

The Quantitative Theory of Diffraction by Spiral Nanotubes

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Abstract

The quantitative theory of diffraction by spiral nanotubes of any chemical composition is offered. Distribution of diffraction intensities along layer lines and layer planes, strong and diffuse reflexes, pseudoorthogonality effect has been simulated and analyzed. The investigation is oriented to electron microdiffraction from a single nanotube.

Introduction

Over the last 50 years, the development of structural analysis of nanotubes by diffraction methods has dedicated, mainly, to nanotubes of coaxial type: chiral and nonchiral nanotubes. However, it's seems obvious that the best part of synthesized nanotubes belong to spiral type: they represent cone structure or roll, when the cone angle is zero [1]. Therefore, the necessity for development of structural analysis of these abundant types of nanotubes is driven by further progress of nanotechnology.

First efforts in investigation of diffraction by spiral structures were related with two works of the middle of the last century: theoretical study performed by Jagodzinski and Kunze [2] and Whittaker's simulative optical experiments [3]. Jagodzinski and Kunze tried to solve the problem of describing spiral structure by approximation of spiral lattice by semi cylindrical layers. It's obvious that such approximation is quite rough, and diffraction from this structure will resemble diffraction from a cylindrical tube rather than from spiral.

Whittaker's simulative optical experiments made significant contributions to the investigation of spiral structures. In this experiments Whittaker performed comparison study of diffraction from artificial two-dimensional models of coaxial and spiral lattices. By the reason of impossibility of making real models of cylindrical lattices because

of small dimensions of the nanotube), Whittaker transferred experiment to larger dimensions – to the range of visible light. Thus, he scaled up the size of artificial models of cylindrical lattices (masks) in accordance with wave length increasing (in comparison with X-RAYS). Experimental results allowed him to describe and analyze azimuthal distribution peculiarity of diffraction intensities in reciprocal space of coaxial and spiral lattices and to make a conclusion that the diffraction patterns from coaxial and spiral structures are very similar and differ only in fine details [3].

The development of quantitative theory of diffraction by spiral nanotubes was being restricted for a long period of time by the lack of crystallographic description of such structures. In the 80 s of last century, description within a framework of model of elastic layer was proposed, and on this basis quantitative theory of diffraction was developed [4]. However, the examination of different types of nanotubes is showed that such model is inapplicable for best parts of nanotubes, and chiral angles that corresponds to the interlayer shift are often have significant value.

In the recent years, the crystallographic description of spiral (roll) nanotubes within a framework of model of strong layer and with arbitrary chiral angle was made [1]. The description is based on the usage of rectangular Bravais lattice, and it's applicable for nanotubes of arbitrary chemical composition. This fact is very important because of the report about synthesis of cylindrical structures that

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have non-hexagonal motif of atoms arrangement [5]. Bravais lattice also allows using well-known coordinates of atoms of flat analogues of nanotubes during the diffraction pattern computation.

This research is dedicated to the development of quantitative theory of diffraction by spiral nanotubes of any chemical composition. Because of the absence of crystallographic description of cone nanotubes, investigation is making on the basis of roll structure [1]. Detailed analysis of the problem,

$$\begin{cases} \rho_{n v j} = \sqrt{\rho_0^2 + 2\tau [(vb + y_j)\cos \varepsilon_c - (an + z_j)\sin \varepsilon_c]} + x_j \\ \varphi_{n v j} = \frac{1}{\tau} \left\{ \sqrt{\rho_0^2 + 2\tau [(vb + y_j)\cos \varepsilon_c - (an + z_j)\sin \varepsilon_c]} - \rho_0 \right\} \\ z_{n v j} = (vb + y_j)\sin \varepsilon_c + (an + z_j)\cos \varepsilon_c \end{cases}, \quad (1)$$

n – index number of spiral-helical site line on the surface of the roll, v – index number of lattice site on the site line, x_j, y_j, z_j – radial, circular and longitudinal linear coordinates of j -th atom in Bravais cell relative to the beginning of this cell, ρ_0 – initial radius of a roll, d – thickness of the layer, $\tau = d/2\pi$, a and b – parameters (dimensions) of rectangular Bravais cell's base, where side a is chosen in the direction closest to the tube axis, and parameter b – in the direction closest to the tube cross-section (side b is perpendicular to a). Index numbers n and v are limited only by dimensions of a nanotube until the roll isn't divided into the turns.

The diffraction amplitude in general form:

$$A(R, \varphi^*, z^*) = \sum_{n, v, j} f_j \exp \left\{ 2\pi i \left[R \rho_{n v j} \cos (\varphi_{n v j} - \varphi^*) + z^* z_{n v j} \right] \right\} \quad (2)$$

where $\{R, \varphi^*, z^*\}$ – the cylindrical coordinate system in reciprocal space of an object, $f_j(R^*)$ – the electron atomic scattering factor of j -th atom in Bravais cell, $R^* = \sqrt{R^2 + z^{*2}}$ – the scalar of radius-vector of a certain point in reciprocal space. From (1) and (2) it can be assumed that analytical estimation of lattice sums (over n and v) in general is complicated, and calculation of diffraction intensity that corresponds to amplitude (2) can be done only numerically.

Let's consider the structure of the nanotube in case of small chiral angle ε_c – this approach, according to [1], allows dividing spiral structure into turns. Thus, in practically important case then generator $g = 2\pi d/b$ [1] is odd (in case of chrysotile

uncovering essential differences between diffraction from coaxial and spiral structures and comparison with experimental data will be done in our next articles.

The Diffraction Amplitude

Atoms of roll nanotube (Fig. 1) with arbitrary chiral angle ε_c within the model of strong layer have cylindrical coordinates [1]:

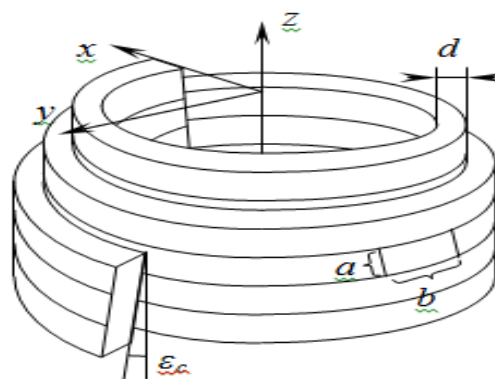


Fig. 1. Lattice parameters of roll nanotube.

nanotube) and semi-integer $p_0 = 2\pi\rho_0/b$ coordinates (1) of j -th atom of v -th primitive unit cell on m -th turn (index number of m begins from zero) of n -th spiral-helical site line in the first approximation represent relatively simple expression:

$$\begin{cases} \rho_{m n v j} \approx \sqrt{\rho_m^2 + 2\tau [vb + y_j - (an + z_j)\varepsilon_c]} + x_j \\ \varphi_{m n v j} \approx \frac{1}{\tau} \left\{ \sqrt{\rho_m^2 + 2\tau [vb + y_j - (an + z_j)\varepsilon_c]} - \rho_m \right\} \\ z_{m n v j} \approx an + (2\pi\rho_0 m + \pi d m^2 + vb + y_j)\varepsilon_c + z_j \end{cases} \quad (3)$$

where $v = 0 \div p_m - 1$, $p_m = p_0 + mg + \frac{g}{2}$.

Let's neglect parameter z_j in (3) and expand radical into a Taylor series in powers of the smallness

$$\sqrt{\rho_m^2 + 2\tau[vb + y_j - (an + z_j)\varepsilon_c]} \approx \sqrt{\rho_m^2 + 2\tau(vb + y_j)} - \frac{\tau an \varepsilon_c}{\sqrt{\rho_m^2 + 2\tau vb}} \quad (4)$$

Substituting (4) into (3) and neglecting relatively small terms gives coordinates of atoms:

$$\begin{cases} \rho_{mnvj} \approx \rho_{mv} + x_j = \rho_{mvj} \\ \varphi_{mnvj} \approx \varphi_{mvj} - \varphi_{mn} - \varphi_m \\ z_{mnvj} \approx an + b\varepsilon_c v + z_{mj} \end{cases}$$

where

$$\begin{aligned} \rho_{mv} &= \sqrt{\rho_m^2 + 2\tau vb}, \\ \varphi_{mnvj} &= \frac{1}{\tau} \sqrt{\rho_m^2 + 2\tau(vb + y_j)}, \\ \varphi_{mn} &= \frac{an\varepsilon_c}{\rho_m}, \quad \varphi_m = \frac{\rho_m}{\tau}, \\ z_{mj} &= (2\pi\rho_0 m + \pi dm^2)\varepsilon_c + z_j. \end{aligned}$$

For this reason diffraction amplitude (2):

$$A(R, \varphi^*, z^*) \approx \sum_{m=0}^{M-1} \sum_j f_j \exp(2\pi i z^* z_{mj}) \sum_{v=0}^{p_m-1} \exp(2\pi i z^* b \varepsilon_c v) \times \sum_{n=0}^{N-1} \exp(2\pi i z^* an) \exp[2\pi i R \rho_{mvj} \cos(\varphi_{mnvj} - \varphi^*)]$$

where N – the length of the nanotube in units of a , and M – number of layers. Let's expand the last exponential function into cylindrical waves in accordance with equation

$$\exp(i\alpha \cos \gamma) = J_0(\alpha) + 2 \sum_{q=1}^{\infty} i^q \cos(q\gamma) J_q(\alpha)$$

$$A(R, \varphi^*, z^*) = A_0(R, z^*) + A_1(R, \varphi^*, z^*),$$

where

$$A_0(R, z^*) = \sum_{m,j} f_j \exp(2\pi i z^* z_{mj}) \sum_v \exp(2\pi i z^* b \varepsilon_c v) J_0(2\pi R \rho_{mvj}) \sum_n \exp(2\pi i z^* an) \quad (5)$$

$$A_1(R, \varphi^*, z^*) = 2 \sum_{m,j} f_j \exp(2\pi i z^* z_{mj}) \sum_v \exp(2\pi i z^* b \varepsilon_c v) \sum_n \exp(2\pi i z^* an) \times \sum_{q=1}^{\infty} i^q \cos[q(\varphi_{mnvj} - \varphi^*)] J_q(2\pi R \rho_{mvj}) \quad (6)$$

Let's consider summands of diffraction amplitude (5) and (6) sequentially. When, estimate summands of q -series that make a strong contribution to amplitude of reflexes, and also achieve analytic relations governing regions of existence of intensity's maxima in reciprocal space. Simulated diffraction profiles will be calculated in case of electron microdiffraction on single nanotube. We also didn't take into account any fudge factors (for absorption, etc) on this stage of development.

Reflexes $h0$ u $h00$

Let's consider diffraction amplitude (5). Sum taken over n has a sharp maximum when

$$z^* = \frac{h}{a}, \quad h = 0, \pm 1, \pm 2, \dots, \quad (7)$$

Such equation governs coordinates of so called «layer planes» of reciprocal space of the nanotube. Near or on this layer planes stand maxima of diffraction amplitude. When the flattish Ewald's sphere of electron beam in TEM cuts reciprocal space of the nanotube, layer planes transform into «layer lines» in diffraction pattern. Indexes of these lines coincide with the value of index h .

By using the Bessel function approximation, we can simplify our algebraic expression for finding maximum condition of sum over v :

$$J_0(x) \approx \sqrt{\frac{2}{\pi x}} \cos\left(x - \frac{\pi}{4}\right)$$

Therefore, with regard of expression (7):

$$\sum_{\nu} \exp\left(2\pi i h \frac{b\varepsilon_c}{a} \nu\right) J_0(2\pi R \rho_{m\nu j}) \approx \frac{1}{\pi \sqrt{R \rho_m}} \sum_{\nu} \exp\left(2\pi i h \frac{b\varepsilon_c}{a} \nu\right) \cos\left[2\pi R(\rho_{m\nu} + x_j) - \frac{\pi}{4}\right]$$

Let's expand $\rho_{m\nu}$ into a Taylor series in powers of the smallness of its second term:

$$\sqrt{\rho_m^2 + 2\tau b \nu} \approx \rho_m + \frac{\tau b}{\rho_m} \nu, \quad (8)$$

$$\begin{aligned} \sum_{\nu} \cos\left(2\pi h \frac{b\varepsilon_c}{a} \nu\right) \cos\left[2\pi R(\rho_{m\nu} + x_j) - \frac{\pi}{4}\right] + i \sum_{\nu} \sin\left(2\pi h \frac{b\varepsilon_c}{a} \nu\right) \cos\left[2\pi R(\rho_{m\nu} + x_j) - \frac{\pi}{4}\right] = \\ = \frac{1}{2} \sum_{\nu} \left\{ \cos\left[2\pi\left(h \frac{b\varepsilon_c}{a} \nu + R\rho_{m\nu} + Rx_j - \frac{1}{8}\right)\right] + \cos\left[2\pi\left(h \frac{b\varepsilon_c}{a} \nu - R\rho_{m\nu} - Rx_j + \frac{1}{8}\right)\right] \right\} + \\ + \frac{i}{2} \sum_{\nu} \left\{ \sin\left[2\pi\left(h \frac{b\varepsilon_c}{a} \nu + R\rho_{m\nu} + Rx_j - \frac{1}{8}\right)\right] + \sin\left[2\pi\left(h \frac{b\varepsilon_c}{a} \nu - R\rho_{m\nu} - Rx_j + \frac{1}{8}\right)\right] \right\}. \end{aligned}$$

These sums have maxima when

$$\pi b \left(\frac{h}{a} \varepsilon_c \pm R \frac{\tau}{\rho_m} \right) = k\pi \Rightarrow R = \pm \frac{1}{d} \left(k \frac{2\pi \rho_m}{b} - \frac{h}{a} 2\pi \rho_m \varepsilon_c \right), \quad k = 0, \pm 1, \pm 2, \dots$$

The first term in brackets is approximately equal to $k\rho_m$ having relative high value that, even after dividing by d , goes far beyond the scope of limits of considered region of R coordinate. Therefore, $k = 0$ and the amplitude (5) governs strong reflexes [6, 7]. The next term corresponds to locations of maxima of m -th summands of the diffraction amplitude of $h00$ reflex for monoclinic, and when $\varepsilon_c = 0$ – for an orthogonal polytypic modification of nanotube structure [1].

$$A_S^{h00}(R) = N \sum_j f_j \sum_{m=0}^{M-1} \exp\left(2\pi i \frac{h}{a} z_{mj}\right) \sum_{\nu=0}^{p_m-1} \exp\left(2\pi i \frac{h}{a} b \varepsilon_c \nu\right) J_0(2\pi R \rho_{m\nu j})$$

where N – value of sum over n , index «S» signify that these reflexes are strong.

Figure 2 shows calculated profiles of the beginning of 2-nd layer line for monoclinic roll nanotubes with different chiral angles. Each curve is a summation of pseudoorthogonal $h0$ and monoclinic $h00$ reflexes (when the chiral angle is small reflexes merge with each other). The pseudoorthogonality effect was analyzed earlier in case of chiral and nonchiral nanotubes [6, 7]. In this case, as for nonchiral nanotubes, pseudoorthogonal reflexes are formed by primary maximum of Bessel functions with zero index and thus reflexes are located in $R = 0$. Let's consider the amplitude (6) and related diffraction effects.

Therein is lies the method of linear approximation for coordinates of atoms that allows us to continue our analysis. As a result, the last sum can be cast into:

Consequently, the amplitude (5) governs series of pseudoorthogonal $h0$ [6] and $h00$ reflexes from a roll nanotube in case of strong layer. Arithmetical sign « \pm » provides positive value of R coordinate in both sides of reciprocal space of an object, where layer planes with $h < 0$ and $h > 0$ stand. In the case of $h > 0$ we must choose negative value. With these results we can estimate expression for amplitude (5):

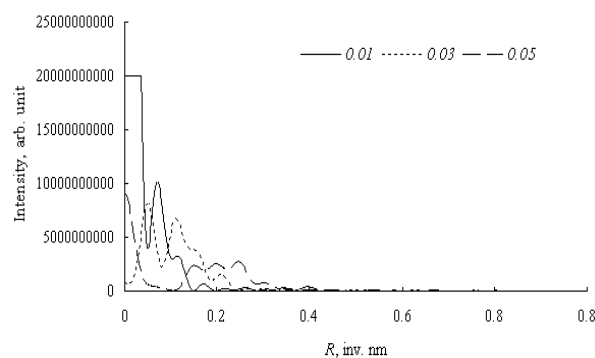


Fig. 2. Profiles of the beginning of 2-nd layer line of monoclinic roll nanotubes with different chiral angles ε_c (degrees). The maximum intensity ($1,69 \cdot 10^{11}$) is synthetically limited.

Reflexes of general position

The amplitude (6) can be cast into such form:

$$A_1(R, \varphi^*, z^*) = \sum_{m,j} f_j \exp(2\pi i z^* z_{mj}) \sum_q i^q \sum_v \exp(2\pi i z^* b \varepsilon_c v) J_q(2\pi R \rho_{mvj}) \times \\ \times \left\{ \exp[iq(\varphi_{mvj} - \varphi_m - \varphi^*)] \sum_n \exp\left[2\pi i \left(z^* - \frac{q \varepsilon_c}{2\pi \rho_m}\right) an\right] + \right. \\ \left. + \exp[-iq(\varphi_{mvj} - \varphi_m - \varphi^*)] \sum_n \exp\left[2\pi i \left(z^* + \frac{q \varepsilon_c}{2\pi \rho_m}\right) an\right] \right\}. \quad (9)$$

Sums over n have sharp maxima when

By introducing the following notation

$$\pi a \left(z^* \pm \frac{q \varepsilon_c}{2\pi \rho_m} \right) = h\pi \quad \Rightarrow \quad z_m^* = \frac{h}{a} \mp \frac{q \varepsilon_c}{2\pi \rho_m}, \quad S_{mq}^\pm = \sum_{n=0}^{N-1} \exp\left[2\pi i \left(z^* \pm \frac{q \varepsilon_c}{2\pi \rho_m} \right) an\right], \quad (11)$$

$$h = 0, \pm 1, \pm 2, \dots$$

(10) we reduce the amplitude (9) to

$$A_1(R, \varphi^*, z^*) = \sum_{m,j} f_j \exp(2\pi i z^* z_{mj}) \sum_q i^q \times \left\{ \exp[-iq(\varphi_m + \varphi^*)] S_{mq}^- \sum_v \exp(2\pi i z^* b \varepsilon_c v + iq \varphi_{mvj}) J_q(2\pi R \rho_{mvj}) + \right. \\ \left. + \exp[iq(\varphi_m + \varphi^*)] S_{mq}^+ \sum_v \exp(2\pi i z^* b \varepsilon_c v - iq \varphi_{mvj}) J_q(2\pi R \rho_{mvj}) \right\}. \quad (12)$$

For estimation of the maximum condition of lattice sums over v, we should use the Bessel function approximation:

$$J_q(x) \approx \begin{cases} \cos\left(x - \frac{\pi}{2}q\right), & x \geq q \\ 0, & x < q \end{cases}$$

It allows us to reduce sums over v in expression (12) to:

$$S_{mqj}^\pm \approx \frac{1}{2} \sum_{v=0}^{\rho_m-1} \exp\left[i(2\pi z^* b \varepsilon_c v \pm q \varphi_{mvj})\right] \left\{ \exp\left[i\left(2\pi R \rho_{mvj} - \frac{\pi q}{2}\right)\right] + \exp\left[-i\left(2\pi R \rho_{mvj} - \frac{\pi q}{2}\right)\right] \right\}. \quad (13)$$

For further analysis we use linear approximation again. Let's expand φ_{mvj} into a Taylor series in powers of the smallness of $2\tau(bv + y_j)$ to the linear term:

$$\sqrt{\rho_m^2 + 2\tau(bv + y_j)} \approx \rho_m + \frac{\tau b}{\rho_m} v + \frac{\tau y_j}{\rho_m}$$

And use also the expansion (8). Thus, when $2\pi R \rho_m \geq q$, sums (13) may be expressed as follows

$$S_{mqj}^\pm \approx A_{mqj}^\pm B_{mqj}^\pm \sum_{v=0}^{\rho_m-1} \exp\left[i\left(2\pi z^* b \varepsilon_c + 2\pi R \frac{\tau b}{\rho_m} \pm \frac{qb}{\rho_m}\right)v\right] + A_{mqj}^\pm B_{mqj}^\mp \sum_{v=0}^{\rho_m-1} \exp\left[i\left(2\pi z^* b \varepsilon_c - 2\pi R \frac{\tau b}{\rho_m} \pm \frac{qb}{\rho_m}\right)v\right], \quad (14)$$

$$\text{where } A_{mqj}^\pm = \frac{1}{2} \exp\left[\pm iq\left(\varphi_m + \frac{y_j}{\rho_m}\right)\right] \quad B_{mqj}^\pm = \exp\left[\pm i\left(2\pi R \rho_m + 2\pi R x_j - \frac{\pi q}{2}\right)\right],$$

The upper arithmetical sign in arguments of exponential functions and in value A_{mqj}^\pm corresponds

to the first term of amplitude (12), and lower – to the second term.

Consequently, the amplitude (12) can be cast into such form:

$$\begin{aligned}
 A_1(R, \varphi^*, z^*) &\approx \sum_{m,j} F_{mj} \sum_q i^q \left\{ \exp[-iq(\varphi_m + \varphi^*)] S_{mq}^- S_{mqj}^+ + \exp[iq(\varphi_m + \varphi^*)] S_{mq}^+ S_{mqj}^- \right\} = \\
 &= \sum_{m,j} F_{mj} \sum_q i^q \left\{ \exp[-iq(\varphi_m + \varphi^*)] S_{mq}^- A_{mqj}^+ B_{mqj}^+ \sum_{v=0}^{p_m-1} \exp \left[i \left(2\pi z^* b \varepsilon_c + 2\pi R \frac{\tau b}{\rho_m} + \frac{qb}{\rho_m} \right) v \right] + \right. \\
 &\quad + \exp[-iq(\varphi_m + \varphi^*)] S_{mq}^- A_{mqj}^+ B_{mqj}^- \sum_{v=0}^{p_m-1} \exp \left[i \left(2\pi z^* b \varepsilon_c - 2\pi R \frac{\tau b}{\rho_m} + \frac{qb}{\rho_m} \right) v \right] + \\
 &\quad + \exp[iq(\varphi_m + \varphi^*)] S_{mq}^+ A_{mqj}^- B_{mqj}^+ \sum_{v=0}^{p_m-1} \exp \left[i \left(2\pi z^* b \varepsilon_c + 2\pi R \frac{\tau b}{\rho_m} - \frac{qb}{\rho_m} \right) v \right] + \\
 &\quad \left. + \exp[iq(\varphi_m + \varphi^*)] S_{mq}^+ A_{mqj}^- B_{mqj}^- \sum_{v=0}^{p_m-1} \exp \left[i \left(2\pi z^* b \varepsilon_c - 2\pi R \frac{\tau b}{\rho_m} - \frac{qb}{\rho_m} \right) v \right] \right\}, \quad (15)
 \end{aligned}$$

where $F_{mj} = f_j \exp(2\pi i z^* z_{mj})$.

Sums over v in the expression (15) have sharp maxima when

$$z^* \approx \frac{h}{a} + \frac{k}{b} \varepsilon_c \quad (17)$$

$$z^* \varepsilon_c \pm R \frac{\tau}{\rho_m} \pm \frac{q}{2\pi \rho_m} = \frac{k}{b}, \quad k = 0, \pm 1, \pm 2, \dots \quad (16)$$

Therefore, the diffraction amplitude consist of four summands, each of which contains product of sum over n (S_{mq}^\pm multiplier) by sum over v . Maxima of amplitude could be achieved when conditions (10) and (16) are fulfilled simultaneously. These conditions generate a set of equations for defining z^* and q . Results of defining q for four summand of the amplitude (15) are noted in fourth column in Table 1 in which we neglected a value containing ε_c^2 multiplier.

By substituting q from the fourth column into the second, and by neglecting summands of second order of smallness (values of first order of smallness are ε_c and $1/2\pi\rho_m$), we can achieve coordinates of layer lines

for all four terms, where is necessary to take into account arithmetical signs of k and ε_c . From (17) we see that in this case, in comparison to diffraction by chiral nanotubes, coordinates of layer lines in a first approximation are independent of the layer number m .

Let's consider the fourth column of Table 1. It's obvious that among the three summands contributing to q largest on modulus value, when $k \neq 0$, has the first summand. Thus, this summand governs arithmetical sign of q . By taking into account the fact that $q \geq 1$ by convention, it may be deduced that 1-st and 2-nd summands of amplitude (15) govern reflexes with $k > 0$, and 3-th and 4-th - with $k < 0$. In consequence of $R \geq 0$ by convention, the amplitude of strong reflexes is governed by 2-nd и 3-th summands when $k = 0$. Because of symmetry of reciprocal space, we will consider only layer lines with $h \geq 0$.

Table 1
Values of z^* and q , at which maxima of amplitude are reached

Summand number	Maximum condition for sum over n	Maximum condition for sum over v	q
1	$z_m^* = \frac{h}{a} + \frac{q\varepsilon_c}{2\pi\rho_m}$	$z^* \varepsilon_c + R \frac{\tau}{\rho_m} + \frac{q}{2\pi\rho_m} = \frac{k}{b}$	$q_1 = k \frac{2\pi\rho_m}{b} - 2\pi\rho_m \frac{h}{a} \varepsilon_c - Rd$
2		$z^* \varepsilon_c - R \frac{\tau}{\rho_m} + \frac{q}{2\pi\rho_m} = \frac{k}{b}$	$q_2 = k \frac{2\pi\rho_m}{b} - 2\pi\rho_m \frac{h}{a} \varepsilon_c + Rd$
3	$z_m^* = \frac{h}{a} - \frac{q\varepsilon_c}{2\pi\rho_m}$	$z^* \varepsilon_c + R \frac{\tau}{\rho_m} - \frac{q}{2\pi\rho_m} = \frac{k}{b}$	$q_3 = -k \frac{2\pi\rho_m}{b} + 2\pi\rho_m \frac{h}{a} \varepsilon_c + Rd$
4		$z^* \varepsilon_c - R \frac{\tau}{\rho_m} - \frac{q}{2\pi\rho_m} = \frac{k}{b}$	$q_4 = -k \frac{2\pi\rho_m}{b} + 2\pi\rho_m \frac{h}{a} \varepsilon_c - Rd$

Therefore, our estimation shows that strong reflexes of the diffraction pattern from a roll nanotube with small chiral angle stand on layer lines (7), and diffuse reflexes are shifted from lines by the value proportional to chiral angle in direction corresponding to its sign and sign of k index. By considering the fourth column as a rule for choosing terms of series over q in the amplitude (12), we will get expressions for the amplitude of strong reflexes.

Strong reflexes of zero layer line

From the Table 1 for $h = k = 0$ we can estimate $q_2 = q_3 = Rd$, and, if it's remembered that q must be integer, we can get an expression:

$$q_2 = q_3 = l \Rightarrow R_l = \frac{l}{d}, \quad l = 1, 2, 3, \dots \quad (18)$$

$$I_S^{00l}(R, \varphi^*) = 4N^2 \left\{ \sum_j f_j \sum_{m=0}^{M-1} \sum_{v=0}^{P_m-1} \cos[l(\varphi_{mvj} - \varphi_m - \varphi^*)] J_l(2\pi R \rho_{mvj}) \right\}^2 \quad (19)$$

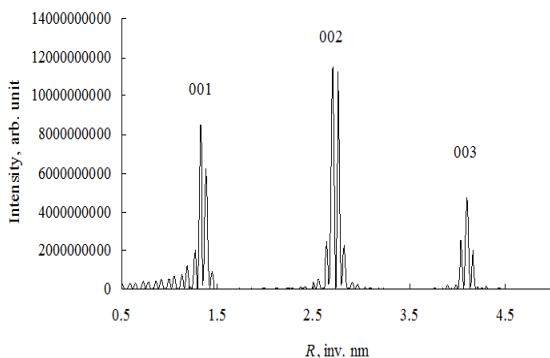


Fig. 3. Strong reflexes of zero layer line from roll nanotube for $\varphi^* = 0$.

Strong Reflexes Standing on the Layer Lines with $h > 0$

Here from the Table 1 and for $k = 0$ we can estimate:

$$q_2 = Rd - 2\pi\rho_m \frac{h}{a} \varepsilon_c, \quad q_3 = Rd + 2\pi\rho_m \frac{h}{a} \varepsilon_c. \quad (20)$$

Integrality requirement for q gives:

$$R_{h0l} = \frac{l}{d} \pm h \frac{2\pi\rho_m \varepsilon_c}{ad},$$

$$A_S^{h0l}(R, \varphi^*) \approx 2Ni^l \sum_{m,j} f_j \exp\left(2\pi i h \frac{z_{mj}}{a}\right) \sum_v \exp\left(2\pi i h \frac{b\varepsilon_c}{a} v\right) \cos[l(\varphi_{mvj} - \varphi_m - \varphi^*)] J_l(2\pi R \rho_{mvj}), \quad (21)$$

- this expression describes locations of so called «basal» reflexes 00l on the layer line with $z^* = 0$. Therefore, 00l reflexes are described by primary summands of series over q in the expression (12), moreover each reflex is described by its own summand with $q = 1$. As a result, in case of inessential overlap of Bessel functions the amplitude (12) can be written as:

$$A_S^{00l}(R, \varphi^*) = 2i^l N \sum_{m,j} f_j \sum_v \cos[l(\varphi_{mvj} - \varphi_m - \varphi^*)] J_l(2\pi R \rho_{mvj})$$

where maxima of S_{ml}^\pm equal to N are taken into account. Corresponding intensity is independent of chiral angle, but has an angular dependence to φ^* . Figure 3 shows profiles of 00l reflexes calculated from the expression (19). It's interesting to note, that only 001 reflex has small-angle tail.

where the index l is governed by the expression (18). Thus in this case, as in the preceding subject, strong reflexes $h0l$ (except $h00$ reflexes) are also described by primary terms of series over q in the expression (12). However, by comparing with similar expressions for monoclinic polytypic modifications of circle, chiral and also spiral nanotubes in model of elastic layer, it's easy to see that the variable $2\pi\rho_m \varepsilon_c$ plays the role of interlayer shift Δz . With the result of 2-nd section of the article, it allows to write an expression for locations of maxima of m -th summands of strong reflexes $h0l$ on the layer line in traditional way [6]:

$$R_{h0l} = \frac{1}{d} \left| l + h \frac{2\pi\rho_m \varepsilon_c}{a} \right|, \quad l = 0, \pm 1, \pm 2, \dots$$

In the same way as in the previous section of sum (11) let's set:

$$S_{mq_2}^\pm \approx S_{mq_3}^\pm \approx N$$

And the amplitude (12) for $q = 1$, $l = 1, 2, \dots$, can be conceived of as:

This expression for $h = 0$ totally identical to (19). Thus, expression (21) governs amplitudes of couples of strong reflections $h0l - h0\bar{l}$ from roll monoclinic nanotube with small chiral angle in the model of strong layer.

Figure 4 shows profiles of reflexes 20+200 taken from Fig. 2, and profiles of 20l reflexes calculated for intensity corresponding to the amplitude (21), with structural parameters of chrysotile and different chiral angles. As expected during the analysis, the diffraction profile is a summation of pair $h0\bar{l} - h0l$ reflexes for $l > 0$ and $\varepsilon_c = -0,04^\circ$. In case of the orthogonal polytypic modification of roll nanotube ($\varepsilon_c = 0$), reflexes from pairs join together and make a summary single reflex, which routinely [8] identify as h0l reflex.

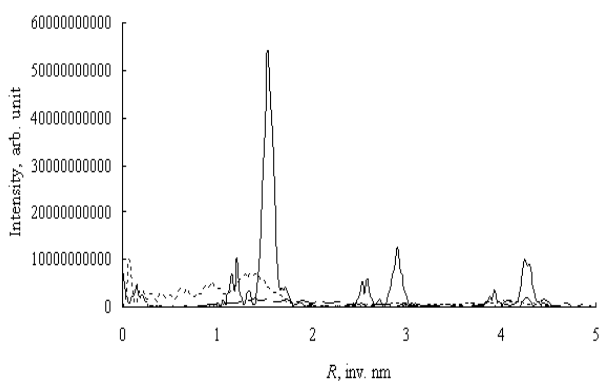


Fig. 4. Strong reflexes on the second layer line from chrysotile monoclinic roll nanotube with $\varphi^* = 0$ and $\varepsilon_c = -0,04^\circ$ (solid line), $-0,5^\circ$ (dotted line) and -1° (dashed line).

Increasing of chiral angle leads to degradation of diffraction conditions (Fig. 4). It must be emphasized that such effect isn't a result of our approximations. It's obvious that within the framework of assumed model small angle ε_c is a good simulation parameter. However, from (3) it follows that increasing of chiral angle will lead to strong change in z coordinates of an atoms from one layer to another. This leads to «destruction» of scattering planes h0l and, as a result, to deterioration of diffraction conditions.

Diffuse reflexes

Locations of layer lines of diffuse reflexes are governed by the expression (17) with regard to algebraic sign of k index. The Amplitude (12) describes the profile of diffuse reflex $hk0$. In this am-

plitude selection of terms of series over q should be done in accordance with Table 1: q_1 and q_2 - for $k > 0$, and q_3, q_4 - for $k < 0$. However, selection of terms of series that contribute significantly to diffraction amplitude must be done in slightly complicated way - this way will be discussed below.

Our findings allow estimating locations of main maxima of diffuse reflexes. Let's use one of the well known properties of the Bessel function lies in the fact that its main maximum located near the value of an argument equal to index of the function. For the amplitude (12) and noted in Table 1 q this gives:

$$\begin{aligned} k > 0: \quad R_{hk0} &\approx \frac{k}{b} - \frac{h}{a} \varepsilon_c \\ k < 0: \quad R_{h\bar{k}0} &\approx \frac{-k}{b} + \frac{h}{a} \varepsilon_c \end{aligned} \quad (22)$$

where we neglect relatively small values. By comparing expressions (17) and (22), it's easy to see that for $\varepsilon_c > 0$ reflex $hk0$ lies above the layer line with $z^* = h/a$ and for smaller values of R , and $h\bar{k}0$ reflex-under the layer line with biggest R . For $\varepsilon_c < 0$ reflexes will interchange places.

For estimation of an angular splitting relatively to the center of reciprocal space of such reflexes in microdiffraction pattern, we determine the formula for scalar vector of main maximum of diffuse reflex from (17) and (22)

$$R_{hk0}^* = \sqrt{R_{hk0}^2 + z^{*2}} \approx \sqrt{\left(\frac{k}{b}\right)^2 + \left(\frac{h}{a}\right)^2} \quad (23)$$

- the splitting is independent on the value of the chiral angle. It means that the splitting of diffuse reflexes occurs on the arc of a circle with the center coinciding with the center of reciprocal space. From (17) and (22) also follows that the distance between two main maxima of diffuse reflexes having opposite signs of k index may be written as

$$\Delta^* = 2\varepsilon_c \sqrt{\left(\frac{k}{b}\right)^2 + \left(\frac{h}{a}\right)^2} \quad (24)$$

Sought value of splitting angle can be estimated from (23) and (24)

$$\frac{\Delta^*}{R_{hk0}^*} \approx 2\varepsilon_c$$

Let's get expressions describing diffuse reflexes in numerical terms. The integrality requirement of q and results of previous sections give that each m -th summand of amplitude of diffuse reflex is described by the group of terms of the series over q in the amplitude (12). Each group consists of q -tuple, indexes of which are varied sequentially near the value $|k|(p_0 + mg)$. Limits of this group can be easily obtained from the last column in the Table 1:

$$q \approx \left[|k|(p_0 + mg) - l_{\max} \right] \div \left[|k|(p_0 + mg) + l_{\max} \right], \quad (25)$$

where l_{\max} – the smallest integer greater than Rd , that is used during simulation. Indexes of corresponding Bessel functions in the amplitude (12) are also differ by one, and for this reason, these functions are closely adjacent to each other in R scale. This means that we can't neglect their overlap, and therefore, we must add diffraction amplitudes rather than diffraction intensities. On the other hand, for increment of k difference between indexes of two adjacent groups correspond to the value $|k|(p_0 + mg)$. In case of such significant distance in

R scale and inessential overlap of Bessel functions, we may consider diffraction amplitudes of diffuse reflexes independently of each other.

Note that in this case q indexes of terms of the series that governs diffuse reflexes are not small, therefore we can't neglect second term in round brackets of sums (11), as we did in case of strong reflexes. For this reason maximum condition of sums gives:

$$\pi \left(z^* \pm \frac{q \varepsilon_c}{2\pi \rho_m} \right) a = h\pi \Rightarrow$$

$$z^* = \frac{h}{a} \mp \frac{q}{2\pi \rho_m} \varepsilon_c \approx \frac{h}{a} \mp \frac{k}{b} \varepsilon_c,$$

where k should be taken modulo. By comparing this expression with (17), it may be concluded that in case of diffuse reflexes, S_{mq}^- sum corresponds to reflexes with $k > 0$ and S_{mq}^+ – to reflexes with $k < 0$.

By taking into account the expression (17), the amplitude (12) in case of diffuse reflex with $k > 0$, it can be conceived of as:

$$A_D^{hk0}(R, \varphi^*) \approx N \sum_{q,m,v,j} f_j \left[i^q \cos \gamma_{qmvj} J_q(2\pi R \rho_{mvj}) + i^{q+1} \sin \gamma_{qmvj} J_q(2\pi R \rho_{mvj}) \right], \quad (26)$$

where «D» index means «diffuse» and

$$\gamma_{qmvj} = 2\pi \left(\frac{h}{a} + \frac{q}{2\pi \rho_m} \varepsilon_c \right) (z_{mj} + b \varepsilon_c v) + q(\varphi_{mvj} - \varphi_m - \varphi^*)$$

A similar estimate can be made for diffuse reflex with $k < 0$:

$$A_D^{h\bar{k}0}(R, \varphi^*) \approx N \sum_{q,m,v,j} f_j \left[i^q \cos \gamma_{qmvj} J_q(2\pi R \rho_{mvj}) + i^{q+1} \sin \gamma_{qmvj} J_q(2\pi R \rho_{mvj}) \right], \quad (27)$$

where

$$\gamma_{qmvj} = 2\pi \left(\frac{h}{a} - \frac{q}{2\pi \rho_m} \varepsilon_c \right) (z_{mj} + b \varepsilon_c v) - q(\varphi_{mvj} - \varphi_m - \varphi^*)$$

limits of summation over q in expressions (26) and (27) are defined by the expression (25).

Let's consider peculiarities of the intensity distribution of diffuse reflexes in cross-section (relatively to the axis of nanotube) of reciprocal space of a roll nanotube. For theoretical estimation the Bessel function has to be approximated by cosine. Terms and multipliers that contribute a significant value to estimation of the amplitude (27) for $q \approx kp_m$ are then approximately represented by

$$\sum_m i^{kp_m} \cos \left(2\pi \frac{h}{a} 2\pi \rho_0 m \varepsilon_c - kp_m \varphi^* \pm 2\pi R \rho_m \right)$$

Addition of summands in real and imaginary part of the amplitude depends on the parameter kg_m . It's obvious that for even kg cosinusoidal summands come only into real part of the amplitude and sinusoidal – only into imaginary part. In case of uneven kg summands come into real and imaginary

part alternately. In that case we should change m to $2m$ and modify the limits of summation. In this analysis limit of summation is doesn't matter, and therefore, considering expression can be approximated by

$$\sum_m \cos \left[2 \left(\frac{2\pi h}{a} 2\pi \rho_0 \varepsilon_c - kg \varphi^* \pm 2\pi R d \right) m + A \right],$$

where A consist summands that are independent of summation index.

Sum have maxima when

$$\frac{2\pi h}{a} 2\pi \rho_0 \varepsilon_c - kg \varphi^* \pm 2\pi R d = n\pi,$$

where n – integer. This expression is equation for class of right-handed and left-handed Archimedean spirals arranged in layer plane (17) in reciprocal space. Let's deduce φ^* from the expression near the spiral beginning, where $R \approx |k|/b$ (Since we wish to study points where spirals begin we should consider only right-handed spirals):

$$\varphi^* = -\frac{\pi}{kg} n + \frac{2\pi h}{a} \cdot \frac{2\pi \rho_0}{kg} \varepsilon_c + \frac{2\pi d}{kg} R \approx -\frac{\pi}{kg} n + \frac{2\pi h}{a} \cdot \frac{2\pi \rho_0}{kg} \varepsilon_c + \frac{|k|}{k}$$

From the first term at the right side of the equation it follows that the pattern is repeated every π/kg angle and it turns out that it has $2kg$ -fold symmetry. It's easy to see that for even kg in imaginary and real parts of amplitude summands are twice as much and this yields that the pattern has a kg -fold symmetry. Therefore, the pattern has a symmetry center in both cases. Note that we can use such analytic simplification only for qualitative evaluation, but not for exact calculation.

Obtained results allow us to pass to simulation of diffraction profiles of diffuse reflexes along the layer line using (26) and (27). For this purpose according to (17) it's necessary to choose z^* coordinate of layer line and azimuthal angle φ^* , at which the reciprocal space of the nanotube is cut by Ewald sphere of electron beam.

Figure 5 shows simulated distribution of intensity of 110 diffuse reflex from the roll orthogonal chrysotile nanotube in the $\{R, \varphi^*\}$ plane with coordinate z^* expressed in (17). In accordance with our estimation this distribution has a helical fashion that is very similar to diffuse reflexes from coaxial nanotubes [6, 7]. Distortion of $2kg$ -fold symmetry (generator g of chrysotile is equal to 5) on the lower

levels of intensity connected with existence of ends points of spiral lattice in $\{\rho, \varphi\}$ plane, angle locations of which in this simulation are agreed.

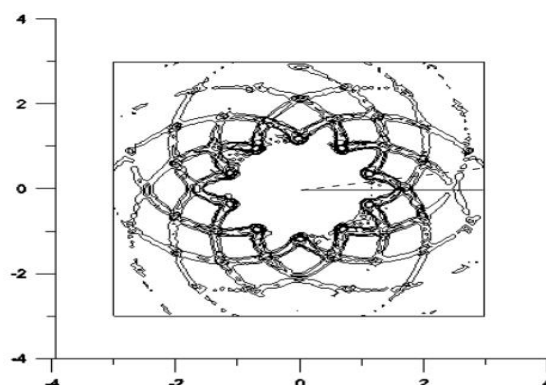


Fig. 5. Simulated distribution of intensity of 110 diffuse reflex from roll chrysotile nanotube in the $\{R, \varphi^*\}$ plane.

Figure 6 shows simulated profiles of 110 reflex along the layer line (17) for different φ^* , showed at Fig. 5 by straight lines of the same type. From the picture it follows that the profile of diffuse reflex depends on the nanotube orientation relatively to electron beam. This peculiarity has a significant importance for lattice parameters (b) measuring technique that uses microdiffraction pattern from single nanotube.

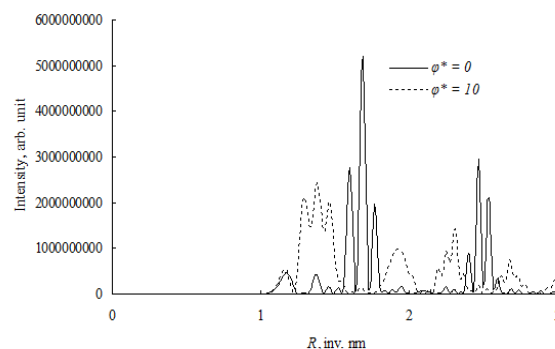


Fig. 6. Simulated profiles of 110 diffuse reflex for different φ^* showed at Fig. 5 by straight lines of the same type.

The truth is that anyone of several points of the beginning of pair spiral reflexes in Fig. 5 could be associated with the main maximum of diffuse reflex $hk0$. Its polar radius is about $R_{hk0} \approx k/b$, and here « \approx » sign means that the point is slightly shifted from the k/b value in the direction of large R according to average radius of the nanotube [9]. However, for random orientation of the nanotube relatively to its axis, every point of intersection between spiral-reflex and Ewald sphere could be the

maximum of diffuse reflex in the microdiffraction pattern. This may cause serious errors while measuring lattice parameters. Therefore, it's necessary to rotate nanotube about its axis for finding the point where Ewald sphere cuts the beginning of spiral pairs (Fig. 5) during the registration of microdiffraction pattern from single nanotube.

Conclusion

Presented diffraction theory allows explaining the origin of local maxima of intensity in the region of «tails» of diffuse reflexes that typically occurs in microdiffraction patterns from single nanotube. Performed analysis and simulated profiles in Figs. 5, 6 state that it's a result of cutting of spiral reflexes set, that represents diffuse reflex, by Ewald sphere. The maxima indexing problem and the peculiarities of spiral reflexes will be considered in next articles of this series.

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