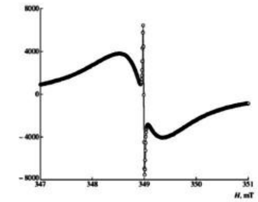
II Int. Conf. “NanoBioPhysics”
Kiev, Ukraine, October 6-9, 2011



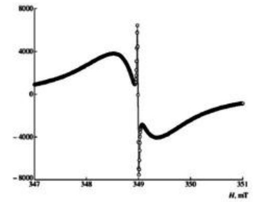
Collective excitation at nanodiamond-protein interaction

Peter I Belobrov, Ivan A Denisov
Molecular Architecture Group at MOLPIT, Siberian Federal University,
Kirensky Institute of Physics & Institute of Biophysics SB RAS
660036 Krasnoyarsk, Russia

Oral talk, 6.10.2011

molpit
International open
laboratory of advanced
science and technology

Outlook of protein & 5 nm diamond ball



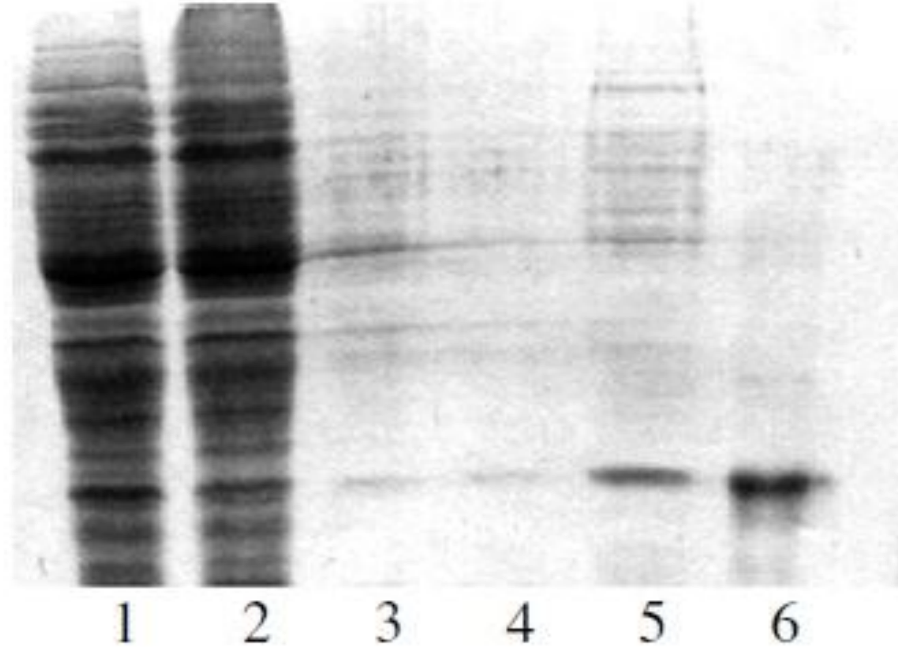
- Problem 1
  - high “effective specificity” of ND-protein interaction
- Problem 2
  - Nanodiamond exhibits free electron, i.e. collective unpaired spins with **g=2.0027** in EPR
    - T-spin & floating Tamm electron in ND shell
    - ψ-function of collective Tamm excitation
  - ND-protein docking with self-consistent boundary conditions
    - 2D-2D & 2D-3D T-layers shell & ND core
    - 1D-2D T-layers shell & proteins
- Conclusion
  - Tamm collective excitations – quasi-particles – of T-layer of diamond surface net in 5nm diamond ball with any protein

Oral talk, 6.10.2011

molpit
International open laboratory of advanced science and technology

Problem 1

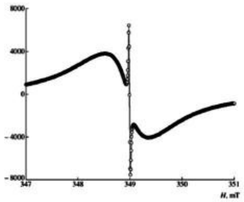
- Till now nobody have explained such high “effective specificity” of ND to the protein



Bondar, Puzyr 2000

An electrophoretogram of protein samples obtained as a result of apoobelin isolation from the *E. coli* cell extract. Apoobelin was isolated from the bacterial cell extract using the ND particles synthesized at the Department of Physics and Highly Dispersed Materials, Krasnoyarsk Research Center. (1) The initial extract, (2) the extract treated with ND particles, (3) and (4) solution collected after washing the pellet of ND particles coated with apoobelin, (5) the final sample of apoobelin after elution with DTT, (6) a marker protein (apoobelin isolated by the standard procedure [10]). Electrophoresis was performed in 12.5% polyacrylamide gel in the presence of 0.1% sodium dodecylsulfate (SDS).

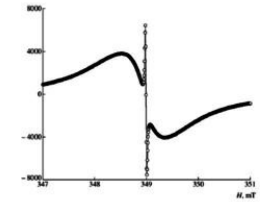
Oral talk, 6.10.2011



References 1 (it is made for the first time):

1. *Belobrov P. I., Voevodin V. A., Erokhin V. V., Lvov Y.M., Petushkov V.N., Puzir A.P., Rodionova N.S.* Interaction of bacterial luciferase with amphiphilic molecules in solution, on water surface, and in Langmuir-Blodgett films // *Preprint of the Institute of Physics* No. 92B, Krasnoyarsk, 1988, 28 p.
2. *V.A. Voevodin, P.I. Belobrov, V.V. Erokhin.* Obtaining and some properties of Langmuir films from bacterial luciferase // In: Biological Luminescence, Singapore: World Scientific, p.375-385 (1990).
3. *V.A. Bondar, A.P. Puzyr.* Use of nanodiamond particles for rapid isolation of recombinant apoobelin from Escherichia coli // *Doklady Biochemistry*, **373**, 129-131 (2000).
4. *A.P. Puzyr, V.S. Bondar, P.I. Belobrov, A.A. Bukaemskii*. Preparation of complexes *nanodiamond-protein-\delta-aluminum oxide // Doklady Biochemistry*, **373**, 139-141 (2000).
5. *A. P. Puzyr, A. A. Bukaemskii, P. I. Belobrov, and T. G. Volova*. Uniform distribution and stabilization of nanoparticles in a bacterial poly-beta-hydroxybutyrate gel // *Doklady Biochemistry and Biophysics*, **376**, 23-25 (2001).

Oral talk, 6.10.2011



Problem 2

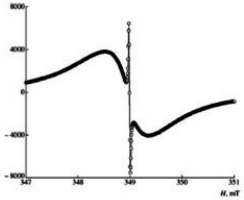
Nanodiamond exhibits free electron, i.e. collective unpaired spins with **g=2.0027** in EPR, 13C NMR, M(H,T)

T-spin (paramagnetic susceptibility)

Tamm collective excitation

T-layer of diamond surface net

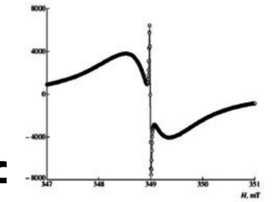
molpit
International open laboratory of advanced science and technology



References 2 (it is made for the first time):

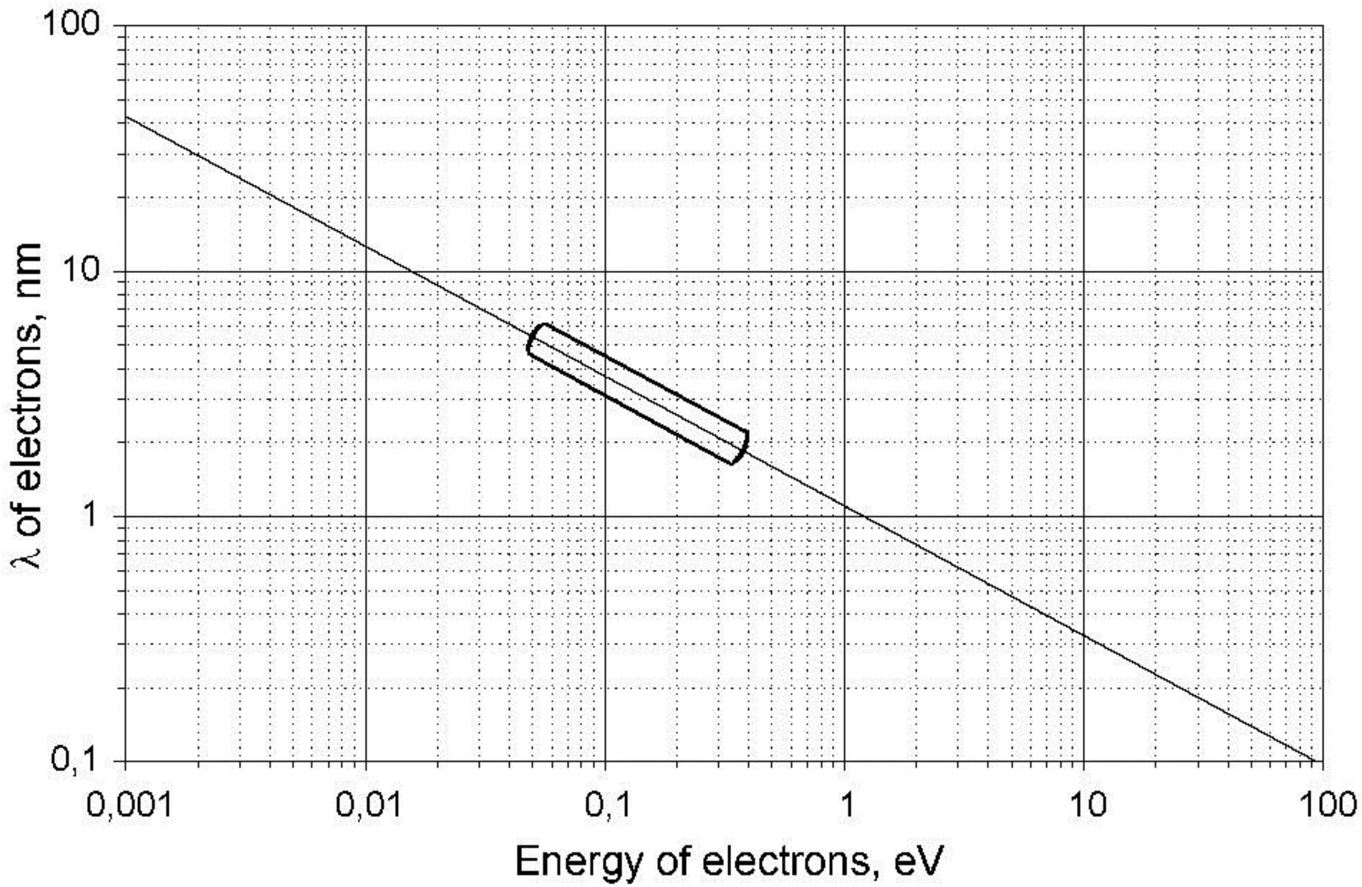
1. *S. K. Gordeev, S. G. Zhukov, P. I. Belobrov, A. N. Smolianinov, and Ju. P. Dikov.* Method of producing a composite, more precisely a nonoporous body and nanoporous body produced thereby U.S. Patent No. 6 083 614 (4 July 2000), Russian Patent No. 95116683 (27 September 1995).
2. *S.K. Gordeev, P.I. Belobrov, N.I. Kiselev, E.A. Petrakovskaya, T.C. Ekstrom.* Novel Solid Nano Diamond/Pyrocarbon Semiconductor Materials *Mat. Res. Soc. Proc.*, **638**, F18.4.1-6 (2001).
3. *P.I. Belobrov, S.K. Gordeev, E.A. Petrakovskaya and O.V. Falaleev,* Paramagnetic properties of nanodiamond. *Doklady Physics*, **46**, 459 (2001).
4. *Peng, J., Bulcock, S., Belobrov, P., and Bursill, L.* Surface bonding states of nano-crystalline diamond balls. *Int J Modern Phys* **B 15**, 4071-4086 (2001).
5. *P.I. Belobrov, L.A. Bursill, K.I. Maslakov, and A.P. Dementjev.* Electron Spectroscopy of Nanodiamond Surface States // *Appl. Surf. Sci.* **215**, No. 1-4, p.169-177(2003).

Oral talk, 6.10.2011



Tamm quasi-particle is de Broglie wave of electron at T-layer

The region of the thermodynamical stability of ND is shown



C atoms ~

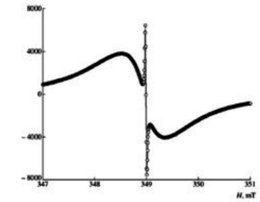
1,100-25,000

- 1.9-5.2 nm

∀ λ ~ 4 nm

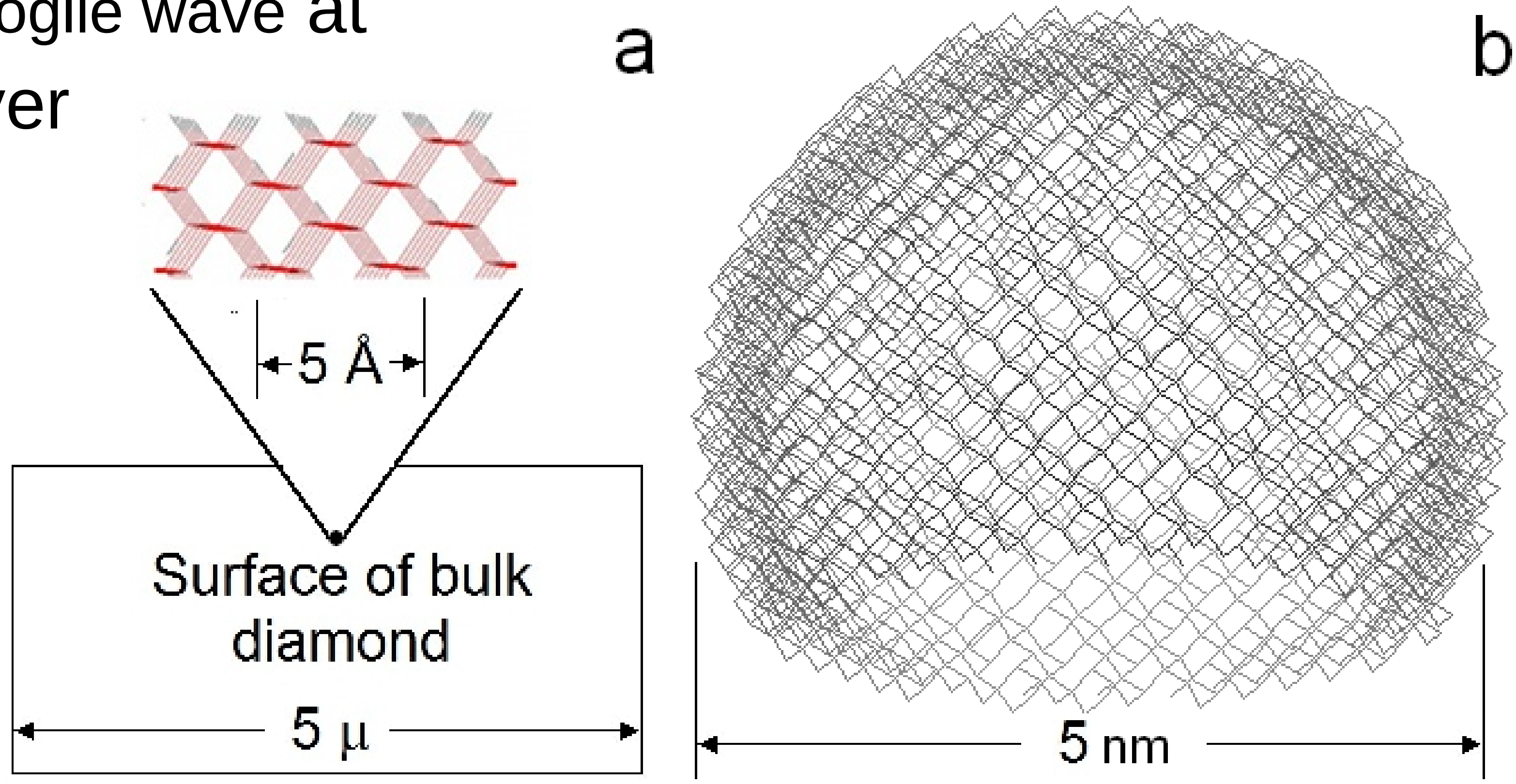
- E ~ 0.1 eV
- *E*, *p*; $\nu = E/h$; $\lambda = h/p$; $p = m_e c$; $h = 6{,}6748 \cdot 10^{-27}$.

Oral talk, 6.10.2011



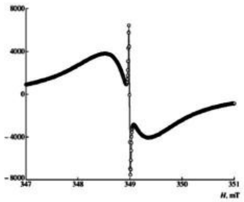
a) T-layer model of ND surface
b) T-layer shell of any diamond

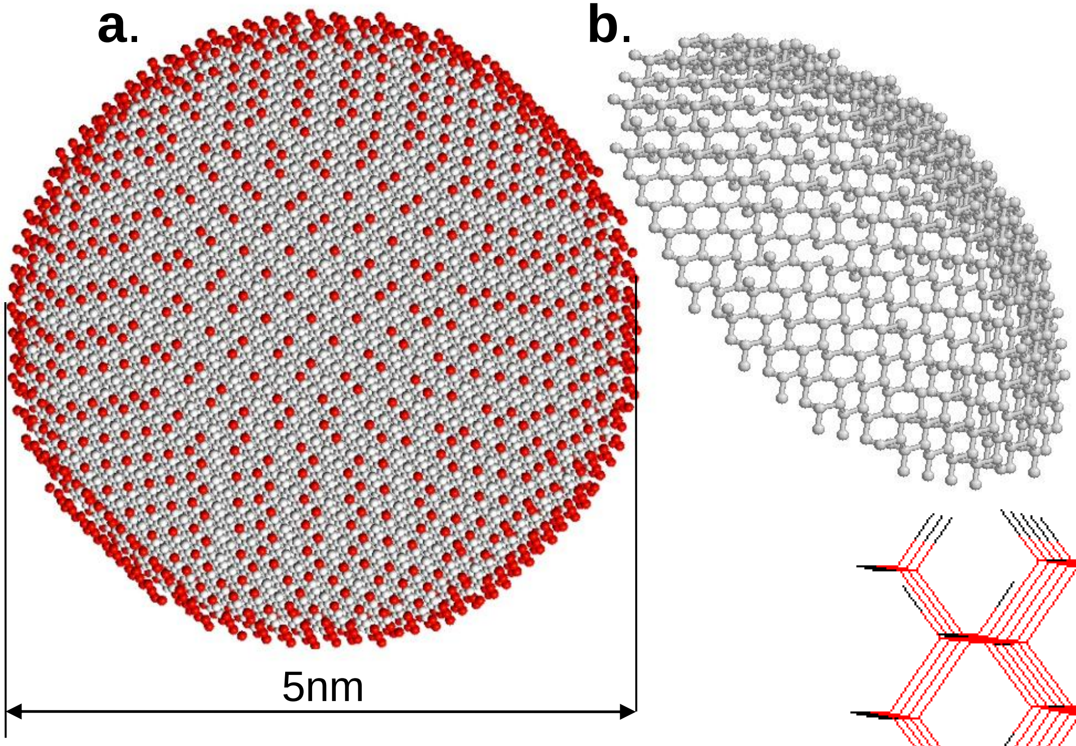
de Broglie wave at
T-layer

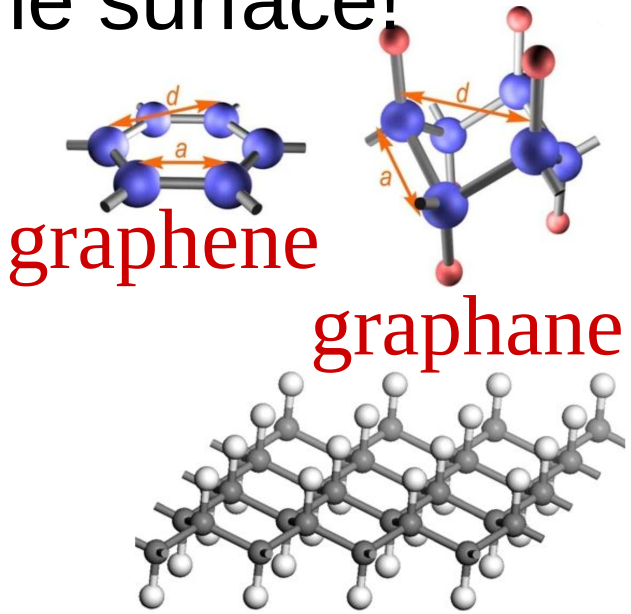


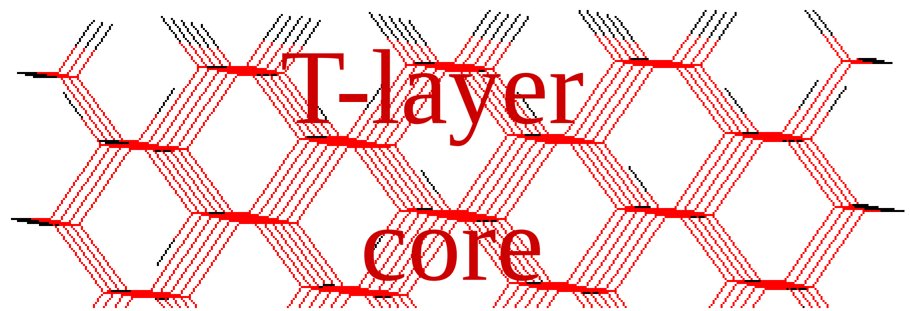
Oral talk, 6.10.2011

Any diamond always and anywhere has a T-layer of the surface!



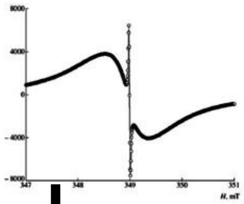






a. Diamond ball 5 nm, terminal atoms marked.

b. T-layer incrustation (extracted from **a**) = sheet from cyclohexanes



1st physical theorem of diamond

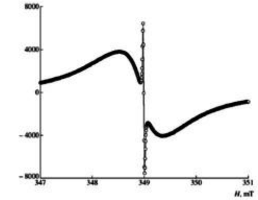
- Any diamond of any shape and size has a T-layer of carbon atoms formed by diamond surface net.

Notes: often used approximations of T-layers are rough enough:

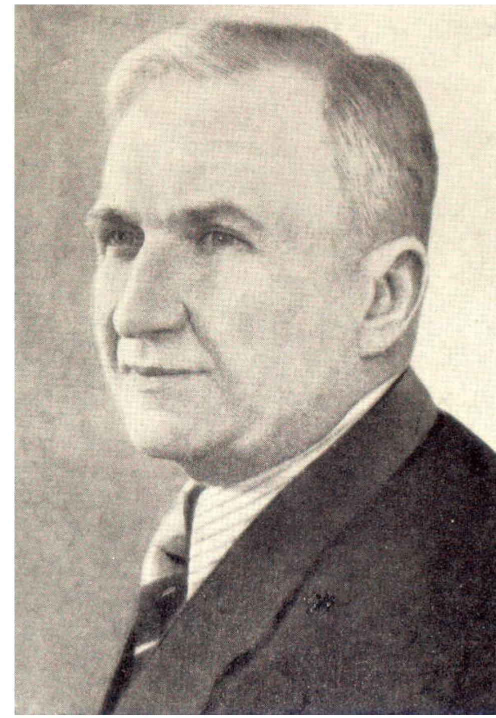
- Thin surface of zero thickness
- Spherical graphene (Russian egg, doll etc.)
- Diamond graphane
- Graphane-like shell

molpit
International open laboratory of advanced science and technology

Electronic-vibrational Tamm surface state of 5 nm diamond ball



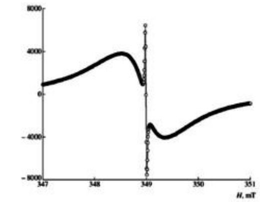
- 1925 – Quantum theory of paramagnetism – contribution of the orbital moment
- 1929 – The concept of vibrational quanta in solid (later called phonons by Frenkel) ⇒ *Idea of sound quantum at ND*
- 1933 – «Tamm levels» - certain electron states were due to the existence of the surface ⇒ *1D & 2D ë states at ND*
- 1934 – Any system with virtual separated charges should have magnetic moment ⇒ *Nature of free spin at ND*
  - In 1934, Altshuler and Tamm predicted the existence of the magnetic moment of neutron and correctly estimated its value and sign. This idea was so unusual then that even Niels Bohr who visited Moscow in 1934 could not accept it.



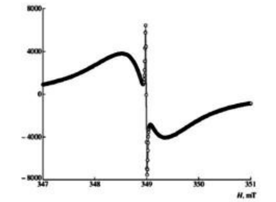
Igor Evgen'evich **Tamm**
(8/07/1895 – 12/04/1971)
1958 – Nobel Prize for the Vavilov-Cherenkov effect

Oral talk, 6.10.2011

Classical papers of Tamm



- Ig. Tamm. Zur Quantentheorie des Paramagnetismus. *Z. Phys.* **32** (1), 582-595 (1925). ***the orbital moment***
- Ig. Tamm. Über die Quantentheorie der molekularen Lichtzerstreuung in festen Körpern. *Z. Phys.* **60**(5-6), 345-363 (1930). ***quantum of sound***
- Ig. Tamm. Über eine mögliche Art der Elektronenbindung an Kristalloberflächen *Z. Phys.* **76** (11-12), 849 -850 (1932). ***Tamm levels*** *(abs)*
- I. E. Tamm, Uber eine mogliche Art der Electronenbildung an Kristalloberflachen *Z. Phys. Sowjetunion*. **1**, 733-746 (1932). ***Tamm levels*** *(paper)*
- CA Altshuler, I. E. Tamm. Magnetic moment of neutron // Doklady Akad. Nauk SSSR, 8, 455 (1934). ***Quantum Nature of free spin***



Toward wave ψ-function of ND

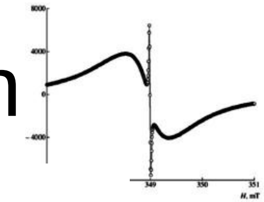
- Diamond quantum dot has own electronic states $\sigma_s^1\sigma_p^2\pi^1$ (no π-band)
- "Plasmon" in low-loss spectrum and pre-peak in core-loss (EELS, X-ray absorption)
- This ë state $\sigma_s^1\sigma_p^2\pi^1$ is not sp^2 or linear combination of sp^1, sp^2, sp^3
- Self-consistent sound quantum exists in ND
- Free spin (unpaired electron) at T-layer of ND

Oral talk, 6.10.2011

Belobrov P I (2004) Cambridge

molpit
International open laboratory of advanced science and technology

Q model of T-spin – Hopf Soliton



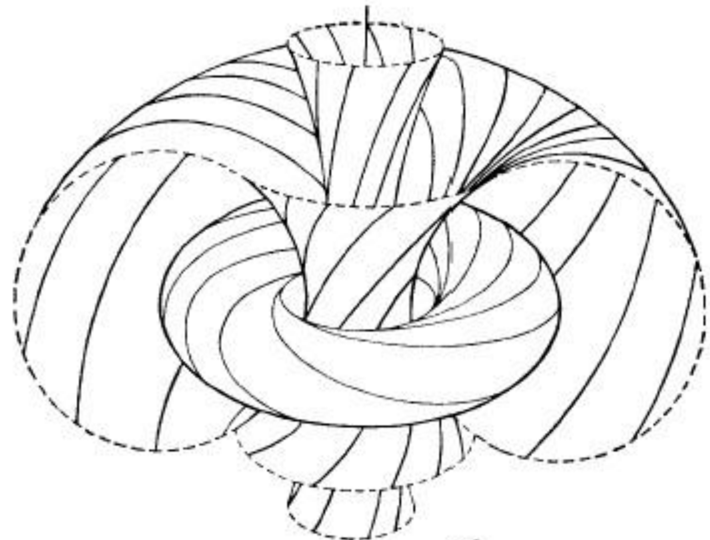
$$\boldsymbol{m}(x,y,z)$$

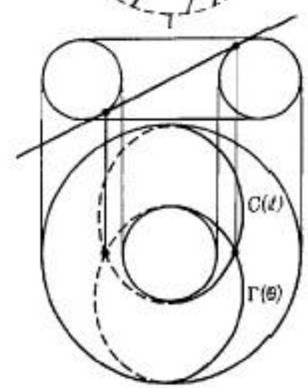
$$m_1(x,y,z)=\left(\frac{2}{1+r^2}\right)^2[-y-2xz+yr^2],$$

$$m_2(x,y,z)=\left(\frac{2}{1+r^2}\right)^2[x-2yz-xr^2],$$

$$m_3(x,y,z)=-1+\left(\frac{2}{1+r^2}\right)^2[2x^2+2y^2].$$

$$\mu=\frac{2}{1+r^2}$$



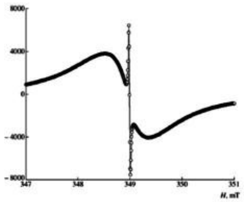


Belobrov P.I., Ermilov I.V., Tsikh A.K. Stable and ground state of dipolic // *Preprint TRITA/MAT-91-0020* (1991), Dept Mathematics, Royal Institute of Technology, S-100 44 Stockholm, Sweden, 1991, 25 p.

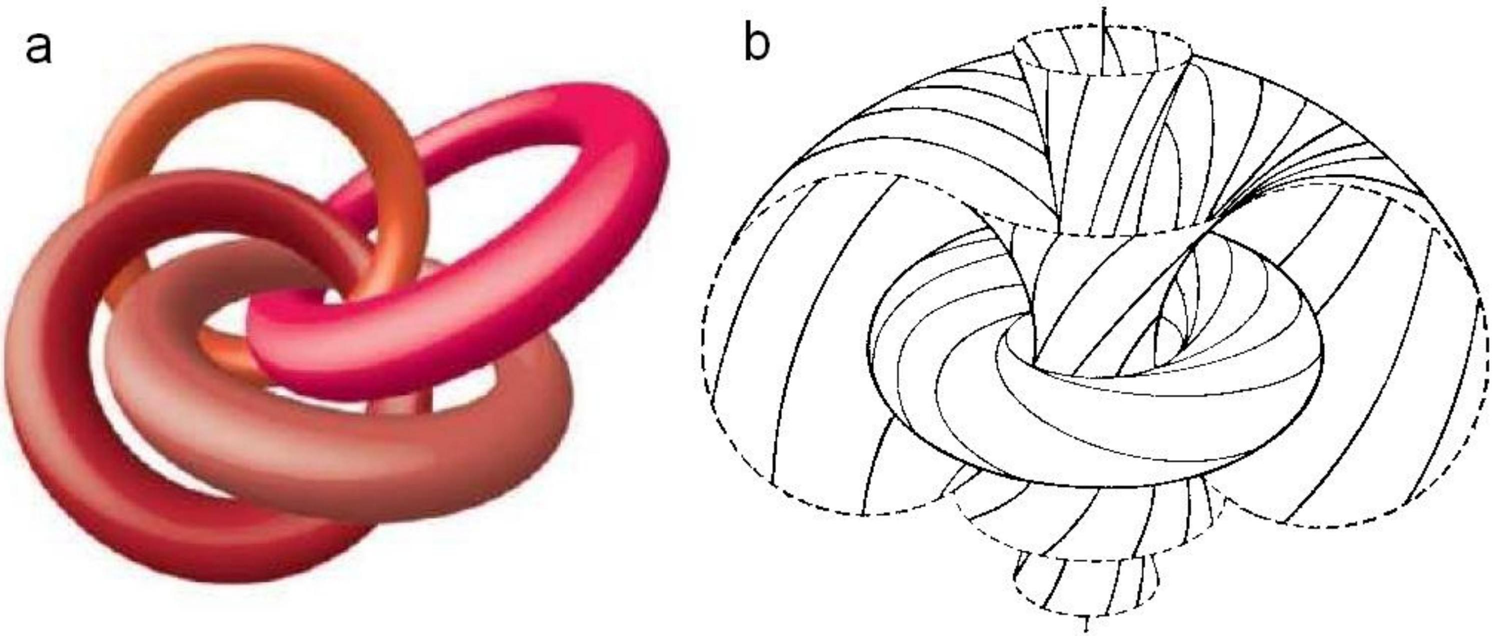
P.I. Belobrov. Nature of nanodiamond state and new applications of diamond nanotechnology // *Proc. IX Int. Conf.* "High-tech for Russian Industry", Russia, Moscow, 11-13 September, vol. **1**, p.235-269 (2003). **It is in Nanodiamond !**

Oral talk, 6.10.2011

Topological insulators



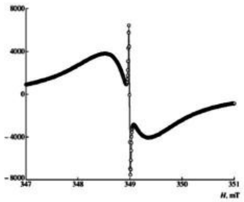
Topological insulators – insulator inside, conducting on the surface.



Hoph map R3 ⊂ S3 → S2

a) Moore J. E. (2010) The birth of topological insulators. Nature, 464(7286), 194-8.

b) Belobrov PI (2003) Nature of nanodiamond state and new applications of diamond nanotechnology // *Proc. IX Int. Conf.* "High-tech for Russian Industry", Russia, Moscow, 11-13 September, vol. **1**, p.235-269 **It is true for Nanodiamond !**



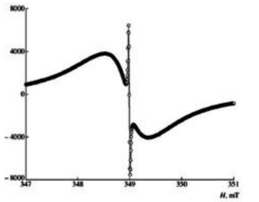
Tamm & Topological insulators

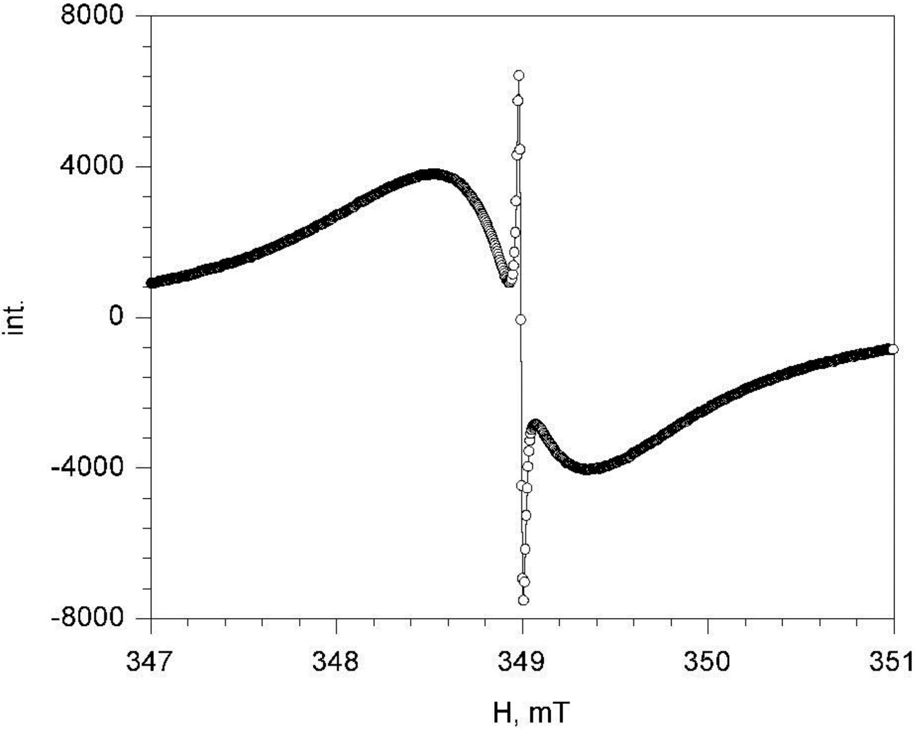
"Surface electronic states of insulator can be metallic" I E Tamm 1932

"If the topological invariants are always defined for an insulator, then the surface must be metallic."

J Moore 2010

Paramagnetic invariant





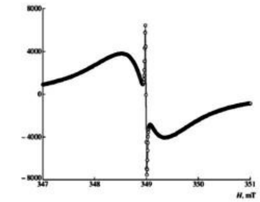
EPR spectrum of ND (NDC 10) with Li standard (g = 2.0023). Scan - 50 mT, modulation 0.01 mT.

- N ≈ $4*10^{19}$ spin / g
- N ~ 1 T-spin per ND particle
- g-value, $g = 2.0027 \pm 10^{-4}$
- line width, $\Delta H = 0.86 \pm 0.02$ mT
- are independent of the
  - temperature (77 - 1000 K)
  - composition of ND
  - structure of ND
  - atoms on its surface Cl, CH3 etc.
  - and state of ND surface
- The absence of saturation up 5 mW

P.I. Belobrov, S.K. Gordeev, E.A. Petrakovskaya and O.V. Falaleev, Paramagnetic properties of nanodiamond. *Doklady Physics*, **46**, 459 (2001).

Oral talk, 6.10.2011

molpit
International open laboratory of advanced science and technology



ND has true Paramagnetic Invariant

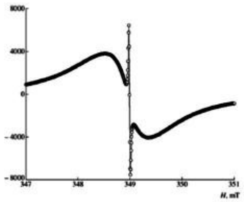
Table 1

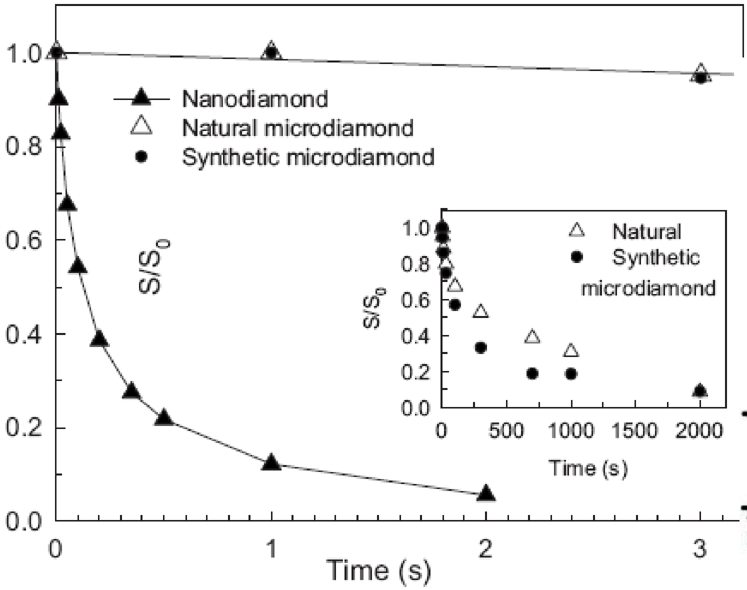
Item	Description of samples	*g*-value	Δ*H*, mT
1	Preparation [1], purification [7], 4% ash	2.0030(4)	0.85(7)
2	Sample no. 1, modification of the surface by chlorine	2.0028(7)	0.88(8)
3	Sample no.1, modification of the surface by CH_3	2.0029(6)	0.84(9)
4	Preparation and purification [3], 2% ash	2.0022(3)	0.86(6)
5	Sample no. 4, purification by sedimentation, 0.3% ash	2.0026(2)	0.86(2)
6	Preparation [3], purification by ozone, 1% ash	2.0027(5)	0.88(1)
7	Sample no. 4, modification of the surface by a protein	2.0024(1)	0.97(1)
8	Preparation and purification [3], 1% ash	2.0024(2)	0.85(3)
9	NDC 0	2.0026(1)	0.84(2)
10	NDC 0.5	2.0026(1)	0.86(1)
11	NDC 5	2.0027(1)	0.85(1)
12	NDC 10	2.0026(1)	0.84(4)
13	NDC 20	2.0025(1)	0.85(1)
14	NDC 30	2.0026(1)	0.85(1)
15	NDC 40	2.0027(1)	0.86(3)
	Mean values	2.0027(1)	0.86(2)

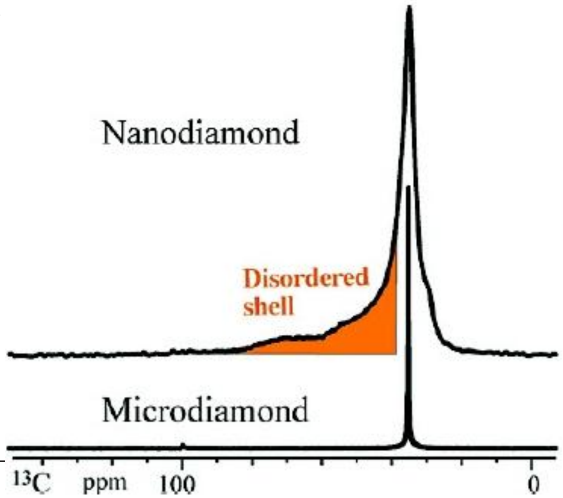
Note: Composites nos. 9-15, (NDC γ) made of nanodiamond (sample no. 1) and pyrocarbon are obtained using the method described in [9]. The carbon content [C] > 99 wt % in contrast to nos. 1–8, in which [C] < 85 wt %.

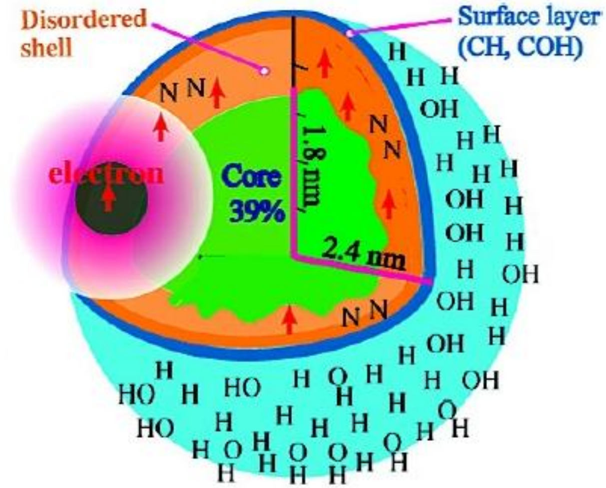
Oral talk, 6.10.2011

Recent confirmation of our results

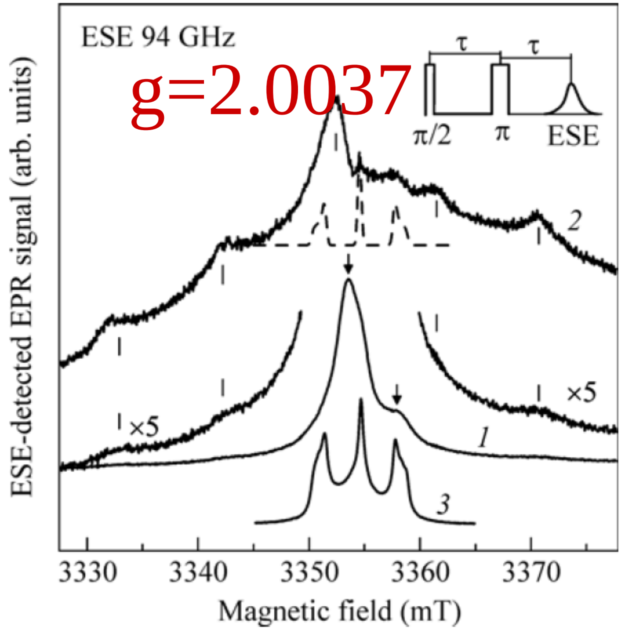






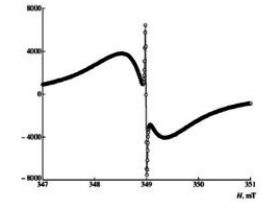


- E. M. Levin at al. Magnetization and C13 NMR spin-lattice relaxation of nanodiamond powder. *Phys. Rev. B.* **77**, 054418 (2008).
- X-W Fang at al. Nonaromatic Core-Shell Structure of Nanodiamond from Solid-State NMR Spectroscopy. *J Am Chem Soc*, **131**, 1426 (2009).
- P G Baranov at al. Electron paramagnetic resonance detection of the giant concentration of nitrogen vacancy defects in sintered detonation nanodiamonds // JETP Lett, 92, 102 (2010).



Oral talk, 6.10.2011

Novel Methods & Tech-s of Biological Computing

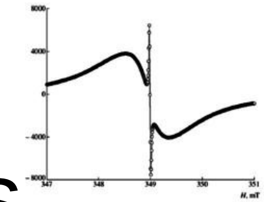


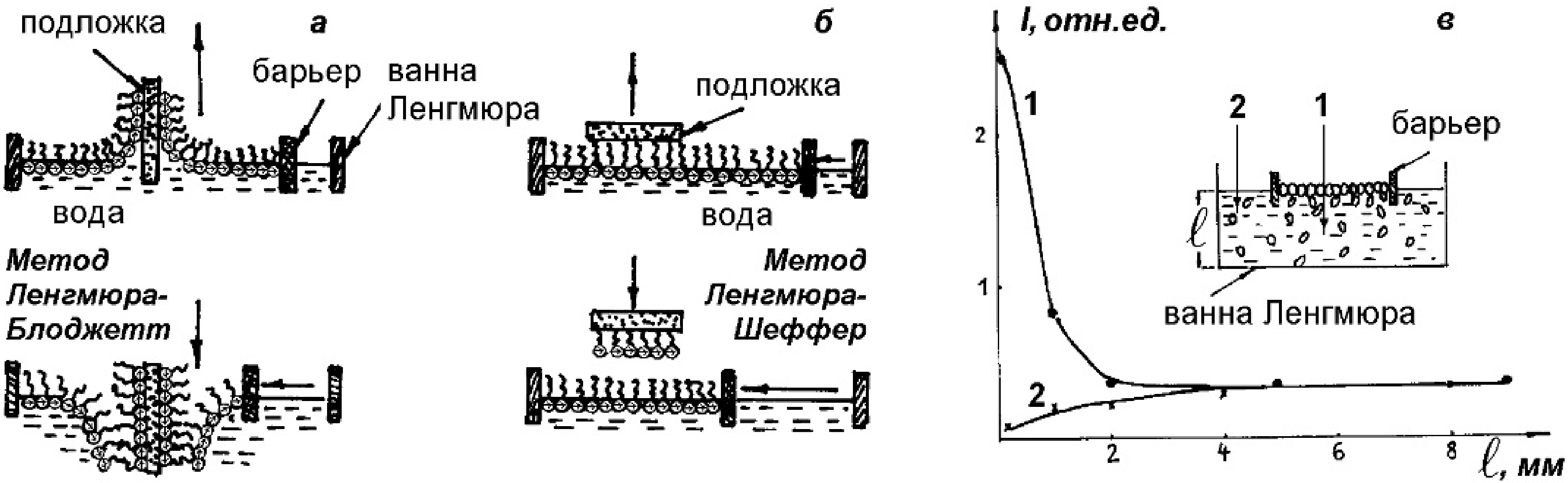
Microemulsion platforms for molecular and biological calculations:

- Langmuir-Blodgett & Langmuir-Schaeffer methods of Molecular Architecture
- Blot, Blotter & Blotting Technologies
- Microemulsion amplification
- Microemulsion platforms for massive parallel sequencing of DNA & RNA

Oral talk, 6.10.2011

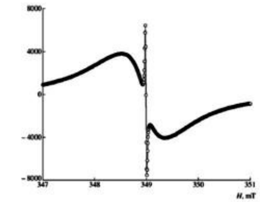
Langmuir-Blodgett & Langmuir-Schaeffer methods of Molecular Architecture





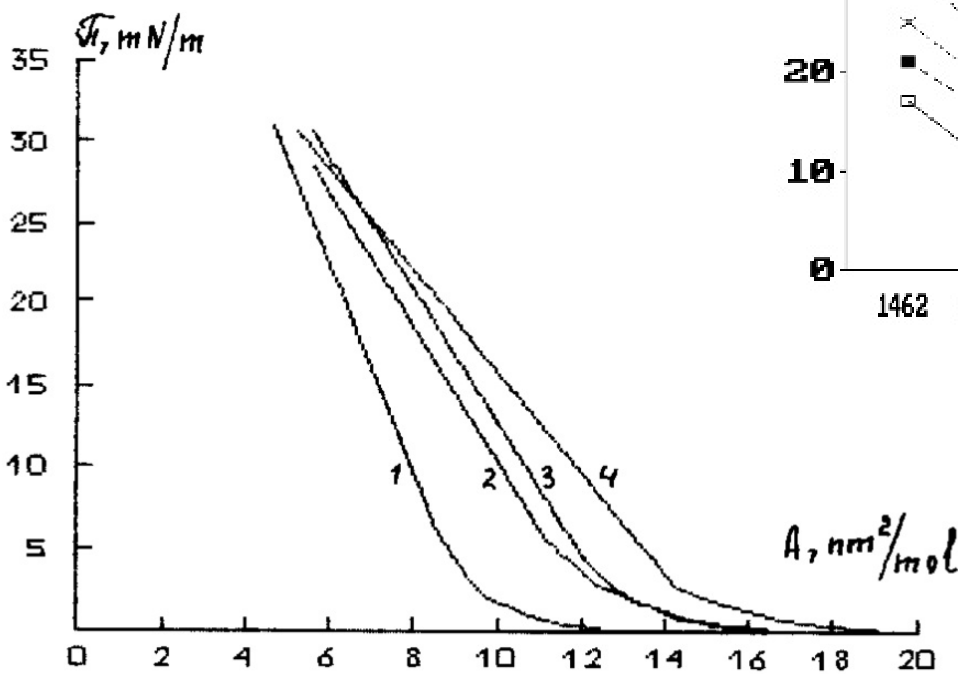
Oral talk, 6.10.2011

Molecular Architecture of Langmuir-Blodgett films



LB films of Bacterial Luciferase

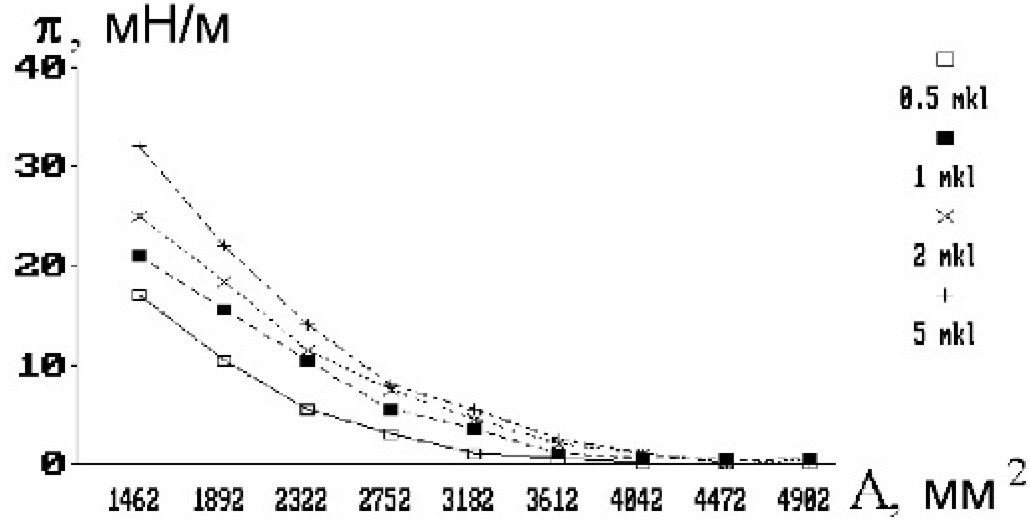
Belobrov at al. (1988)
Preprint of Kirensky Institute of Physics # 92B



Oral talk, 6.10.2011

LB films of Nanodiamond

Belobrov at al. (1991) unpublished



Bacterial Lucifrase (BL),
Fatty Acid (K),
Aldehyde (A),

1 – BL+ K 1:50 M/M

2 – BL ~ 10^{-5} M

3 – BL + A 1:50 M/M

4 – BL + A 1:10 M/M

Nanodiamond weght %

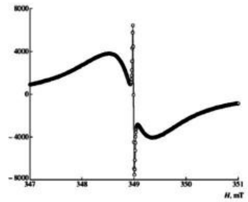
1 – 10^{-2}

2 – 2x10^{-3}

3 – 5x10^{-4}

4 – 5x10^{-5}

molpit
International open laboratory of advanced science and technology



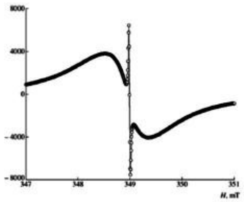
Blotting Tech

- Blot - quantum image of chemical signal
- Blot-blotter interaction
- Is it calculation of blot by blotter?

Клякс-папир! Ау!

- Клякса - квантовый образ химического и биологического сигналов
- Новые методы био и хим вычислений

MASSIVELY MULTIPLEXED SEQUENCING



MP Strathmann - US Patent App. 20,100/113,283, 2009

Note the complementary oligos may be peptide nucleic acids or any other molecule that specifically interacts with a segment of the tag. A slight modification to the procedure would allow the use of **microemulsion amplification**

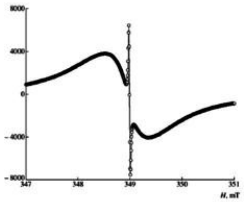
(Ghadessy et al. (2001) Proc. Natl. Acad. Sci. USA 98 p4552;

Dressman et al. Proc. Natl. Acad. Sci. USA 100:8817-8822, 2003)

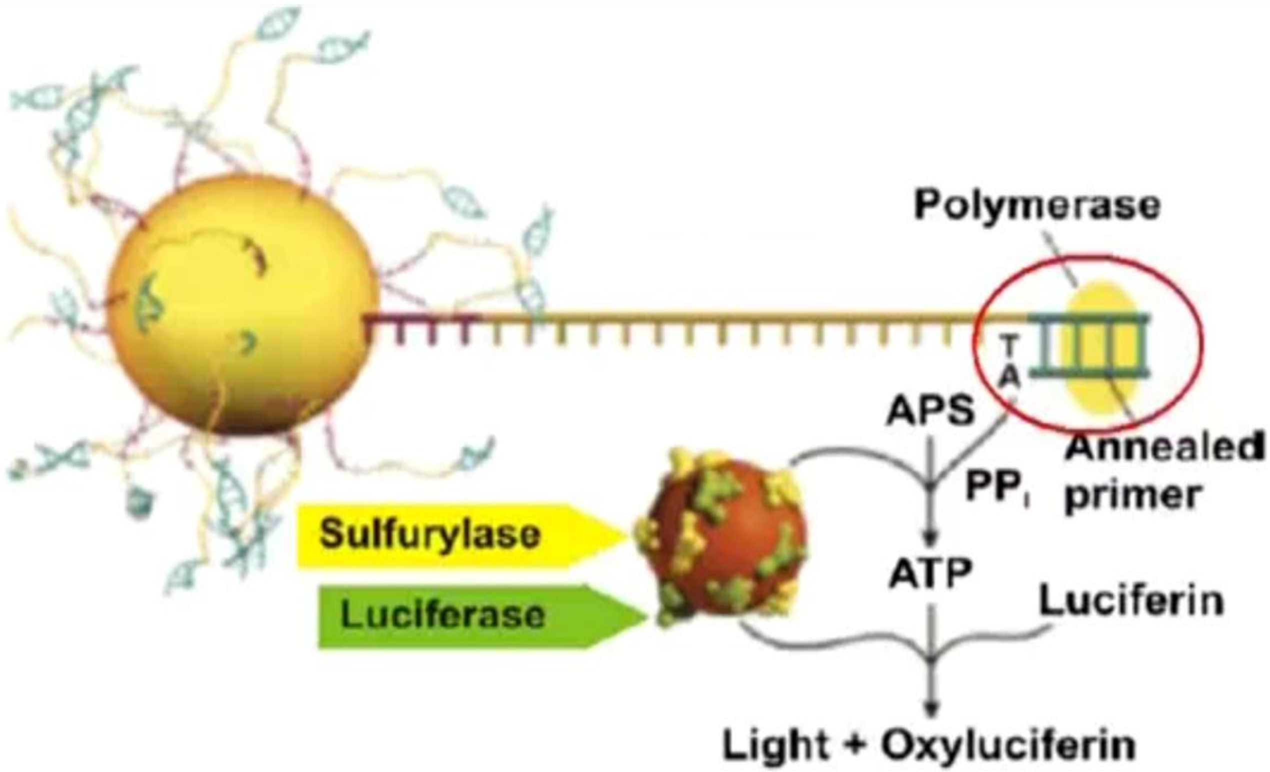
prior to flow cytometry or fixed-position imaging. If the microemulsions are not broken, then the complementary oligos could be present prior to amplification in a quenched form for example Molecular Beacons

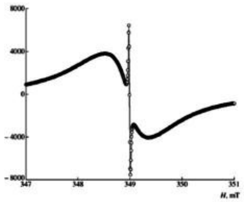
(Tyagi et al. (1998) Nat. Biotechnol. 16 p49)

molpit
International open laboratory of advanced science and technology



Microemulsion amplification





Direct Molecular Diagnosis of Fetal Aneuploidy

HC Fan - US Patent 20,110,151,442, 2011

A **microemulsion platform** was developed to increase the scale of the assay [17, 18], and it is now being used as a sample preparation technique for massively parallel sequencing [19]. However, all these previously described methods are cumbersome to implement, take a long time and require significant labor.

17. Dressman D, Yan H, Traverso G, Kinzler K W, Vogelstein B. Transforming single DNA molecules into fluorescent magnetic particles for detection and enumeration of genetic variations. Proc Natl Acad Sci USA 2003; 100: 8817-22.

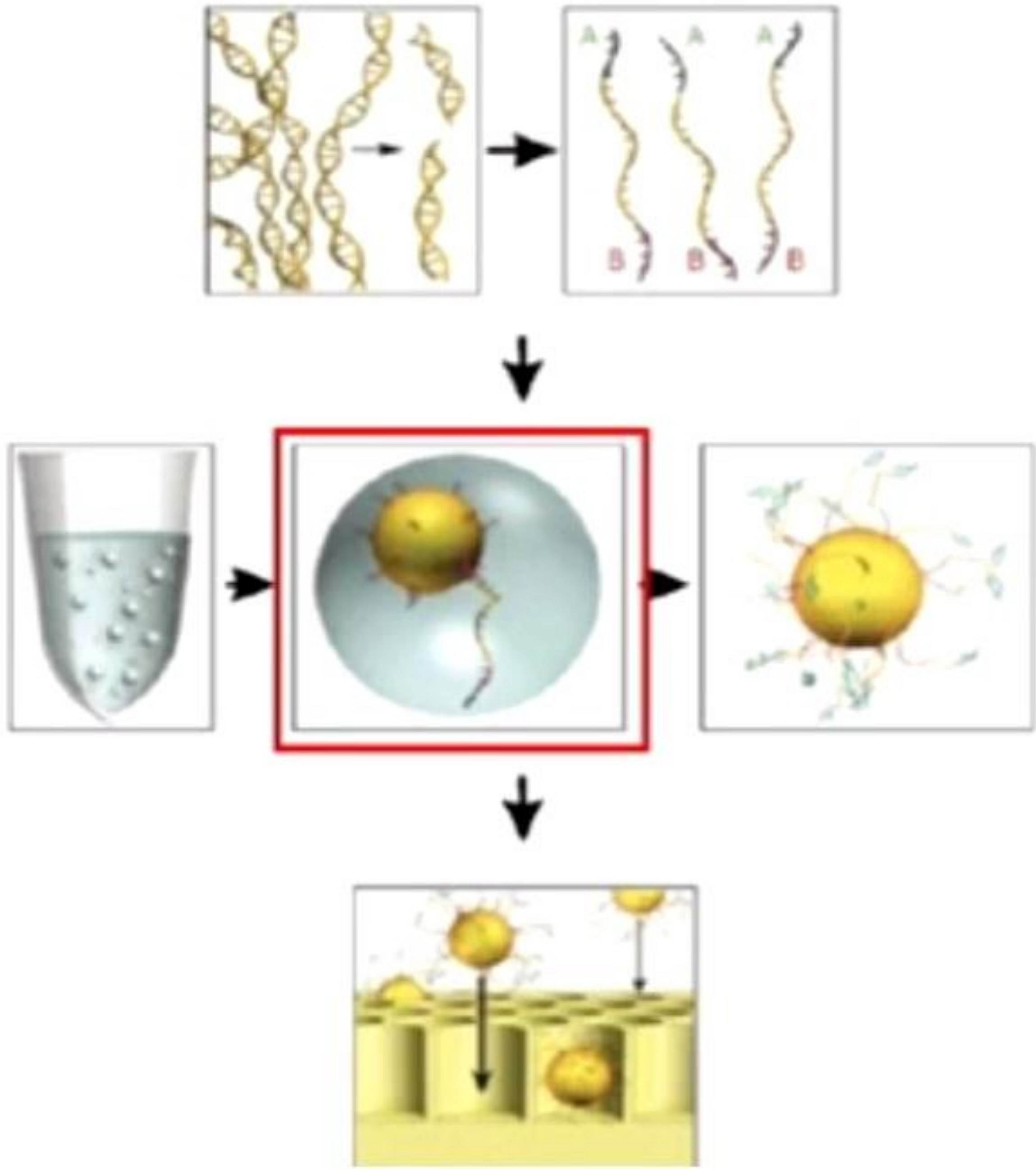
18. Diehl F, Li M, Dressman D, et al. Detection and quantification of mutations in the plasma of patients with colorectal tumors. Proc Natl Acad Sci USA 2005; 102:16368-73.

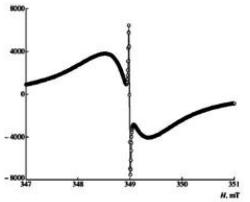
19. Margulies M, Egholm M, Altman W E, et al. Genome sequencing in microfabricated high-density picolitre reactors. Nature 2005; 437: 376-80.

molpit
International open
laboratory of advanced
science and technology

Microemulsion platforms for massive parallel sequencing of DNA & RNA

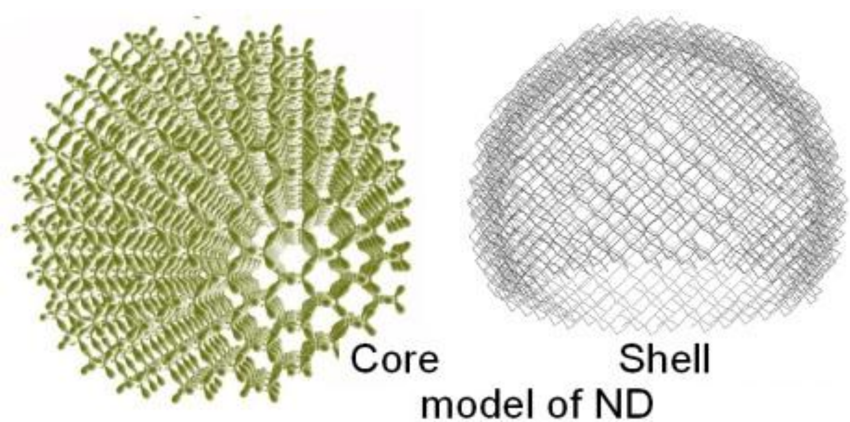
Oral talk, 6.10.2011

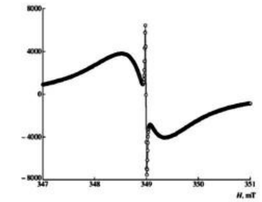




Conclusions

1) ND has diamond surface net = T-layer
2) There is collective excitations ND-protein
3) LB films of ND with Luciferase
4) Tamm quasi-particle is de Broglie wave of electron at T-layer
5) ND-Microemulsion platform of tiny tech





Acknowledgments

- Kirill A Lukyanenko, Viktoriya V Savchenko, Polina E Lisitsa, Daniil A Fedotov, Stig E Friberg

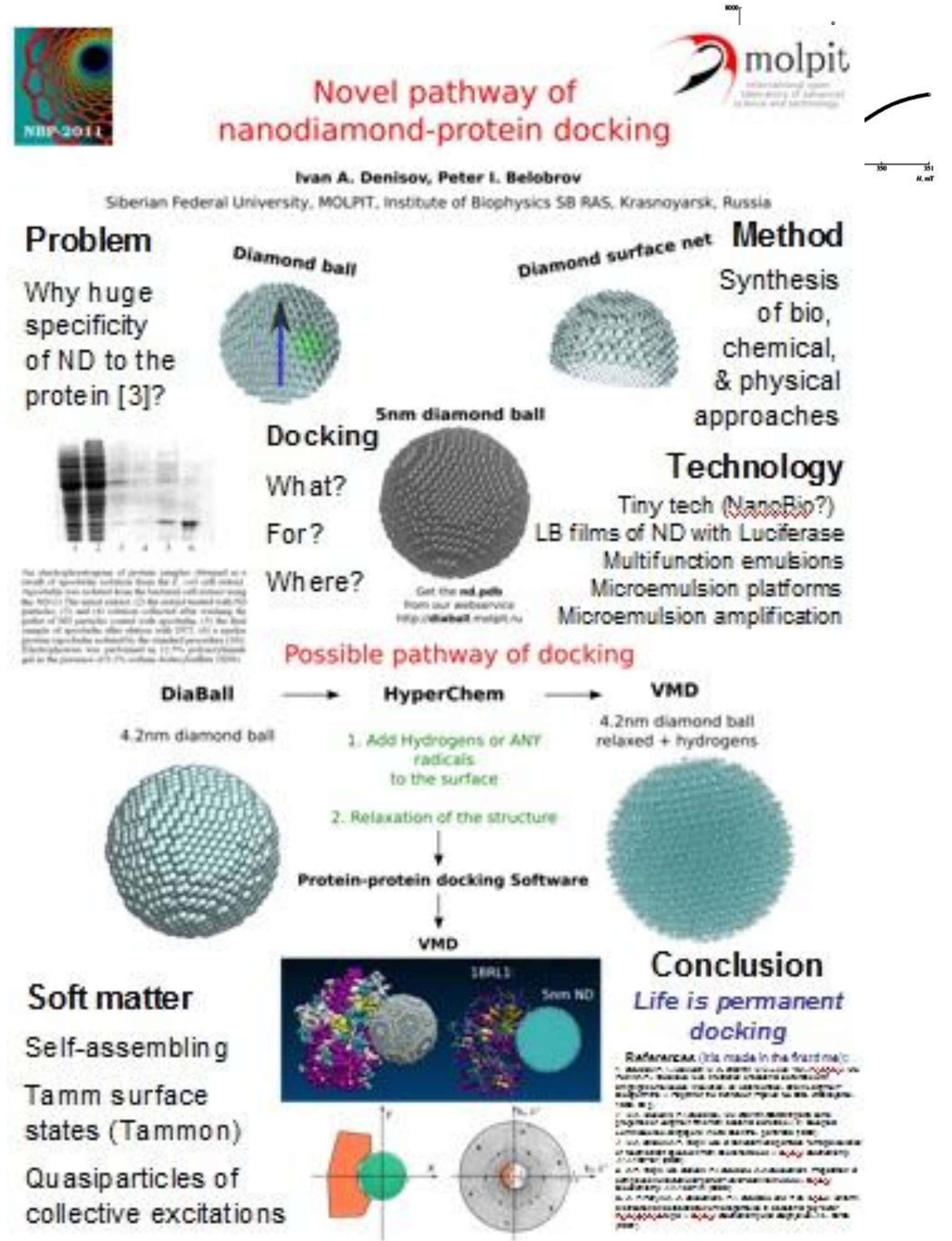
- This research was supported by RFBR Grants 07-04-01340-a, 08-02-00259-a and (# 09-08-98002-p_sibir_a) , ME&S of RF Grant No. 2.2.2.2/5309 and U.S. CRDF Grant RUX0-002-KR-06/BP4M02.

Oral talk, 6.10.2011

molpit
International open laboratory of advanced science and technology

Novel pathway of nano-diamond – protein docking

Poster #19
Abstract book
pp. 46 & 60



Oral talk, 6.10.2011