

THE MECHANISM OF GRAPHITIZATION IN CARBON MATERIALS

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Introduction

Two processes proceed simultaneously at heat treatment structurally of imperfect carbon materials: formation of graphite and growth of the crystallite sizes. The main attention is traditionally given to the structural aspect of graphitization - transformation of crystal structure. The differences of average interplanar distances in disorder carbons from those characteristic for graphite are treated as a consequence of plenty of defects present in the structure. The formation of graphite, from such point of view, results from the elimination of defects at heat treatment. The estimation of adequacy of such approach, and also research of interrelation of formation of crystal structure and growth of the crystallite sizes is made by methods of computer modeling.

Technique of computer simulation

The modeling is carried out for soft carbon and carbon fibres. It was assumed in the computations that carbon atoms are sp^2 bonded in layers as in the graphite structure, and carbon crystallite was assumed to be defect free. In layers the carbon atoms are connected by covalent bonds. Interplanar bond come true van der Waals interaction. The models of crystallite structure of soft carbon and carbon fibre are submitted on figures 1 and 2.

The account of interatomic distances is carried out on the basis of estimations of the degree of bonds in crystallite of the different size, proceeding from empirical relation:

$$R_{C-C} = F_0 + F_1 / \chi,$$

where the values of factors $F_0 = 0.1068$ nm, $F_1 = 0.0472$ nm are found on known values of interatomic distances in various carbon materials. Degree of bonds there is as the size, equal to the relation of the greatest possible of number of covalent bonds to number of really formed bonds. Change of the sizes of layers at accounts carried out on the basis of the way offered in [1] (fig. 3).

The crystal structure is designed by the method of atom-atom potential [2]. This method found mutual arrangement of layers in crystallite, at which the van der Waals energy of their interaction, calculated as the sum of pair energy of interaction of each atom of one layer with each atom other is minimum:

$$E = \sum_{i=1}^N \sum_{j=1}^N [-Ar_{ij}^{-6} + B \exp(-\alpha r_{ij})],$$

where N - number of atoms in a layer, r_{ij} - distance between atoms, A , B , α - empirical factors. The mutual arrangement of layers was set by an interlayer spacing d_{002} and vector of relative shift S . The relative rotation of layers were not considered, since was established earlier, that to a minimum of energy of interaction there corresponds zero rotation [3]. The circuits of simulation

of energy of interaction depending on relative shift for soft carbon and carbon fibres are resulted on figure 4.

Result and Discussion

The computations established, that the interatomic distances and interlayer spacing d_{002} in soft carbon are function of the sizes of crystals L_a in a direction of an a -axis [4-6] (fig.5). In a carbon fibres interplanar distances is function of the sizes of layers of the sizes of layers $L_{a\perp}$ in the direction perpendicular to the axis of the fibres [7] (fig.6). Moreover relative energetically the favourable shifts of layers, also depends on the sizes of layers as for carbon fibre (fig.7), and for soft carbon (fig.8). Established in result of computer simulation of dependence d_{002} and R_{c-c} from the crystallite sizes L_a look like is similar observable experimentally [5, 8, 9] (fig.6).

The small crystal sizes L_a or $L_{a\perp}$ cause equilibrium energetically favourable structures with the values of interplanar distances and mutual arrangement of the next layers different from the values characteristic for graphite. Transformation of such turbostratic structure in graphite was possible probably only during growth of the crystal sizes. Thus the change of the crystal sizes is the reason of graphitization, and transformation of their structure only a consequence.

References

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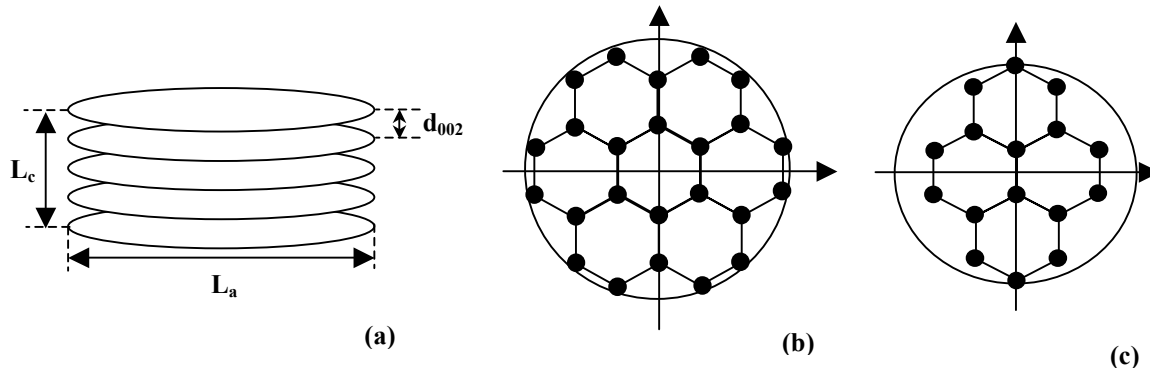


Fig.1. Model of a crystal of a carbon material: (a) the crystal as has stack of layers; (b) structure of a separate layer, model 2 ($L_a=0.9$ nm, $N=24$, $m=12$); (c) structure of a separate layer, model 1 ($L_a=0.75$ nm, $N=16$, $m=10$). N - number of atoms in a layer, m - number of extreme atoms

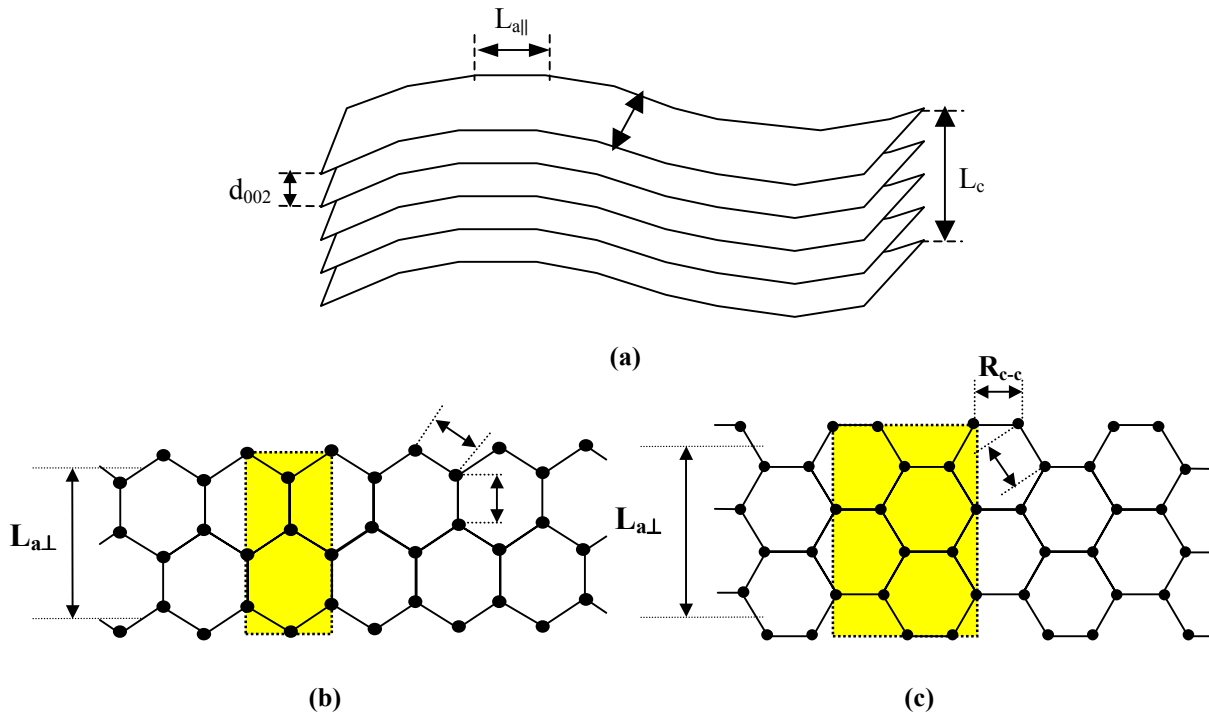


Fig.2. Model of a crystal of a carbon fibre: (a) crystal as a stack of layers; (b) structure of a separate layer, PAN-structure ($L_a=0.426$ nm); (c) structure of a separate layer, HC-structure ($L_a=0.492$ nm). The yellow colour allocates elementary cells of a layer

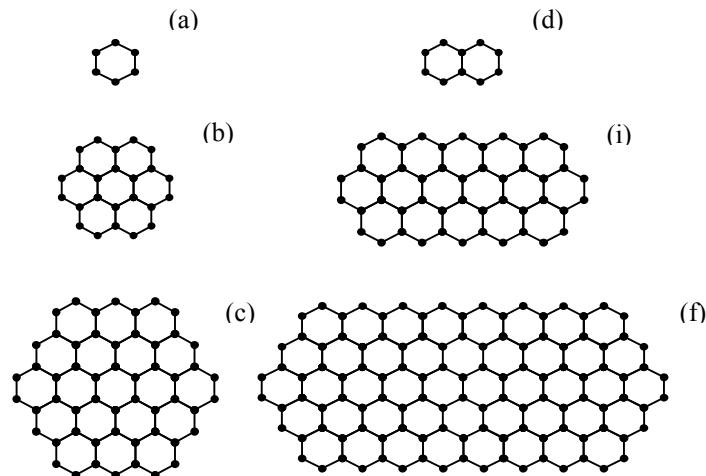


Fig.3. Image of layers of carbon atoms: (a) $p=1$, $f=1$; (b) $p=1$, $f=2$; (c) $p=3$, $f=3$; (d) $p=1$, $f=2$; (i) $p=2$, $f=2$; (f) $p=3$, $f=2$.

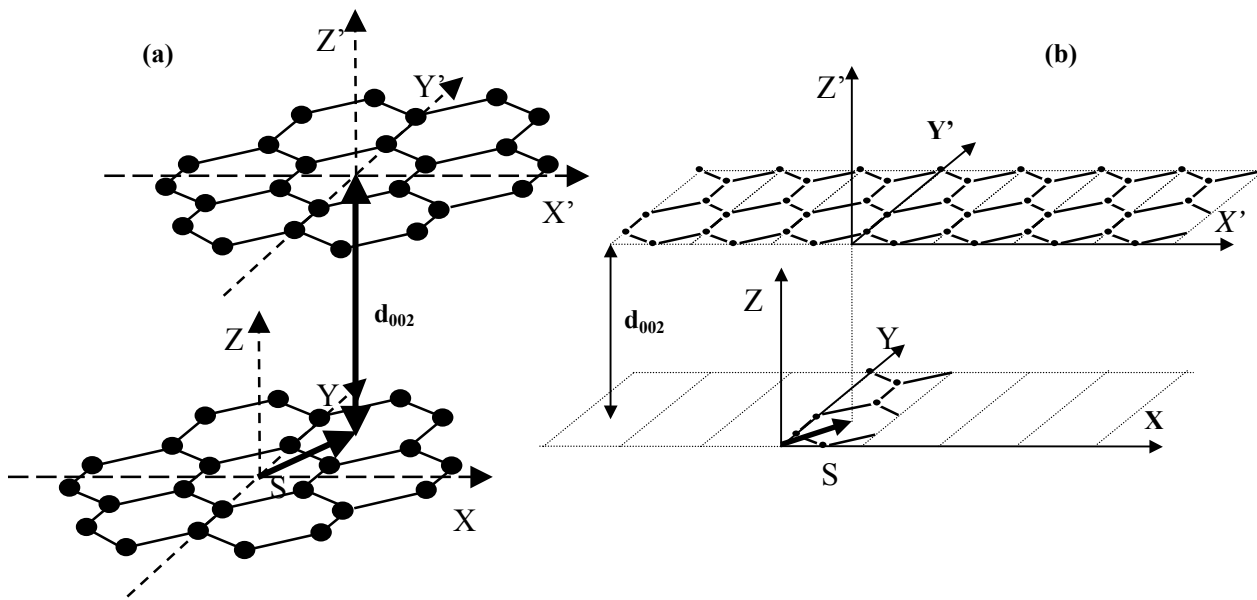


Fig. 4. Circuit of the task of relative shift between layers: (a) soft carbon; (b) carbon fibre.

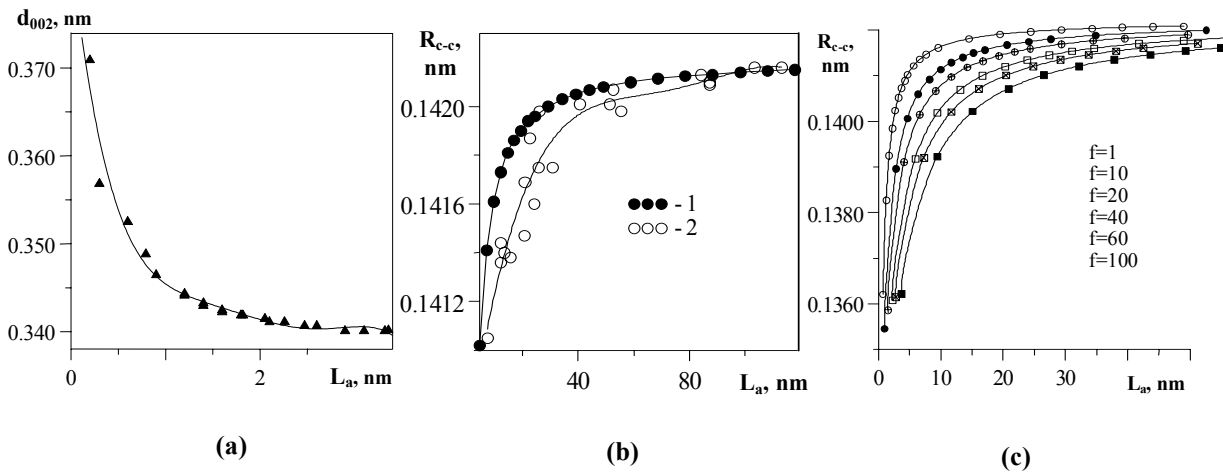


Fig. 5. Dependence of interlayer spacings d_{002} (a) and internuclear distances R_{c-c} (b) (c) from the sizes of crystals L_a in cokes (on (b) 2 - experimental, 1 - model dependence $f=1$)

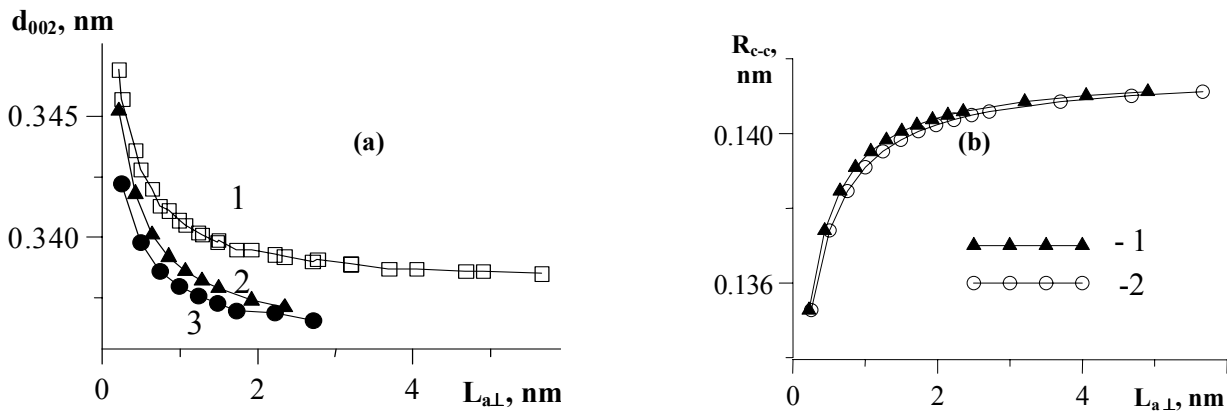


Fig. 6. Dependence of interlayer spacings d_{002} (a) and internuclear distances R_{c-c} (b) from the sizes of crystals L_a in a carbon fibre: (a) 1 - PAN- and HC- of structure $S=0$, 2 - PAN-structure $S \neq 0$, 3 - HC-structure $S \neq 0$; (b) 1 - PAN-structure, 2 - HC-structure

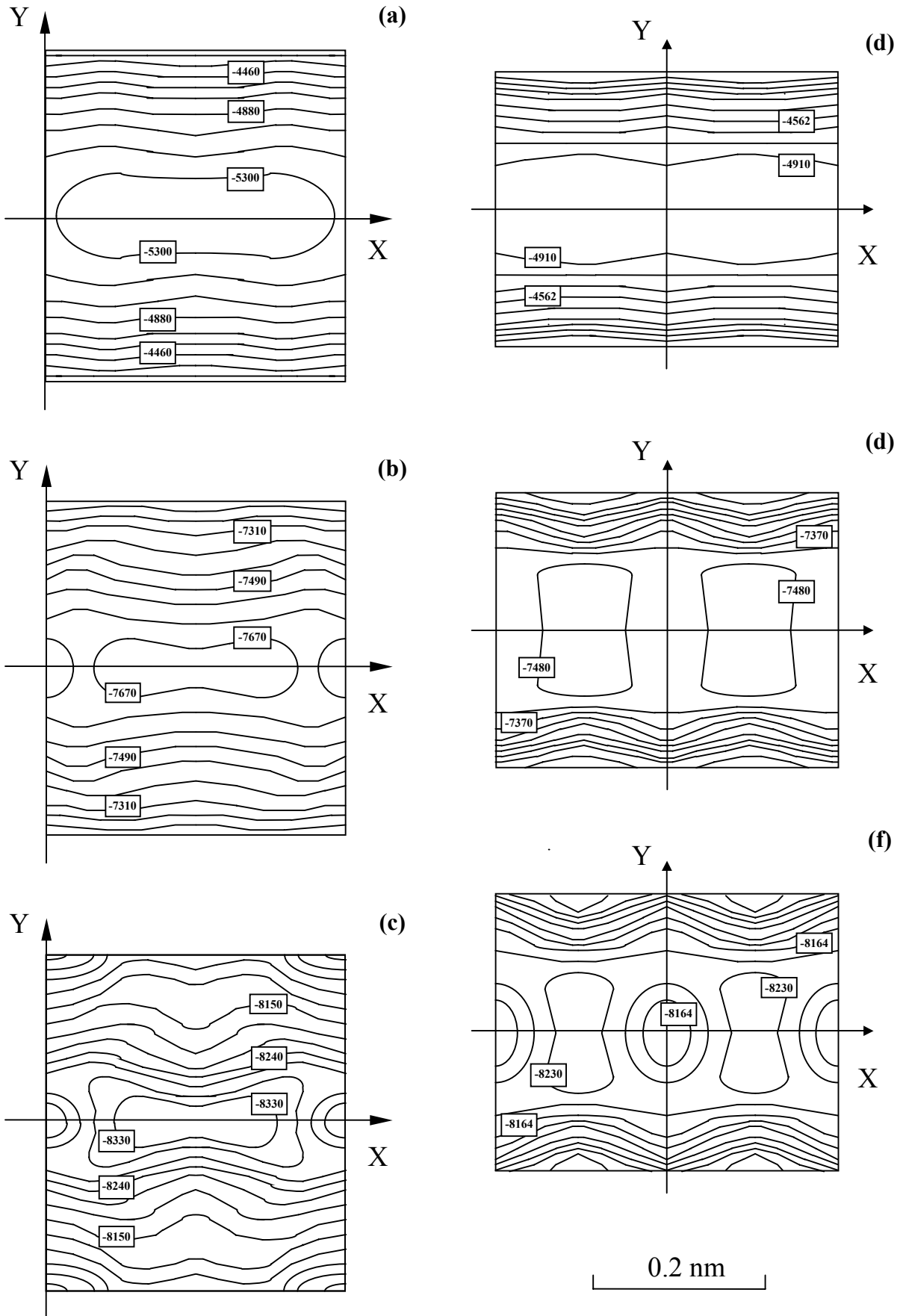


Fig.7. Change of energy van der Waals of interaction in carbon fibres (dimension J/mol), on 2 atoms of a layer, depending on their mutual arrangement, set by the vector S , and cross sizes of layers L_{aL} : (a), (d) - 2 atoms; (b), (e) - 6 atoms; (c), (f) - 12 atoms; (a) - (c) - HC-structure; (d) - (f) - PAN-structure

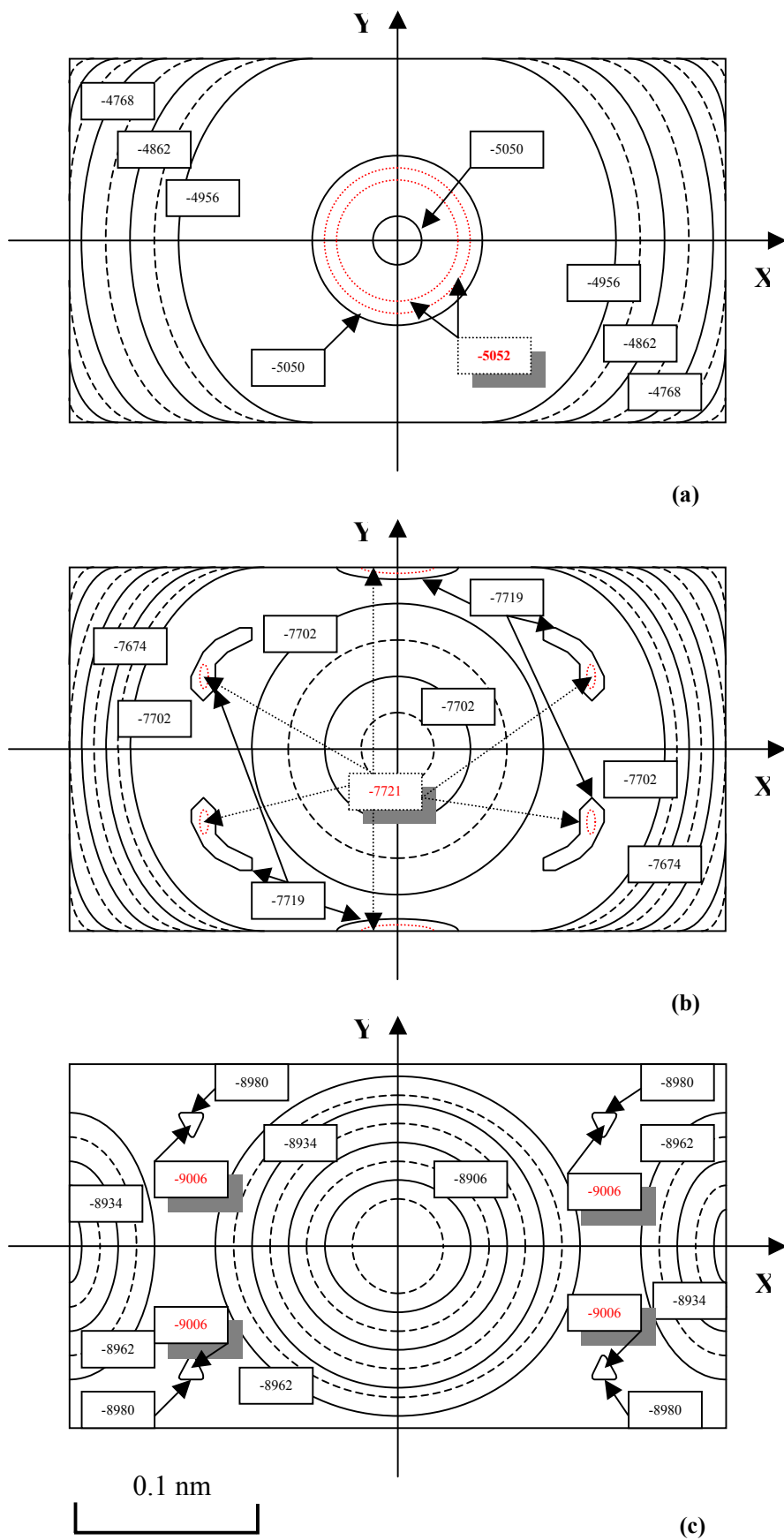


Fig.8. Change of specific energy van der Waals of interaction in soft carbon (dimension J/mol), on 2 atoms of a layer, depending on a mutual arrangement of layers, set by the vector S , and sizes of layers L_a : (a) 0.9 nm; (b) 3.1 nm; (c) (structure of graphite!). The red colour designates borders of area with the minimum energy of interaction