-1)^M J_{m-M}(\kappa_{|M_b N} R_\alpha). \tag{12}$$

Here, r_α^{MT} is the radius of the MT-sphere α; u'_l and $\dot{u}'_l$ are radial derivatives of functions u_l and $\dot{u}_l$ at $r=r_\alpha^{MT}$ respectively. Finally, I_1 and I_2 are

$$I_1=\int_0^{\pi} \exp\{i(K_P r_\alpha^{MT}\cos\theta)\}\, J_m(\kappa_{|M_1|N} r_\alpha^{MT}\sin\theta)\, P_l^{|m|}(\cos\theta)\sin\theta d\theta \tag{13}$$

$$I_2=\int_0^{\pi} \exp\{i(K_P r_\alpha^{MT}\cos\theta)\}\, \{iK_P\cos\theta J_m(\kappa_{|M_1|N} r_\alpha^{MT}\sin\theta) + (1/2)\kappa_{|M_1|N}\sin\theta \times$$

$$[J_{m-1}(\kappa_{|M_1|N} r_\alpha^{MT}\sin\theta) - J_{m+1}(\kappa_{|M_1|N} r_\alpha^{MT}\sin\theta)]\}\, P_l^{|m|}(\cos\theta)\sin\theta d\theta, \tag{14}$$

where $P_l^{|m|}$ is the Legendre polynomial. Using the obtained base functions, which we call the augmented cylindrical waves, one can calculate the overlap and the Hamiltonian matrix elements:

$$\begin{aligned}
\langle P_2M_2N_2|P_1M_1N_1\rangle = {} & \delta(P_2M_2N_2,M_1N_1P_1) - 2\pi\{\Omega|J'_{|M_2|}(\kappa_{|M_2|N_2}a)J'_{|M_1|}\kappa_{|M_1|N_1}a)|\}^{-1}\times \\
& \sum_\alpha \exp\{i[(\boldsymbol{K}_{P_1}-\boldsymbol{K}_{P_2})\mathbf{Z}_\alpha+(M_1-M_2)\Phi_\alpha]\}\,(-1)^{M_1+M_2}\times \\
& \sum_{m=-\infty}^{\infty} J_{m-M_2}(\kappa_{|M_2|N_2}R_\alpha)\, J_{m-M_1}(\kappa_{|M_1|N_1}R_\alpha)\times \\
& \left\{ I_3 - (r_\alpha^{MT})^4 \sum_{l=|m|}^{\infty} \left\{\frac{(2l+1)[(l-|m|)!]}{2[(l+|m|)!]}\right\} C_{lm,\alpha} \right\},
\end{aligned} \tag{15}$$

$$\begin{aligned}
\langle P_2M_2N_2|H|P_1M_1N_1\rangle = {} & \{K_{P_1}K_{P_2}+\kappa_{|M_1|N_1}\kappa_{|M_2|N_2}\}\delta(P_2M_2N_2,M_1N_1P_1) - \\
& 2\pi\{\Omega|J'_{|M_2|}(\kappa_{|M_2|N_2}a)\, J'_{|M_1|}(\kappa_{|M_1|N_1}a)|\}^{-1}\sum_\alpha \exp\{i[(\mathbf{K}_{P_1}-\mathbf{K}_{P_2})\mathbf{Z}_\alpha+(M_1-M_2)\Phi_\alpha]\}\times \\
& (-1)^{M1+M2}\sum_{m=-\infty}^{\infty} J_{m-M_2}(\kappa_{|M_2|N_2}R_\alpha)\, J_{m-M_1}(\kappa_{|M_1|N_1}R_\alpha)\times \\
& \{K_{P_2}K_{P_1}I_3(J)+\kappa_{|M_2|N_2}\kappa_{|M_1|N_1}I_3(J')+m^2I_4-(r_\alpha^{MT})^4\sum_{l=|m|}^{\infty}\left\{\frac{(2l+1)[(l-|m|)!]}{2[(l+|m|)!]}\right\}(E_lC_{lm,\alpha}+\gamma_{lm,\alpha})\}.
\end{aligned} \tag{16}$$

Where

$$I_3=2\int_0^{\pi/2}\int_0^{r_\alpha^{MT}} \cos[r(K_{P_1}-K_{P_2})\cos\theta]J_m(\kappa_{|M_2|N_2}r\sin\theta)J_m(\kappa_{|M_1|N_1}r\sin\theta)\sin\theta r^2 d\theta dr$$

$$I_3(J')=2\int_0^{\pi/2}\int_0^{r_\alpha^{MT}} \cos[r(K_{P_1}-K_{P_2})\cos\theta]J'_m(\kappa_{|M_2|N_2}r\sin\theta)J'_m(\kappa_{|M_1|N_1}r\sin\theta)\sin\theta r^2 d\theta dr$$

$$I_4=2\int_0^{\pi/2}\int_0^{r_\alpha^{MT}} \cos[r(K_{P_1}-K_{P_2})\cos\theta]J_m(\kappa_{|M_2|N_2}r\sin\theta)J_m(\kappa_{|M_1|N_1}r\sin\theta)(\sin\theta)^{-1} d\theta dr$$

$$C_{lm,\alpha} = (I_2^* \dot{u}_l - I_1^* \dot{u}'_l)\,(I_2 \dot{u}_l - I_1 \dot{u}'_l) + N_{l,\alpha}\,(I_1^* u'_l - I_2^* u_l)\,(I_1 u'_l - I_2 u_l).$$

$$\gamma_{lm,\alpha} = (I_2^* I_1 + I_1^* I_2)\,\dot{u}_l u'_l - I_2^* I_2 \dot{u}_l u_l - I_1^* I_1 \dot{u}'_l u'_l$$

Finally, using the secular equation

$$\det \| \langle P_2 M_2 N_2 | H | P_1 M_1 N_1 \rangle - E(\boldsymbol{k}) \langle P_2 M_2 N_2 | P_1 M_1 N_1 \rangle \| = 0 \qquad (17)$$

we calculate dispersion curves $E(\boldsymbol{k})$.

Applications

The developed method was applied to study the band structure of linear equidistant chains $(M)_\infty$ for all metal of the third period from the K to Zn and to analogous chains $(M_2)_\infty$ with bond length alternation. In the former case the interatomic distances were chosen to be equal to a sum of atomic radii and in the later one the bonds were shortened and elongated by 10 %. A potential cylinder radius was supposed to be equal to 3.5 Å, which may be considered as radius of the host carbon nanotubes. One-electron potential was supposed to coincide with the atomic one inside the MT-spheres and zero in the intersphere region.

The results of calculations show that all chains but those formed by the Ca and Zn atoms have a metal band structures. The $(Ca)_\infty$ ultrathin wire is one-dimensional semiconductor with closed nondegenerate mainly 4*s*-band and indirect energy gap equal to 2.4 eV, the doubly degenerate conduction band being formed by $4p_X$- and $4p_Y$-functions mainly (Fig.1). The conduction band minimum and valence band maximum are located in at $k=0$ and at $k=\pi/c$, respectively. The $(Zn)_\infty$ wire is a low-gap semiconductor with a direct energy gap equal to 0.15 eV corresponding to transition at $k=\pi/c$. Bonds alternation results in the band gap reduction in case of the Ca and its growth for the Zn approximately by 1 eV.

The dispersion curves of 3*d*-transition metals are generally analogous. As a typical example, Fig.2 shows the band structures on the $(Mn)_\infty$ and $(Mn_2)_\infty$ chains. Origin of the low-lying states for equidistant $(Mn)_\infty$ chain can be interpreted in terms of tight binding method. The nondegenerate $E_1(1)$ and $E_3(1)$ bands are mainly σ-bonding and antibonding combinations of 4*s*- and $3d(z^2)$-functions. A doubly degenerate $E_2(2)$ band located in a gap between $E_1(1)$ and $E_3(1)$ states is build up from $3d(x^2\text{-}y^2)$- and $3d(xy)$-functions; orientation of these orbitals results in the δ-type bonding interactions. The next is doubly degenerate π-type antibonding band that originates from $3d(xz)$- and $3d(yz)$-functions. Bond alternation results in a folding and splitting of bands and growth of band width as compared to those of the equidistant $(Mn)_\infty$ chain; a metal character of band structure retains its validity.

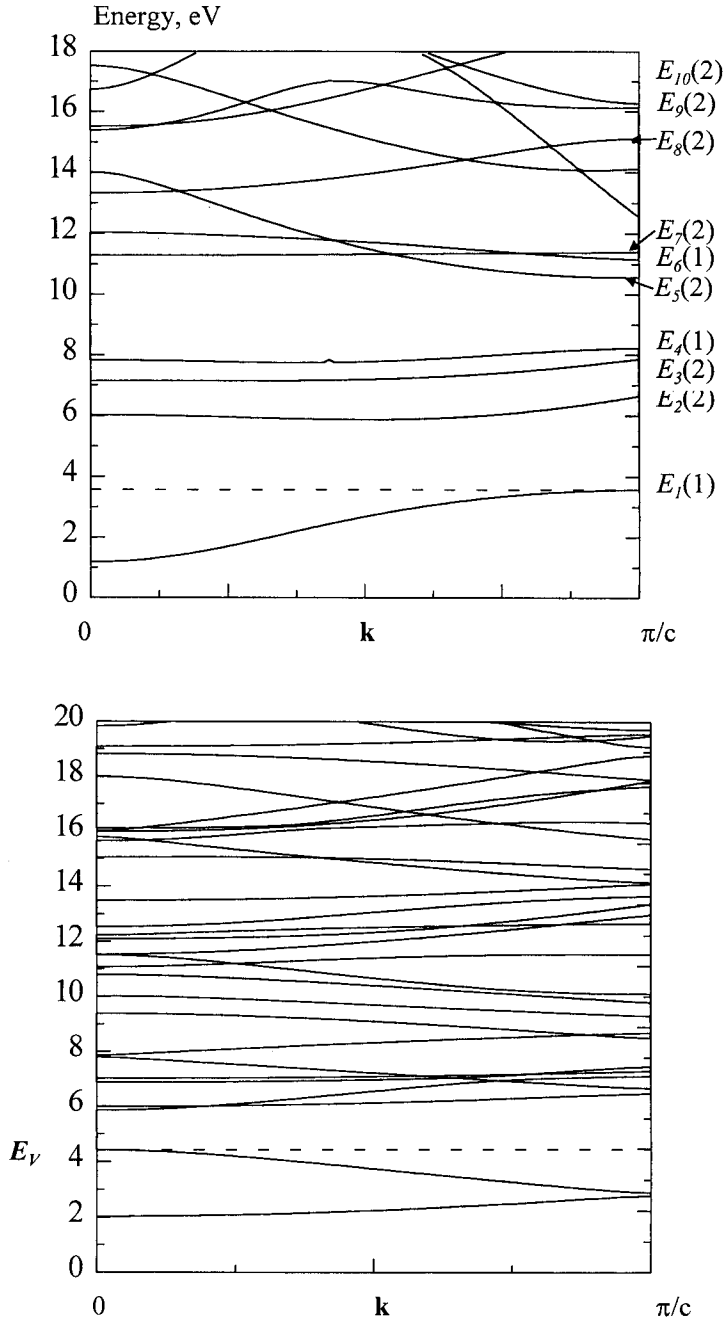

Fig. 1. Band structure of $(Ca)_\infty$ and $(Ca_2)_\infty$ chains

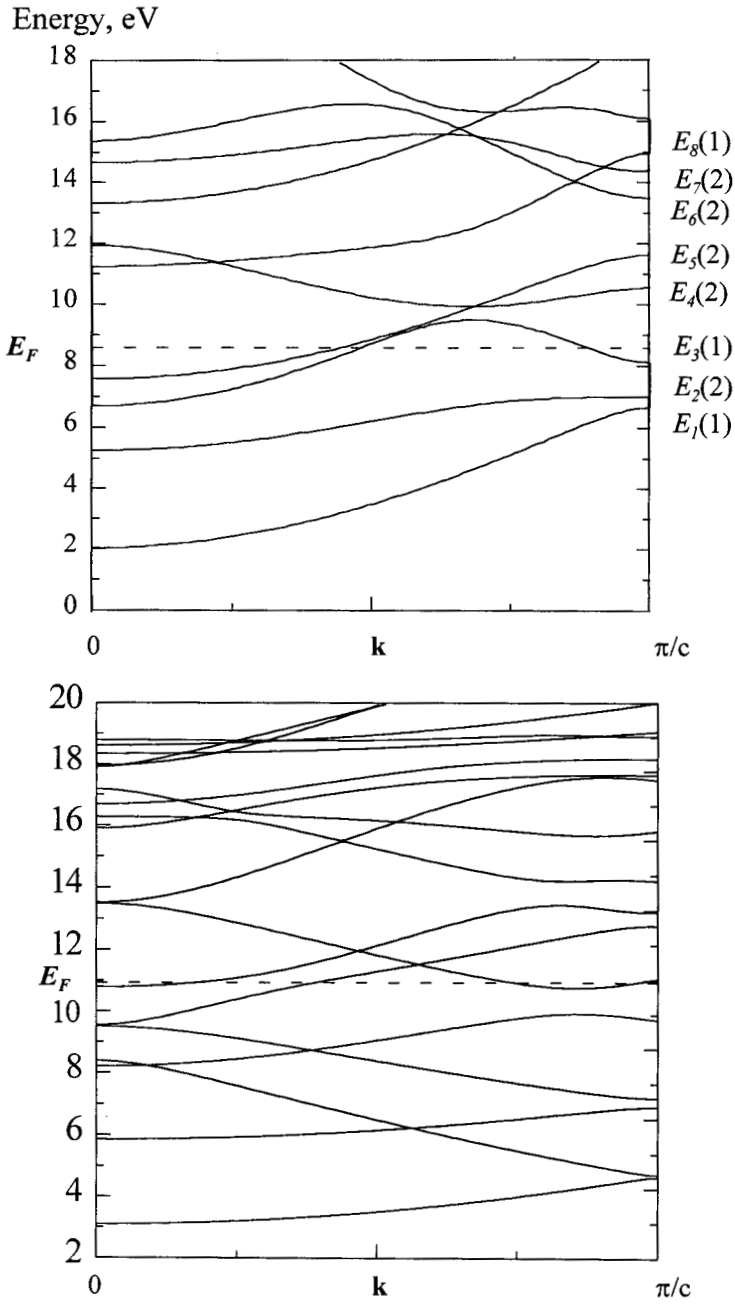

Fig. 2. Band structure of $(Mn)_\infty$ and $(Mn_2)_\infty$ chains

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REFERENCES

[1] S. Iijima, *Nature*, **351** (1991), 56.

[2] S. Iijima and T. Ichihashi, *Nature*, **363** (1993), 603.

[3] W. Kratschmar, *Nuovo Cimento*, **107** (1994), 1077.

[4] T. W. Ebbesen, *Physics Today*, **49** (1996), 26.

[5] Y. K. Tsang, Y. K. Chen, P. J. F. Harris, and M. L. H. Green, *Nature*, **372** (1994), 152.

[6] O. Zhou, R. M. Fleming, D. W. Murphy, and C. H. Chen, *Science*, **263** (1994), 1744.

[7] R. Beyers, C.-H. Kiang, R. D. Johnson, and J. R. Salem, M. S. de Vries, C. S. Yannoni, D. S. Bethune, H. C. Dorn, P. Burbank, K. Harich, and S. Stevenson, *Nature*, **370** (1994), 196

[8] T. Yamabe, *Synth. Metals*, **70** (1995), 1511.

[9] L. Lou, P. Nordlander, and R. E. Smalley, *Phys. Rev.* B., **52** (1995), 1429.

[10] L. Langer, V. Bayot, E. Grivei, J.-P. Issi, J. P. Heremans, C. H. Olk, L.Stockman, C. Van Haesendonck, and Y. Bruynseraede, *Phys. Rev.Lett.* **76** (1996), 479.

[11] M. Kosaka, T. W. Ebbesen. H. Hiura, and K. Tanigaki, *Chem.Rev.Lett.*, **233** (1995), 47.

[12] W. A. de Heer, A. Chatelain, and D. Ugarte, *Science*, **270** (1995), 1179.

[13] L. A. Chernozatonskii, Yu. V. Gulyaev, Z. Ja. Kosakovskaja, *Chem. Phys. Lett.*, **233** (1995), 47.

[14]. P. N. D'yachkov and A. V. Nikolaev, *Dokl. Akad. Nauk Russ.*, **344** (1995), 633.

[15] A. V. Nikolaev and P. N. D'yachkov, *Dokl. Akad. Nauk Russ.*, **348** (1996) 57.

[16] P. N. D'yachkov and A. V. Nikolaev, *Dokl. Akad. Nauk Russ.*, **353** (1997), 203.

[17] K. Schmidt, M.Springborg, *Solid State Commun.*, **104** (1997), 633

[18] V.M.Galitskii, B.M.Karnakv, V.I.Kogan., *Problims of Quantum Mechanics*, Moscow, Nauka (1984) (in Russian).

[19] G.A.Koran, T.M.Korn, *Mathematical Handbook for Scientists and Engineers*, New York, McGrow-Hill, (1961).

[20] G.N.Watson, *A Treatise on the Theory of Bessel Functions,*(1945).

[21] L. D. Landau and E. M. Lifchitz, *Quantum Mechanics*, Moscow, Nauka (1974) (in Russian).

[22] V. V. Nemoschkalenko and V. N. Antonov, *Methods of Computational Physics in Solid State Theory. Band Structure of Metals*, Kiev, Naukova Dumka (1985) (in Russian).