

*In memory of the outstanding scientist
B.N. Sharupin is dedicated*

ELECTRONIC LEVELS AND CRYSTAL STRUCTURE

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Abstract. The well-known phrase "the electron is also not exhausted, like the atom" must start with an atom. Atom is still engaged in a whole section of physics, but as is now accepted, digging in details, do not reach generalizations that could be properly used by chemists, and physicists of related fields. So there are no qualitative conclusions from modern physical physics even from many fields of physics, than from chemistry. While the basic atomic representations, if they are slightly combed and corrected, and the accumulated reference data are sufficient to better connect with a macroscopic real atom.

First, it is necessary to correct the reference point - for most chemical elements it is necessary to go from a hydrogen-like atom to a graphite-like one. So carbon not only spawned life. Most of the other chemical elements are made in its image and likeness. its electronic structure, in principle, is preserved, only scaled. But the principal features of the carbon atom, unimportant for the hydrogen-like volume and, as a consequence, not taken into account in the elementary model, for most atoms of other chemical elements remain. Namely, the dependence of the energy levels on additional quantum numbers, on the s-p interaction, and even on the spin interaction.

In this paper, the problem of rigorous calculation of the quasi-atom model based on carbon was not posed. This, to some extent, is a technical problem using the algorithm developed for the hydrogen atom. The problem was to show which features of the electronic spectrum in the basic model should be initially taken into account, would not be obtained as the tenth correction to the original model. And these features were revealed as a result of a comprehensive study of "elementary", but not primitive C & BN.

From the analysis of the allowed electronic levels, the worldview question also arises: What are these quanta on which quantum mechanics was constructed, when there are some shares from them, determined by additional quantum numbers? We will not go into this issue for now (because it goes far beyond the scope of this work). Normal quanta - this piece of energy is needed to tear an electron into a vacuum. So in this paper we simply analyzed what patterns for allowed energy levels (with allowance for shares) and allowed hybridized orbitals based on refined carbon orbitals are observed in the structure and properties of materials.

The revealed regularities are of the most general nature, which not only did not put, but even helped in the construction of the crystal structure and in the design of semiconductor structures for highly effective local thermoelectric conversion.

Keywords: carbon, boron nitride, resolved states, atomic orbitals, hybridization, crystal structure, semiconductor structures.

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1. Introduction

Well-known graphite and its white, dielectric analogue of boron nitride, first obtained from chlorides on laboratory work by Boris Sharupin, a student of the 3rd year of the Leningrad Institute of Technology, were correctly considered theorists as extremely anisotropic crystals of the crystals existing on the Earth. But their high

anisotropy was associated not with their most rigid connection of hexagons, but with the complete absence of chemical bonds in the crystal lattice between mono-atomic layers along the C axis. Although such so-called Van der Waals crystals without chemical bonds can exist only at helium temperatures, and C & BN do not fall apart and at 3000C, theorists "skidded".

The beginning of this "drift" can be related to the name of the classic Linus Pauling, who invented sigma and pi-electrons (Pauling, 1947). Although he personally found errors in his concept, and tried to introduce new, "curved" chemical bonds, the Van der Waals crystal model firmly entered the textbooks on solid-state physics under a modified name-two-dimensional crystals (Bassani & Pastori-Parravicchini, 1983). So firmly that the differences of real C & BN crystals were tried to describe, introducing quasi-two-dimensionality, in the form of small corrections, and for a non-existent "graphene" they even gave the Nobel Prize.

Originally I had certain doubts in some basic physical models originated in the analysis of the anomalies of crystal optics of disproportionate crystals, which I considered quite natural for a qualitatively new, four-dimensional object (Ordin, 2011). But I decided to check the crystal-optical models of plasma and lattice oscillators on the asymptotics of the anisotropy of classical crystals, on an "ideally" anisotropic conductor-graphite and on an "ideally" anisotropic dielectric-boron nitride.

But the first experiments on C & BN samples (both on the grown by B. N. Sharupin (Sharupin, 1976) crystals and on the American ones), showed that:

1. the samples are far from ideal crystals,
2. their properties are not described by ideal models in any way (as indicated by the authors of the first papers (Handbook of Opticsed, 1974)).

And then, after 7 years of our joint work, B.N. Sharupin grew "ideal" C & BN crystals, and I experimentally examined them, and showed that:

3. properties of C & BN can not be described by two-dimensional models, since they do not take into account chemical bonds between atomic planes.

And then, a great scholar B.N. Sharupin invited me, a young scientistsist yet at that time, to a conference he was holding at the First Atomic Station of the USSR. He invited me with a report refuting that was written in the books, including what was written in his own book, with a report refuting the Van der Waals interaction between monoatomic layers in C & BN.

Perestroika, one can say bluntly, killed Boris Nikolaevich Sharupin. And I was able to publish in a physical journal the results we have obtained only after including it in co-authors posthumously (Ordin *et al.*, 1998a).

But there was a gap between purely physical, inconsistent with the usual notions, the conclusions of our publication and a huge layer of purely technological research by Sharupin's staff, without which it would be impossible to obtain perfect crystals and, as it turned out, understand and accept our conclusions.

This gap was reflected in the books published after our work. Even in the handbook published in Schringer by the employee of our Institute, the conclusions of our publication on the basis of a huge number of little-known works by the best technologists of the world were not reflected (when Japanese and Americans learned to grow perfect crystals 5 microns thick, Boris Nikolayevich gave me more than palm-sized one on which I measured all the crystal optics, and not just the normal planes, which is reflected in our publication). Partially this gap I tried to fill with physical research, spent some time with the former (in GIPH) B.N. Sharupin's associates. But

the great purity of the results obtained was published only in the works of Russian conferences (Ordin *et al.*, 1998b; Ordin *et al.*, 1998c; Ordin *et al.*, 1998d; Ordin *et al.*, 2001a; Ordin *et al.*, 2001b; Ordin *et al.*, 2003) and are not known in the world so far.

Now, when the world began to be interested in my previous publications, I was asked to send their originals. But in post-perestroika time not all reports of Russian conferences were published. To some extent, this prompted me to write a book in which not only the final conclusions for ideal anisotropic crystals are shown, but also a purely experimental basis for the observed regularity - the dependence of the physical properties of the pyrocrystals on the ordering degree of both their crystal lattice and the complex ordering hierarchy crystallites.

But when analyzing the structure and properties of C & BN (Ordin, 2018a; Ordin, 2018b; Ordin, 2018c), a catastrophic discrepancy was revealed in the most general physical laws. The dependence of the upper filled level on the atomic number within the base model of the hydrogen-like atom is qualitatively different from the experimental data on the first ionization potential, and the atomic orbitals calculated to arbitrarily large principal quantum numbers are not the first approximation even for the elementary carbon atom (require 100%).

So it turned out that

4. that an elementary, but at the same time, non-primitive carbon atom, and not an ideal model based on the hydrogen atom, is a "brick" for atomic physics and the description of chemical bonds.

So it turned out that carbon is not only a "brick" of organic life, but also a "brick" of atomic physics.

So we had to postpone the preparation of the book "Local Thermoelectric Effects" - the completion of the expansion of the phenomenology of thermoelectricity to the nano-level (Ordin, 2017a; Ordin, 2017b; Ordin *et al.*, 2017c; Ordin, 2017d; Ordin, 2018d; Ordin, 2018e; Ordin, 2018f) and first deal with publications on C & BN.

2. Analysis of resolved energy level of electron

For chemical bonds, first of all, the upper electron-filled atomic level (which corresponds to the first ionization potential of the atom and the work function of the solid body formed from these atoms) is important, and the empty level closest to the filled level (which corresponds to the electron affinity).

On the example of the "elementary" C & BN, the relationship of the macroscopic properties of a substance with properties at this "elementary" atomic level can be continued, at the same time, and correcting it, rather than confining itself to its statement in the introduction. And on the atomic level, this chain has necessarily continued with the correction of the basic model of the crystal bonds of the "elementary" C & BN (Ordin *et al.*, 1998a). Only He and Li can be considered simpler than C & BN, but only the simplest *s*-orbital is filled with them. And for most materials used, the electronic structure is richer and it needs to be represented in the first approximation.

Such a correct approximation, in fact, is the model of the electronic structure of C & BN, and not the model of the hydrogen atom. While most calculations of atomic orbitals of complex atoms (electron density distribution) are conducted in the form of numerous corrections to the model of the hydrogen atom. Here is a refinement of the C

& BN crystal model based on electronic orbitals and led to the need to comb the model of the atom, which, in principle, is correct only for the hydrogen atom.

The basic formula describing the allowed energies of ALL electronic levels (respectively, and all orbitals) and used for any atoms has long been obtained by quantum mechanics and is well known:

$$E_n = -\frac{hcRZ^2}{n^2} \tag{1}$$

where eZ - nuclear charge, an - principal quantum number (Pimentel & Spratley, 1969).

The sign in the formula stands minus, as is customary in semiconductor physics, but traditionally ionization potentials are depicted as positive, which separates chemical and some physical letters of the type of solid-state physics. Adhering to the correct sign in Formula 1 and putting the world's constants equal to unity, one can construct a graph of the dependence of the energy of each allowed (according to the main quantum number n) energy level of the electron E_n on the atomic nucleus charge (Fig. 1).

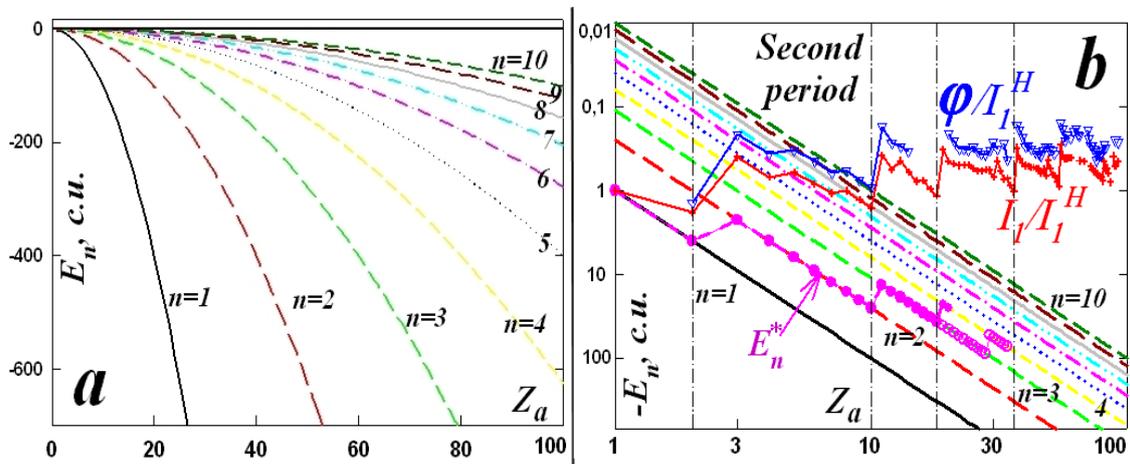


Figure 1. Dependence of the energy of allowed electronic levels (in conventional units) on the atomic number in linear (a) and double logarithmic scale (b). Pink dots show the maximum filled levels (within the framework of the elementary model). Red crosses and blue triangles show normalized reference data on the first ionization potential I_1/I_1^H and the work function ϕ/I_1^H .

In order to avoid confusion, I note at once that the generally accepted term “first ionization potential I_1 ,” refers to the minimum excitation energy of an electron of an atom i.e. to the most highly filled level E_n^* . So I_1 relates to the first quantum $n = 1$ only for the first period, for the second period I_1 refers to the level with $n = 2$. And so on, the electrons of the atom tend to occupy an energetically favorable state at the allowed energy levels, i.e. the filling of levels by electrons begins with the deepest, first, then second and so on up to the total number of electrons equal to the atomic number on (in Fig. 1b the pink lines and points are E_n^* in accordance with the experimental period, pink circles - E_n^* in accordance with the model of the hydrogen-like atom).

But each level of electron energy resolved (the main quantum number) corresponds to a different number of allowed states of the electron, distinguishable both in spin-2 and in orbital quantum number- $\{l = 0, 1, 2, \dots n - 1\} \Rightarrow k = n$ and in terms of the magnetic quantum number having the number of values determined by the chosen orbital number- $\{m_l = l, l - 1, \dots - l\} \Rightarrow r = 2l + 1$ (c taking into account the spin-the

placement of two electrons on the level, the number of states doubles and by additional quantum number-states). So the filling of the levels with the increasing principal quantum should go stepwise, as shown by the pink dots in Fig. 1b.

However, as can be seen from Fig. 1, the basic model of a hydrogen-like atom widely used (in introductions) gives the level filling by electrons (pink dots) qualitatively different from reality (red crosses and blue triangles in Fig. 1b). The observed first ionization potentials of atoms demonstrate that the energy of the top-filled allowed atomic level for $Z_a \gg 1$ (for long periods) does not increase by orders of magnitude, as would follow from the hydrogen-like model (pink dots in Fig. 1b).

In this case, for the second "elementary" period, the number of elements is 10, which is in full accordance with the model. In addition to filling two s-states, we have two more orbital numbers- $n = 2 \Rightarrow \{l = 0, 1\}$ and, correspondingly, four additional allowed states of the electron $\{l = 0, m_0 = 0\}, \{l = 1, m_1 = 1, 0, -1\} \Rightarrow 1 + 3$, and taking into account the spin, eight (points in Figs. 1b and 2 are the normalized first ionization potential).

This long-known violation is simply accompanied by words about the greater difference in energy levels within the period than between periods. But this difference is so great that it casts doubt on the very expediency of using the calculations of the electron orbitals of large atoms based on the nucleus of the hydrogen atom.

So a completely filled s-p-hybridized electron shell of neon is similar to a completely filled s-shell of helium, and neon itself with a partially shielded nucleus is similar to helium. In general, the weakly increasing course of the first ionization potential observed in Fig. 1b qualitatively differs qualitatively from the model, which decays quadratically. It is more qualitatively more accurate to describe each period using its quasi-nucleus, a core shielded by internal and external electron shells. Moreover, the shape of the outer orbitals calculated on the basis of a bare core, as will be shown in the next section, can in no way be used as the first approximation for describing the crystal structure.

So when using the bare nucleus to describe the atom already in the third period, the formalism itself is violated even in the number of states. And one can use formalism only where the amendments to it are small. But they are not small, as can be seen from Figures 1 and 2, already in the second period.

Of course, there are quantitative differences already in the first period, but there are few points for analyzing the regularity. So, let's take a closer look at the "informal first" period - the second.

The analysis of quantitative differences in the second period gives an understanding that the elementary model for each period has its own "reference point" at approximately the same energy level (see $I_1/I_1(H)$ and $\varphi / I_1(H)$ in Fig. 1b), and not quadratically decreasing. Therefore, the main attention was paid to a careful analysis of the quantitative differences between the elementary model and the experimental data of this period, the "elementary" and the base for more complex periods (Fig. 2).

As can be seen from the lower Fig. 2, all reliable data on the work function and electron affinity correlate well with the first ionization potential. In this case, the first ionization potential decreases not monotonically, but has two characteristic discontinuities. The first at the beginning of the p-orbit filling determines the s-p-splitting Δ_{S-P} , the second jump is observed when the p-orbital filling begins with the electrons of the opposite spin and determines the spin splitting of p-levels Δ_{Spin} .

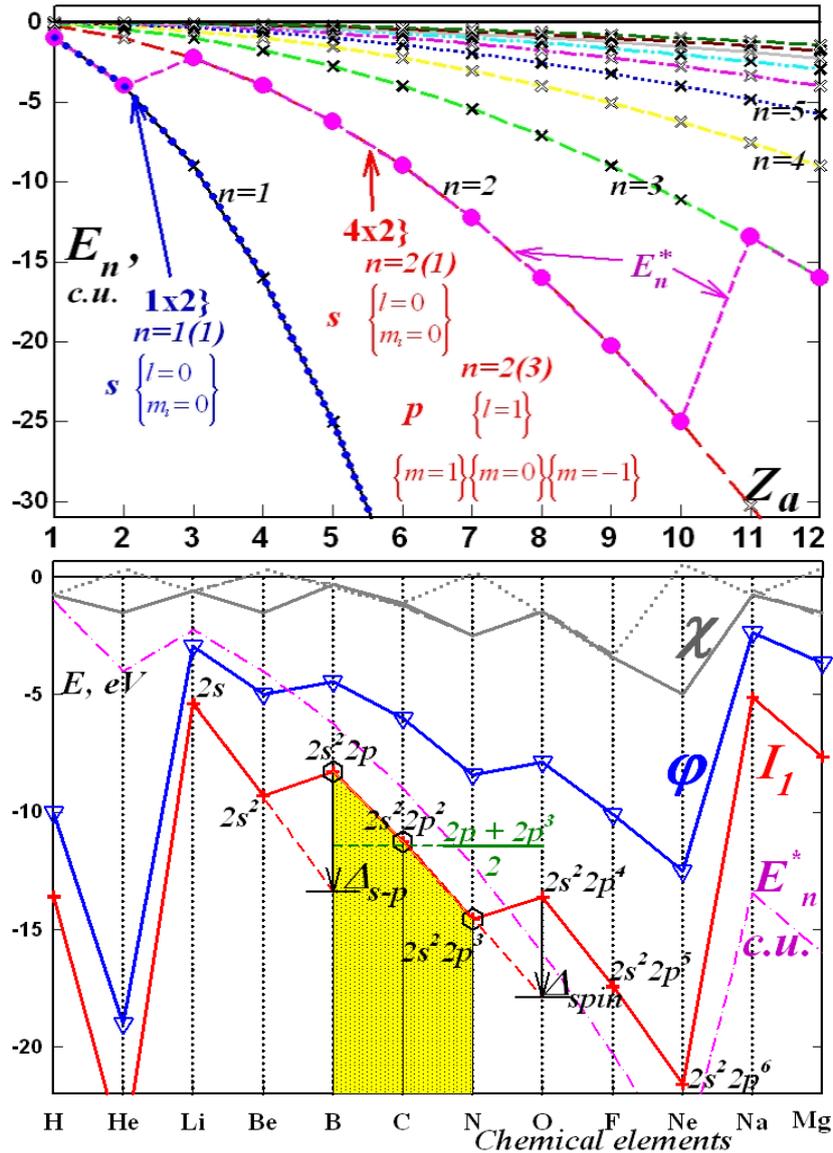


Figure 2. The progress of the upper filled state E_n^* (pink dots is at the top and the pink dotted curve is from below) from the model dependence of the energy E_n on the atomic number and the lower figure is the experimentally observed dependences on the atomic number of the first ionization potential I_1 , the work function ϕ and the electron affinity χ (the data contradicting the definition of affinity are represented by a dotted line)

Therefore, it follows from the foregoing that for the third period the helium quasi-atom model also gives the correct length of the period. And the model following from the analysis of the second period, it is possible and it is necessary to use as base model. Instead of using the "through formalism" of a hydrogen-like atom with a level energy that depends only on the principal quantum number.

Moreover, the electronic structure of the elements of the second period clearly demonstrates the regular dependence of the energy of the electron levels on the additional quantum numbers (Fig. 2), and in a slightly modified form these regularities of filling the levels of the second period are almost completely repeated for the third

period (in spite of the elementary model having the same number elements, as well as the second period), and the main ones are observed for all subsequent periods (Fig. 1b).

Namely, the first ionization potential of the second period does not have a monotonous dependence on the atomic number of the element (in accordance with the elementary model), but three, clearly expressed regions. The period begins with the filling of the s-orbitals first with one and then with the second electron with the opposite spin. As far as the spin of the second s-electron itself raises the second level qualitatively (by deviation from the ideal model for the first period of the core already shielded by the s-shell), it is difficult to determine, since and the first s-level is not lower, but above the corresponding s-level of hydrogen.

But when going to p-levels (further filling), a characteristic jump is seen, indicating that the orbital quantum number raises the energy of the level allowed by the principal quantum number. I. e. already at the atomic level there is an s-p-splitting. The filling of the p-level by the first three electrons of one spin again goes in qualitative agreement with the ideal dependence on the atomic number (the yellow band in the lower Fig. 2). But the filling of the p-level by the next three electrons of the opposite spin again begins with a jump, but continues in qualitative accordance with the ideal dependence on the atomic number of the element. That is, in addition to the traditionally considered s-p-splitting, there exists and is observed at the atomic level spin splitting.

Conducted analysis of the conformity / non-conformity of an ideal model with experimentally observed regularities allows us to make a number of fundamental amendments and conclusions.

1. The larger size of the screened (by internal electron shells) nucleus-quasidron raises (significantly) the allowed (near the quasinuclear) energy level for the external electron.

2. For the third period, the maximum orbital number remains equal to unity, as for the second period, i.e. this is a quasi-second period with "n" = 2.

3. Only for the fourth period does the orbital quantum number reach 2 and d-shells arise, i.e. period with quasi- "n" = 3.

4. For the properties of materials, the nearest, first unfilled level-the broadening of the electronic levels-their transformation into bands also determines the metal, semiconductor or dielectric properties of the resulting materials. But for barrier effects, this is not enough - a significant difference in the work function from affinity to electron not only in dielectrics and semiconductors, but also in metals directly indicates that the broadened first unfilled level does not reach the level of vacuum (zero). It follows that in the nano-size barriers the maximum height of the barrier is determined by the second unfilled level, which also manifests itself in the electron affinity.

Carbon and its dielectric analogue of boron nitride refer specifically to the second period, which determines their elementarity for a whole class of more complex materials. As can be seen from the lower figure 2, carbon also has on the upper shell two s-electrons with different spins and two p-electrons with identical spins and boron nitride, too, only on average per atom two p-electrons with exactly the same spins, since the spins of the p-electrons of the boron and nitrogen are the same. This is the similarity of the C & BN atomic orbitals and determines the similarity of their crystalline orbitals and many properties, which makes it possible to construct a base element model for most complex chemical elements. So carbon not only spawned Life. Most of the other chemical elements are made in its image and likeness. Basically its electronic structure is preserved, only scaled.

Also, one more general statement follows from the dependence of the first ionization potential in the second and third periods. The above-mentioned spin splitting Δ_{Spin} (Fig.2), in principle, violates the Pauli principle, which, by and large, requires registration in Fermi-Dirac statistics (and most likely in Bose-Einstein statistics). This, of course, goes well beyond the work on C & BN. Therefore, I only note that these statistics work well in solid bodies, where, as noted above, the atomic repulsion of opposite spins can be offset by the spatial separation of their electron carriers (as analyzed in the framework of the ballistic model - see the article with the same name on the site Nanotechnological Society of Russia (Ordin, 2015) and in the book "Refinement of basic physical models" (Ordin, 2017d).

3. Zone structure and potential barriers on the boundary of two materials

When creating semiconductor devices, the main parameter of the material is the width of the forbidden zone. At the same time, when creating interfaces, the work of the output was not given much importance. The potential barriers at the boundary for semiconductors of the same type were also determined by the width of the forbidden band. But for dissimilar materials, the magnitude of the potential barriers was an order of magnitude smaller than the difference in the work yields of the contact materials of the plates, and as a result, they believed it did not correlate with it in any way. When creating semiconductor structures for local thermo-EMF, this issue had to be given special attention (Ordin, 2015).

As can be seen both from the general figure 1 and from the more detailed figure 2 (lower), the work function of metals clearly correlates with the first ionization potential, and for silicon depends on the type of its conductivity, i e, it correlates with the top of the valence band and bottom of the conduction band. This correlation is determined by the fact that the work function corresponds to the ceiling of the allowed zone (the blue band in Fig. 3) formed from the level of the first ionization potential I_1 .

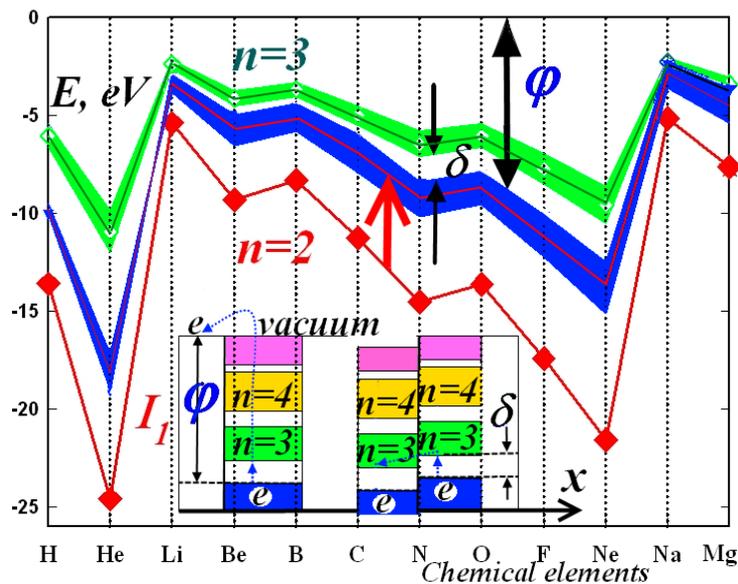


Figure 3. The scheme of the appearance of allowed and forbidden zones and the internal work function of δ at the boundary of different materials

As noted earlier, the first ionization *potential* I_1 corresponds to the maximum electron-filled level of the resolved level, and for the second period shown in Fig. 3 this is the second level in the principal quantum number: $n=2$. Qualitatively, for each chemical element, being tied to its I_1 , it is possible to estimate the position of the nearest to the filled, free allowed level by the formula 1.

To this level, for $n=3$, whose energy is $4/9 \cdot I_1$, there is a corresponding band of the color of the sea wave - a band of free states, a valence band, which is also present in metals, but overlapping with the band of filled states. The asymmetry specified by the polarity of the boundary leads to an external work function φ and to the external photoelectric effect at the boundary with the vacuum, and to the inner work function δ and to the internal photoelectric effect at the interface of the two materials. Wave functions of empty levels of different materials on the boundary overlap.

Since the internal work function is generally unequal to zero, it follows that the energy widths of the bands of allowed states are much less than the difference between the level I_1 and the corresponding external work φ . So in this case, due to the crystalline interaction, there is a rise in the level filled with electrons, and the energy gain necessary for the appearance of the condensed state is apparently connected with the interaction of the nuclei with each other, which on the state of the external electrons only appears as compression and extrusion onto the surface. It is more correct to say, as was shown above, with quasinuclear interaction, which leads to a fundamental difference in the experimental characteristics obtained from the hydrogen-like atom model shown in Fig.1.

In order not to overload Fig. 3, there is no strip on it - the dependence on the atomic number of the following free states: $n=4$. The ceiling of this band correlates well with the experimental values of the electron affinity χ . Levels corresponding to quantum numbers greater than 4 are condensed near the vacuum level (Fig. 1), and the corresponding zones merge (the pink region on the inset showing how electrons flow across the vacuum boundary and the boundary with another material).

The circuit shown in Fig. 3 can be said to be a working scheme for microcracking of semiconductor structures with highly effective local thermo-EMFs (Ordin, 2017a; Ordin, 2017b; Ordin *et al.*, 2017c; Ordin, 2017d; Ordin, 2018d; Ordin, 2018e).

4. Analysis of the orientation of hybridized atomic orbitals

Logarithmic relativity is a general physical phenomenon (Ordin, 2017e), which manifests itself not only in the energy of allowed electronic states (formula 1), but also in the form of their orbitals - the electron density distribution in various allowed orbits. And quantum mechanics using a hydrogen-like model, not only counted the energy of allowed electron states to an unlimitedly large principal quantum number, but a huge number of orbitals corresponding to additional quantum numbers.

But even with the example of allowed electron energies, it was shown that approximations to infinity without taking logarithmic relativity give an error greater than the base value in the zeroth approximation. Therefore, we restrict ourselves to considering only the shape of the first two orbitals, which correspond to the second period of interest to us: one s-orbital and three p-orbitals (Fig. 3a).

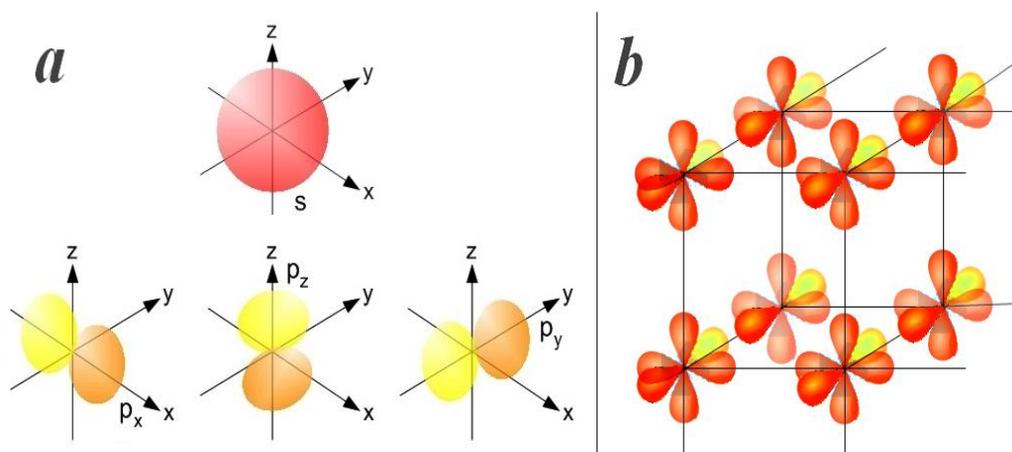


Figure 3. The set of atomic orbitals of the second period (a) and the corresponding elementary translational cell (b) obtained in the framework of the simplest model.

If we assume that when a chemical bond is formed by an unfilled electron, one p-orbit can be neglected, then the same graphite would form a square grid of atoms. This is not observed in nature - the carbon grid is formed by hexagons.

And since chemical orbitals in both micromolecules and macro crystals can differ substantially in orientation and in shape from the calculated atomic orbitals in general, then their hybridization has been invented.

As a matter of fact, hybridization introduced to describe interatomic interactions was attributed directly to a separate atom, which means that the correction for the corrected orbitals (depicted in Fig. 3) is actually calculated, taking into account the macroscopic properties of matter from these atoms.

In fact, such an approach was a refusal to use atomic orbitals. So Pauling drew his model of sigma and pi-electrons (Fig. 4), directly contradicting the ALLOWED (resolved) atomic orbitals of graphite.

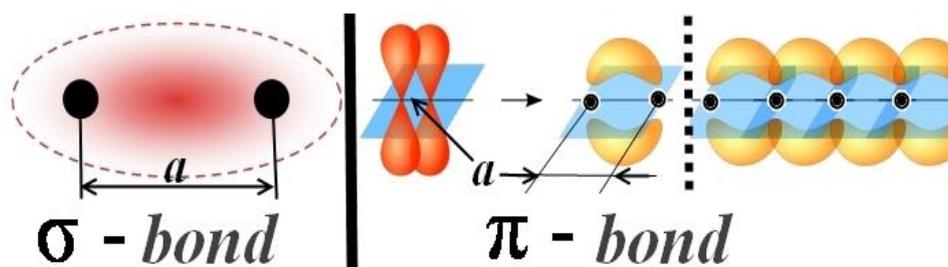


Figure 4. Pauling fit the chemical orbitals (actually macroscopic) under the atomic idealized model (in fact, the terminology)

In principle, it was a beautiful attempt to look into the unknown microcosm. And in itself this attempt to look into the unknown, deserves the Nobel Prize, because it encouraged many chemists and physicists to do this kind of design, including me.

But already in these basic drawings it is clear that the developers (Pauling himself soon realized that the design is contradictory) is "hidden behind the thought": the diversity of the image of the links of the same size (between the nodes and the pi-link, the distance is also intra-planar a , just like this Naturally, as between the nuclei of the sigma bond), and the "equality" of the size (represented) of the p- and s-orbitals, and the

translational smearing of the π -electrons (in contrast to the σ -electrons rigidly fixed between the nuclei).

And the "hidden" blurring of one of the four electrons (true, on both sides of the layer!) Was attributed: both the sliding of the layers along each other, and the high electrical conductivity along the layer, and for one and Van der Waals interaction between the layers. And the atoms of a single layer "liberated" by blurring would seem to be placed anywhere relative to the atoms of the other layer, but from "caution" they drew them (Fig. 5) located strictly above each other (so that all the maxima of the diffused π -bond of the neighboring layers coincide).

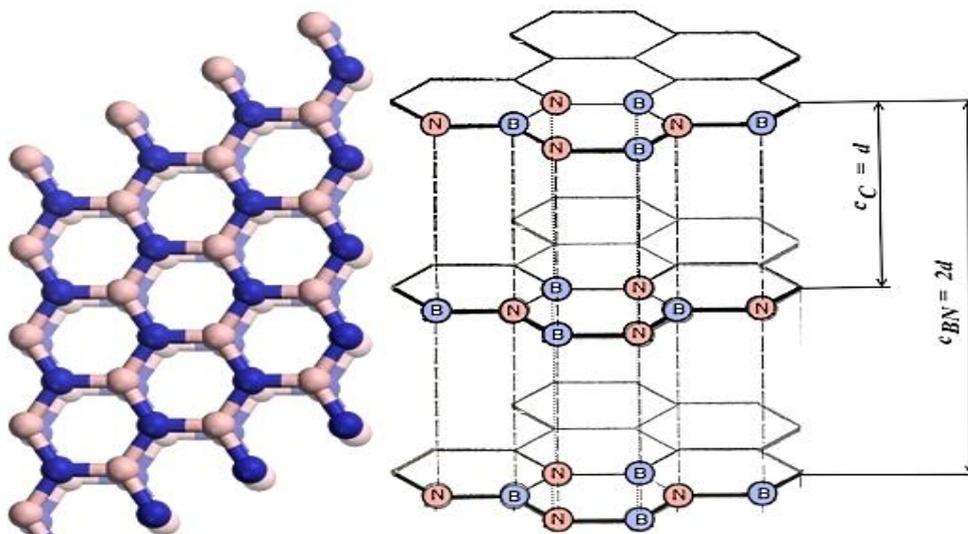


Figure 5. Erroneous, but originally included in the letters, and still redrawn by many graphenologists, including Wikipedia, the basic model of the crystal lattice of the hexagonal phase C & BN (with the replacement of equivalent balls for graphite)

In terms of promoting understanding of the meaning of true rather than idealized allowed atomic orbitals, many results of structural and IR spectral studies were obtained in the growth of pyroxyms of graphite and boron nitride, which, in many ways, supplemented each other (Ordin *et al.*, 1998b; Ordin *et al.*, 1998c; Ordin *et al.*, 1998d; Ordin *et al.*, 2001a; Ordin *et al.*, 2001b; Ordin *et al.*, 2003). The closeness in energy of the upper p-orbital of carbon ($2p^2$) to the average value of the energies of the upper half-filled p-orbitals of boron ($2p$) and nitrogen ($2p^3$) indicates the similarity of external orbitals of boron nitride to carbon orbitals.

Those the flow of an electron from nitrogen to boron leads, as it were, to the formation of two carbon atoms, only one little (as seen from the spectra of the lattice reflection BN) is positively charged and the other negatively. The polarity of the boron nitride molecule made it possible to analyze the interatomic bonds in the crystal lattice, which is practically identical to the graphite lattice in all phases, including the one depicted in Fig. 5, which demonstrates the discrepancy between the Powling orbital and not only the hexagons in the layer, but also the observed translation periods across the layers C & BN. The model of the crystal structure of the hexagonal phase, drawn by the Pulling method, gives a transmission period that does not exist in hexagonal graphite and is equal to one interplanar distance (in the experiment it is at least doubled in 3D

graphite), and in hexagonal boron nitride there is such a period, and the atoms of adjacent layers are not located as in Fig. 5.

In general, the above-mentioned cycle of complex studies allows us to state that the true atomic orbitals of C & BN are inscribed, in strict accordance with symmetry, in the tetrahedron depicted in Fig. 6 (and, as studies have shown, in strict accordance with the four are involved in molecular bonds in C & BN electrons).

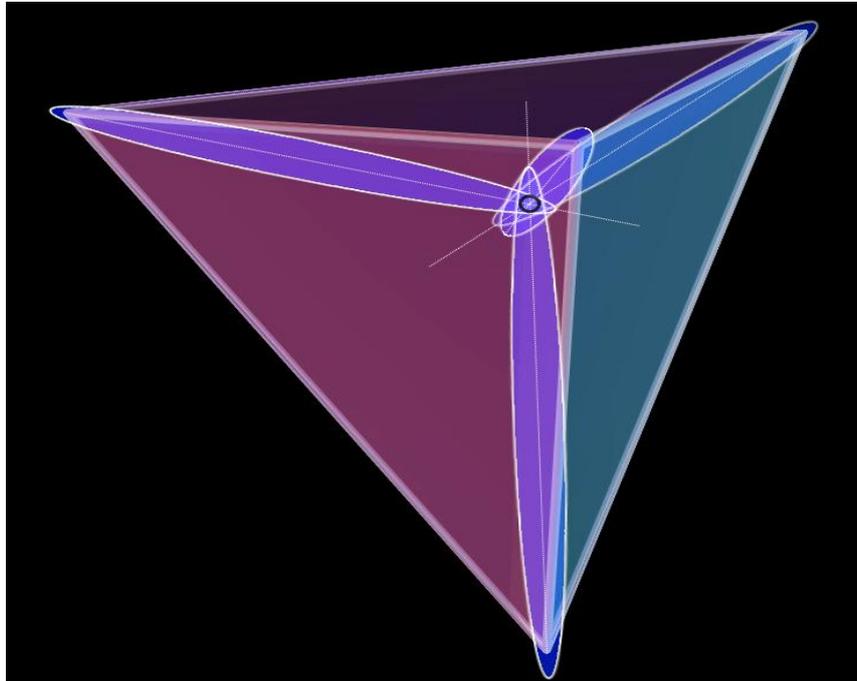


Figure 6. The orientation of the true hybridized atomic orbitals C & BN

The deformation of the atomic orbitals shown in Fig. 6 requires additional energy, which is released during the chemical reaction. However, a large deformation of atomic orbitals requires a large expenditure of energy. Therefore, the formation of chemical orbitals is more probable with a slight change in the orientation of the atomic orbitals.

Therefore, the correct, and not artificial, type of Pauling's constructions is essential, their representation is in first approximation (rather than making numerous corrections to the ideal model, or drawing them not on the basis of the principles of physics, but based on empirical data).

The atomic orbitals shown in Fig. 6 correspond directly to the crystalline orbitals of the cubic C & BN phase and only slightly deform in their other phases.

The analysis shows that it is the model of the carbon atom that should be used as the base for many chemical elements, and also for the correct description of organic life.

5. The real crystal structure of C & BN

The complex research carried out by C & BN touched on a number of the most general issues of the formation of atomic-molecular bonds. And a direct confirmation that the results of the analysis are true and useful are the obtaining of perfect pyrocrystals and the construction of the rhombohedral C & BN structure (Fig. 7) on the

basis of the orbitals depicted in Fig. 6 and the identification of the order-disorder transition upon its transition to the hexagonal phase.

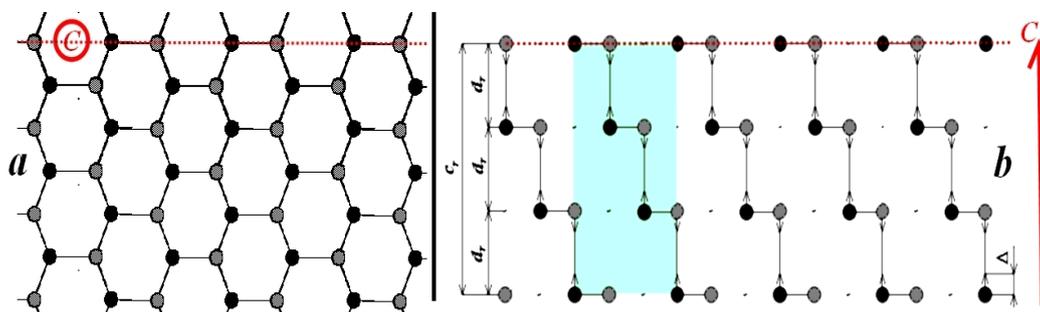


Figure 7. The simplest, but taking into account the displacements of the atoms Δ from the plane perpendicular to the C axis (shown in the figure to the right by small arrows) is the lattice model of the rhombohedral C & BN : a - in the plane perpendicular to the C axis, b - in the plane of the section parallel to the C-axis (indicated in both figures by a dotted red line)

Three of the four orbitals depicted in Fig. 6, overlapping with the orbitals of neighboring atoms form very rigid bonds and form the grid of hexagons depicted in Fig. 7a. The fourth atomic orbital of one monoatomic layer "can find" an analogous orbital from the adjacent layer, but their overlap will be somewhat less because of partial rectification in the plane of the three orbitals involved in the grid of hexagons.

Figure 7b shows the cross-section of the lattice by a plane parallel to the C axis and passing along the sides of a part of hexagons. The interlayer bonds shown in Fig. 7b, which are about one and a half times less rigid than the interlayer ones, can satisfy spatial translation and form a regular lattice from the two-dimensional net of hexagons by the only method depicted in Fig. 7b, which leads to the formation of the rhombohedral phase. These interlayer bonds provide up to about 1000 ° C the existence of a regular rhombohedral phase (Ordin *et al.*, 1998a). But since their stiffness (and, accordingly, the Debye temperature along the C axis) is about one and a half times lower than the stiffness inside the layer bonds, then at higher temperatures, while maintaining ordering in the planes, the interlayer bonds are destroyed. This leads to a one-dimensional solid-state order-disorder transition in the hexagonal phase (Ordin *et al.* 2001b; Ordin *et al.* 2003). So the hexagonal phase existing at room temperatures is metastable (hardened like the same diamond) and has ordering of interlayer bonds of the soliton type, which leads to the formation of small-diameter crystallites. In fact, it is the interlayer bonds that form the fullerenes, and the destruction of their regularity leads, with the integrity of hexagons, to the formation of a small concentration of defects (Fig. 9) in the rhombohedral phase of the C and BN pyrocrystals.

The section shown in Fig. 8 demonstrates how, in principle, the interlayer bonds of the same layer can be closed to each other when one of them is passed. This is how the fullerenes are formed from which crystallization centers are formed, a large number of which lead to the formation of poorly ordered pyrocrystals from sprouting growth cones (Fig. 9).

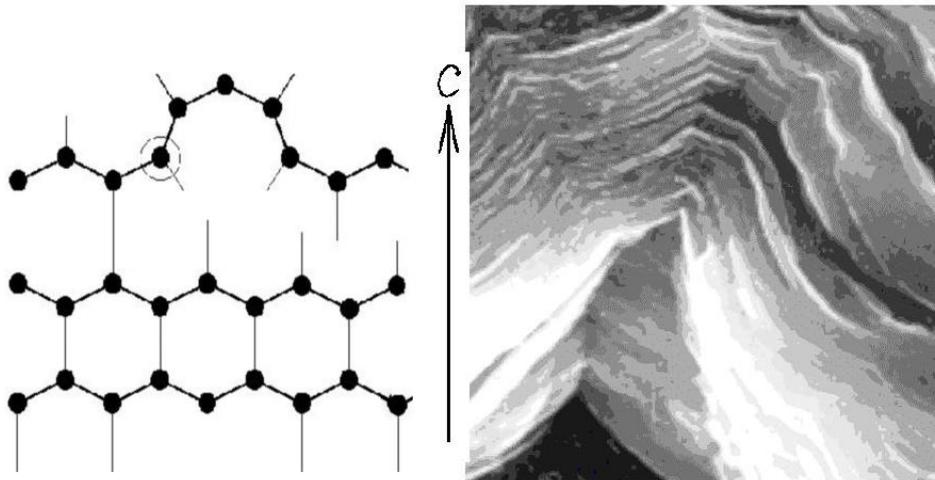


Figure 8. The model for the formation of the interlayer defect and its electronic photograph (100nm x 100nm).

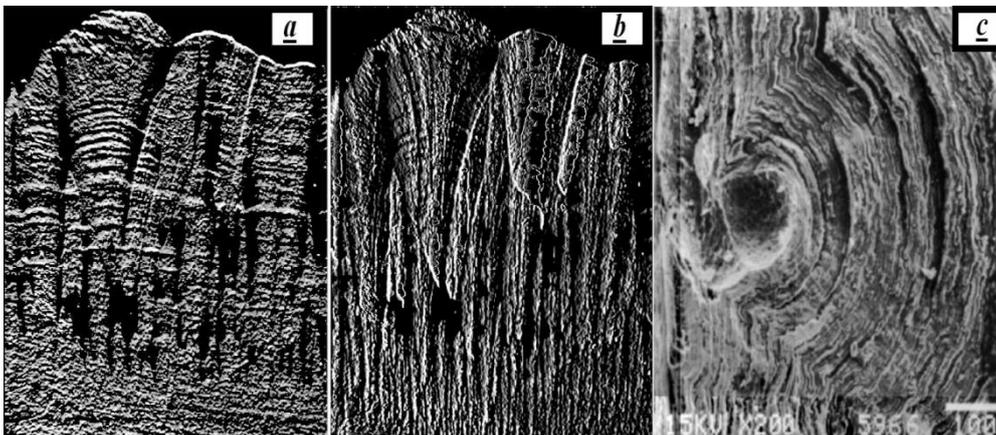


Figure 9. Electron microphotographs of the pyrolytic crystals of the C&BN pipeline stratum: a and b are the plane parallel to the growth axis C (preferential orientation of crystallographic axes C of microcrystallites), c is the plane perpendicular to the growth axis (the edge of the figure is approximately 1 mm)

And most of the published data refer to the type shown in Fig. 9, C & BN samples, in which many properties are determined by large intercrystalline scattering. Whereas our conclusions are based on the results of the measurement of the most perfect samples (Fig. 10a).

Measurements of lattice vibrations in rhombohedral nitride of boron and measurement of plasma oscillations in rhombohedral graphite have the unambiguously confirmed asymptotic behavior of the dependences of the numerous C & BN parameters on the degree of their ordering-there is an ion-covalent bond between monoatomic layers.

The maximum of the anisotropy of C & BN is achieved on highly ordered polycrystalline hexagonal samples (Fig. 10c) and decreases, first, as the dimensions of the hexagonal crystallites increase (Fig. 10b), and then on going to the rhombohedral single crystal (Fig.10a)

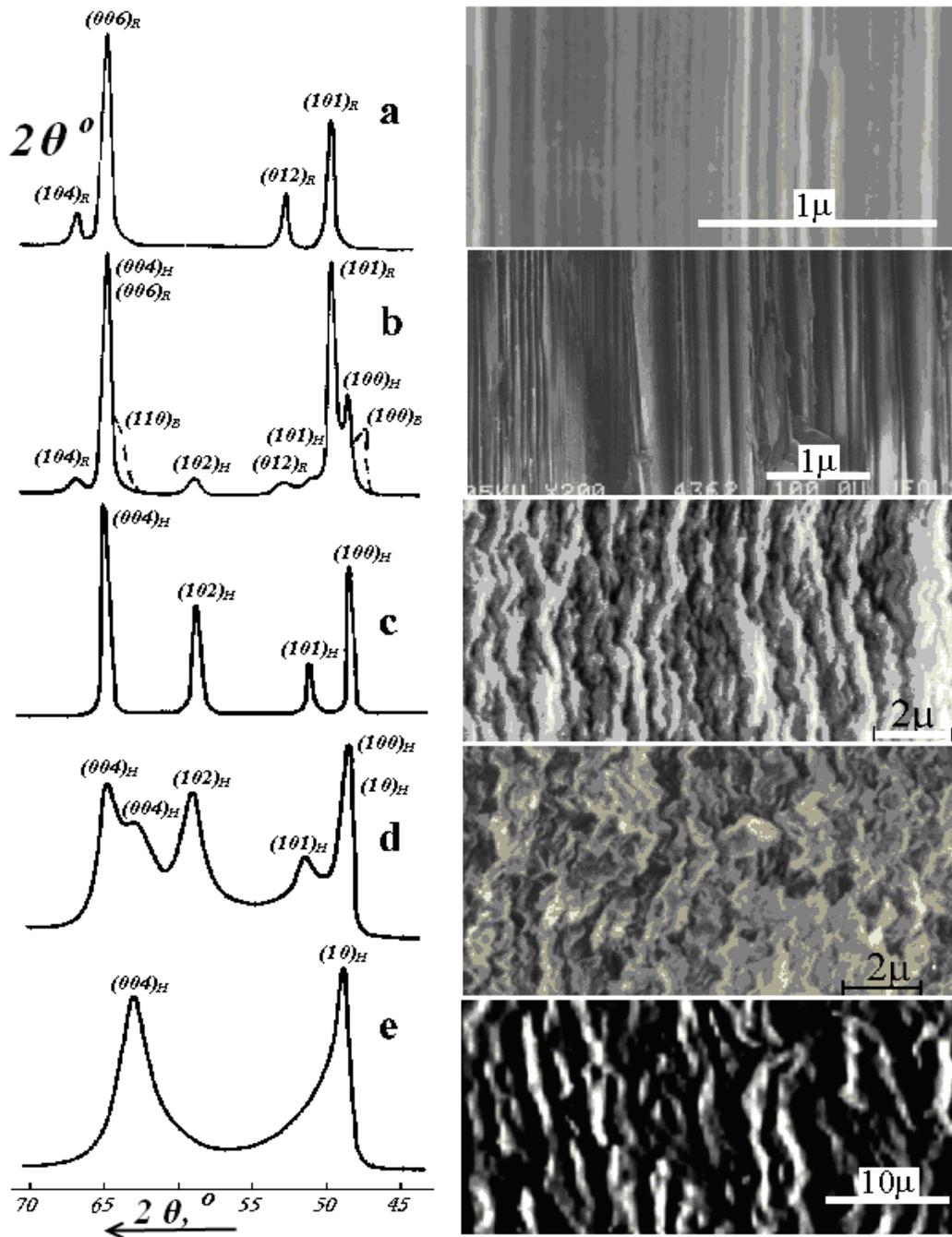


Figure 10. The results of X-ray diffraction measurements and electronic photographs of the plane parallel to the growth axis C of a series of samples of different phases of C & BN with different degrees of ordering of the crystal lattice and microcrystals: a - highly ordered rhombohedral, b - mixture of rhombohedral and hexagonal layers, c - highly textured hexagonal, d and e - hexagonal (the so-called pipe-strat phase).

6. Conclusion

Basically any model has certain limits of applicability. As it is shown in this paper, the widely used model of a hydrogen-like atom is qualitatively broken already in the second period, and for the following periods gives a catastrophic discrepancy with the experimental data.

The complex study of C & BN pyrocrystals not only clarified their crystal structure and properties, but made it possible to obtain perfect pyrocrystals and, on their "elementary" basis, to make a qualitatively new "brick" for the construction of atoms, their electronic orbitals.

Moreover, unlike the generally accepted relativistic refinement of the quantum-mechanical hydrogen-like model, which, as shown, gives a quadratic divergence with experiment, a realistic model of the quasinuclear change is proposed for the transition to the next period. This quasinuclear model strictly, in the first approximation, takes into account the logarithmic relativity, which manifests itself in all and in time, in space, and in energy, and, as follows from this work in the form of an orbital. Namely, the "working" principal quantum number in the transition to a new period remains (it is taken from a new reference point), but the energy and shape of the orbitals is calculated not for the total nuclear charge, but for its effective charge that is not shielded by internal orbitals.

Thus, it has been shown that even in the simplest chemical compounds, even in the "elementary" carbon atom, it is required to refine the concepts of the strength and form of atomic-molecular bonds. At the same time, it is possible and necessary to build models of atomic-molecular bonds of many chemical compounds on the basis of a carbon atom, "elementary" but more complex than a hydrogen atom.

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