Experimental proofs of collective electron states and their localization into porous composites from nanodiamond and pyrocarbon

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PPM2015 Conference, Bilbao-Spain, 12th March 2015

Outline

- The one point 11 years ago exactly
  - A few features of the problem 12/3/2004 $\rightarrow$ 12/3/2014
  - J-M. Len: "Chem is Bio" $\rightarrow$ «Chem is the part of Bio»
- Experiments with diamond KoLoBok
- Theoretical calculations
- Diamond ball ~ 5 nm (KoLoBok) is mist! Why?
  - The little round bun (*en*) $\equiv$ bollo (*es*) $\equiv$ kolobok (*ru*)
- Crystal field (> 20 nm) $\neq$ close packing (2 $\div$ 5 nm)
- Ando, 2015: "The topological materials"
- Outlook
  - In this year; at nearest future; who knows?

EDM Group Seminars: *Lent 2004*

Friday 12th March 2004 Lecture Room 1-4pm

Nature of Nanodiamond State and Applications of Diamond Nanotechnology

Prof. Peter I. Belobrov

(Institute of Biophysics SB RAS & UNESCO chair of KSTU, Krasnoyarsk, Russia)

The brilliancy of nanodiamond has remarkable prospects and the current mists that surround the properties of this **huge diamondoid** are only recently recognized by fundamental research being undertaken for the first time. As such the applied aspects for this diamond molecule are as yet still underestimated. The nature of the nanodiamond state (NDS) based on existing nanodiamond experimental data is surveyed in this lecture. A model of a diamond quantum dot (DQD) is proposed, based on the representation of collective electronic-vibration states at Tamm levels in clusters with a self-consistent boundary. The properties of NDS are universal and are demonstrated in their thermodynamic stability, in X-ray, electronic, EPR, NMR, IR, Raman and Auger spectra and in their magnetic properties. The reconstruction of DQD surfaces will be demonstrated. A brief review of new applications for diamond nanotechnology in physics, chemistry and biology will be made. The outlook for technological developments utilizing nanodiamond in solid-state electronics and vacuum microelectronics and the opportunity for making new devices in nanoelectronics will be considered.

http://molpit.org/?page=46

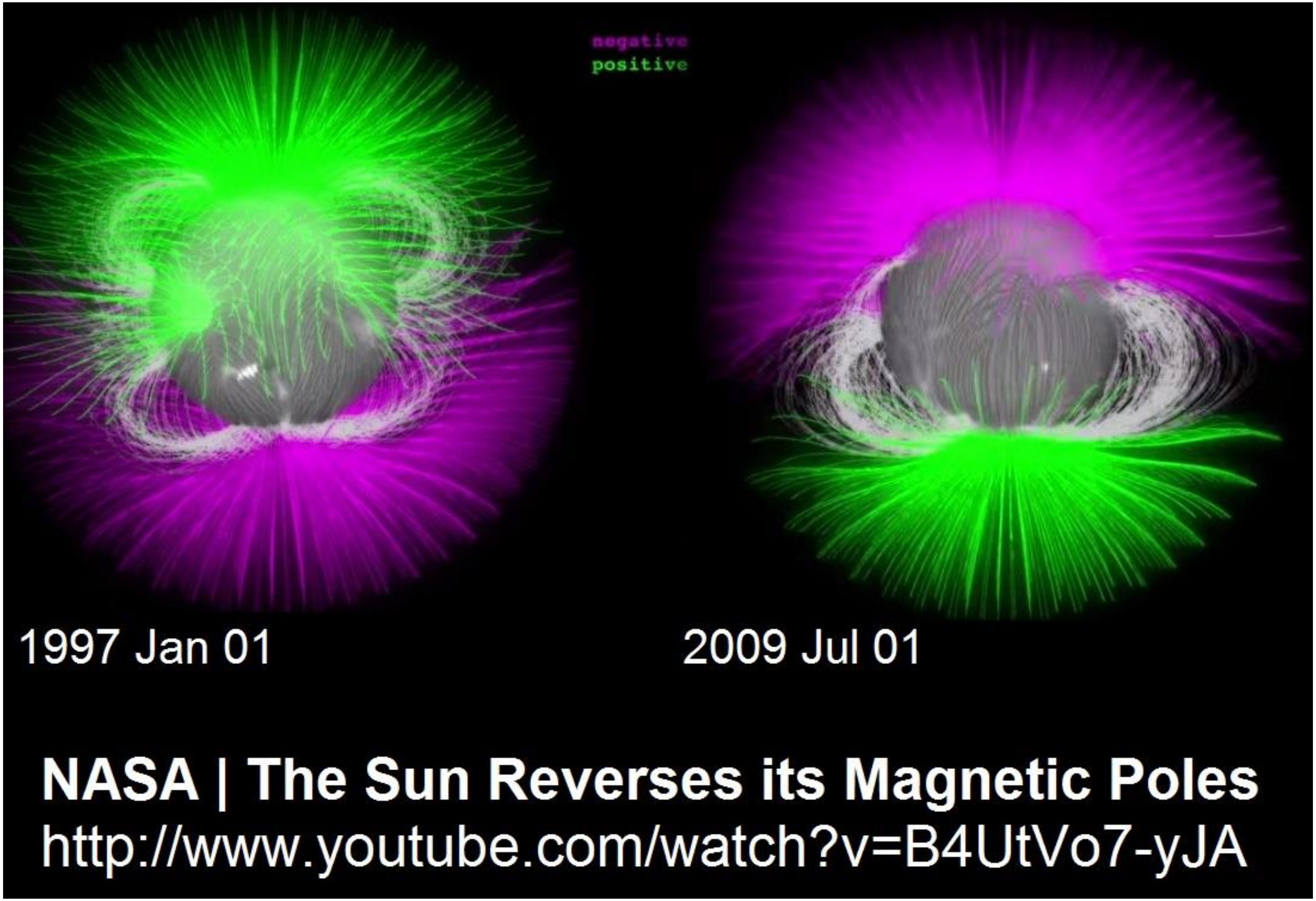
UNIVERSITY OF CAMBRIDGE

ELECTRONIC DEVICES & MATERIALS GROUP

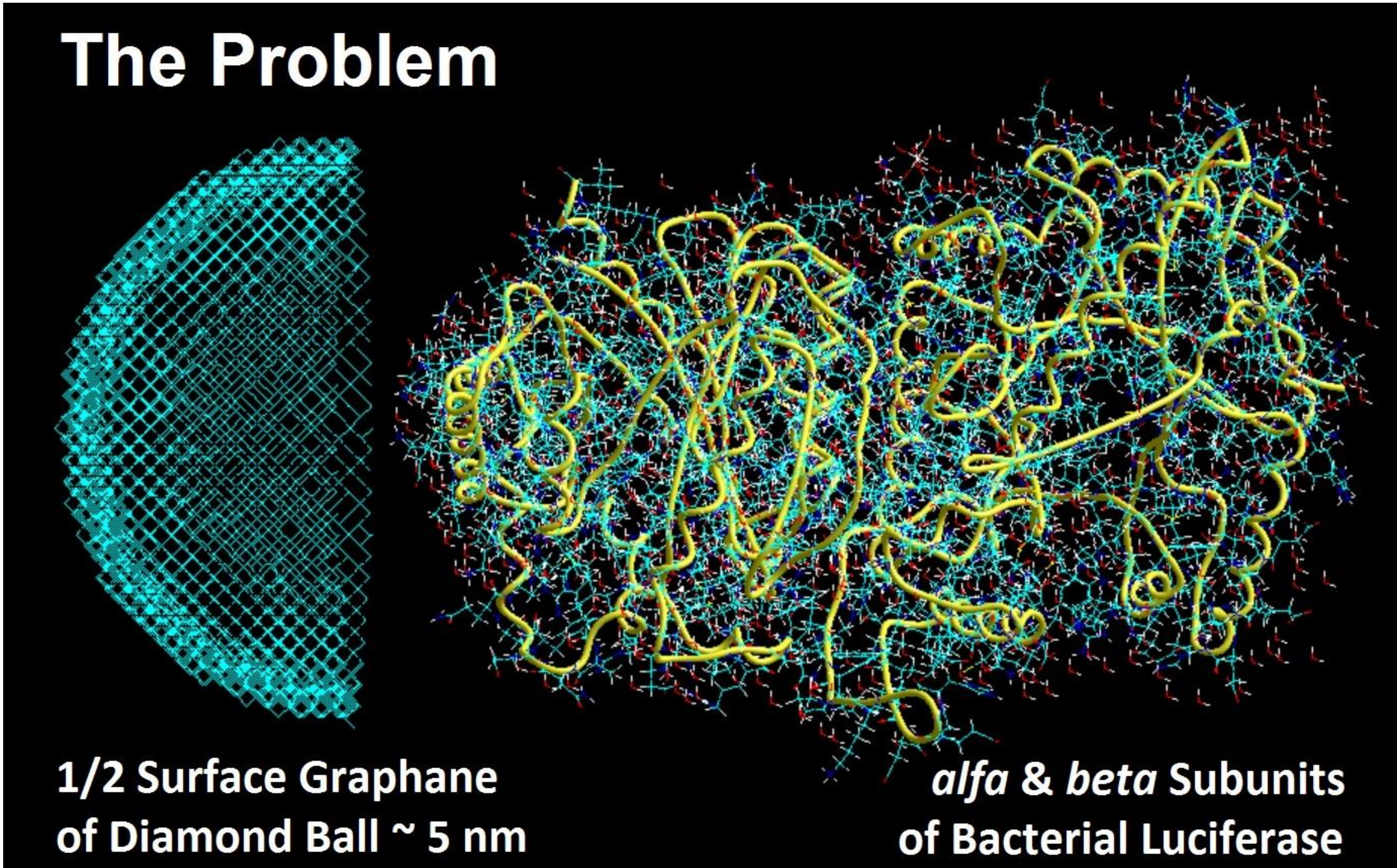
Before 2004 Graphene

- KS Novoselov, 2004 Science 22 Oct, Received 19 July, Accepted 15 Sept 2004.
- KS Novoselov, 2005 Nature 10 Nov, Received 14 July, Accepted 12 Sept 2005
- Y Zhang, 2005 Nature 10 Nov, Received 18 July, Accepted 12 Sept 2005

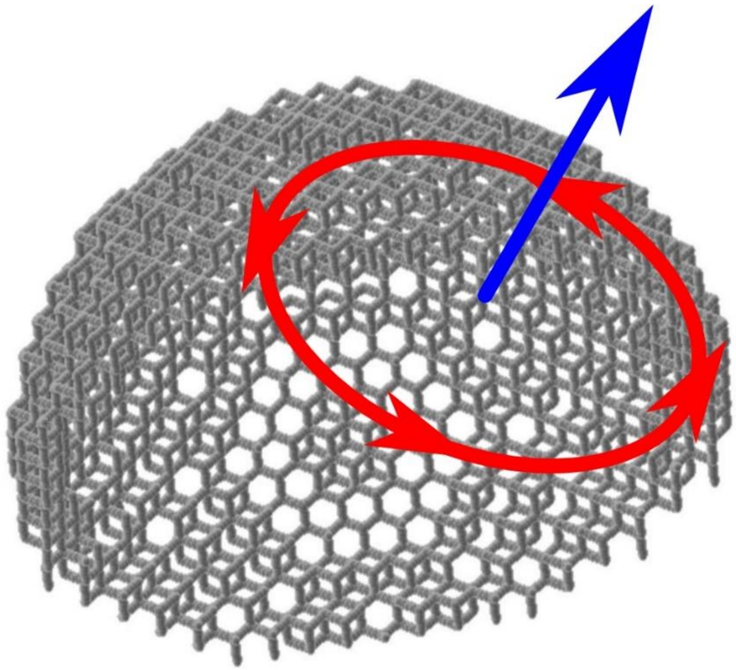
What means the period of 11 years?

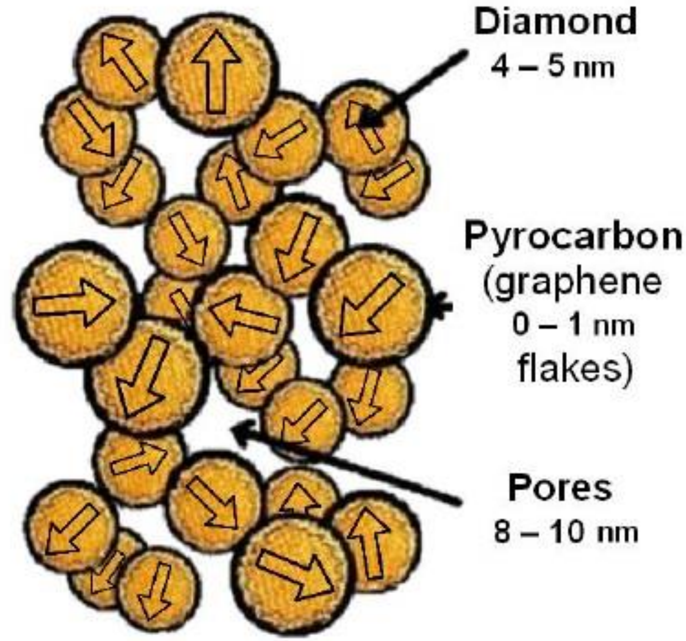


The Problem is …

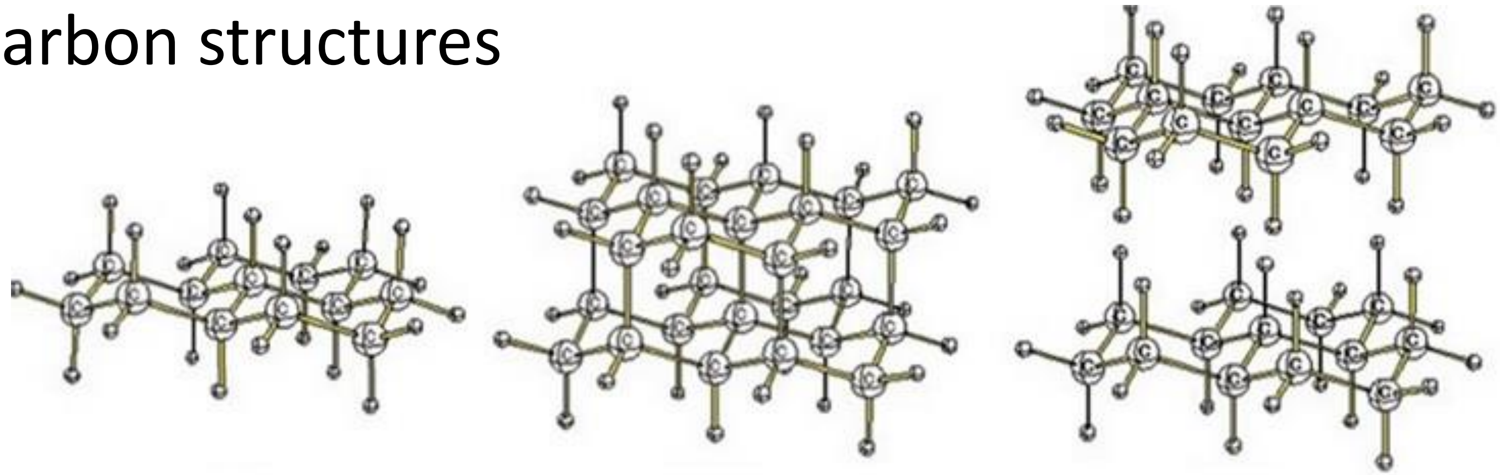


Fractional dimensions of electron density

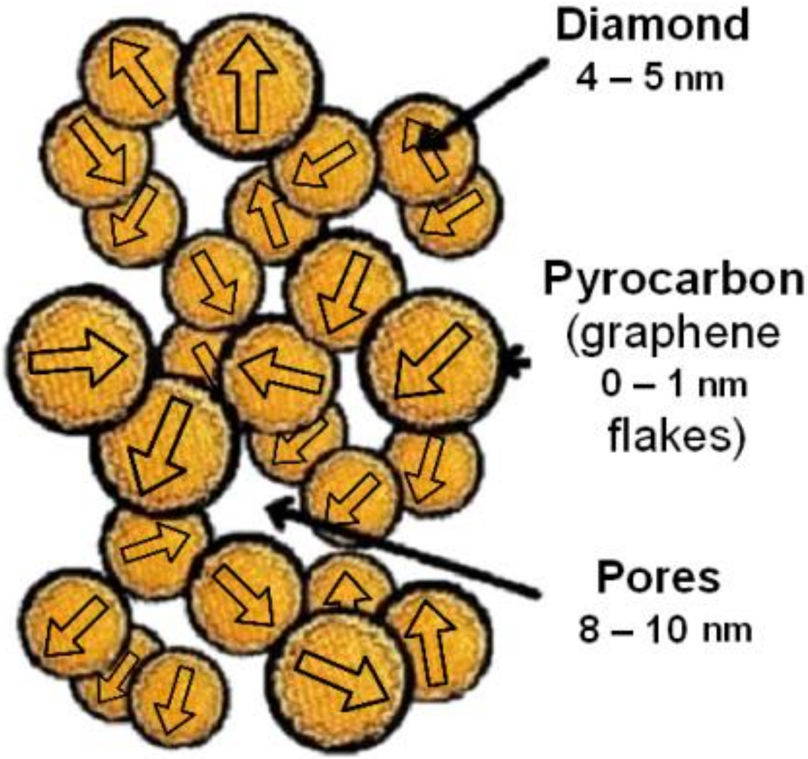




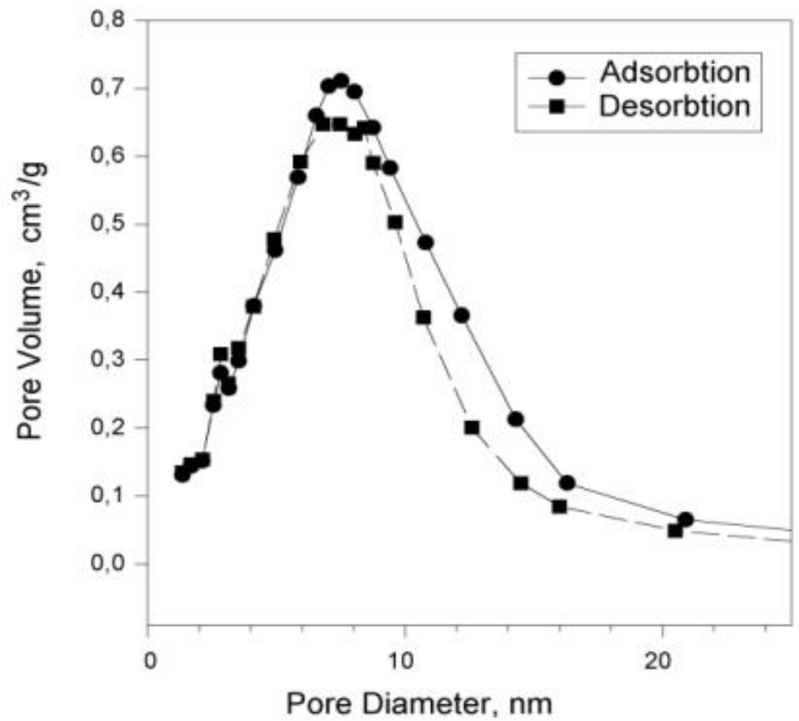
Strong curvature & incommensurate of nearest layers in carbon structures



The experiments with ~10^{19} KoLoBoks

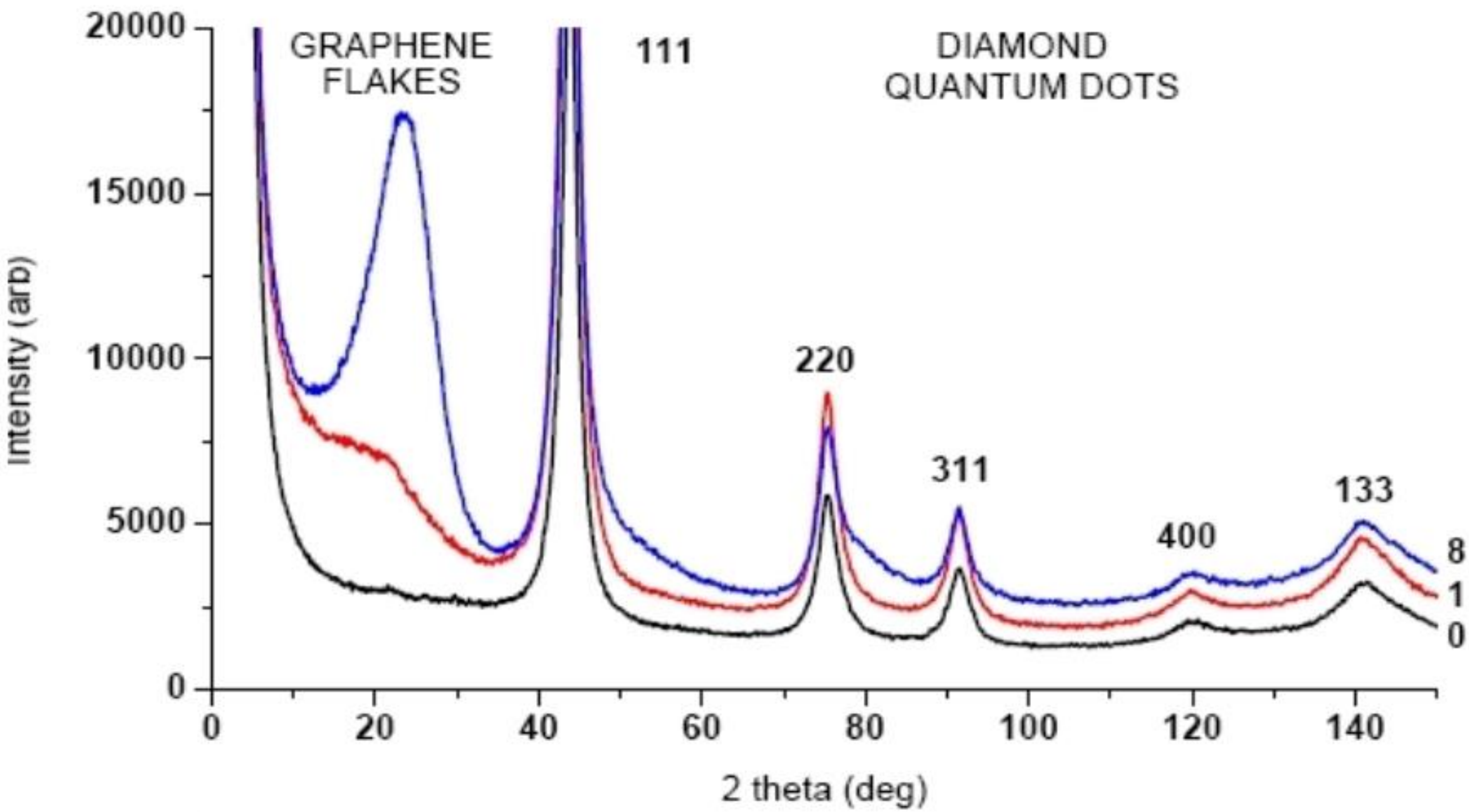


T-spin in NDC

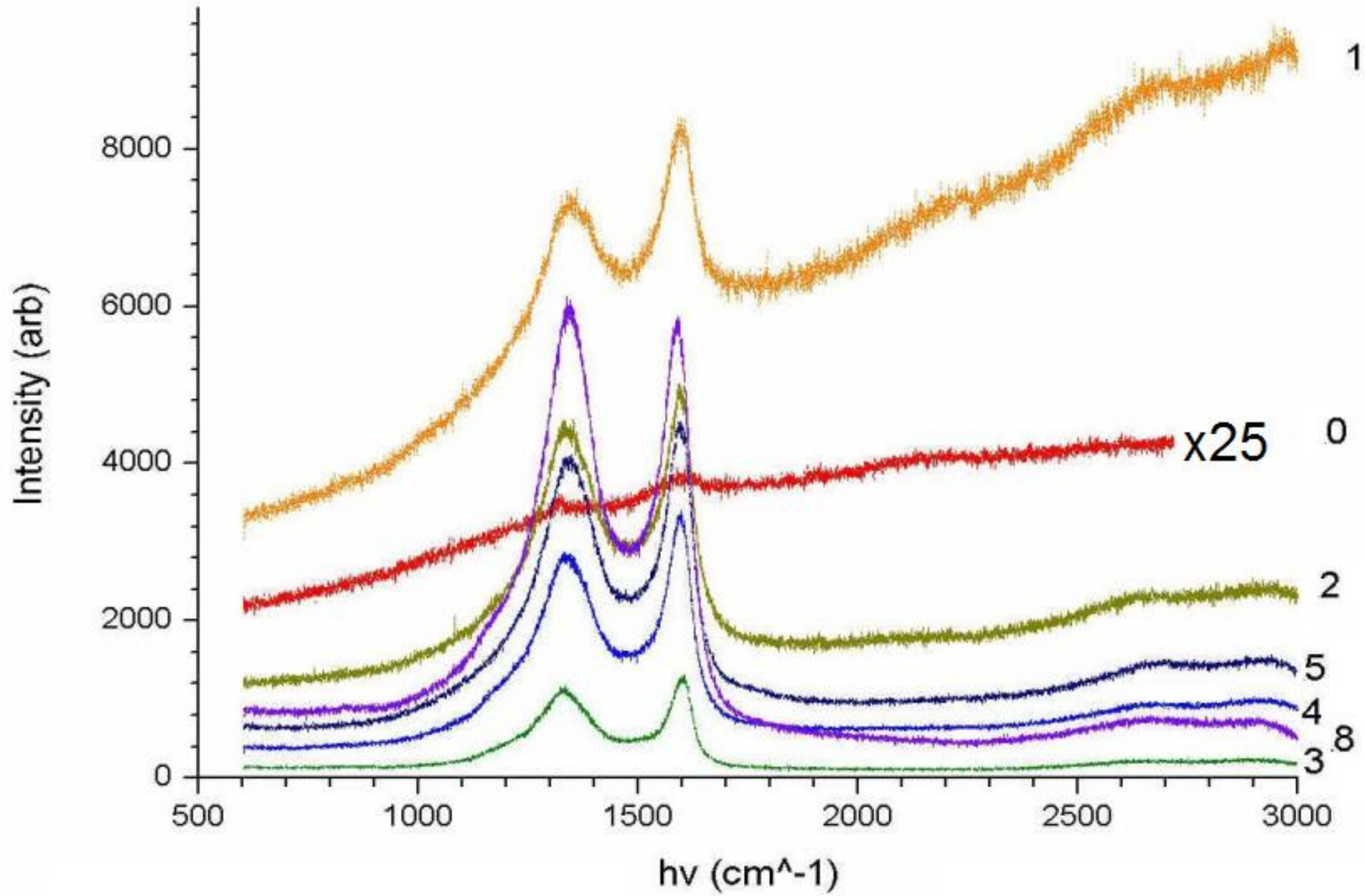


Pore size distribution by N_2

X ray diffraction



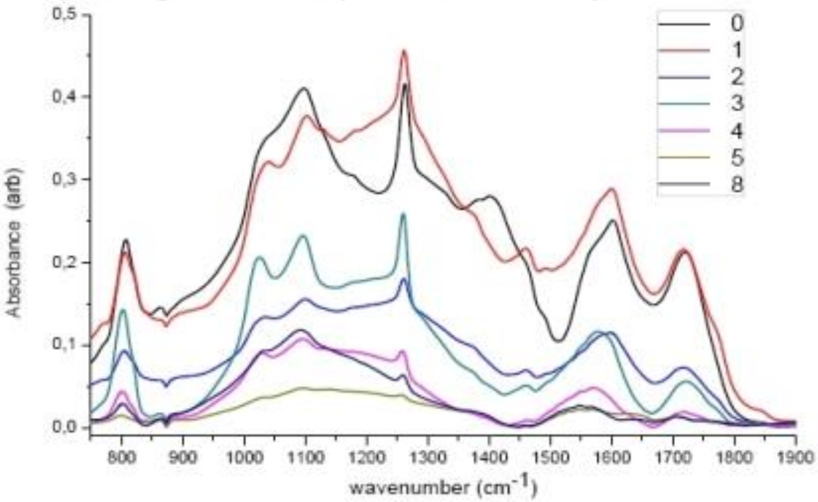
Raman



# code	γ, %
0	0
1	10
2	20
3	30
4	40
5	50
8	80

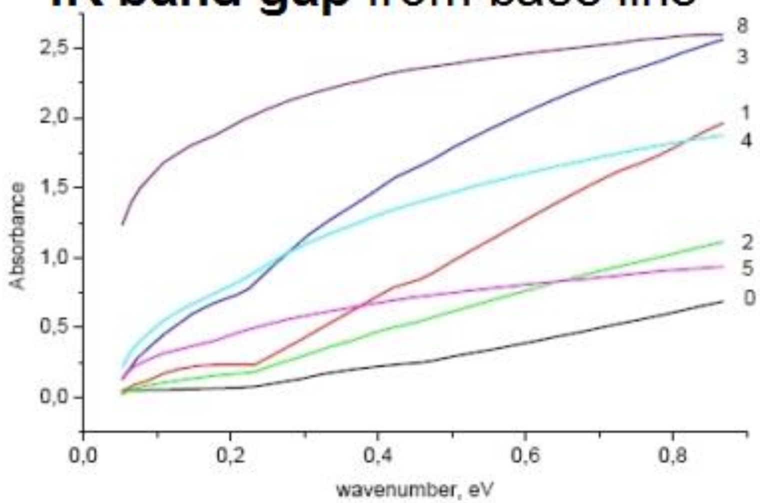
Main experiments

IR spectra (- base line)



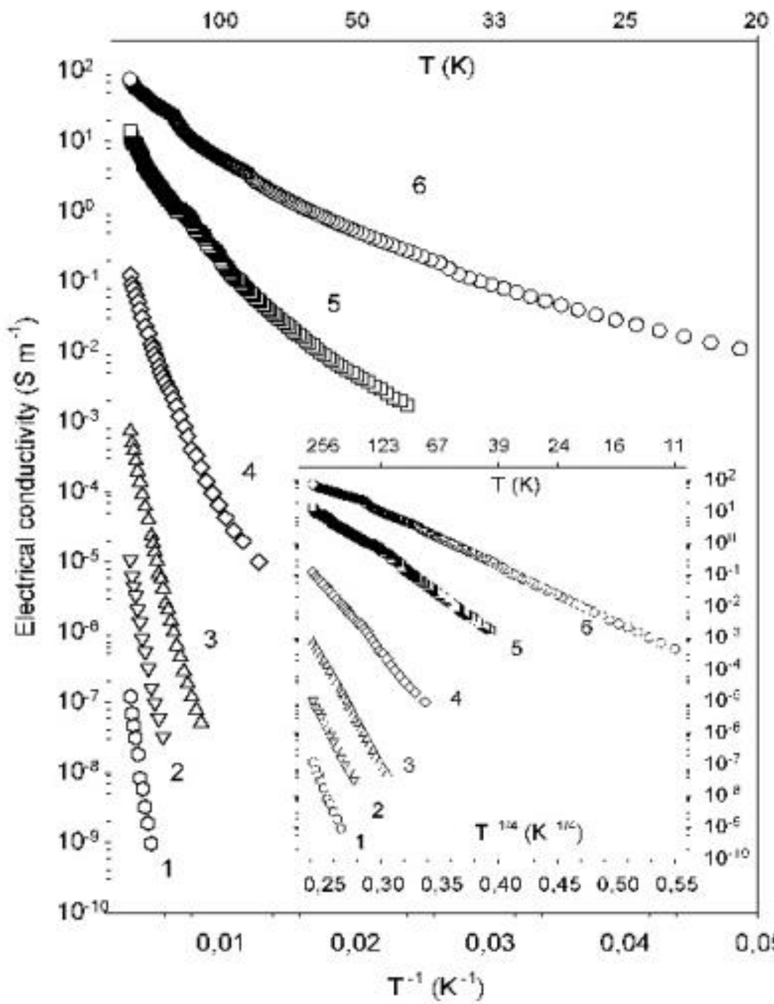
# code	γ, %
0	0
1	10
2	20
3	30
4	40
5	50
8	80

IR band gap from base line

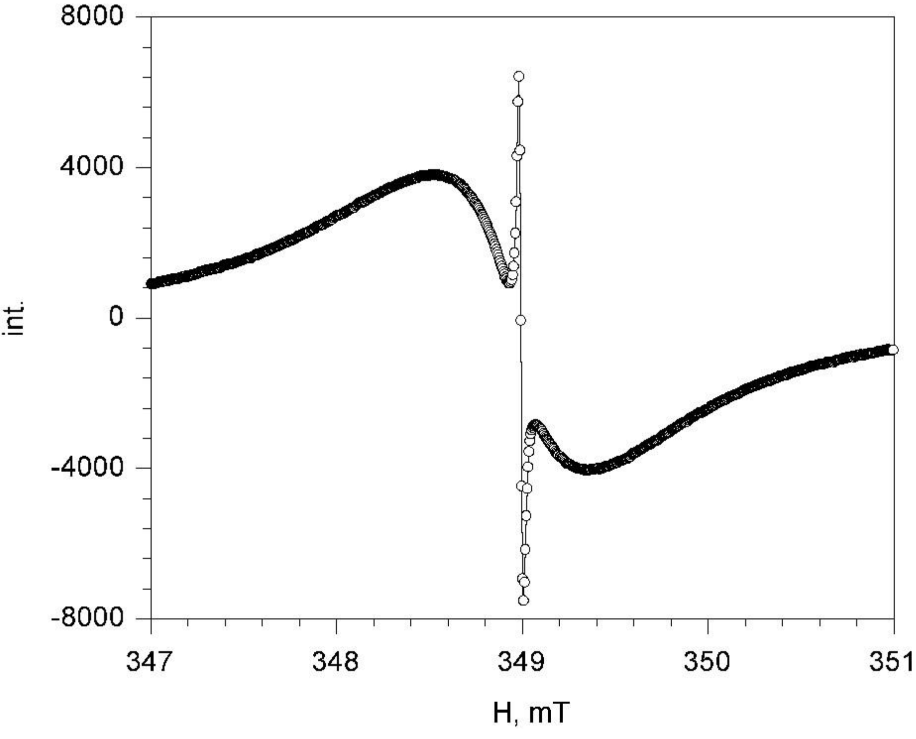


Semiconducting properties

- #1 - #6: γ = 0.5, 5, 10, 20, 30, 40 %



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).

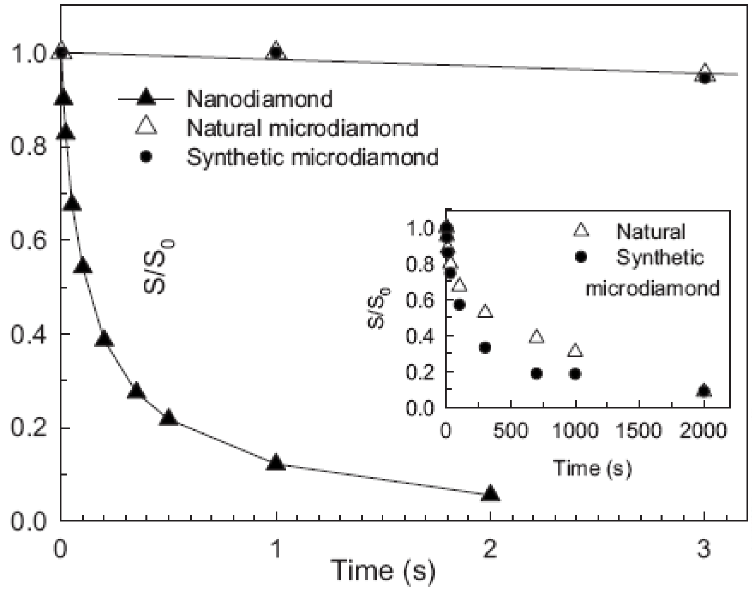
ND has true Paramagnetic Invariant

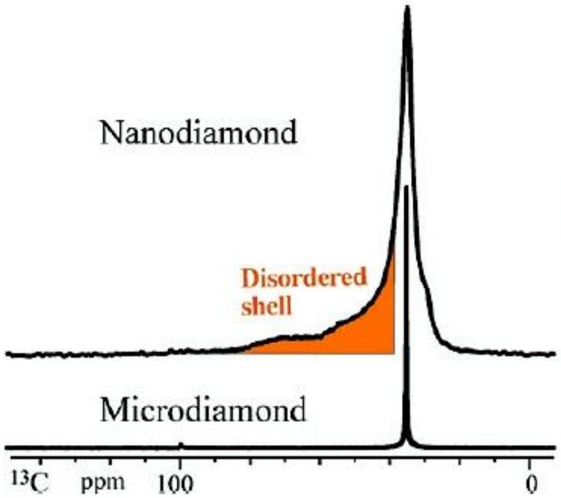
Table 1

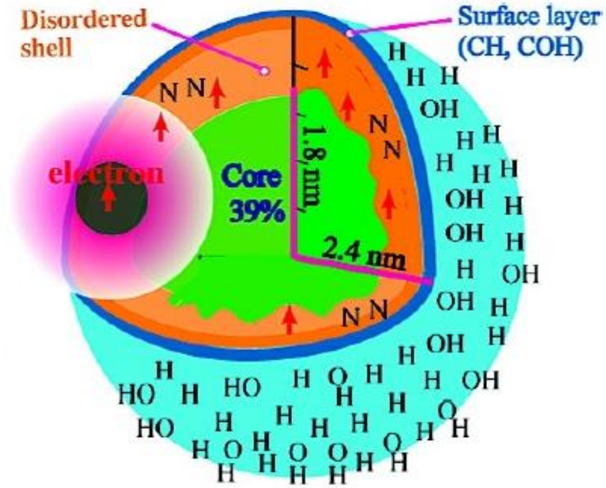
Item	Description of samples	g-value	ΔH, mT
1	Preparation [1], purification [7], 4% ash	2.0030(4)	0.85(7)
2	Sample no. 1, modification of the surface by chlorine	2.0028(7)	0.88(8)
3	Sample no.1, modification of the surface by CH_3	2.0029(6)	0.84(9)
4	Preparation and purification [3], 2% ash	2.0022(3)	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 %.

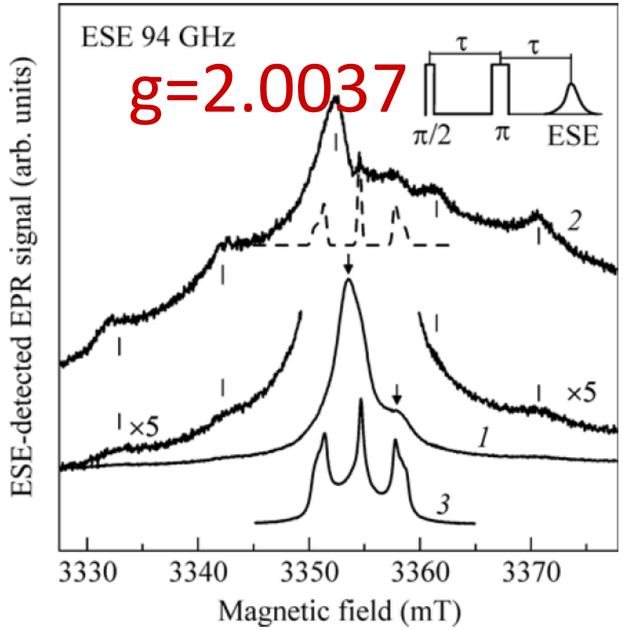
The confirmations of our results

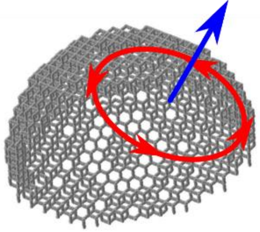




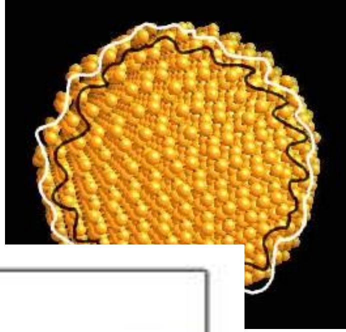


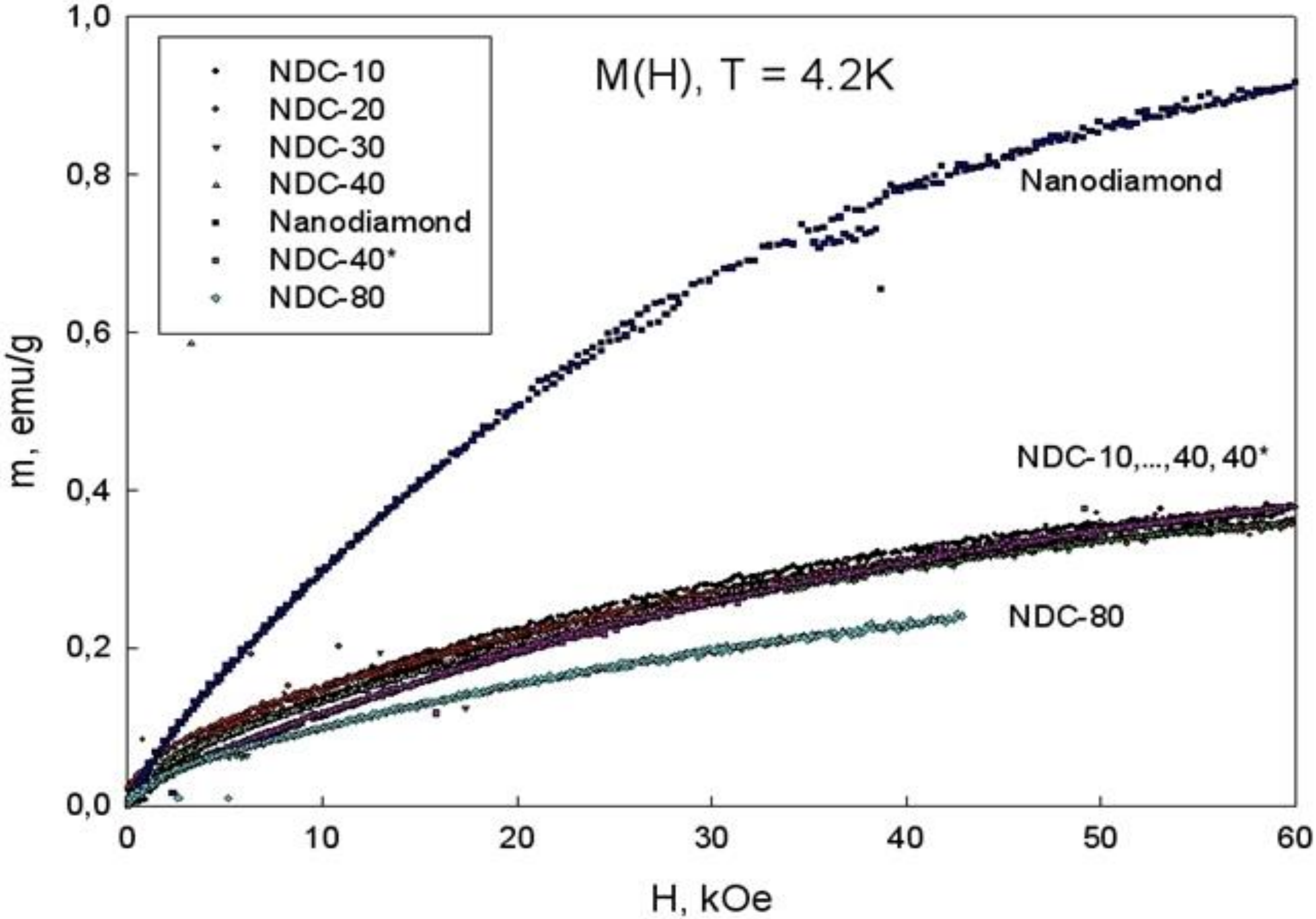
- E. M. Levin at al. Magnetization and C13 NMR spin-lattice relaxation of nanodiamond powder. *Phys. Rev. B.* **77**, 054418 (2008).
- X-W Fang at al. Nonaromatic Core-Shell Structure of Nanodiamond from Solid-State NMR Spectroscopy. *J Am Chem Soc*, **131**, 1426 (2009).
- P G Baranov at al. Electron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



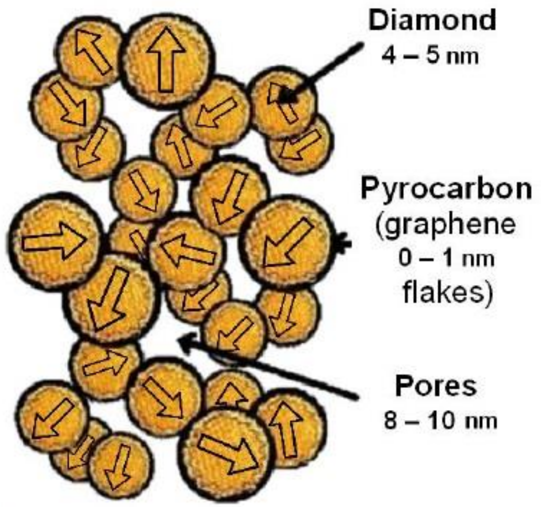


Magnetic susceptibility





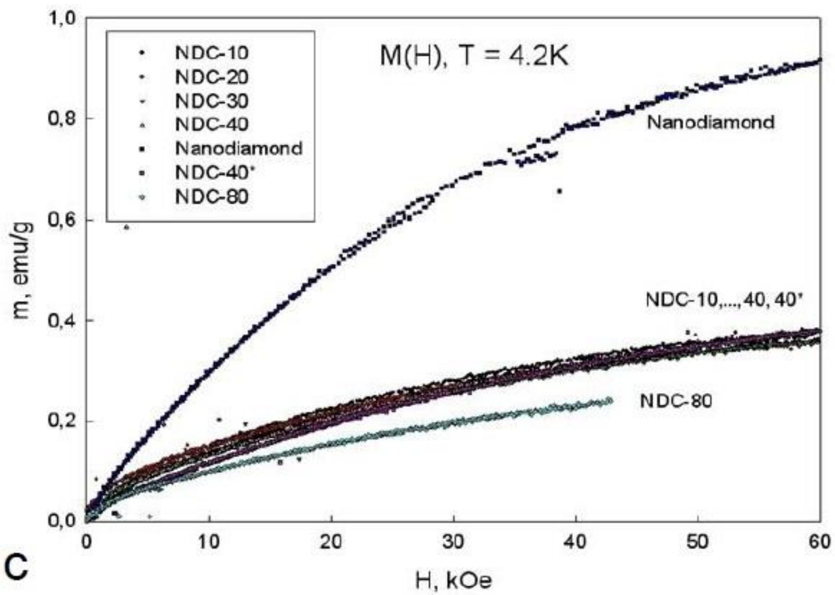
Figures



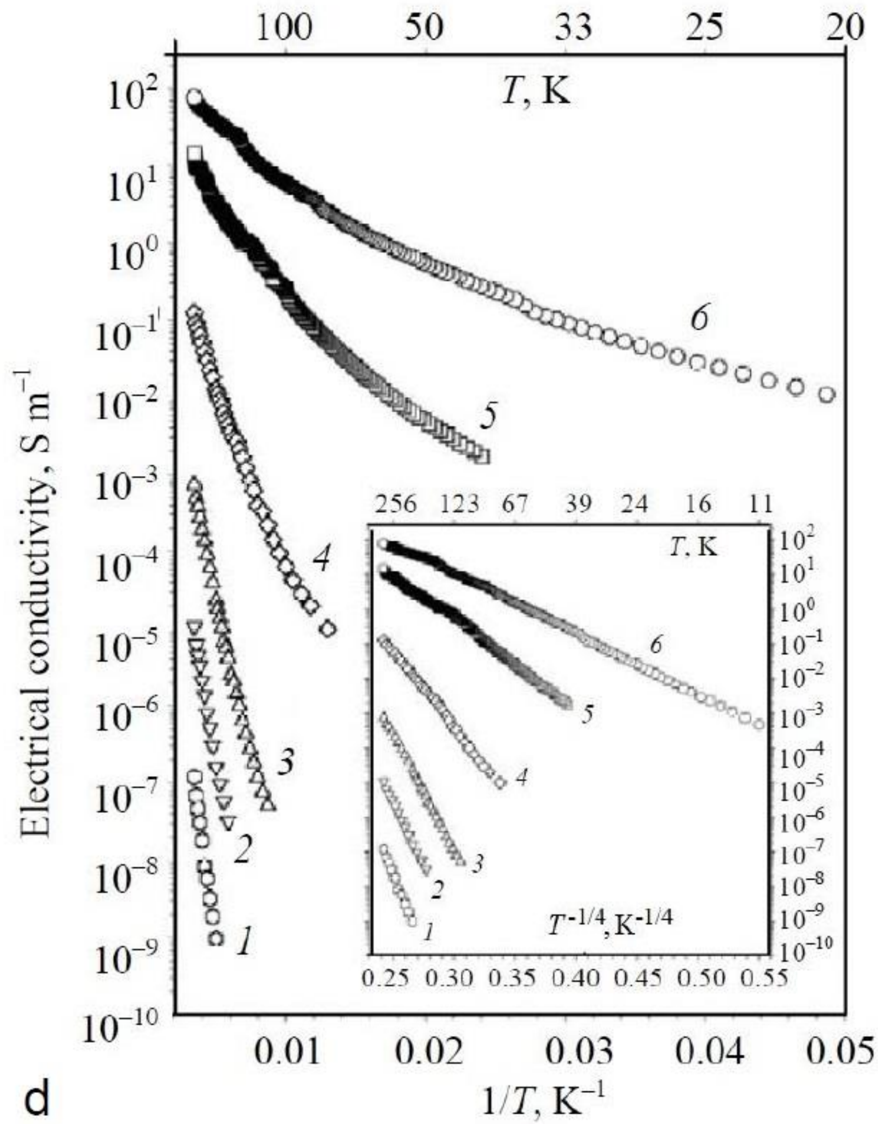
a

b

# code	γ, %
0	0
1	10
2	20
3	30
4	40
5	50
8	80



c



d

Fig.1. a) structure of NDC; b) coding of samples by ratio of sp^2/sp^3 phases; c) magnetic susceptibility; d) semiconducting properties from electrical conductivity (are confirmed by band gap from IR spectra).

Ando: «The topological materials»

- Yoichi Ando, Liang Fu. Topological Crystalline Insulators and Topological Superconductors:
  - From Concepts to Materials // arXiv:1501.00531 [cond-mat.mtrl-sci] (3 Jan 2015).
- But: Tamm & Topological insulators

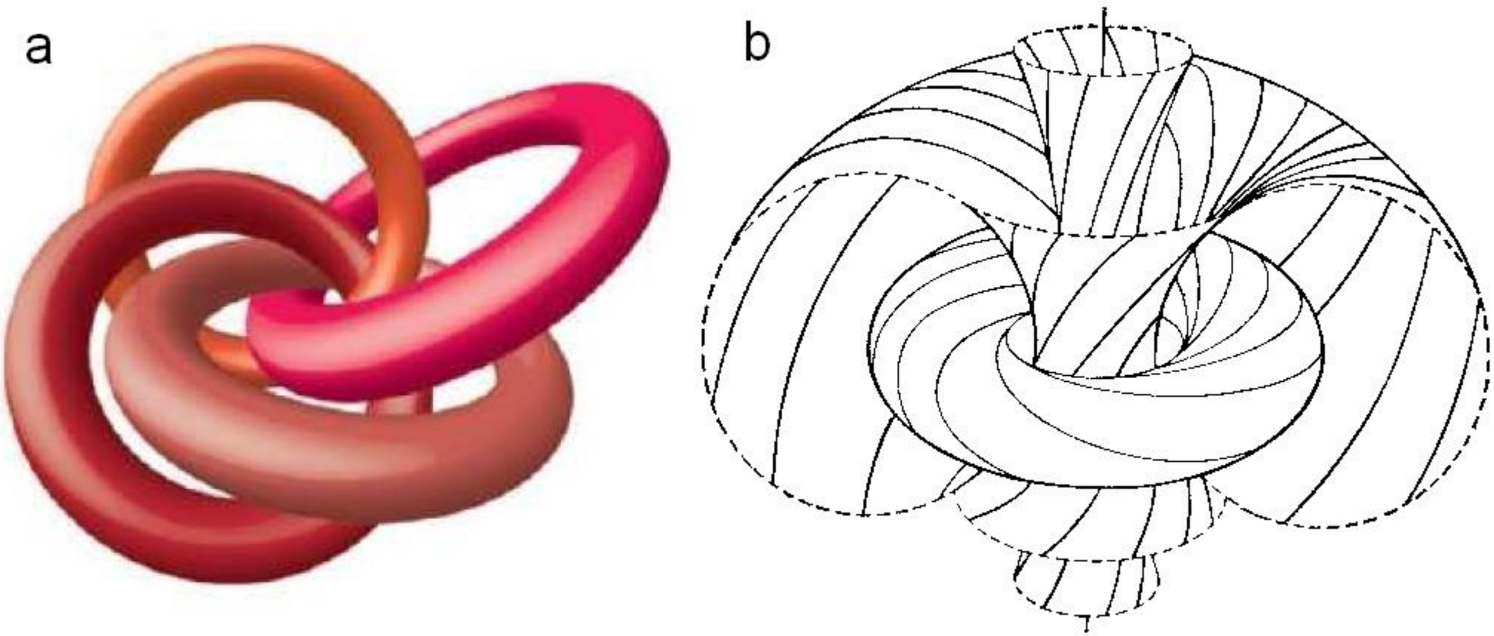
"Surface electronic states of insulator can be metallic" *I E Tamm 1932*

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

J Moore 2010

Topological insulators before Ando

Topological insulators – insulator inside, conducting on the surface.



Hoph map R3 $\subset$ S3 $\rightarrow$ 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 !**

A Model of ND T-Spin – Hopf Soliton

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

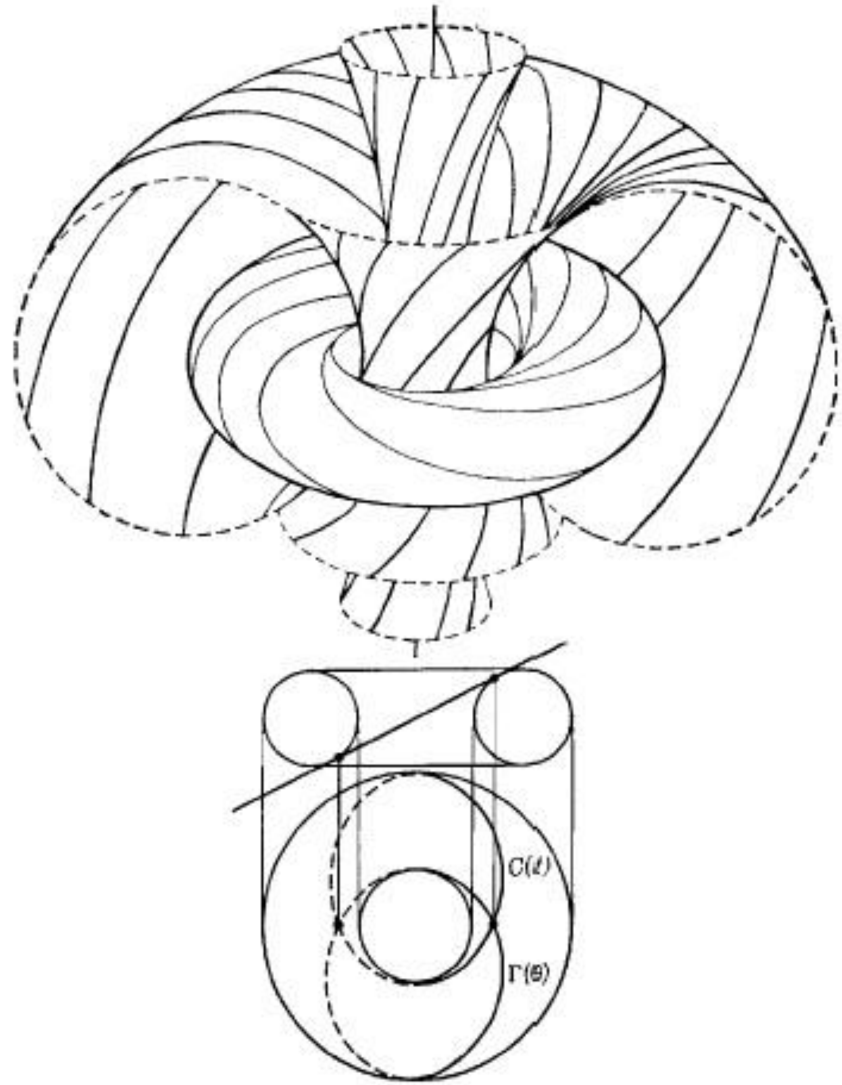
$$m_1(x,y,z) = \left(\frac{2}{1+r^2}\right)^2 [-y - 2xz + yr^2],$$

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

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

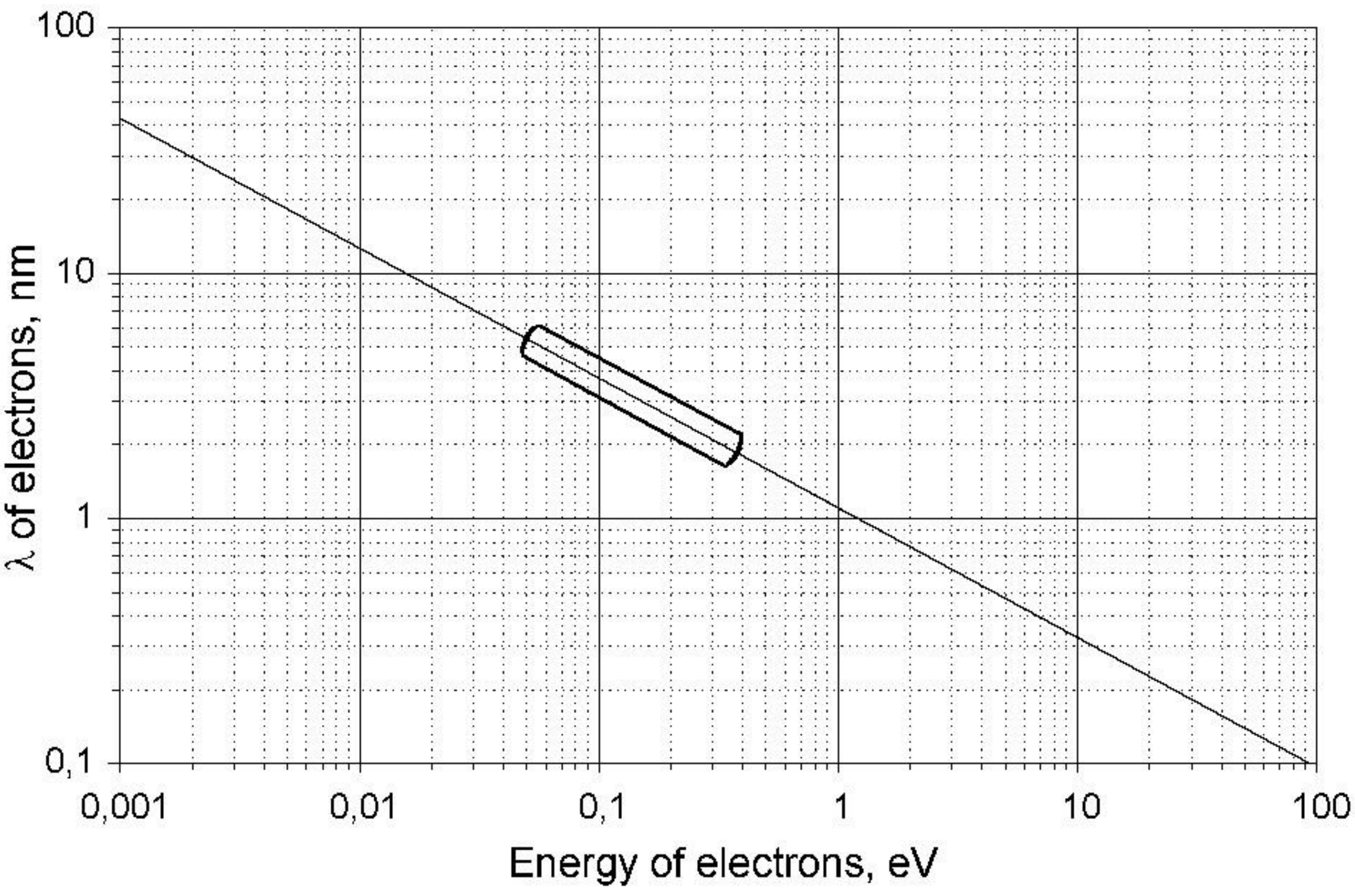
$$\mu = \frac{2}{1+r^2}$$

http://molpit.org/page/36 **Dipolic**



DQD is good defined by associated (de Broglie) waves of electron

The region of the thermodynamical stability is shown



C atoms ~ 1,100-25,000

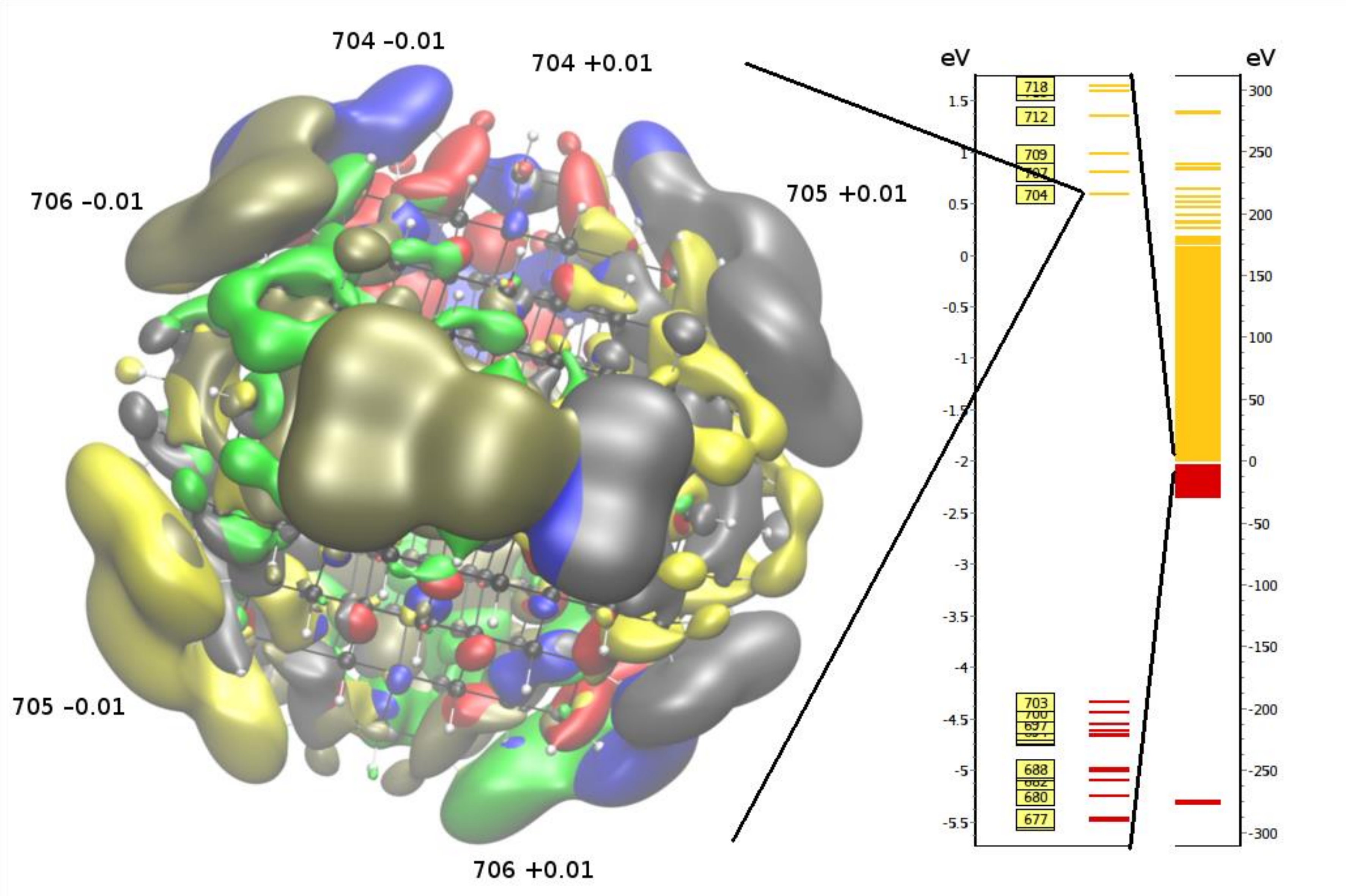
- 1.9-5.2 nm
- λ ~ 4 nm
- E ~ 0.1 eV
- *E, p;* $\nu=E/h$*;* $\lambda=h/p$*;* $p=m_e c$*;* $h=6,6748\cdot10^{-27}$.

Toward wave ψ-function of NDS

- 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 quantum of sound exists in DQD
- Free spin (unpaired electron) at NDS is T-spin

12 March 2004 http://molpit.org/?page=46

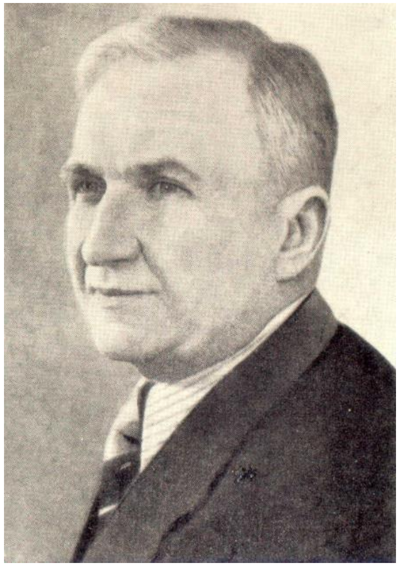
$C_{211}H_{140}$



704 -0.01
704 +0.01
706 -0.01
705 +0.01
705 -0.01
706 +0.01
eV
eV
718
712
709
704
703
697
688
680
677

Electronic-vibrational Tamm surface state of 5 nm diamond ball = KoLoBok

- 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 quantum of sound 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.



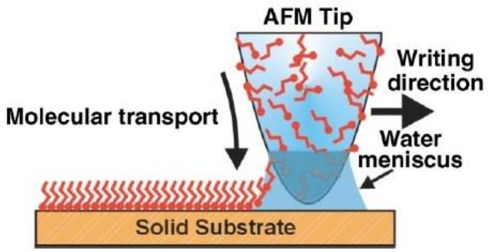
Igor Evgen'evich **Tamm**
(8/07/1895 – 12/04/1971)
1958 – Nobel Prize for the Vavilov-Cherenkov effect

Nd (> 20 nm) ≠ bun (2 ÷ 5 nm)

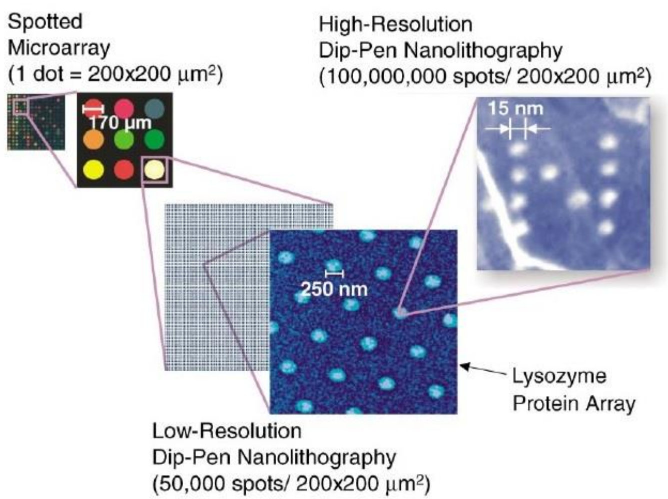
- Crystal field (> 20 nm) ≠ close packing (2 ÷ 5 nm)
- Nobody can take into account,
  - that crystal field ≠ close packing
  - 50 nm & 5 nm are strong differ matters!
- S Singh *et al.*, 2014, ND array + SiV centers by DPN
  - Spatially controlled fabrication of a bright fluorescent nanodiamond-array with enhanced far-red Si-V luminescence, Nanotechnology **25**, 045302.
- <u>ND dot diameter and height</u>
- 735 nm ± 27 nm and 61 nm ± 3 nm
- 820 nm ± 20 nm and, 245 nm ± 23 nm

“Dip-Pen” Nanolithography (DPN)

Chad Mirkin *et al.*, 1999, Science **283** (5402), 661-663 doi:10.1126/science.283.5402.661



Schematic representation of the DPN process.

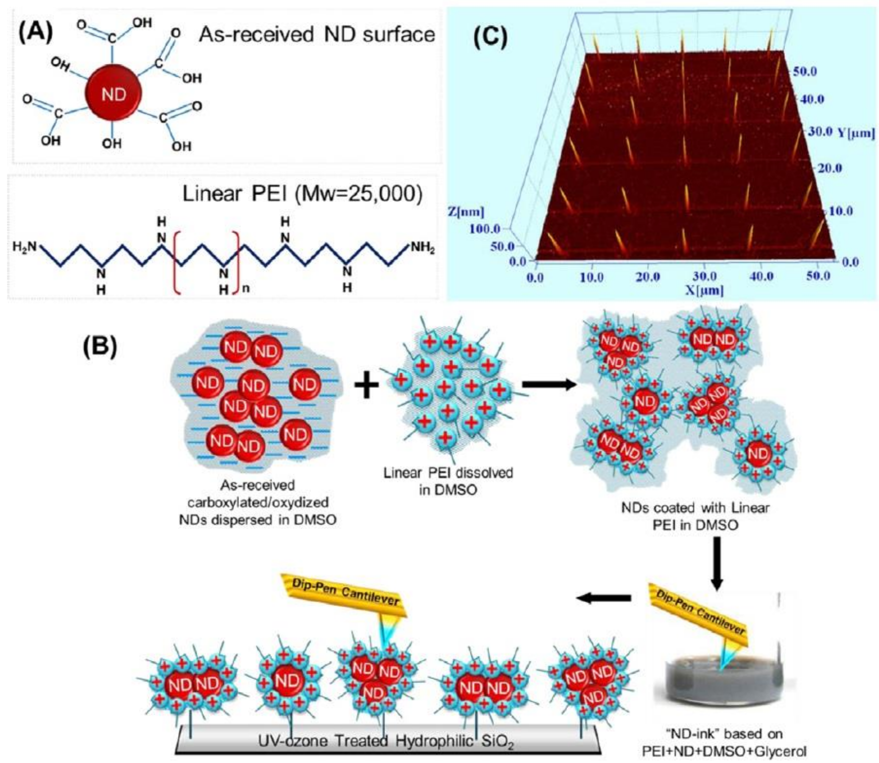


Schematic illustration of the power of DPN resolution in the context of biomolecular nanoarray fabrication.

S Singh *et al.*, 2014, ND array + SiV centers by DPN, Nanotechnology **25**, 045302. <u>ND dot diameter and height</u>

735 nm ± 27 nm and 61 nm ± 3 nm

820 nm ± 20 nm and, 245 nm ± 23 nm

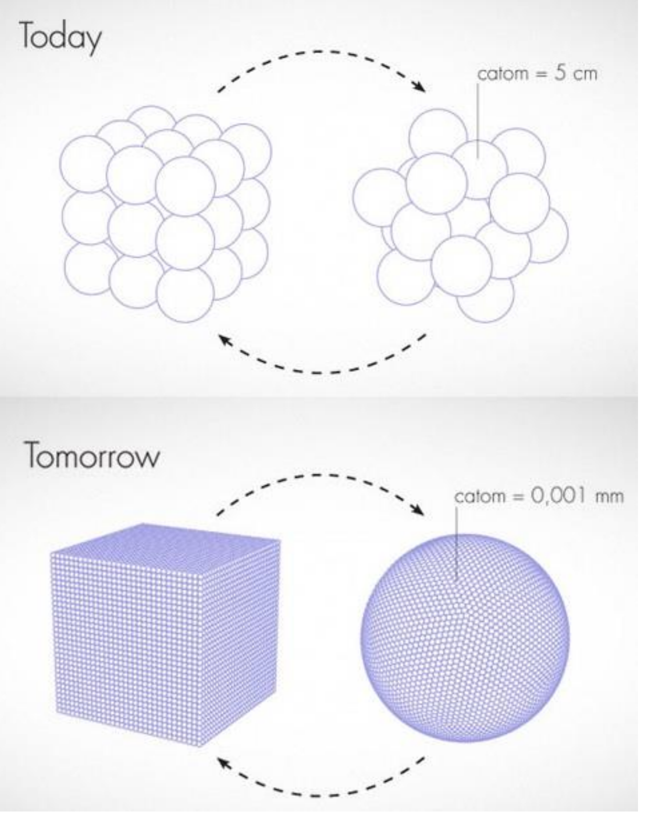


Kitchen Nanotechnology

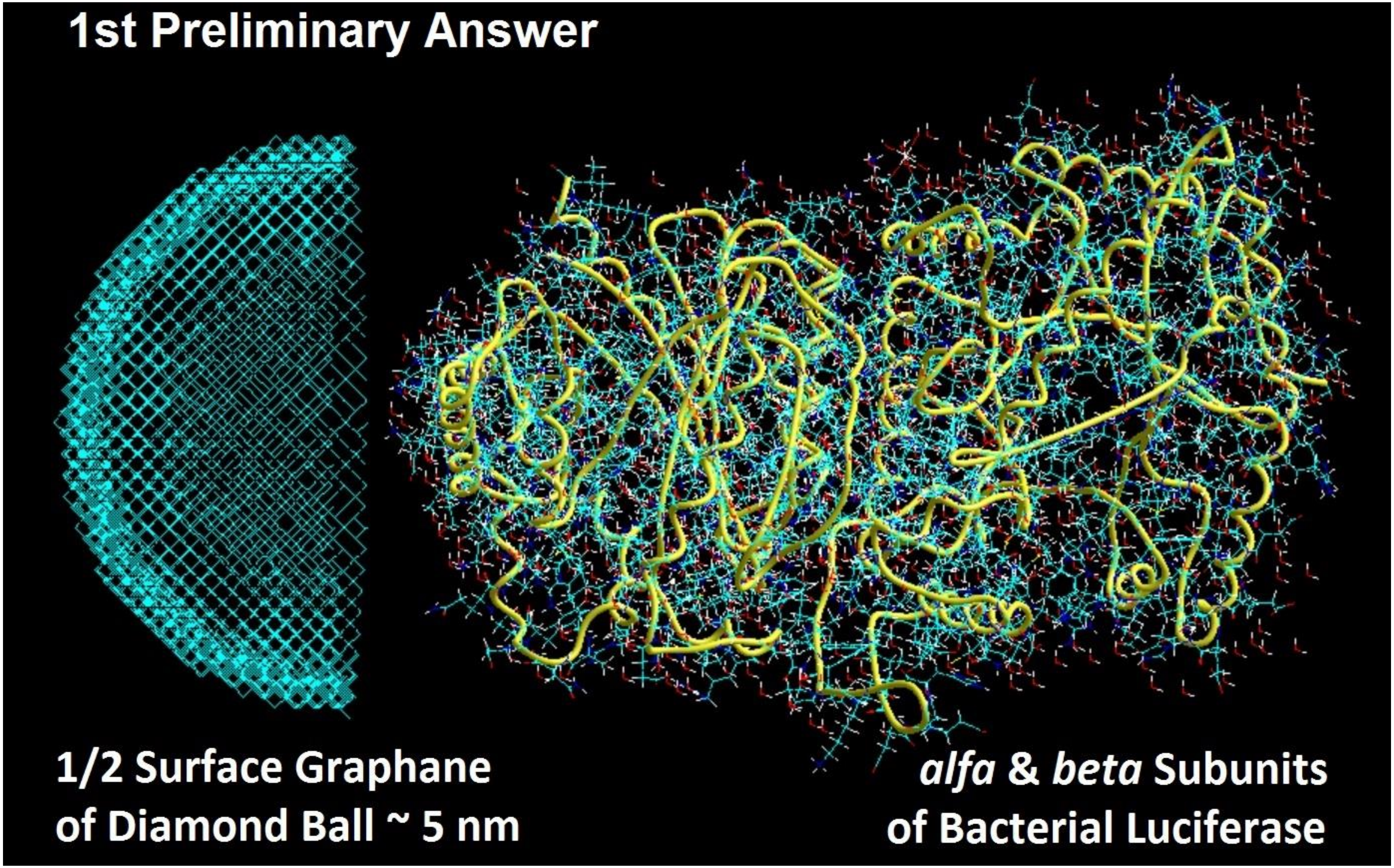
Old before
12 March 2004
https://www.youtube.com/watch?v=QDb83Y_OMts

Living Kitchen (2010)
The Future of NanoTech
http://michaelharboun.com/livingkitchen.html

https://www.youtube.com/watch?v=QDb83Y_OMts



1st Answer: Subsurface current induces the magnetic moment of diamond ball



Outlook

- For what and for whom all those buns?
- Quantum metrology
- Proposed redefinition of SI base units
  - 2011 $\rightarrow$ 2014 $\rightarrow$ 2018
  - Quantum units of Nature, Physical Nature!
- For us and for our happy life
  - Fundamental chemical & biological laws
  - Fundamental chemical & biological constants


SI International System of Units
base units
s
m
kg
A
K
mol
cd
defining constants
$\Delta\nu$
c
h
e
k
N_A
K_{cd}