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The reason for the aggregation of diamond nanoparticles in suspensions

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It is proved that the bond of diamond nanoparticles during their connection — agglomeration, is formed mainly due to a weak — about 0.05 eV — bond of unpaired electrons from the subsurface layers of each particle. This property distinguishes diamond nanoparticles from all known types of nanoparticles.

Keywords: diamond nanoparticles, weak covalent bond, agglomeration, suspension.

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The capacity of diamond nanoparticles (DNs) for agglomeration in suspensions may lead to some interesting phenomena, such as sol-gel transition in hydrosol, demonstrated, for example, in [1]. This type of aggregation (or association), which may be called „contactless", via the layers of dispersion medium, for example, water. In structured systems coagulation or condensation-crystallization structures may arise. Structures of the first type comply with the association via layers of dispersion medium, and they are less strong compared to the structures of the second type. The structures of the second type arise under direct contact of the particles, forming amorphous or crystalline bodies. They are much stronger, but after damage they will not recover, since the arising layers prevent occurrence of such contacts. In the DLVO theory of nanoparticle aggregation, in particular, into chains [2,3], the formation of the first type structures is called coagulation in the far minimum, when there is a balance of exchange attraction and electrostatic repulsion. In such cases dissolution of the system with water causes return to the initial colloidal solution with chaotic distribution of colloidal particles.

The paper will study specifically the features of the DNs bond. Previously the attempts have already been made to explain the agglomeration of the primary DNs with uneven distribution of charge distribution on their surface [4,5].

This paper presents a different point of view.

A model of a DNs bond is proposed, based on the existence of the amorphous subsurface layer containing unpaired electrons (Figure 1) found in [6] by the NMR method in DNs of detonation synthesis.

The method to produce/process/clean the diamond material may be different [7], but in all cases the production of DNs with absolutely „pure" surface is hardly probable, not to mention the unavoidable N-V defects of the crystalline structure.

Further it is suggested that the main part in the agglomeration of DNs is played by the formation of a bond arising due to the unpaired electrons from the subsurface layers (Figure 2).

The calculation of the covalent bond energy is well known (e. g. see [8]). Let us similarly calculate the bond energy of two DNs. The calculation scheme is shown in Figure 3.

As usual, the bond energy is determined mainly by exchange energy of unpaired electrons with the opposed spins. It remains unclear how the regions are actually implemented with the positive charge that correspond to the

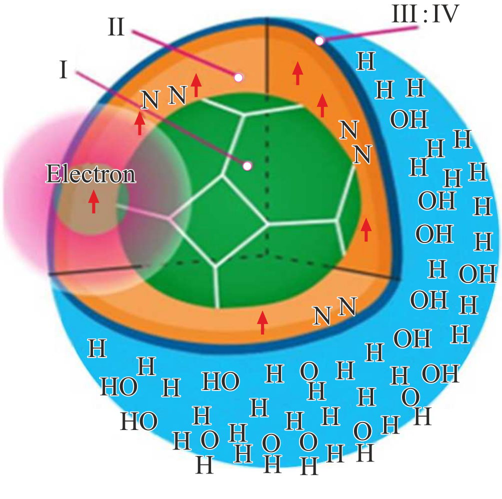

Figure 1. Composition of diamond nanoparticles. I — central faceted crystalline part is enclosed in the non-crystalline subsurface part. II — amorphized layer with unpaired electrons and atoms of nitrogen N; III, IV — transition layer and external surface layer functionalized with hydrogen (H) and hydroxyl groups (OH); arrows ↑ and ↓ show the direction of electron spins. An orbit is shown near one of electrons that corresponds to its state. Other explanations are available in the text.

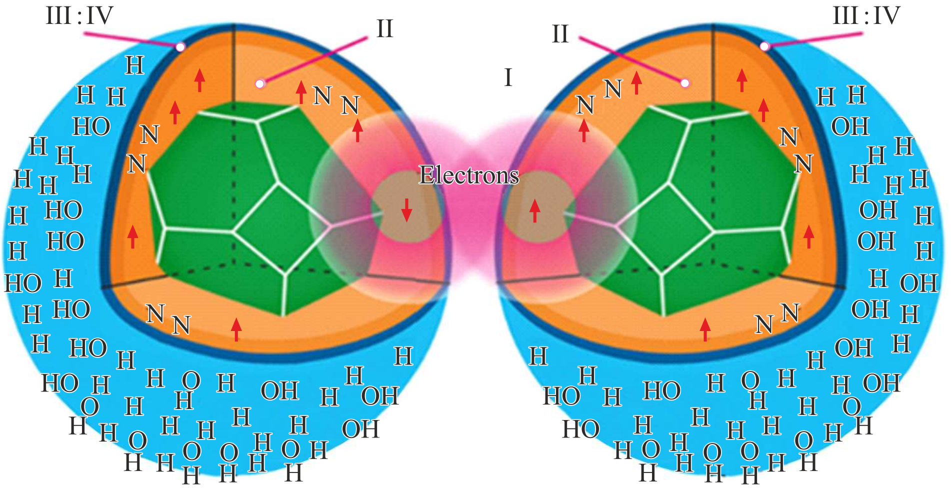

Figure 2. Formation of a bond between unpaired electrons of two diamond nanoparticles. Between the electrons there is an area of orbit overlapping — the main area of exchange interaction. This bond is similar to a covalent bond, but the parts are separated with a layer of dispersion medium. All designations are explained in Figure 1.

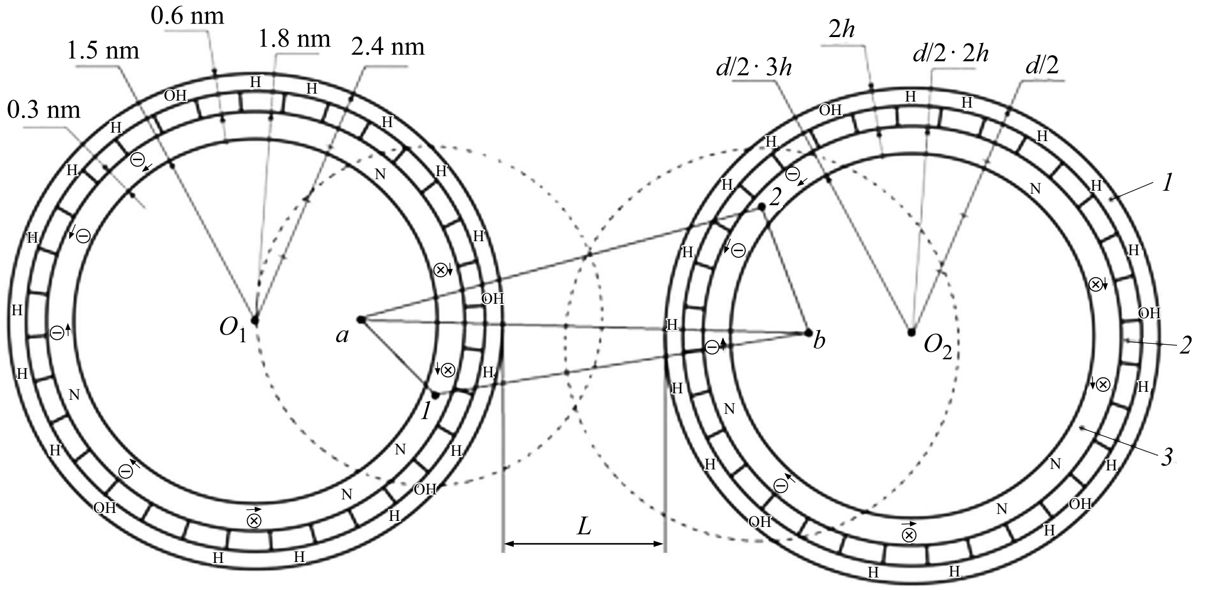

Figure 3. Simplified model of cross section of two DNs with centers in O_1 and O_2. The particles are separated with a layer of dispersion medium with thickness of L. The crystalline part of each nanoparticle is presented as a ball with diameter of d. The external surface layer (*1*); transition layer (*2*) and layer with unpaired electrons and atoms of nitrogen (*3*) are deemed to have the same thickness h. The point circles identify the cross section of orbit areas in unpaired electrons. These electrons are designated 1 in the left particle and 2 in the right one. Electrons 1 and 2 are related to the positively charged parts, which conventionally (see explanations in the text) are deemed to be concentrated in points a and b. Distances necessary to calculate the bond energy: $ab = R$; $a1 = r_{1a}$; $a2 = r_{2a}$; $b1 = r_{1b}$; $b2 = r_{b2}$; $12 = r_{12}$.

available unpaired electrons. Apparently, the answer to this question may only be provided by the ab initio calculation of the structure, similar to the calculation done in [9] for one particle from 328 C atoms. In this paper such calculation is not required to obtain the high-quality results.

For qualitative estimates, and only such estimates will be made further, let us assume that the positive charge is concentrated in the small regions — „points“ compared to the distance from them to the electrons. Let us designate the following: such points in the regions of the positive charge localization „a“ accordingly in the first (Figure 3, on the left) and „b“ in the second (Figure 3, on the right) particles.

The questions on the size (polydispersion) of aggregates stabilized by electrons of the subsurface layer and minimum size of the non-destroyed aggregate must be the subject of a separate study in every specific case of diamond material production/processing/cleaning. In [6] the dimensions of the crystalline nucleus and its surrounding non-crystalline layers of detonation synthesis were estimated. In accordance with these estimates within the considered model the distances between the points noted in Figure 3 may be assumed as follows:

$$d_1 = d_2 = d = 4.8\,\text{nm};\quad O_1O_2 = d + L\,(\text{nm});$$

$$ab/2 = R/2 = r_{12} = h + L\,(\text{nm});$$

$$r_{1a} \approx r_{2b} \approx r;\quad r_{2a} \approx r_{1b} \approx r/2, \tag{1}$$

where r — specific distance to form a bond between unpaired electrons in DNs, specific distance for the phenomenon considered in this paper, L — width of dispersion medium layer, and $h \approx 0.3$ nm width of the external surface layer of the particle; transition layer and layer with unpaired electrons and atoms of nitrogen. All layers are deemed to be having the identical thickness.

The role of valence electrons in formation of a bond between the particles seems to be played by nitrogen-vacancy defect electrons.

Let us proceed to numerical estimates.

The potential energy of electron interaction between each other (see Figure 3) is as follows:

$$W = \beta\left(-\frac{ke^2}{R} - \frac{ke^2}{r_{12}} + \frac{ke^2}{r_{1b}} + \frac{ke^2}{r_{2a}}\right). \tag{2}$$

As usual, the following are designated: electric constant k, Bohr radius r_B, and electron charge e. To calculate covalent bond, it is customary to relate distance r specifically to r_B evident ratio $r = t_B/\beta$. Value β — a dimensionless parameter characterizing the specific considered phenomenon, was introduced. The solvent characteristics were included in parameter α.

Wave functions may be taken in the form corresponding to the main state, namely, for example

$$\psi_a(1) = C\exp(-r_{1a}/r). \tag{3}$$

Accordingly, all other wave functions have the same appearance.

The energy may be qualitatively introduced as

$$E = B - A. \tag{4}$$

Value B is determined by electrostatic interaction, and value A — by exchange interaction of electrons.

Substituting values into electrostatic and exchange interactions, we obtain

$$B = \beta^2 ke^2 \frac{2}{r_B}\exp(-4 - \alpha L/h); \tag{5}$$

$$A = \beta^2 ke^2 \frac{2}{r_B}\exp(-3 - \alpha L/h). \tag{6}$$

Therefore, indeed the energy of interaction is determined by the exchange interaction, $A > B$ and, accordingly, there is a bond.

The energy of interaction between the electrons of various particles will be equal to

$$E = -\beta^2 ke^2 \frac{2}{r_B}\exp(-3 - \alpha L/h)\left(1 - \frac{1}{\exp(1)}\right). \tag{7}$$

If the dispersion medium is absent, it would be $E \approx -\beta^2 2.8$ eV. This result is satisfactorily compliant with the results of the numerical calculation (3.5 eV). Using the estimate of covalent bond energy found by DFT methods in [9] at 2.9 eV for the particles comprising 328 C atoms and believing that there is a single bond that connects them, we will get the estimate of the parameter value $\beta \approx 1$, then $E \approx 0.05$ eV at $\alpha L/h \approx 3$.

Based on the model of the weak covalent bond, the known facts may be explained [10]: 1) preferable formation of chains, and not agglomerates of DNs; 2) decrease of crystallization-freezing temperature for suspensions with DNs; 3) formation of gel from suspensions with the positive electrochemical potential at much smaller concentrations of particles, rather than the formation of gel from suspensions with the negative potential; 4) growth of electrophoretic mobility and heat conductivity of suspensions with the growth of DNs concentration; 5) higher strength of DNs agglomerates under dynamic synthesis — synthesis with addition of graphite into the exploded mixture, compared to the particles produced by synthesis with detonation method.

Undoubtedly, the proposed model requires thorough additional experimental verification. A good verification for the proposed model could be the influence of the nitrogen quantity, and accordingly, of the number of N-V defects at the properties of suspensions with DNs. Therefore, to explain the provided experimental data, it is enough to study the interaction between the non-functionalized diamond nanoparticles.

At the same time the model of agglomeration leading the change of the shape of the particle obtained as a result, differs substantially from the generally accepted model, when the shapes of the nanoparticle and agglomerate are nearly identical.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] A.Y. Vul, E.D. Eidelman, A.E. Aleksenskiy, A.V. Shvidchenko, A.T. Dideikin, V.S. Yuferev, V.T. Lebedev, Y.V. Kul'velis, M.V. Avdeev. *Carbon* **114**, 242–249 (2017). DOI: 10.1016/j.carbon.2016.12.007

[2] I.F. Efremova. Periodicheskie kolloidnye struktury. Khimiya, L. (1971) (in Russian).

[3] N.O. Mchedlov-Petrossyan, N.N. Kriklya, A.P. Kryshtal, A.A. Ishchenko, M.L. Malysheva, V.V. Tkachenko, A.Yu. Ermolenko, E. Osawa. J. Mol. Liq. **283**, *1*, 849–859 (2019). DOI: 10.1016/j.molliq.2019.03.095

[4] A.S. Barnard. J. Mater. Chem. **18**, *34*, 4038–4041 (2008). DOI: 10.1039/B809188A

[5] A.S. Barnard, M. Sternberg. J. Mater. Chem. **17**, *45*, 4811–4824 (2007). DOI: 10.1039/B710189A

[6] X.W. Fang, J.D. Mao, E.M. Levin, K. Schmidt-Rohr. J. Am. Chem. Soc. **131**, *3*, 1426 (2009). DOI: 10.1021/acs.jpcc.5b05507

[7] V.N. Mochalin, O. Shenderova, D. Ho, Y. Gogotsi. Nat. Nanotechnol. **7**, 11–23 (2012). DOI: 10.1038/nnano.2011.209

[8] E.D. Eydelman. Fizika s elementami biofiziki: uchebnik. 2-e izd., pererab. i dop. GEOTAR-Media, M. (2023). Gl. 23 (in Russian).

[9] A.A. Knizhnik, Y.G. Polynskaya, A.S. Sinitsa, N.M. Kuznetsov, S.I. Belousov, S.N. Chvaluna, B.V. Potapkina. Phys. Chem. Chem. Phys. **23**, *1*, 674 (2021). DOI: 10.1039/D0CP05533F

[10] A.T. Dideikin, E.D. Eidelman, S.V. Kidalov, D.A. Kirilenko, A.P. Meilakhs, F.M. Shakhov, A.V. Shvidchenko, V.V. Sokolov, R.A. Babunz, A.Ya. Vul'. Diam. Relat. Mater. **75**, *2*, 85 (2017). DOI: 10.1016/j.diamond.2017.02.009

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