BAND STRUCTURE AND PHOTOELECTRON SPECTRA OF ULTRATHIN CARBON NANOTUBES

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Introduction

The prospect of using carbon nanotubules in various areas of engineering requires diagnostics at all stages of their production and application. A photoelectron spectroscopy has a required sensitivity for this purpose. Besides the photoelectronic emission of ultrathin nanotubes can be used to obtain electronic streams of necessary intensity.

In the given communication it has been carried out the calculation of photoelectronic spectra of ultrathin zigzag carbon tubes. First the energy band and DOS have been defined. Then using empirical values of partial photoionization cross-section the photoelectronic spectra have been calculated.

Calculations

The calculations of electronic properties of the nanotubes were carried out by the self-consistent full-potential linear-muffin-tin-orbital (FP-LMTO) method described in [1]. Since the method is based on the density functional theory and does not include any empirical parameters, it is often refered to as an 'ab initio' method.

The nanotube of "zigzag" type has the shortest period along the tube $\sqrt{3}a_0$ where a_0=1.42 $\overset{0}{A}$ is the nearest-neighbor distance between carbon atoms in graphite. In order to utilize of the band structure method, we constructed the unit cell, in which the height is equal to the period of the tube along z axis and the form of the (x,y)-plane cross-section is determined by the rotational symmetry of the tube. In particular, for the (3,3) nanotube, in which three graphite links fit in the circumference of the tube (12 carbon atoms in the unit cell), we chose the hexagonal form of the cell in the (x,y)-plane. For the (4,4) nanotube, in which four graphite links fit in its circumference (16 carbon atoms in the unit cell), the square form of the cell was chosen in the (x,y)-plane. The use of the symmetric unit cells allows us to calculate the DOS more easily and with reasonable accuracy, since we may integrate over a part of BZ rather than over the whole BZ. The self-consistency was performed

with 15 special points in 1/6th of BZ for (3,3) nanotube and with 18 special points in 1/8th of BZ for (4,4) nanotube. The total and partial DOS were calculated by the linear tetrahedron method using 175 points in 1/6th of BZ in the former case and 325 points in 1/8th of BZ in the latter case. The energy step was 0.027 eV in the calculation of DOS.

Results and discussion

In Fig.1 and 2 the total density of electronic states (e) and partial densities of states (a-d) for (3,3) and (4,4) carbon nanotubes arepresented, accordingly. All histograms are displayed after normalization on the principal maximum. The conventional formula of hybridization obtained from account, $S^{1.4} p_z^1 p^{1.6}$ for both forms of nanotubules.p includes the summarized contribution of p_x- and p_y-orbitals (or π-states) in the common system of valence bands. Due to curving of a graphene sheet π-electrons partially mix with a σ-system. As a first approximation the degree of hybridization doesn`t depend on a tube diameter in. The density of electronic states at the Fermi level is not equal to zero, it testifies to metal properties of the pattern. This result is stipulated by p_x- and p_y-states (a and b), which are almost completely identical except of some fine details, the number of which is more in conduction band. This fact is connected with geometrical singularities and space symmetry of tubules.

In Fig.3 the diagram, defining place of carbon nanotubes in a set allotropy forms of carbon [2] is submitted. As a criterion of classification was used the type of hybridization of the electrons in the carbon atom. Each side of an equilateral triangle in Fig.3 corresponds to a numerical axes i_π (i_π is the number of π-electrons in the atom). Thus an interior part of the triangle corresponds to the phases which are inherent the features of three allotropic forms. For example, the dashed line in Fig.3 (i_π = 1) not only corresponds to the phase state of graphite but also to some more complex formations. Keeping in mind that the number of nonhybrid π-electrons in ultrathin nanotubes, investigated in the given work, is obtained equal 1.6, we find a line inside the triangle with this value (it is shown by rich line). It also corresponds to a phase condition of carbon medium consisting of ultrathin nanotubes. In accordance with increasing tube diameter this line should shift toward the side of the dashed line i_π = 1 (shaded area).

It has produced the calculation of photoelectron spectra (PES) of both carbon model zigzag nanotubes.

Intensity of photoelectron spectra

$$I_F(E) = \sum_{\alpha=1}^{4} N_{\alpha\beta}(E) \cdot Q_\alpha \quad (1)$$

depends on two values: photoionization cross-section $Q_\alpha = \frac{|M_\alpha|^2}{|M_\pi|^2}$ and combined density of states $N_{\alpha\beta}$. Index β defines a final state at photoionization, which is in our case approximate by a flat wave. That is why the partial density of valence states shown in Fig.1 and 2 was used in (1) instead of $N_{\alpha\beta}$. The photoionization cross-section of hybrid electrons differs from atomic Q_s and Q_p cross-section, known from the publications. The Q_α values, chosen for calculation are shown in the table.

In Fig.4,5 the calculated photoelectronic spectra of (3,3) and (4,4) nanotubes, obtained with the help of formulas (1), for the several chosen values of photoionization cross-section are submitted. The signs (a-d) in Fig.4 and 5 correspond to the signs of columns in the table. In our opinion, the variations Q_α shown in the table correspond to photoeffect at excitation photon vacuum ultraviolet (25-30 eV, a) and ultrasoft x-ray radiation (200-300 eV, d). Because of it the form of spectral curves changes rather essentially due to the contribution of s-states near the bottom of the band. However, the position of maxima on the power axes is not changed. It depends on a tube diameter: with increasing tube diameter the displacement of the position of maxima shift toward higher binding energies.

Conclusions

1.The structure of bands of ultrathin carbon nanotubes differs from the similar band structure of graphite. It is stipulated by a curvature of a surface of a graphene sheet at forming tubule. Especially it is important to take into account this effect for very thin nanotubes. Hybridization of valence electrons for them does not satisfy to the formula, known for graphite, $S^1 p^2 \pi^1$, and it is represented as $S^{1.4} p^1 \pi^{1.6}$.

2.Intensity and form of photoelectronic spectra are defined by two principal factors: a density distribution of electrons in subbands and ionization cross-section under influence of light. In the ultraviolet part of the spectrum photoionization cross-sectionof p-electrons prevail. p-electrons in nanotubes have a rather large density of energy distribution. For this reason the basic amount of electrons having gone nanotube at excitation of photons 20-30 eV have a p-symmetry. With increasing energy of excitation the part of emitted s-electrons increases.

References

1. Weyrich K.H. Full-potential linear muffin-tin-orbital method. Phys. Rev. B 1988; 37(17):10269-10282.
2. Carbyne and carbynoid structures. Edited by Heimann R.B., Evsyukove S.E., Kavan L.

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Table. Relative photoionization cross-section Q_α of valence electrons in nanotubes

Signs of subbands	photoionization cross section			
	(a)	(b)	(c)	(d)
s	0	0	1	1.75
p_z	1	1.25	1.25	1.25
p_x,p_y	1	1	1	1

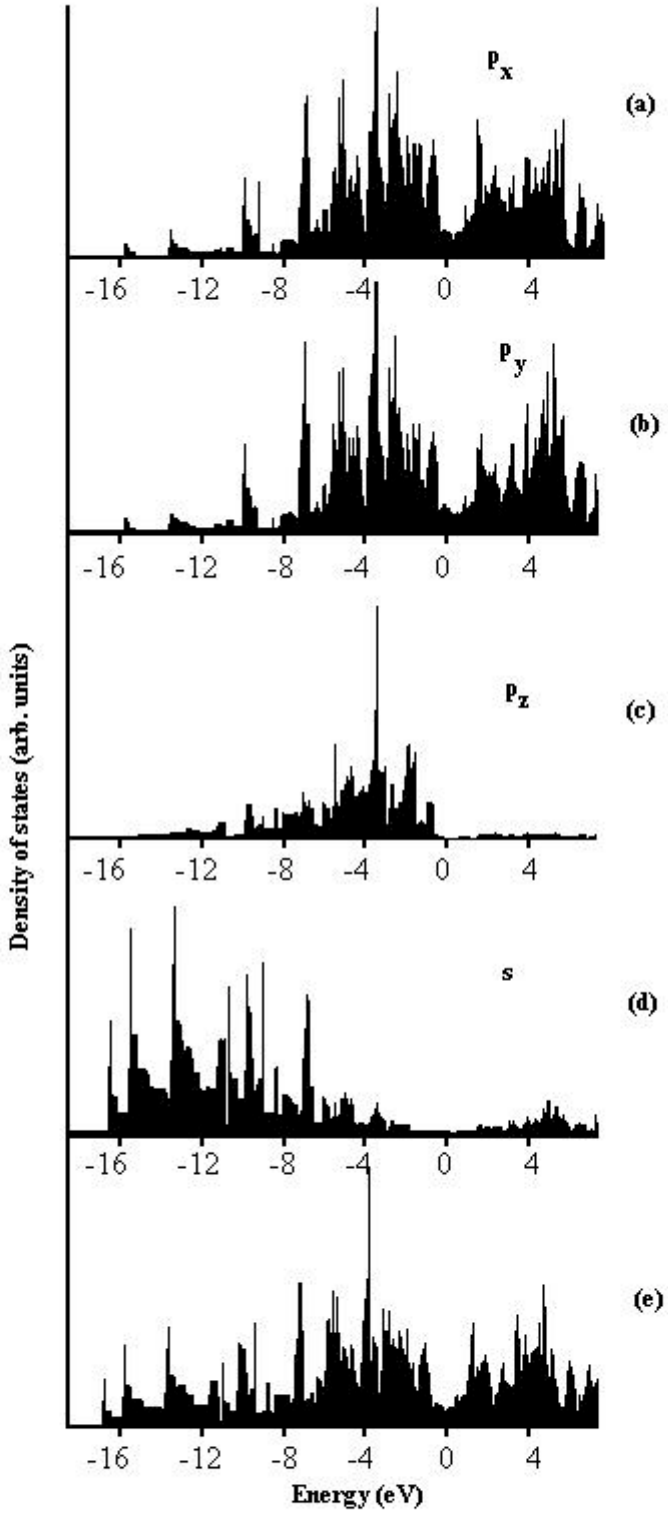

Figure 1. Calculated histograms of density of states of (3,3) nanotube. Zero energy corresponds to the Fermi energy.

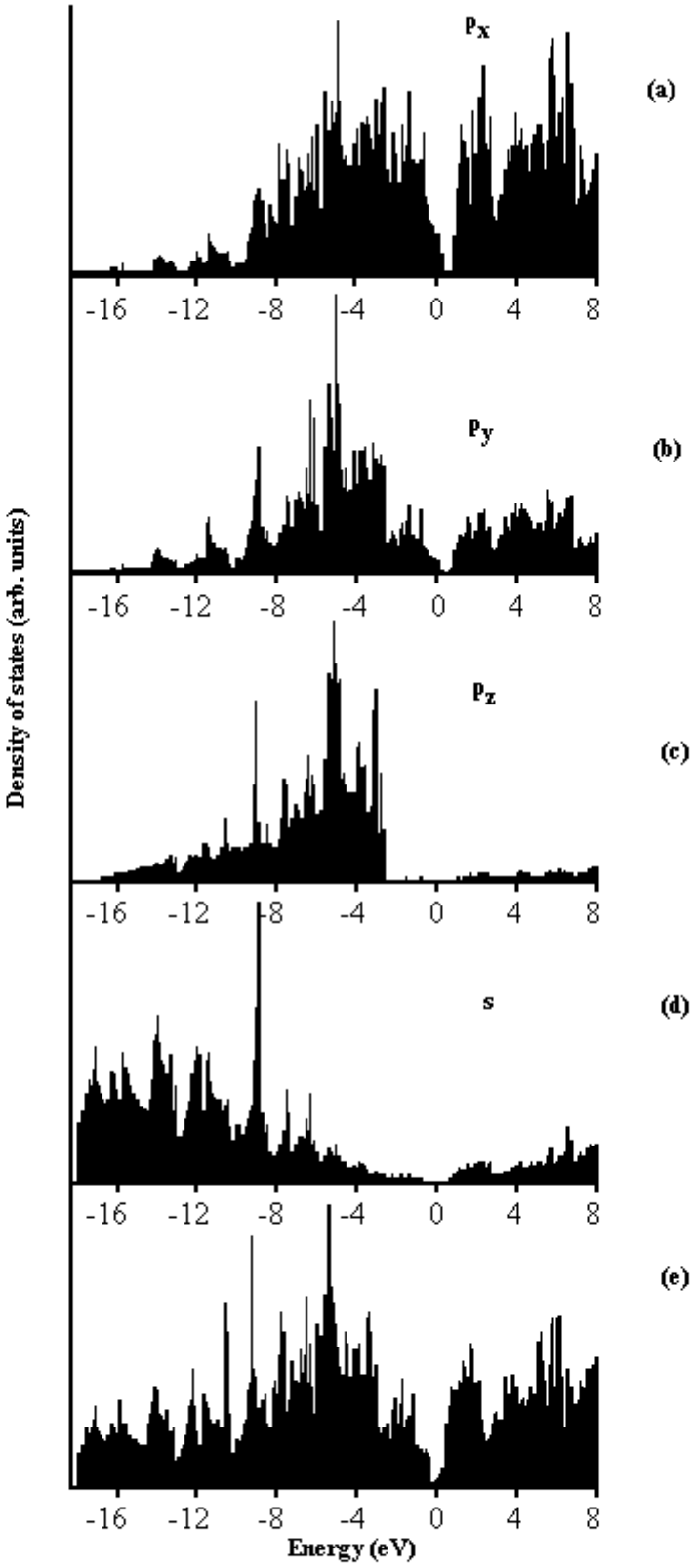

Figure 2. Calculated histograms of density of states of (4,4) nanotube. Zero energy corresponds to the Fermi energy.

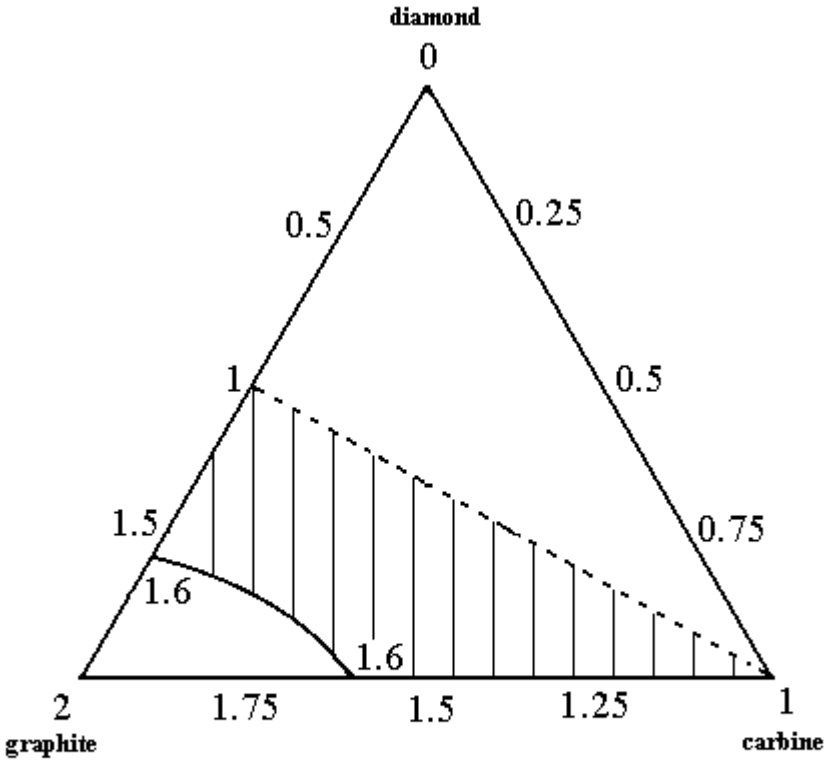

Figure 3. Diagram of condensed carbon. The numbers on diagram correspond to the number of nonhybrid electrons (per atom).
The shaded part of the diagram corresponds to the phase state of nanotubular carbon.

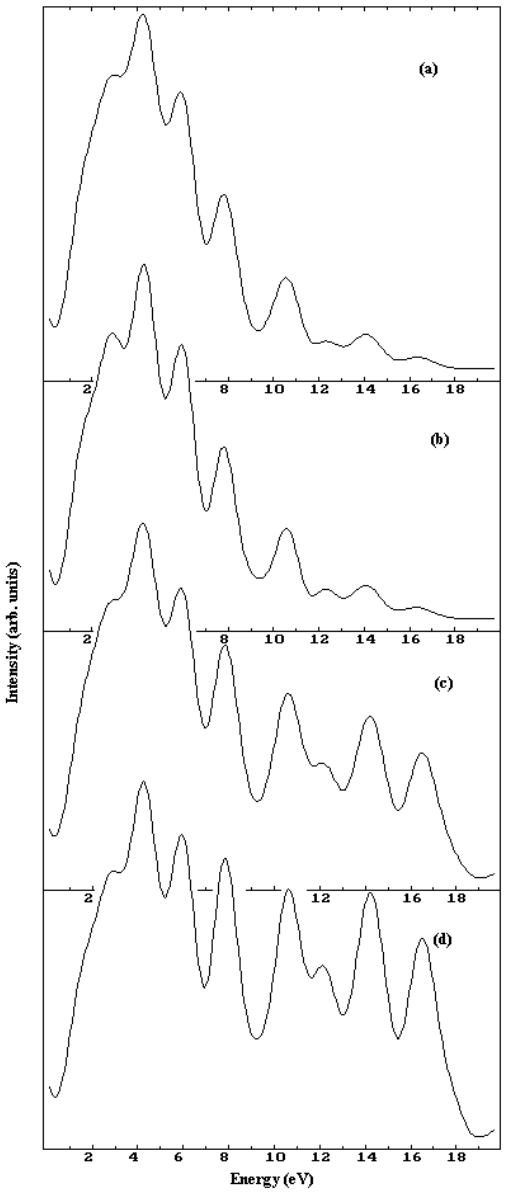

Figure 4. Calculated PES spectra of (3,3) nanotube at different energies stimulated radiation.

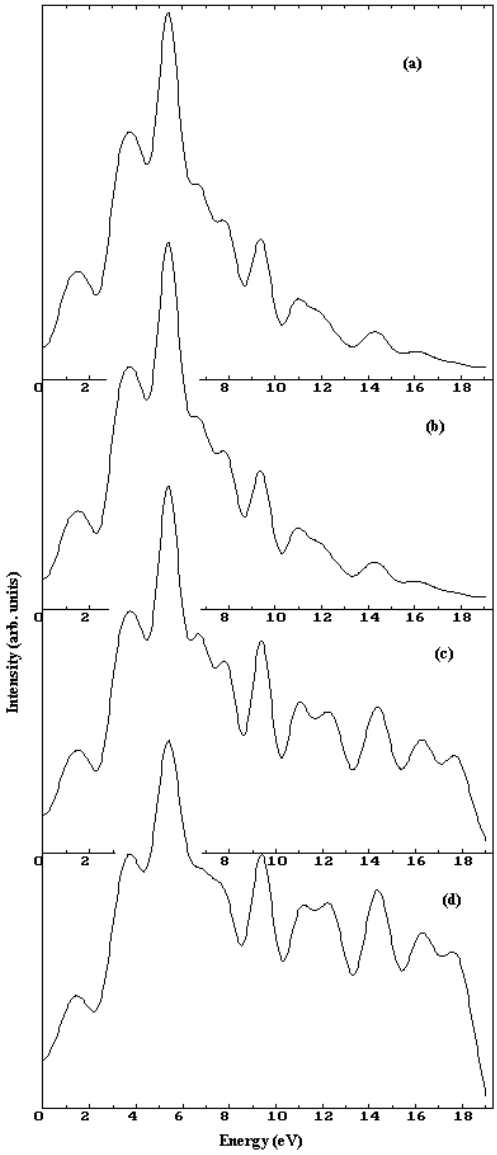

Figure 5. Calculated PES spectra of (3,3) nanotube at different energies stimulated radiation.