Smart Diamond 2-5 nm

(Nature of Tamm states into particles from diamondoids to nanodiamond: theory, experiments and materials)

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Preliminary presentation of my planned manuscript to **Nanomaterials** mdpi

Background

20 years ago [1-3], 10 years ago [4-6] and a few preprints & papers in Russian:

1. P I Belobrov, I V Ermilov, A K Tsikh. Stable and ground state of dipolic // *Preprint TRITA/MAT-91-0020* (**1991**), Dept Math, Royal Inst of Technology, S-100 44 Stockholm, Sweden, 25 p. [PDF] molpit.org
2. 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 Sept., vol. **1**, p.235-269 (**2003**). [PDF] academia.edu {in Russian}
3. P I Belobrov. Nature of Nanodiamond State and Applications of Diamond Nanotechnology // Presentation at Cambridge University, UK (12th March **2004**). [PDF] molpit.org
4. Kiselev N. I. et al. Electrical and magnetic properties of nanodiamond and pyrocarbon composites // *Russian Journal of General Chemistry* 83 (11) , 2173-2181 (**2013**). Original Russian Text: N.I. Kiselev, D.A. Velikanov, S.B. Korchagina, E.A. Petrakovskaya, A.D. Vasil’ev, L.A. Solov’ev, D.A. Balaev, O.A. Bayukov, I.A. Denisov, S.S. Tsegel’nik, E.V. Eremin, D.A. Znak, K.A. Shaikhutdinov, A.A. Shubin, N.P. Shestakov, N.V. Volkov, S.K. Gordeev, P.I. Belobrov (2012), published in Rossiiskii Khimicheskii Zhurnal, (**2012**), Vol. 56, Nos. 1–2, pp. 50–57. https://doi.org/10.1134/S1070363213110376
5. IA Denisov, AA Zimin, LA Bursill, PI Belobrov. Nanodiamond collective electron states and their localization // *Preprint arXiv:1307.4633* (24 Jul 2013). https://doi.org/10.48550/arXiv.1307.4633
6. Belobrov P.I. Self-organization of low-dimensional carbon structures in diamond electronics // «High-tech for Russian Industry». M .: BMSTU, 220-235 (2015). [PDF] academia.edu

Outlook

- Def.: DCs = 1st Diamond Condensed state
- What is diamondoids? Def.: n-mantanes
- Diamondoids, **DC** (2-5 nm), ND (CD < 100 nm)
- Aggregates nDC ($n \sim 10^5$); solid NDC ($N \sim 10^{19}$)
- **NDC** properties depend from γ = mass ratio of (**T_S/DC**)
- We'll compare the experiments with theory that allows to conclude: **NDC** is
  - solid bulk porous semiconductor
  - new pure carbon solid with controlled band structure
  - novel member of topological materials family.
- Discussion all features of Tamm surface states **T_S**

We disclose the DC mist

- The diamond – pyrocarbon composite **NDC**
- **DC** is **Diamond Compass** is introduced by us
- The 10^{19} Diamond Compasses is **smart NDC** semiconducting porous bulk material
- **NDC** was made & patented ~3 decade ago
  - 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**).

DC = diamond 2-5 nm

- «Diamond is a metastable allotrope of carbon».

[*AP Rudenko & II Kulakova,* 1993]

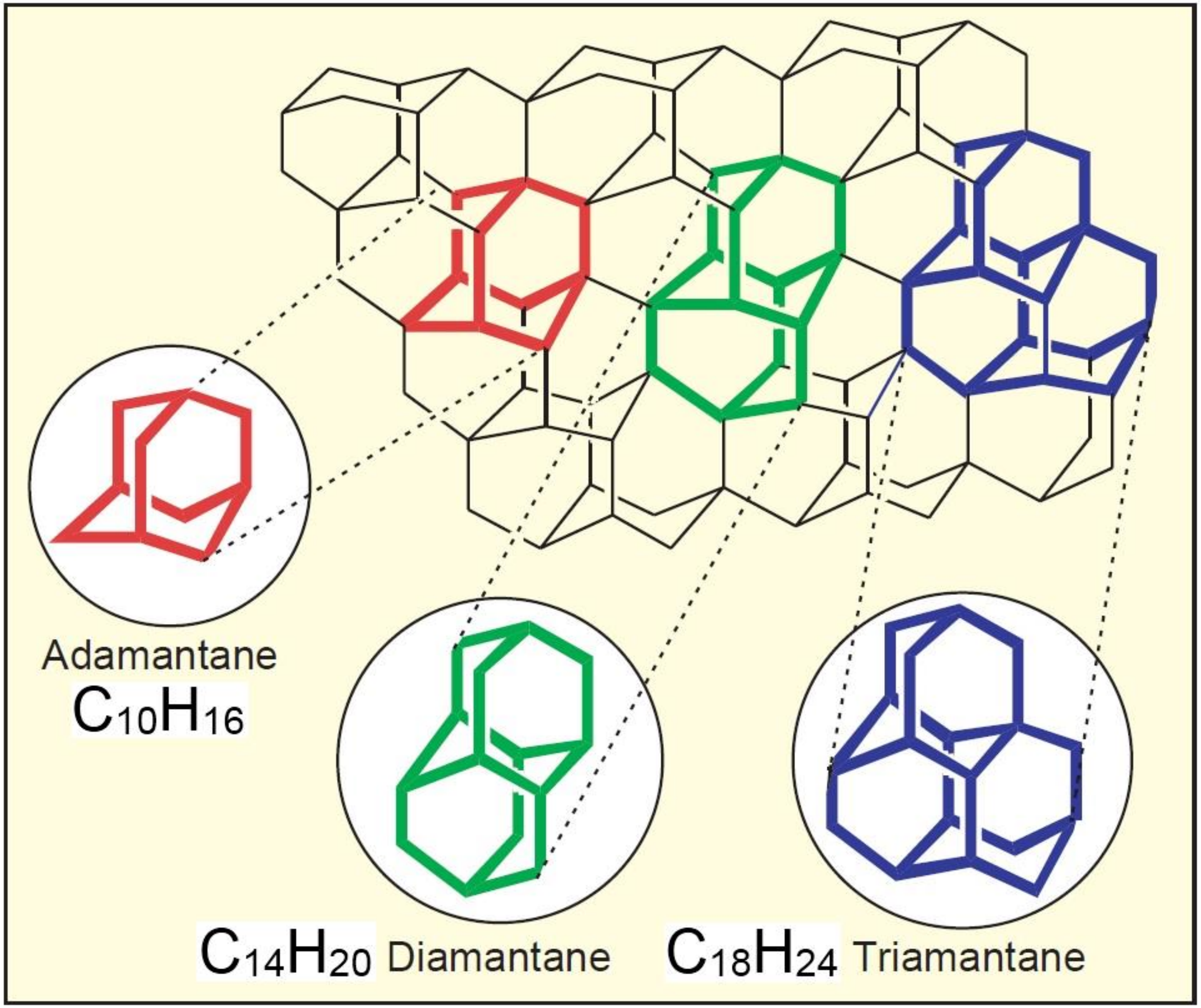
- «Monocrystalline diamond with particle size less than 100 nm (designated as nanodiamond) has been widely studied during the past decades».

[*Y Zhang*, 2018]

DC is a most stable sp^3 allotrope of carbon.

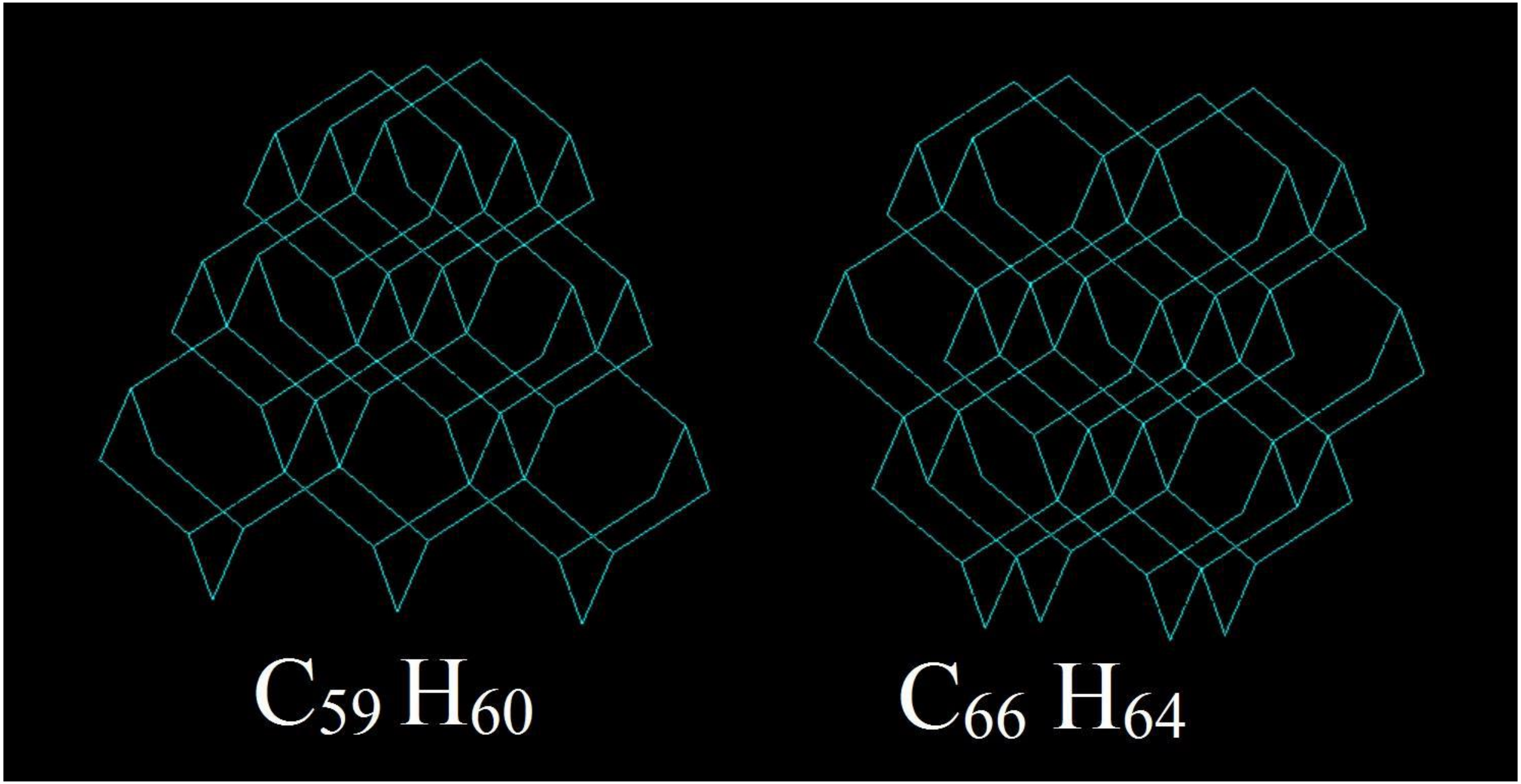
- DC exists between **organic diamondoids** ($C_{10}H_{16}$, $C_{59}H_{60}$, $C_{66}H_{64}$, etc.) and **inorganic nanodiamond** (C_nH_m, $n>10^4$, $m<n/10$).
- ND, size < 100 nm; Diamondoids = n-mantanes

n-mantanes [*A Marchand*, 2003]

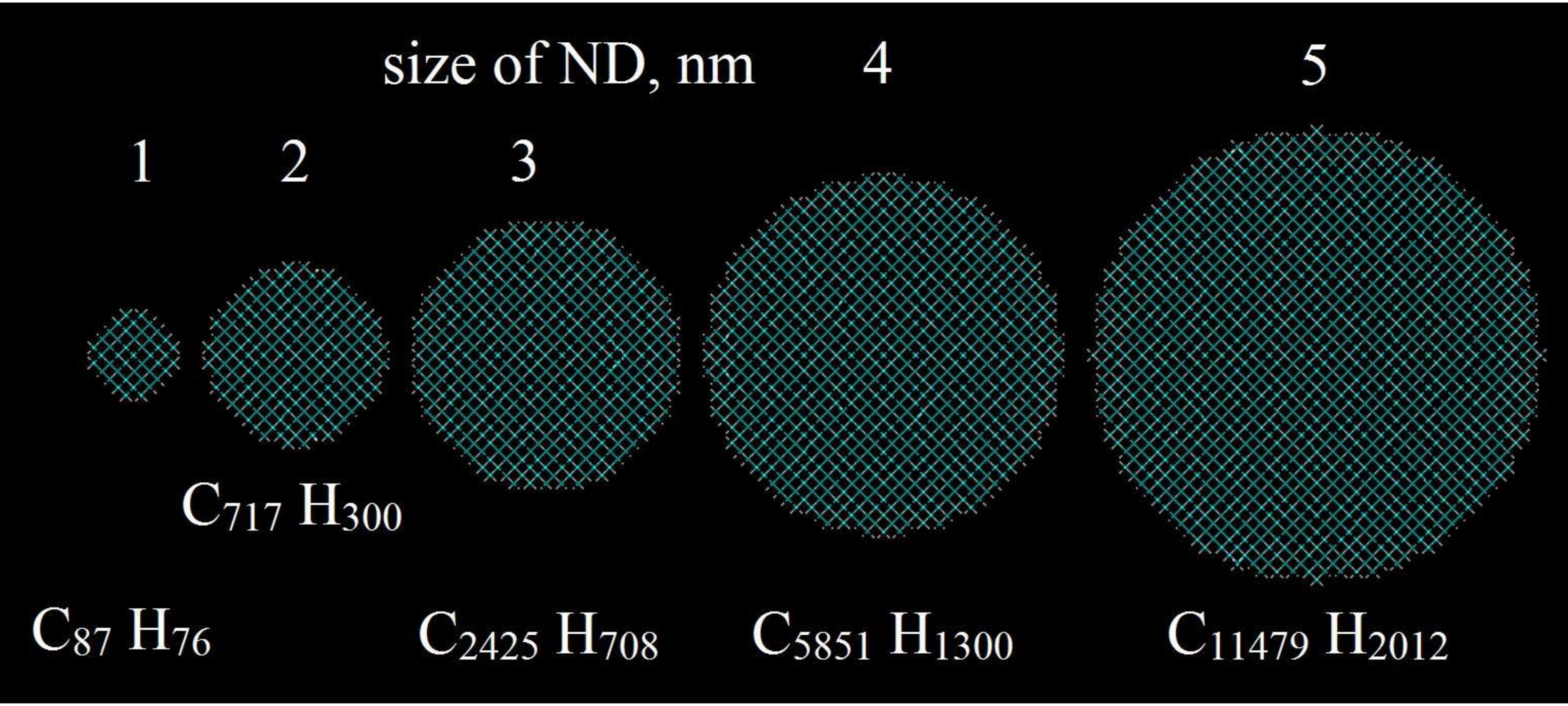


The transition across $C_{60}H_{60}$

$C_{59}H_{60} \leftrightarrow C_{66}H_{64}$

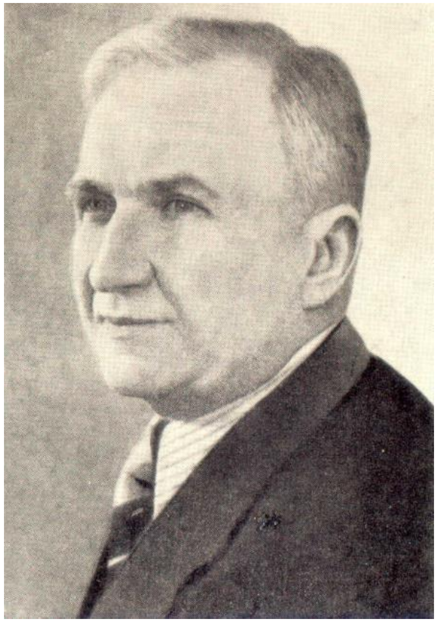


A few structural levels from diamondoids to the DCs (1st diamond condensed state) or DC (diamond compass)



Electronic-vibrational de Broglie – Tamm (T-spin) surface state of diamond compass

- 1925 – Quantum theory of paramagnetism – **contribution of the orbital moment**
- 1929 – The concept of vibrational quanta in solid (later called **phonons** by Frenkel) $\Rightarrow$ *Idea of quantum of sound at DC*
- 1933 – «**Tamm levels**» - certain electron states were due to the existence of the surface $\Rightarrow$ *1D & 2D ё states at DC*
- 1934 – Any system with **virtual separated charges** should have **magnetic moment** $\Rightarrow$ *Nature of free spin at DC*
  - 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.



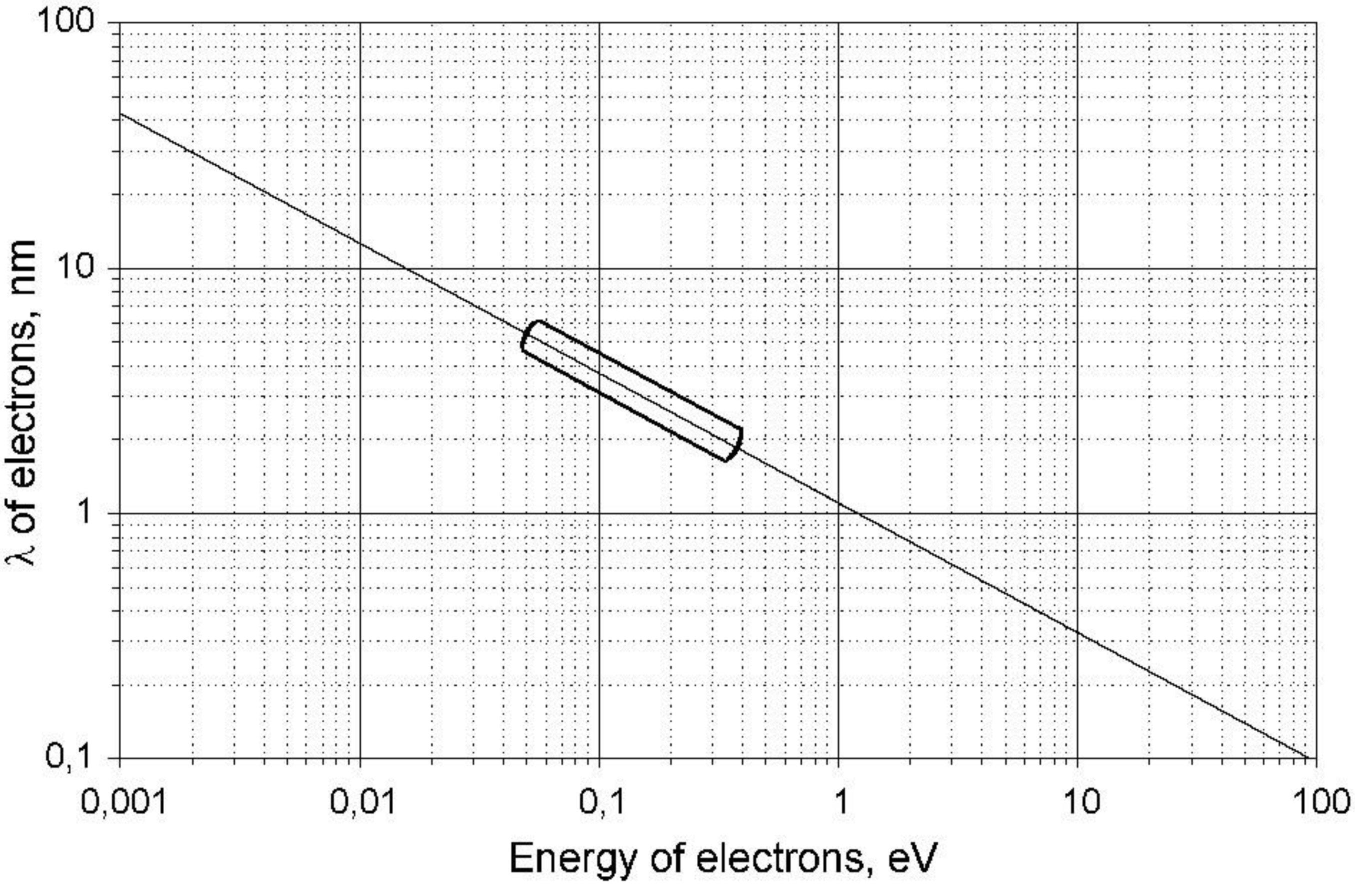
Igor Evgen'evich **Tamm**
(8/07/1895 – 12/04/1971)
1958 – Nobel Prize for the Vavilov-Cherenkov effect

Classical papers of Tamm

- Ig. Tamm. Zur Quantentheorie des Paramagnetismus. *Z. Phys.* **32** (1), 582-595 (1925). ***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***

Tamm quasi-particle is de Broglie waves of electron at T-layer (T-spin)

The region of the thermodynamic stability of DC is shown



^{13}C ~ 12 ÷ 270

^{12}C atoms **~**

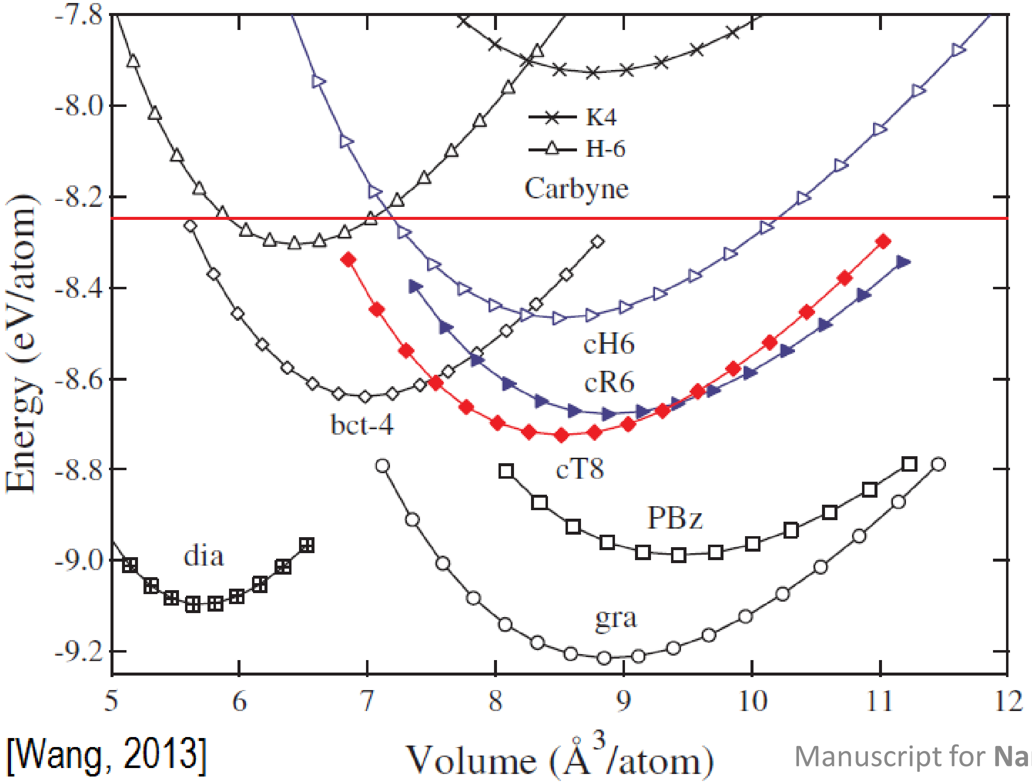
1,100 ÷ 25,000

- 1.9-5.2 nm
- λ ~ 4 nm
- E ~ 0.1 eV
- *E, p; ν = E/h.*

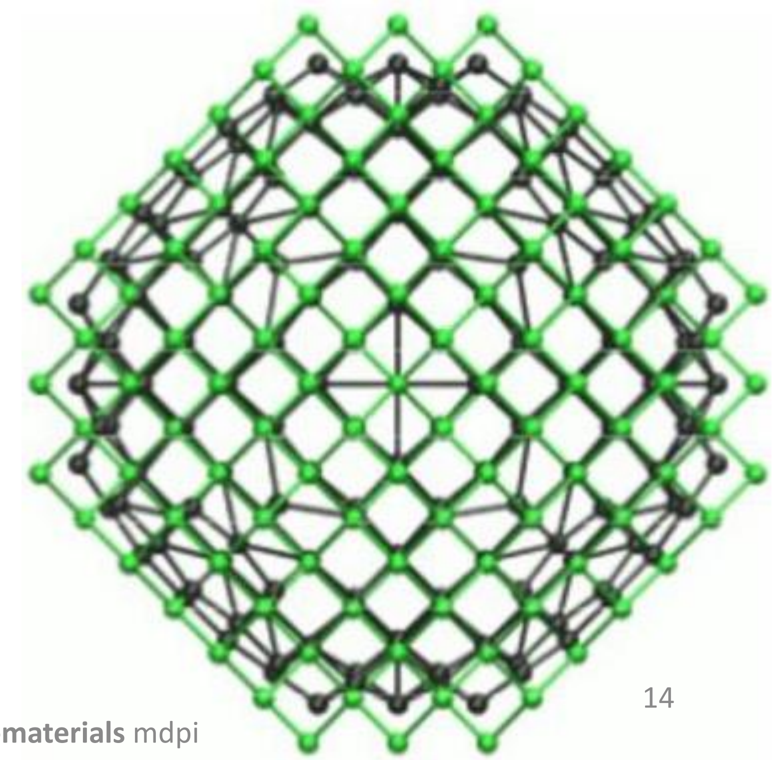
Carbon in Nature: ^{12}C 98,93 % & ^{13}C 1,07 %.

CD (> 20 nm) ≠ DC (2 ÷ 5 nm)

- Cubic Diamond (> 20 nm) ≠ close packing DC (2 ÷ 5 nm)
- Urgent to take into account,
  - **that crystal field ≠ field of close packing structure**
  - **50 nm CD & 2-5 nm DC with T_S are strong differ matters!**



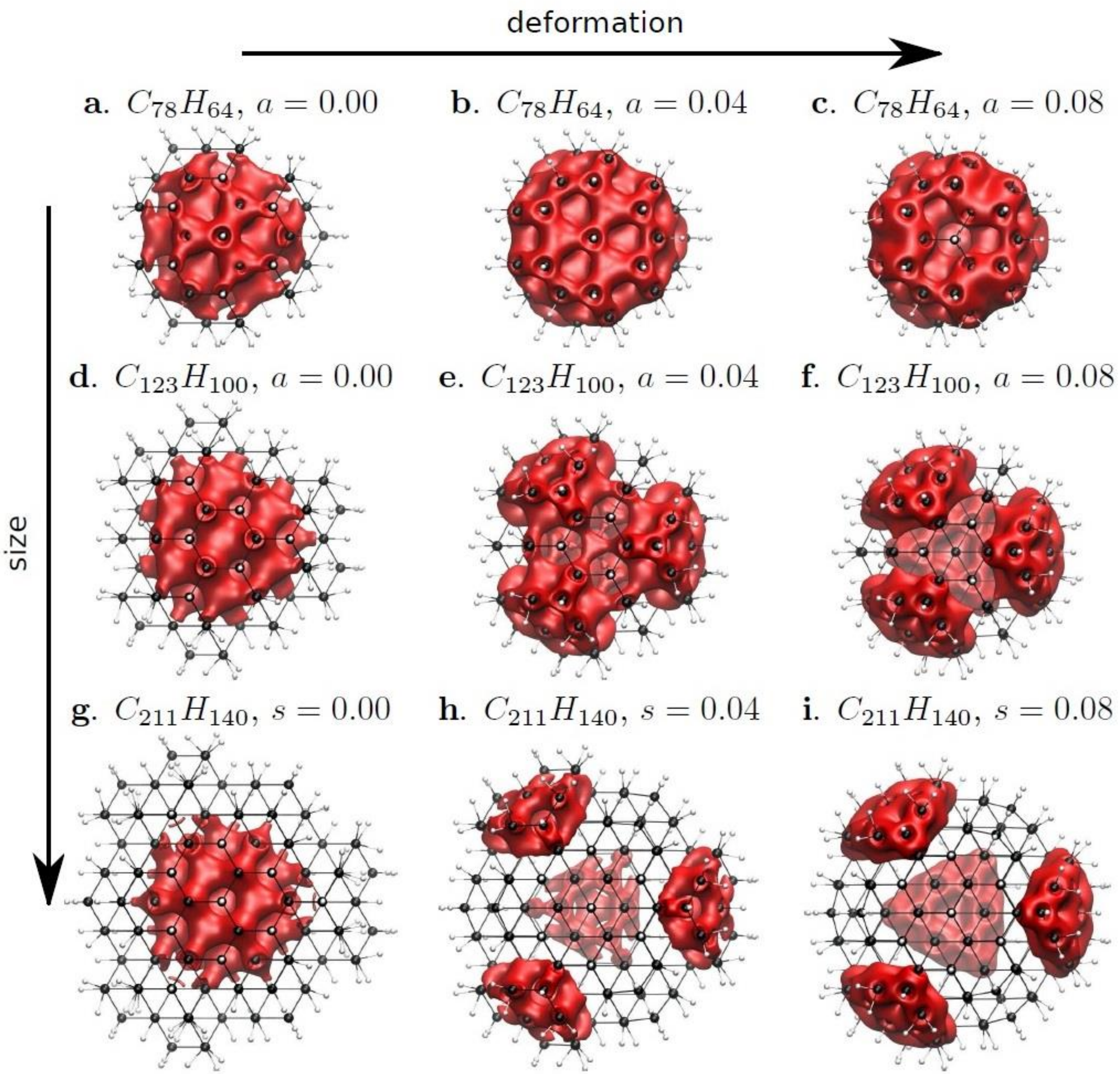
[Wang, 2013]



Wavefunctions isosurfaces (0.02 a.u.) for the lowest bonding orbital of diamond compass of three sizes:

- **(a–c)** C_{78},
- **(d–f)** C_{123},
- **(g–i)** C_{211}

and three fixed compressions

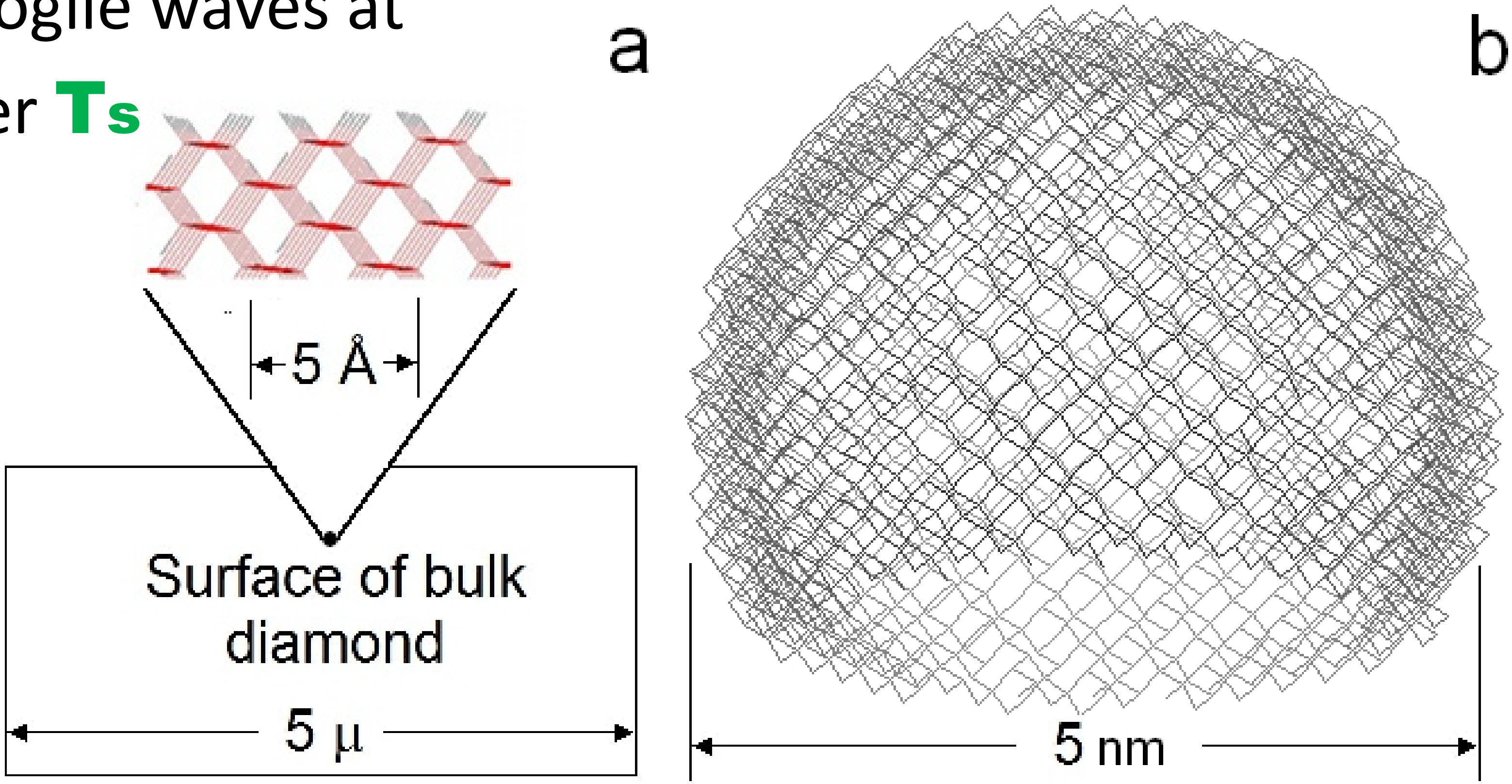


Denisov IA et al. *Preprint arXiv:1307.4633* (24 Jul 2013).

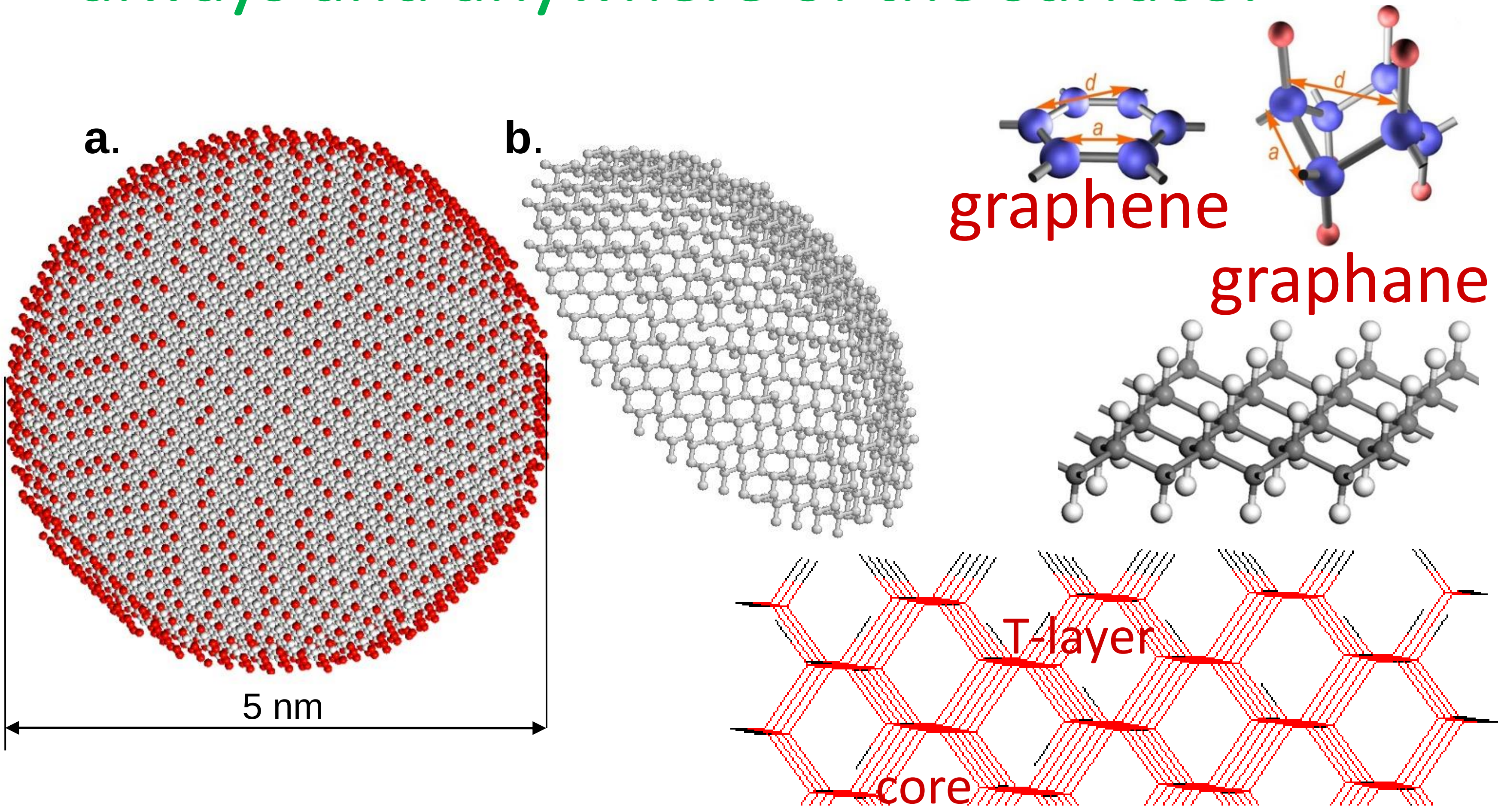
a) T-layer model = **Ts** of DC surface
b) T-layer shell **Ts** is in any diamond

de Broglie waves at

T-layer **Ts**



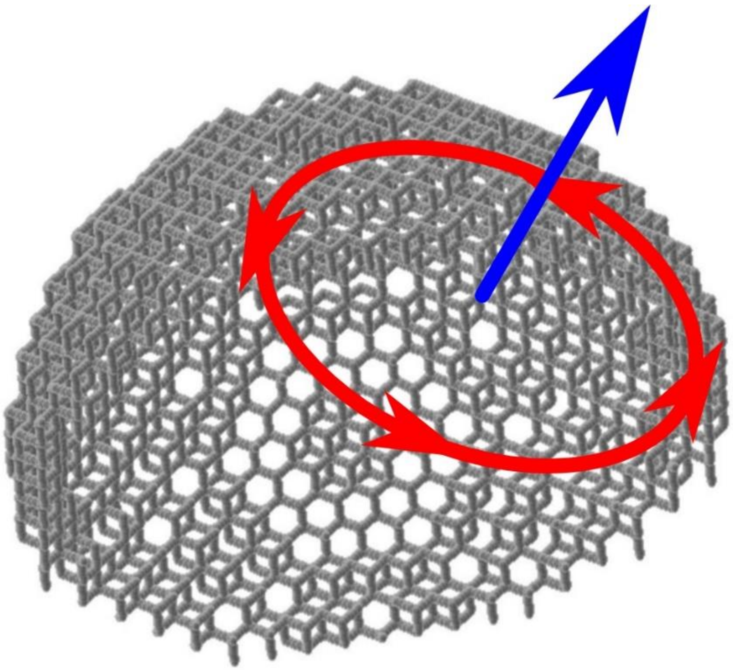
Any diamond encrusted by T-layer **Ts** always and anywhere of the surface!

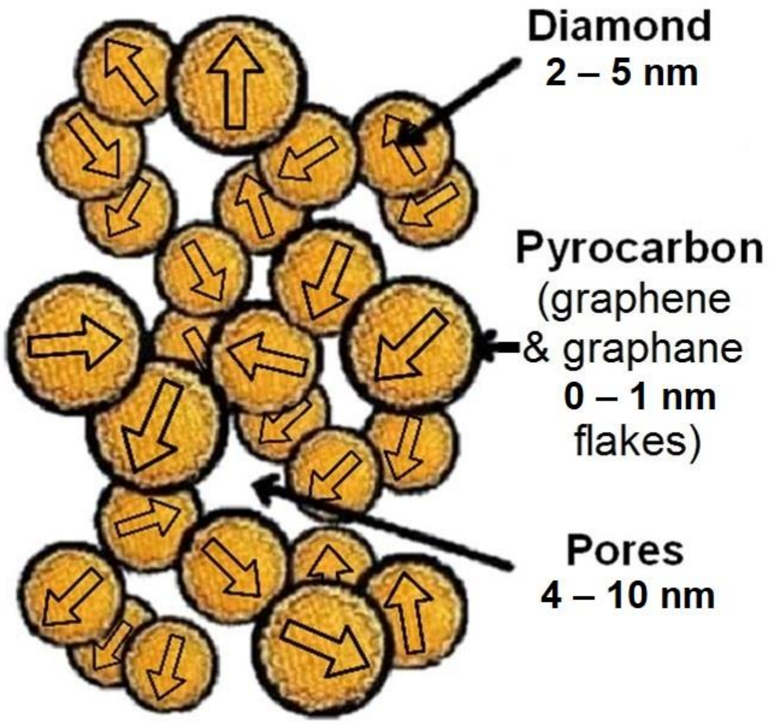


a. Diamond ball 5 nm, terminal atoms marked.

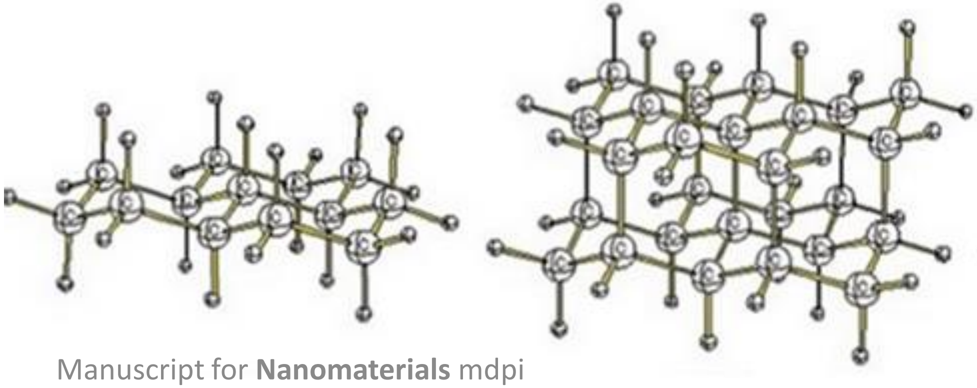
b. T-layer **Ts** incrustation (extracted from **a**) = sheet from **semi-graphane**

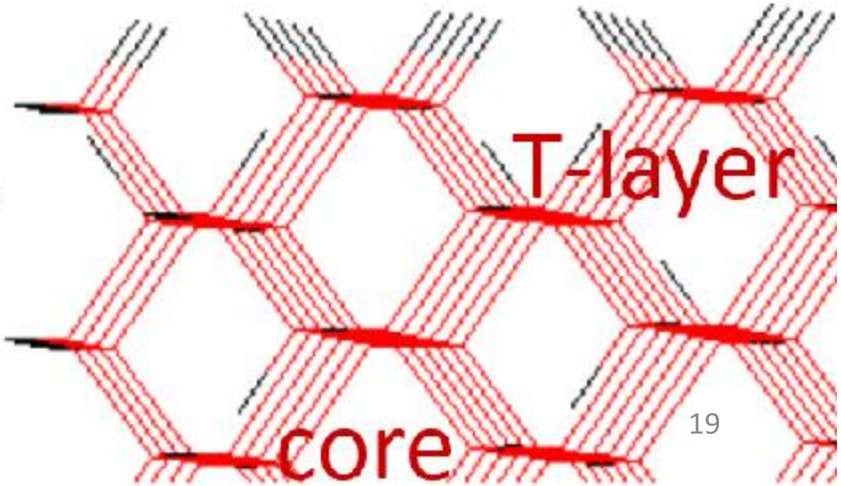
Fractional dimensions of ë density





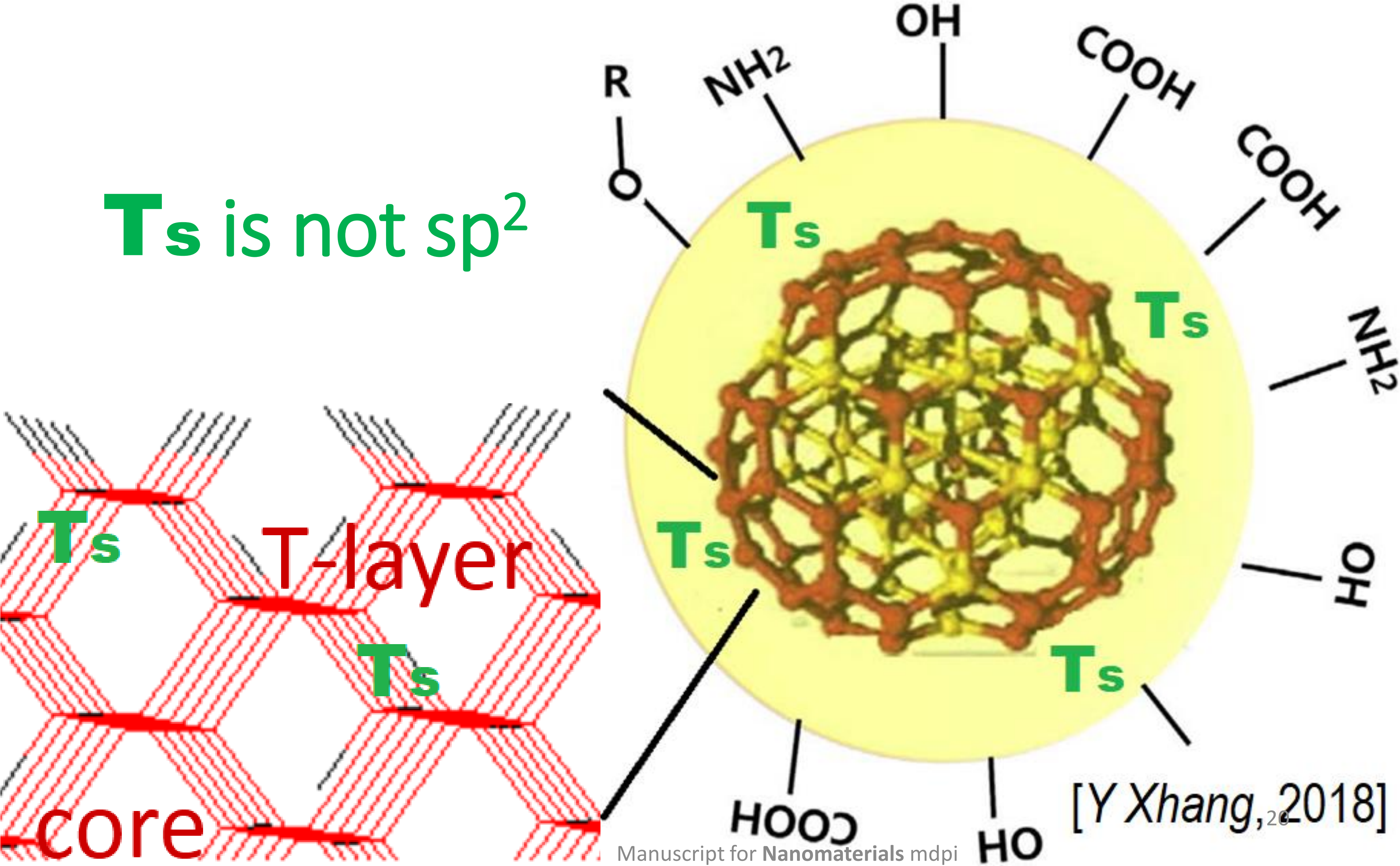
Strong curvature & incommensurate of nearest layers in carbon structures





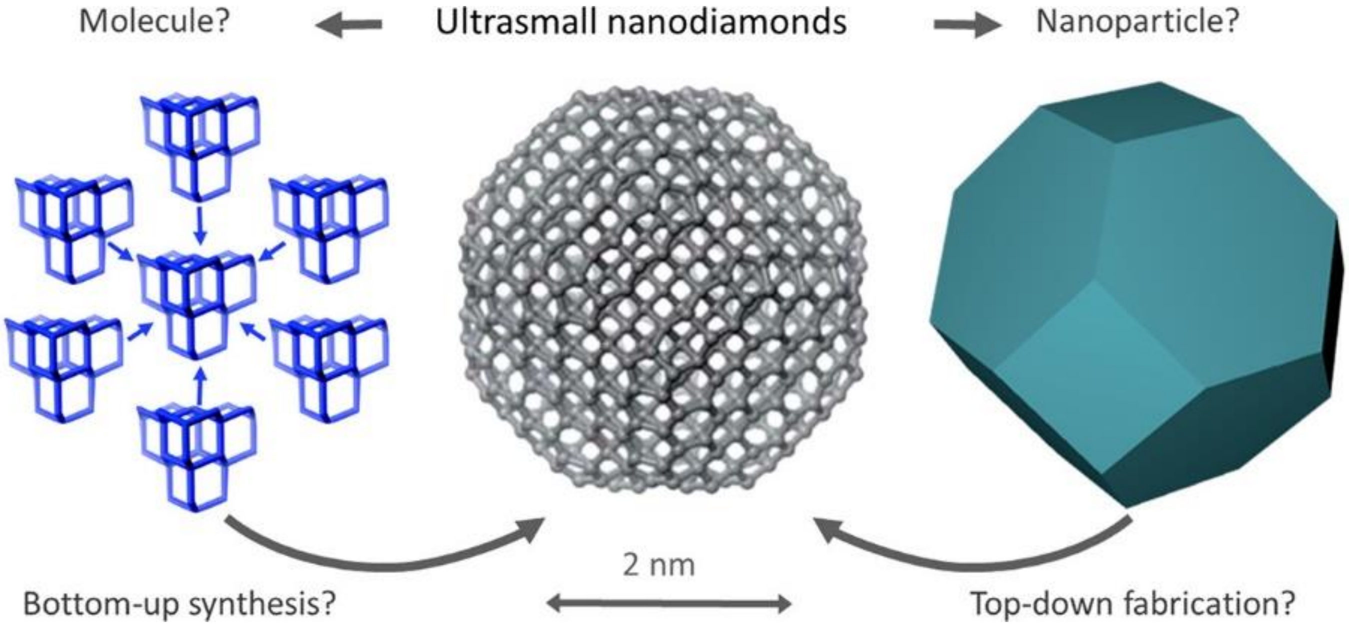
Structure of Tamm surface **Ts**

Ts is not sp^2



[Y Xhang, 2018]

SLY Chang, P Reineck, A Krueger, and VN Mochalin. **U**ltra**S**mall **N**ano**D**iamonds: Perspectives and Questions // *ACS Nano* 16 (6), 8513–8524 (2022).



«Yet today, we are **unable to accurately control** nanodiamond composition at the atomic scale, **nor can we reliably create and isolate particles** in this size range. In this perspective, we discuss recent advances, challenges, and opportunities in the synthesis, characterization, and application of **USND**. We particularly focus on the advantages of bottom-up synthesis of these particles and critically assess the physicochemical properties of **USND**, which significantly differ from those of larger particles and bulk diamond.»

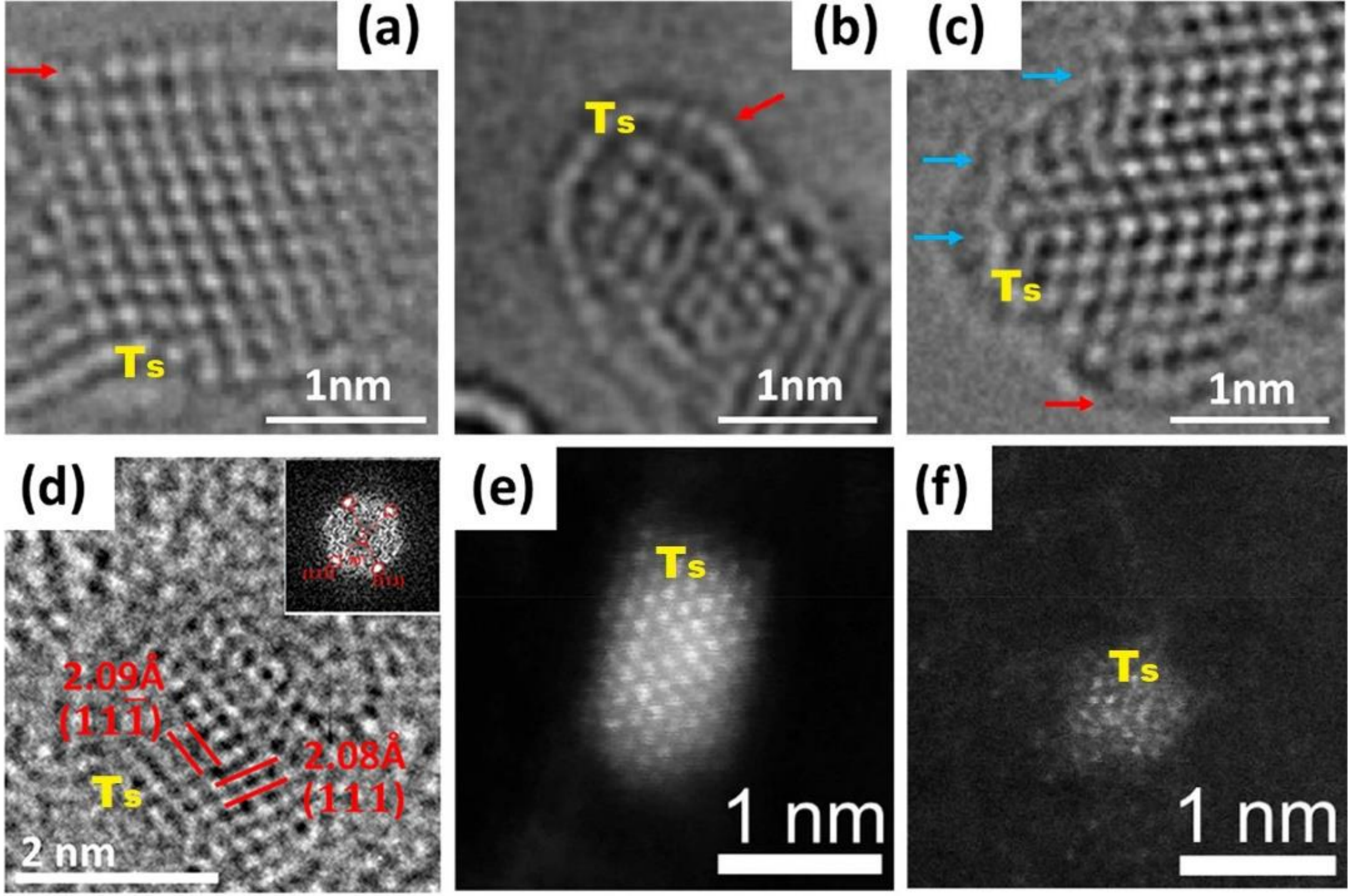


Fig. 5. Imaging of NDs: (a–c) HRTEM images of DNDs of varying sizes, showing the diamond structured core and reconstructed surfaces (red arrows). Blue arrows indicate the twin planes within the particle; (d) HRTEM image and its corresponding amplitude of Fourier transform (inset) of a ~2 nm USND synthesized in mild conditions from nitrated naphthalene. The USNDs are embedded in amorphous carbon and residual precursors; (e,f) annular dark-field scanning transmission electron microscopy image of 1−2 nm NDs showing only the core of the particles [SLY Chang et al. // *ACS Nano* **16**, 8513 (2022)].

Лето

A model of T-spin – Hopf Soliton

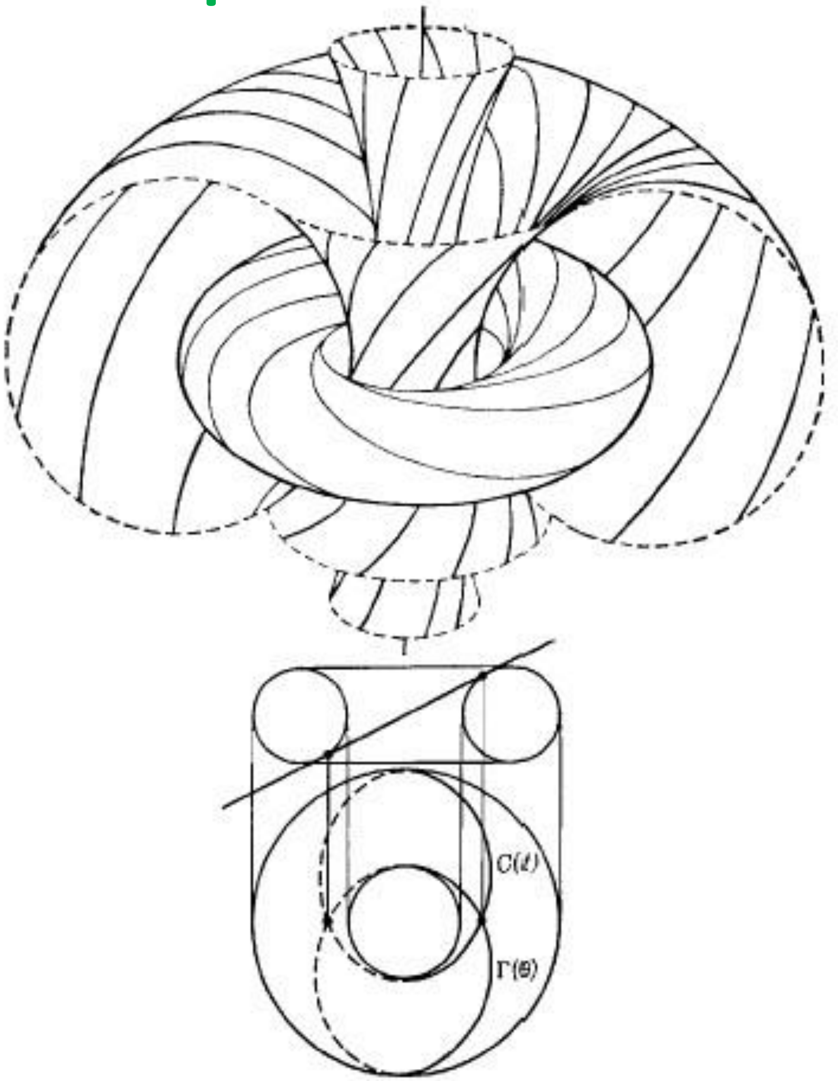
$$\boldsymbol{m}(x,y,z)$$

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

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

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

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

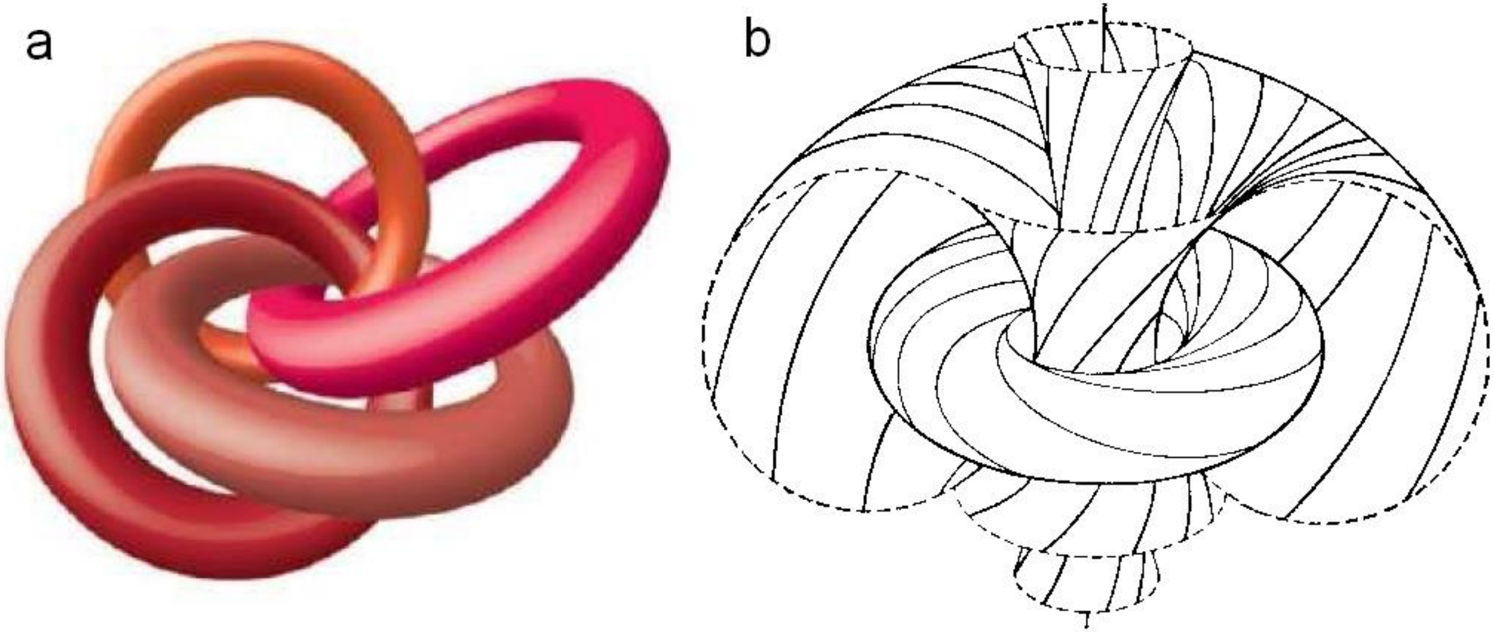


PI Belobrov, IV Ermilov, AK Tsikh. Stable and ground state of dipolic // *Preprint TRITA/MAT-91-0020* (**1991**), Dept Math, Royal Inst of Technology, S-100 44 Stockholm, Sweden, 25 p.

PI 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 Diamond Compass!**

Topological insulators

Topological insulators – insulator inside, conducting on the surface.



Hopf map $R^3 \subset S^3 \to S^2$

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

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

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).
- Tamm & Topological insulators

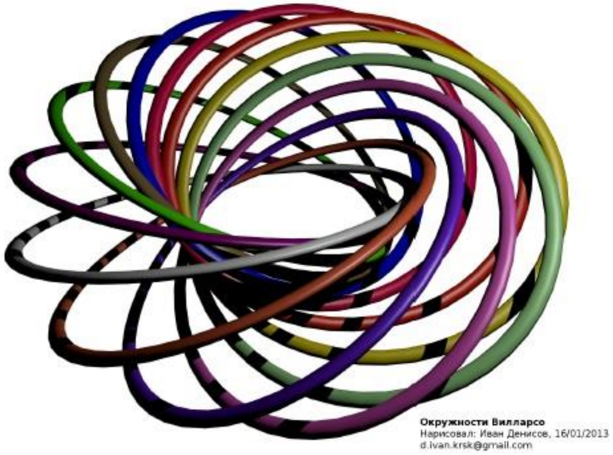
«Surface electronic states of insulator can be metallic» *I E Tamm* ***1932***

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

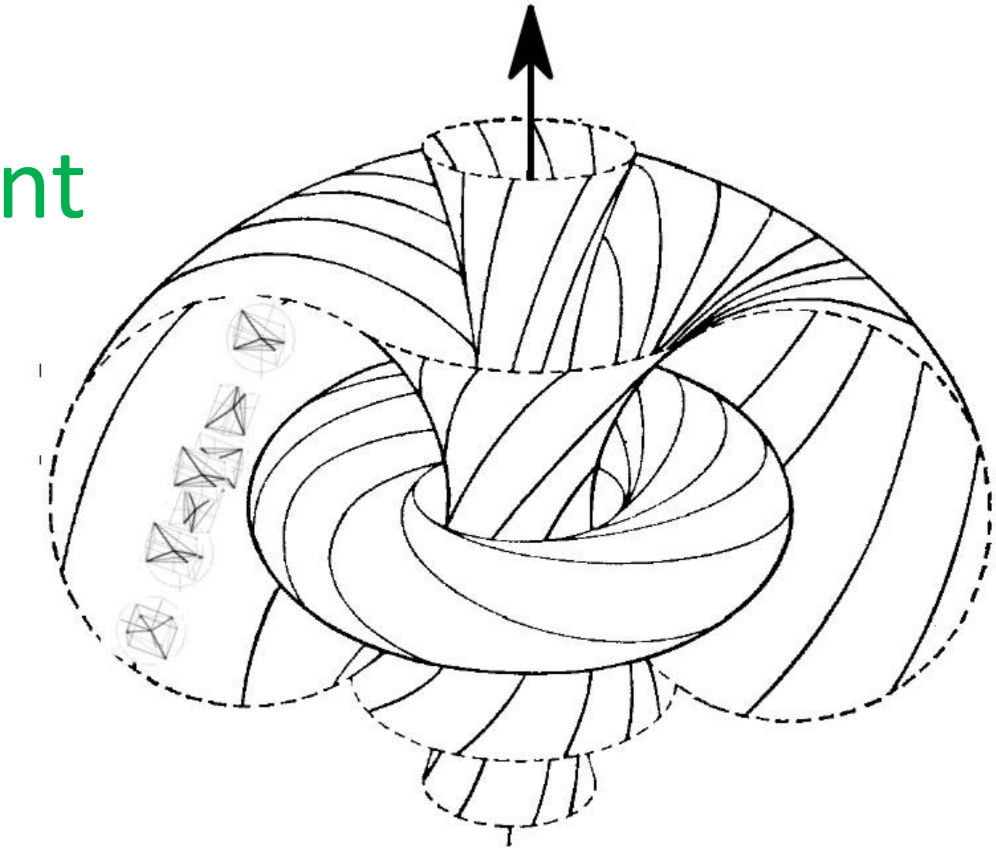
J Moore ***2010***

Paramagnetic nature of diamond compass is Feynman trajectories

Pauli spin current

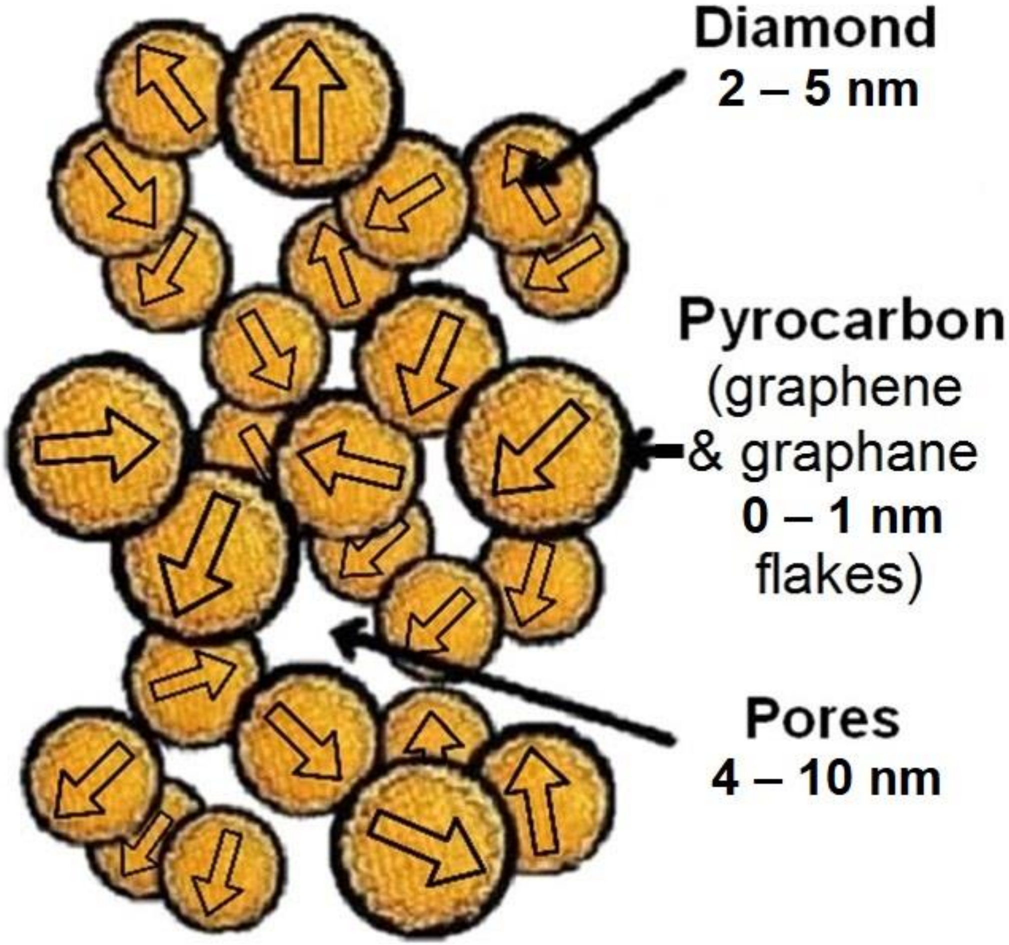


Окружности Вилларсо
Нарисовал: Иван Денисов, 16/01/2013
d.ivan.krsk@gmail.com



Quantum Nonlocal Polarizability of Diamond Compass?

3 phases: Diamond, Graphane, Pores

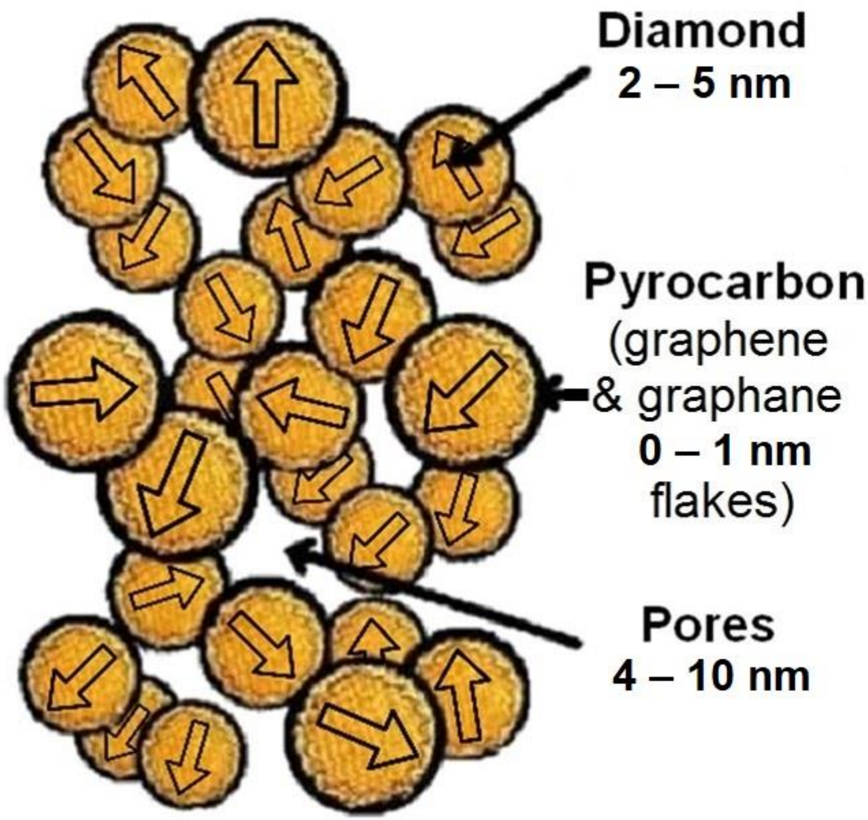


- *All three phases have equal rights and self-consistent*

T-spins into NDC

Solid porous NDC (N ~ 10^{19})

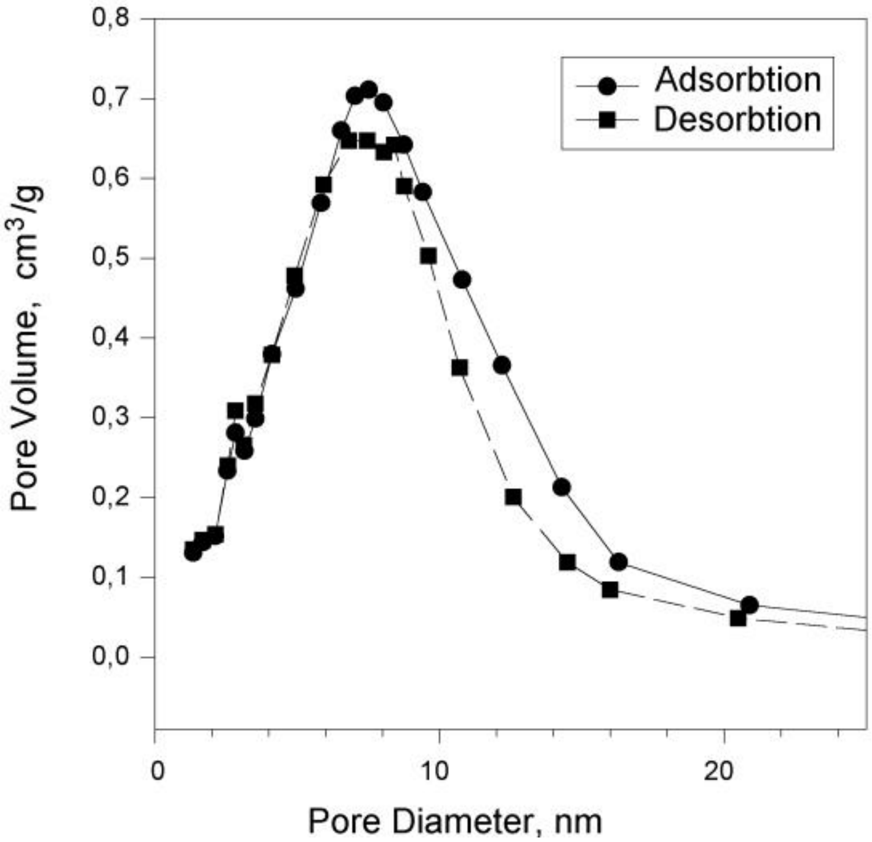
- New family of smart bulk nanomaterials
- High level of properties



Diamond
2 – 5 nm

Pyrocarbon
(graphene
& graphane
0 – 1 nm
flakes)

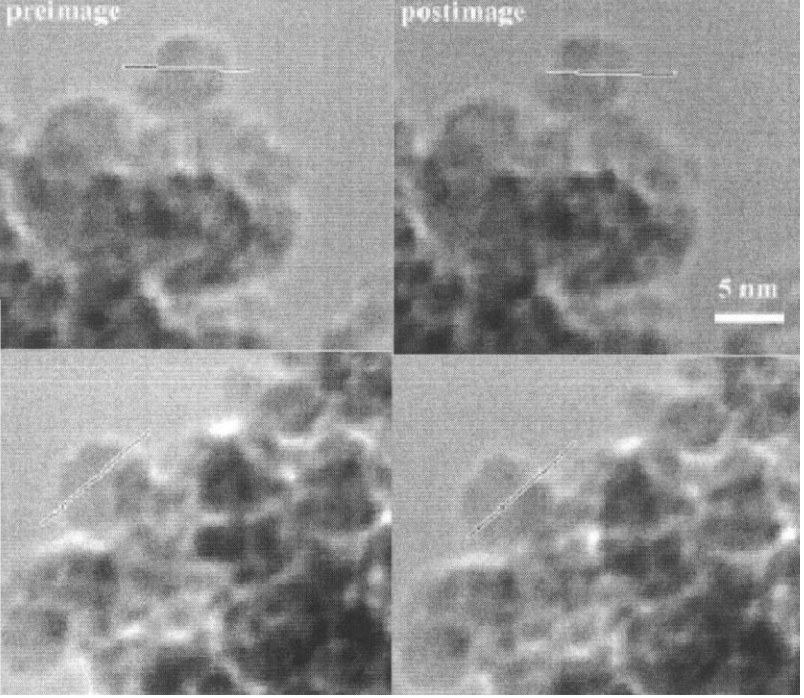
Pores
4 – 10 nm



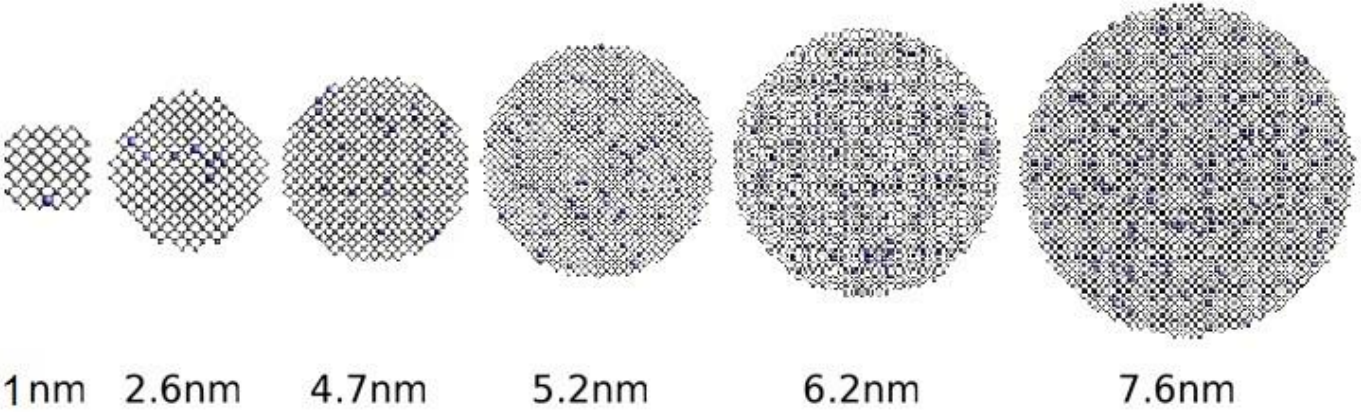
Pore size distribution

N_2, T = 77K, Gordeev (1998)

Line scan PEELS for low-loss and core loss energy ranges



Pre- and post-PEELS images, using to control quality of specimen drift, contamination and beam damage during data collection

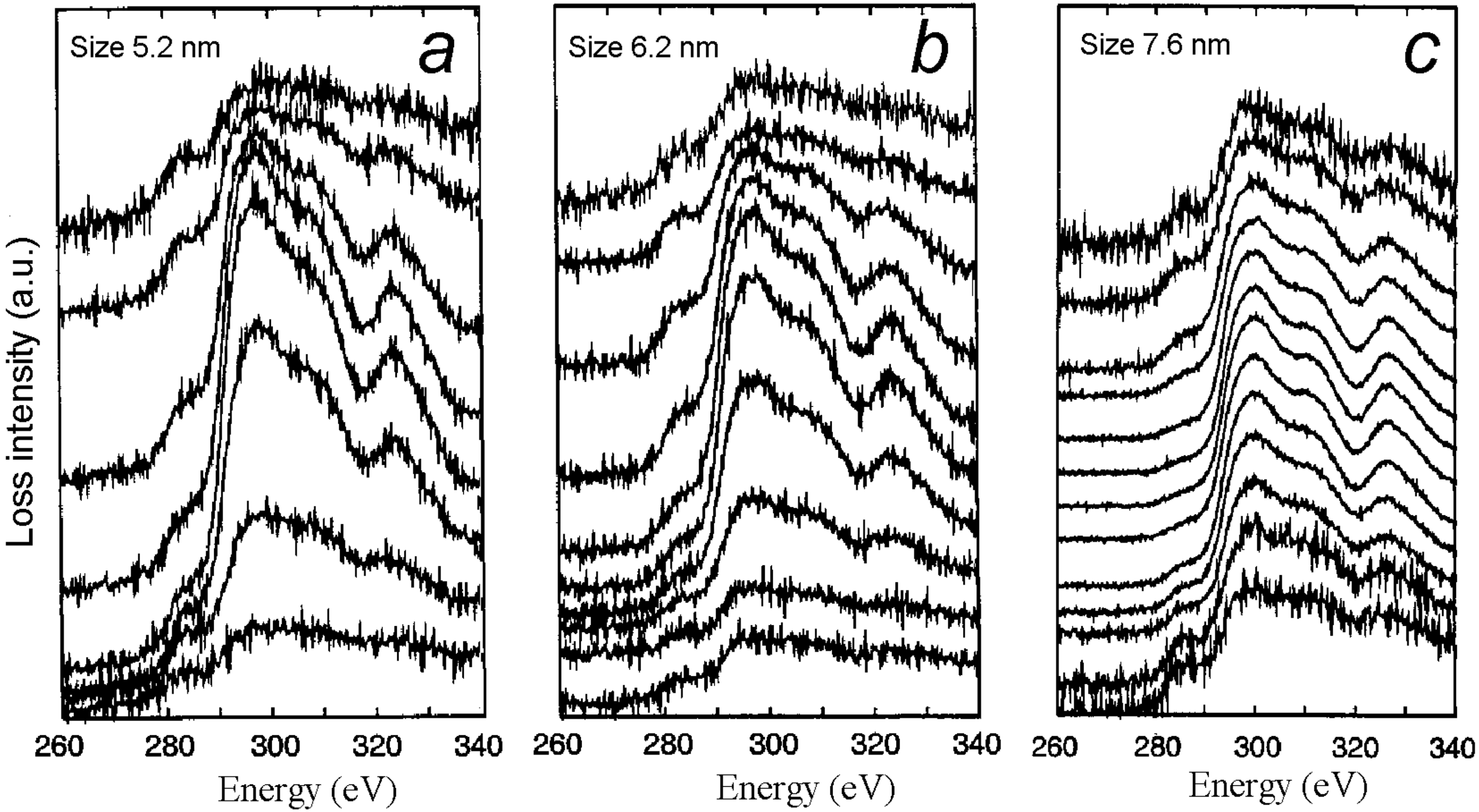


At the low-loss range surface (12–24 eV) & bulk (30–33 eV) plasmons depend on a size of DC.

γ = mass ratio of ~~(sp^2~~/sp^3) (T$_S$/**DC**)

Peng, J., Bulcock, S., Belobrov, P., and Bursill, L. Surface bonding states of nano-crystalline diamond balls. *Int J Modern Phys* **B 15**, 4071 (2001).

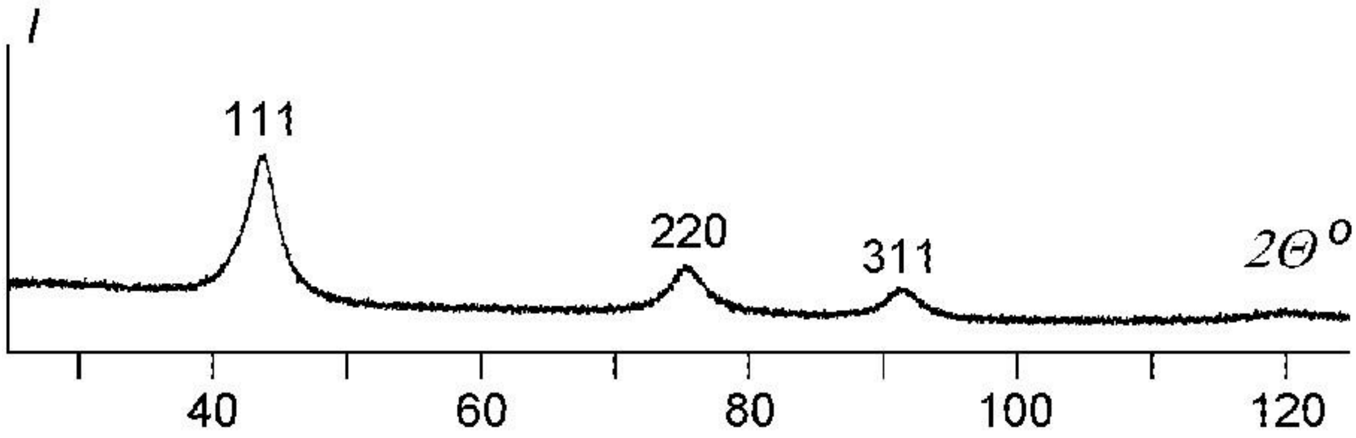
Pre K-edge signal – the property of DC

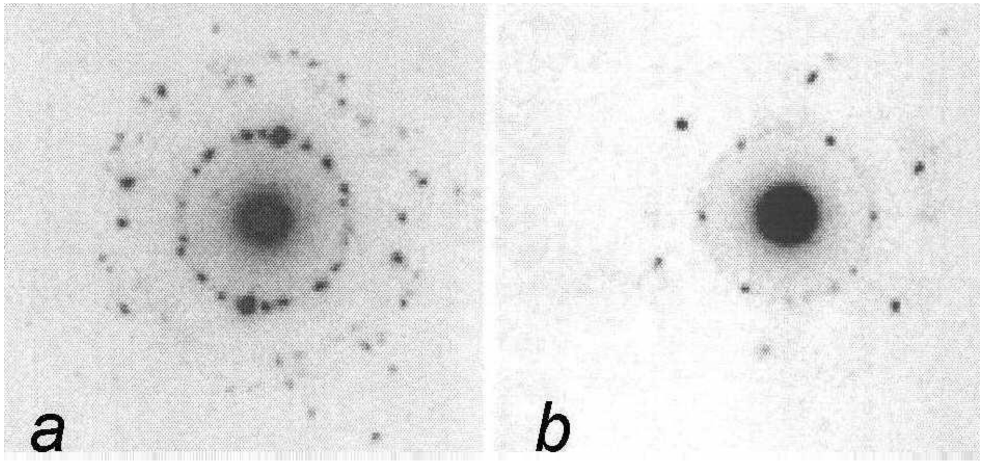


Line scan parallel electron energy loss spectrum for core-loss energy ranges for three DC particles of diameter (a) 5.2, (b) 6.2 and (c) 7.6 nm. Pre-peak (280–295 eV) characterises DC at the core-loss range

J Peng at al. *Int.J.Mod.Phys.***15**, 4071 (2001)

X-ray and electron diffraction of DC

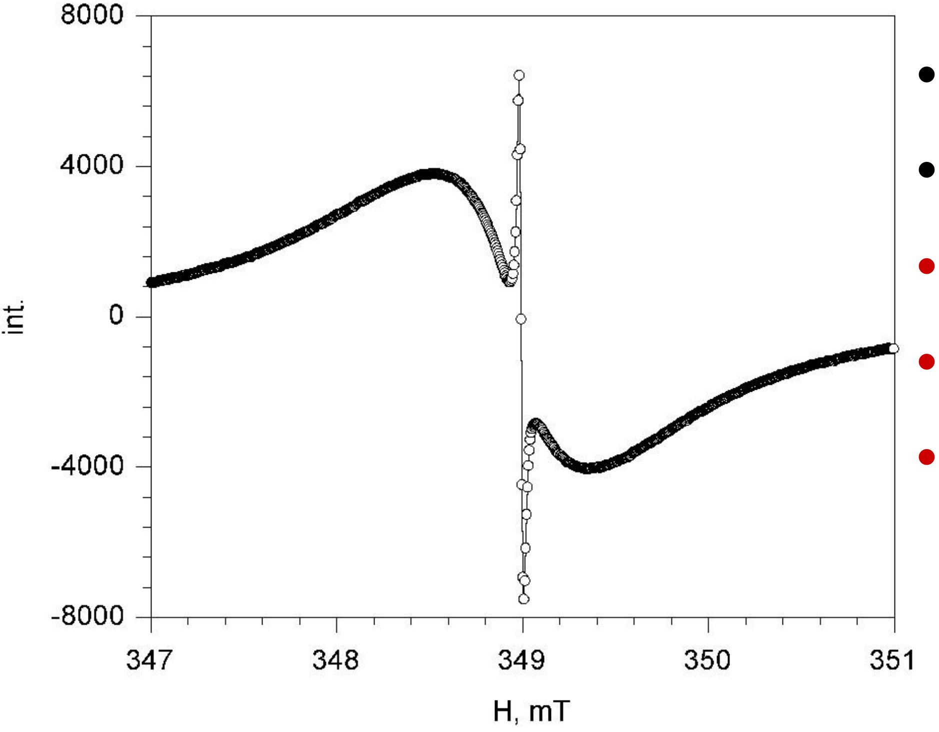




- Nano-diffraction from
- a) several particles
- b) structure of DC ?
  - two DC particles
  - twinning
  - quasicrystal

J Peng at al. *Int.J.Mod.Phys.***15**, 4071 (2001)

Paramagnetic invariant of DC



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

- N ≈ $4*10^{19}$ spin / g
- N ~ a few T-spins per DC 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 CD
  - structure of CD
  - atoms on its surface Cl, CH_3 etc.
  - and state of CD 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**).

DC has Paramagnetic Invariant

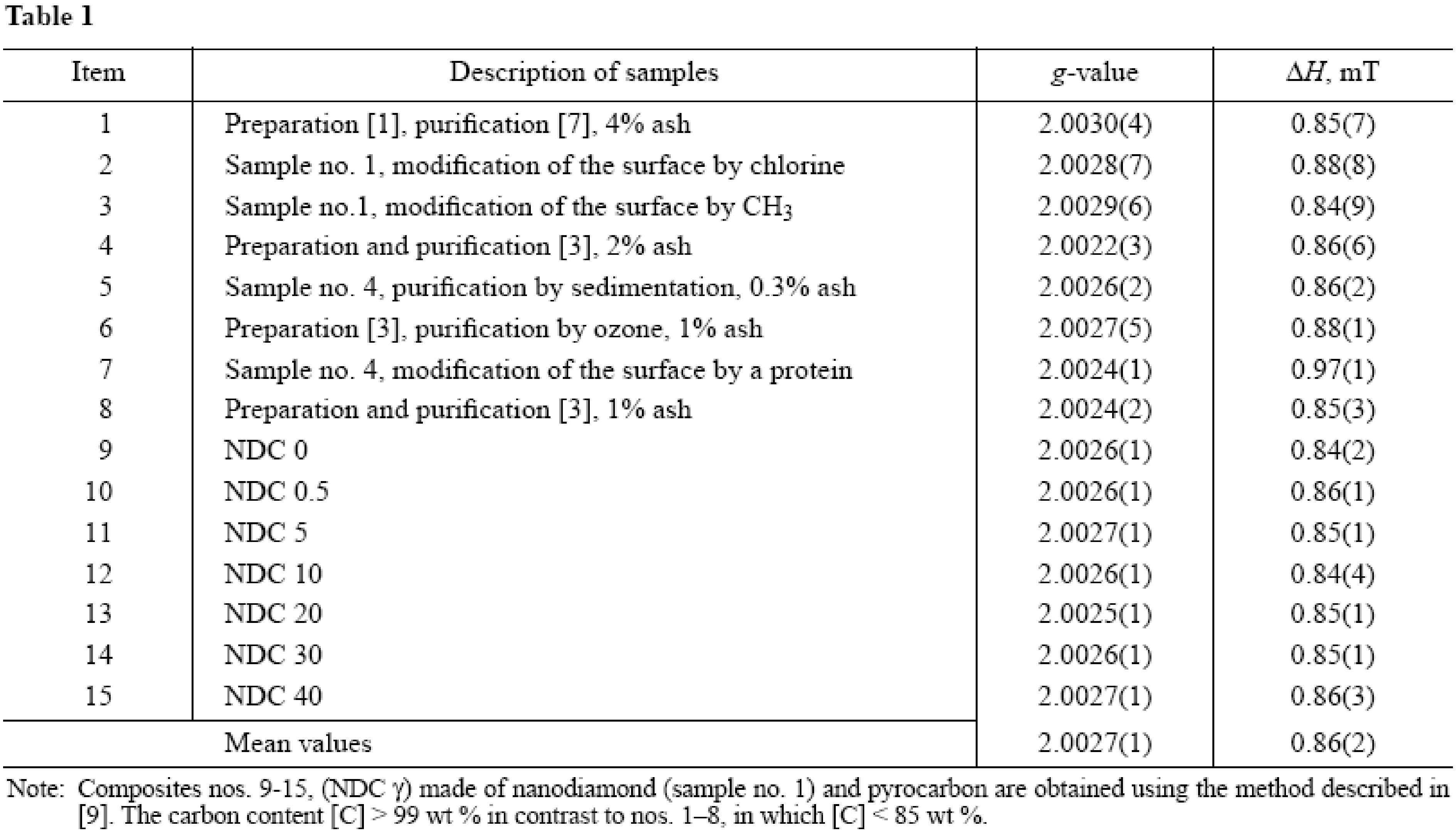
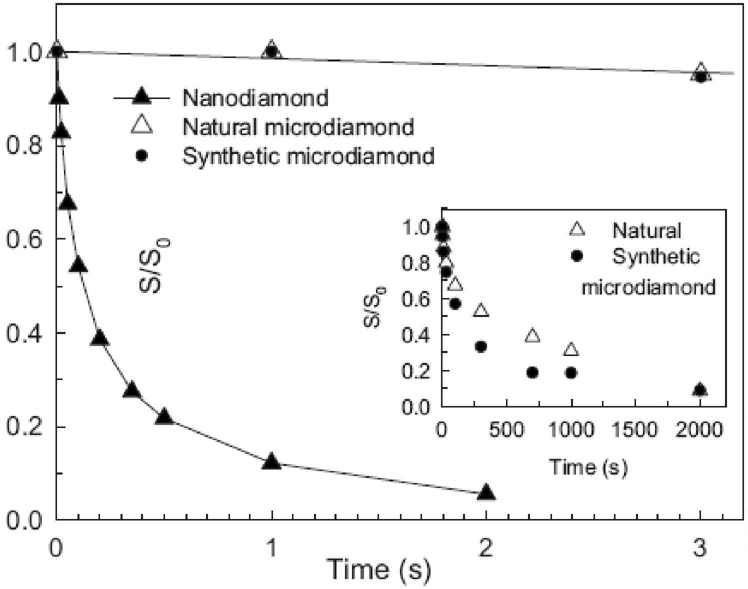


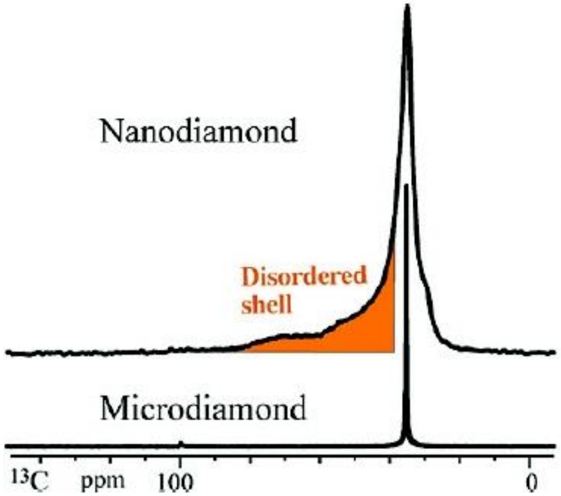
Table 1

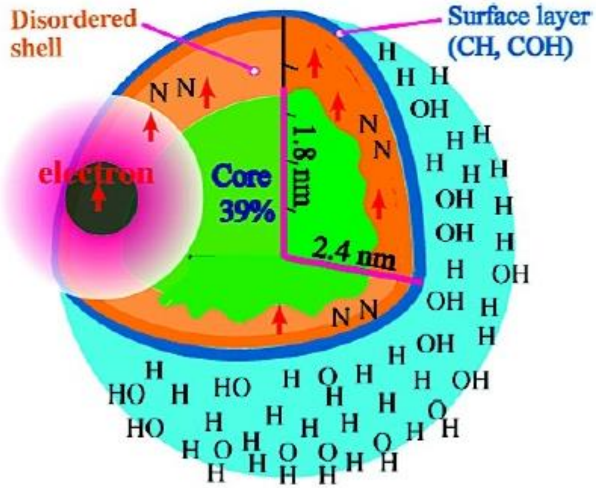
Item	Description of samples	*g*-value	Δ*H*, mT
1	Preparation [1], purification [7], 4% ash	2.0030(4)	0.85(7)
2	Sample no. 1, modification of the surface by chlorine	2.0028(7)	0.88(8)
3	Sample no.1, modification of the surface by CH_3	2.0029(6)	0.84(9)
4	Preparation and purification [3], 2% ash	2.0022(3)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

The results of K Schmidt-Rohr’ team

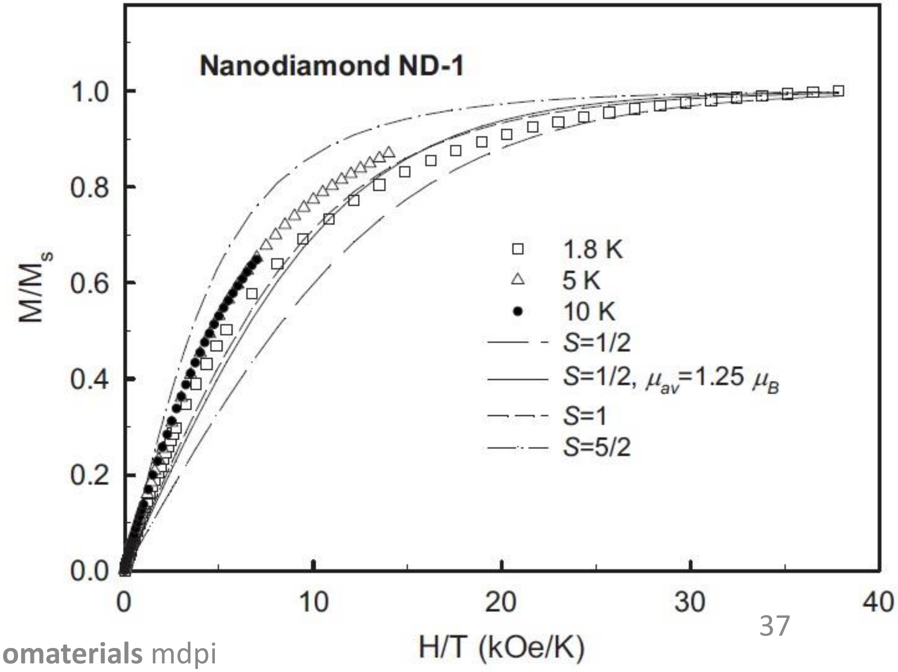




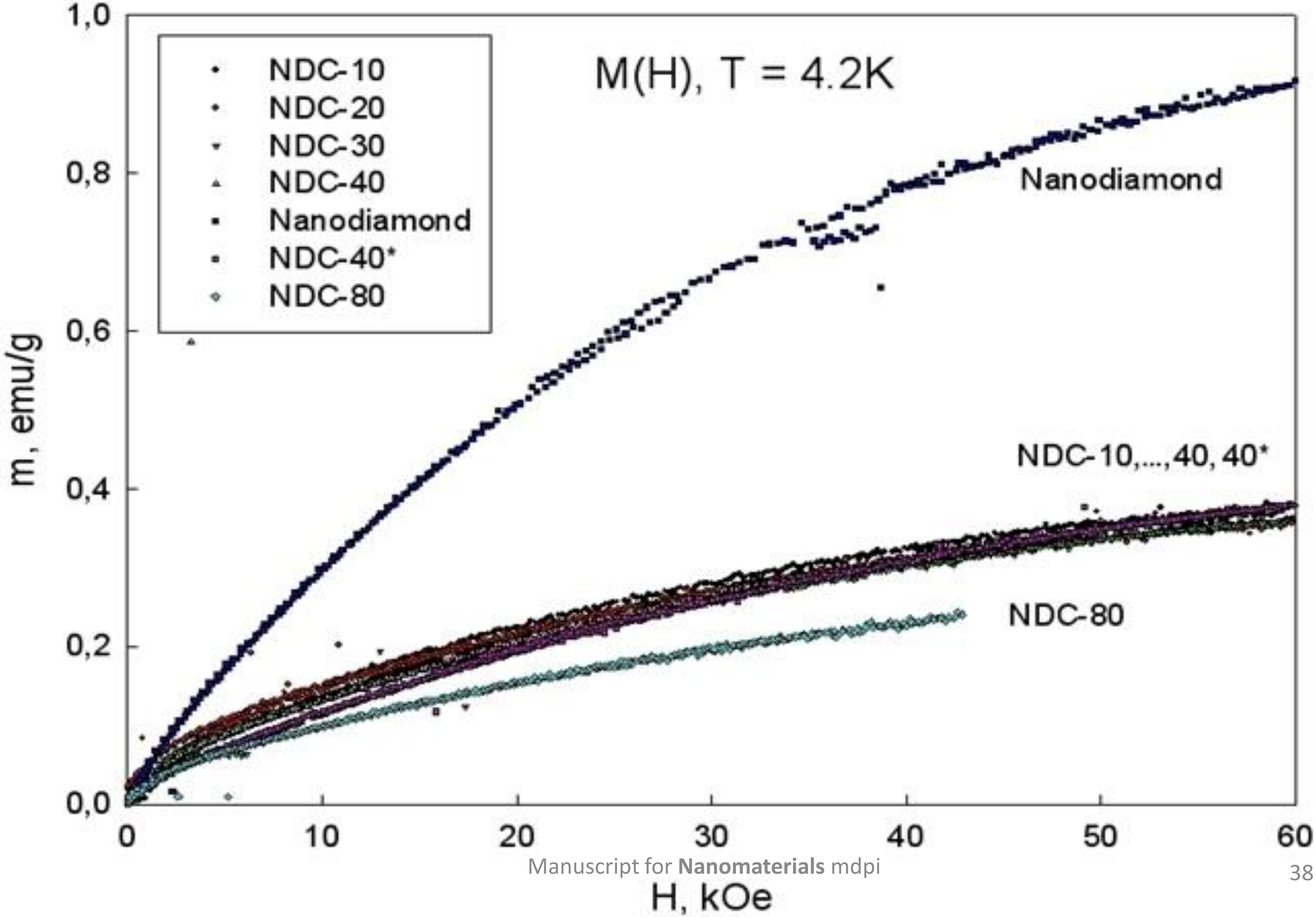


E. M. Levin at al. Magnetization and ^{13}C NMR spin-lattice relaxation of nanodiamond powder. *Phys. Rev. B.* **77**, 054418 (2008).

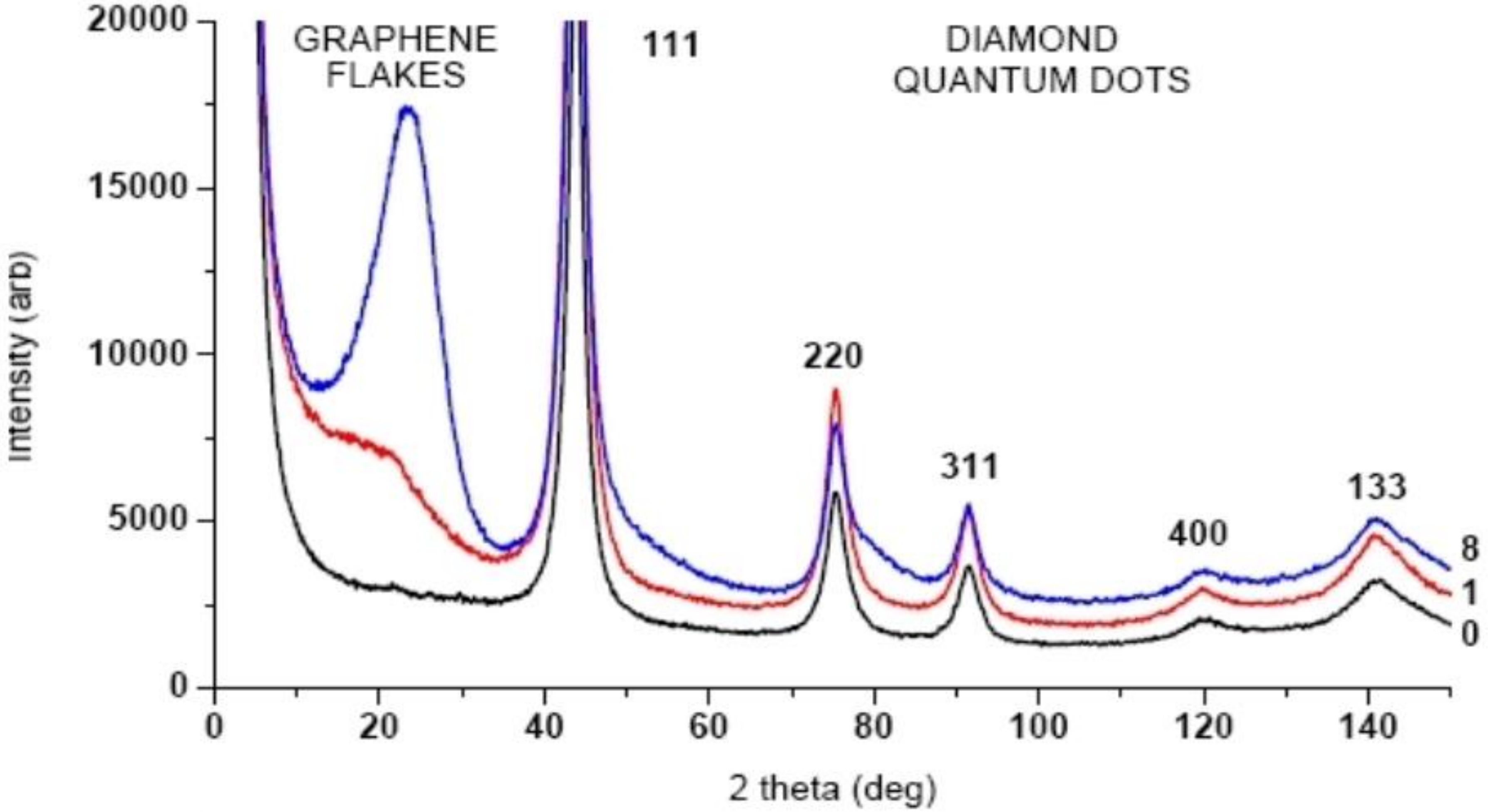
X-W Fang at al. Nonaromatic Core-Shell Structure of Nanodiamond from Solid-State NMR Spectroscopy. *J Am Chem Soc*, **131**, 1426 (2009).



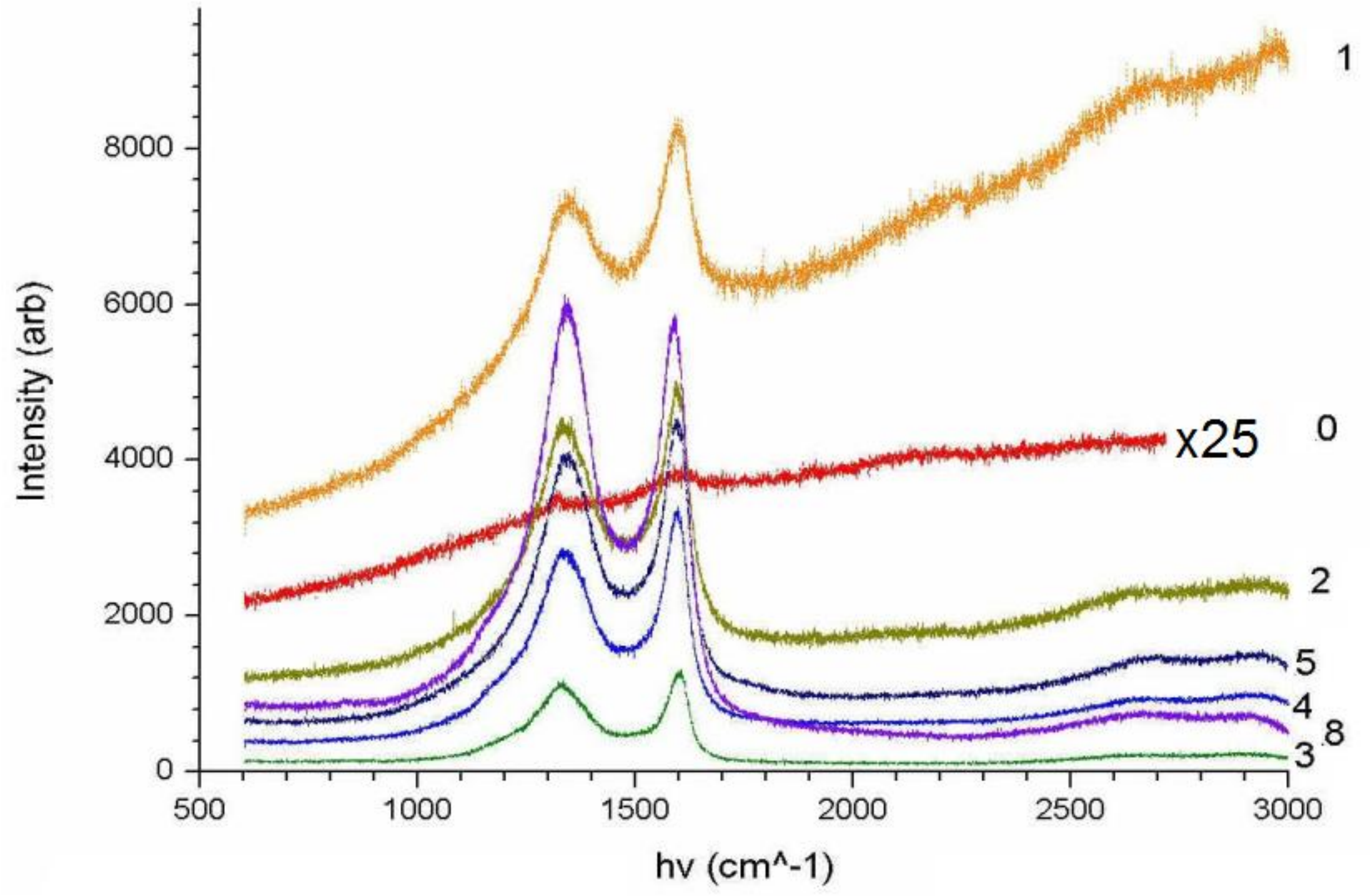
Magnetic susceptibility



X-ray diffraction of NDC

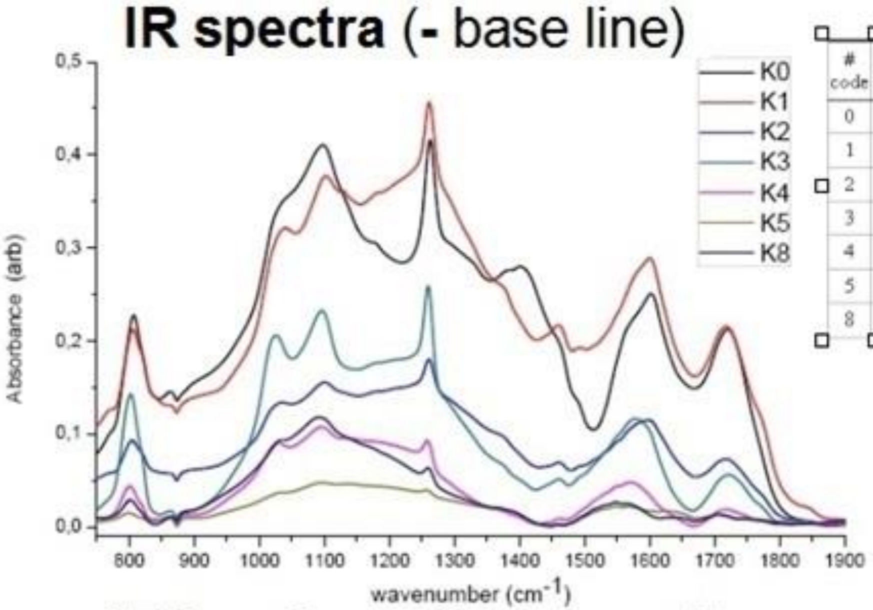


Raman of NDC



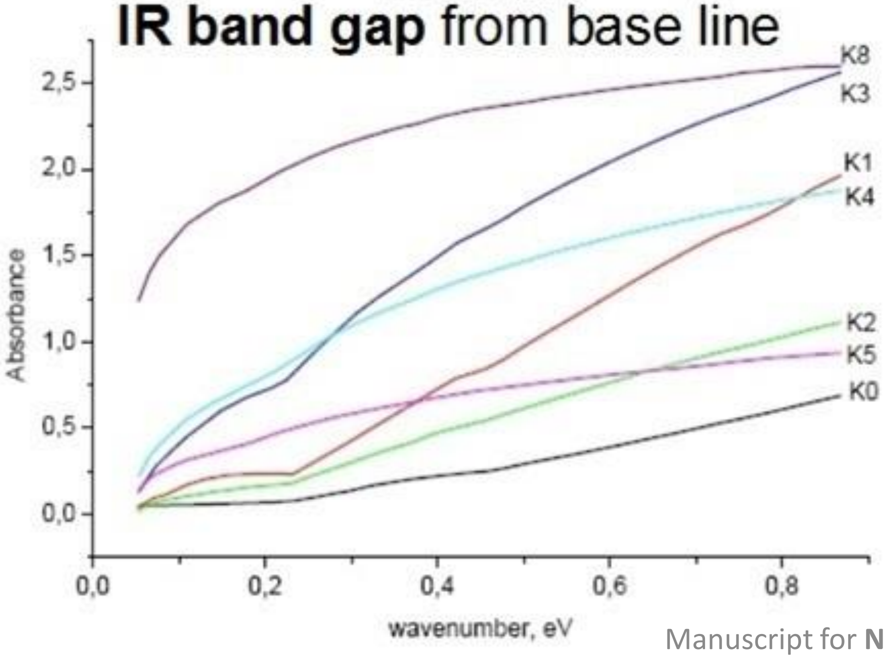
# code	γ, %
0	0
1	10
2	20
3	30
4	40
5	50
8	80

The proof: NDC is semiconductor

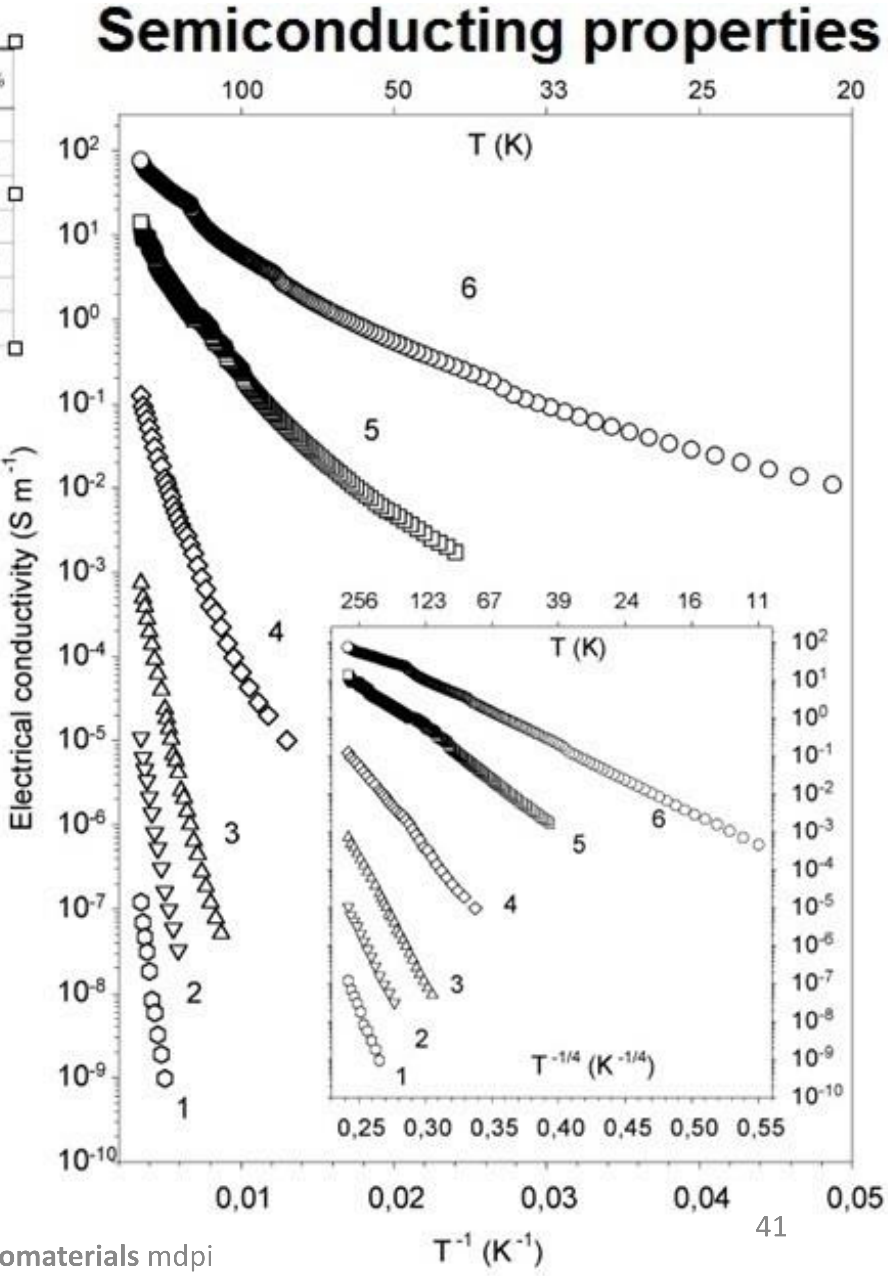


IR spectra (- base line)

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

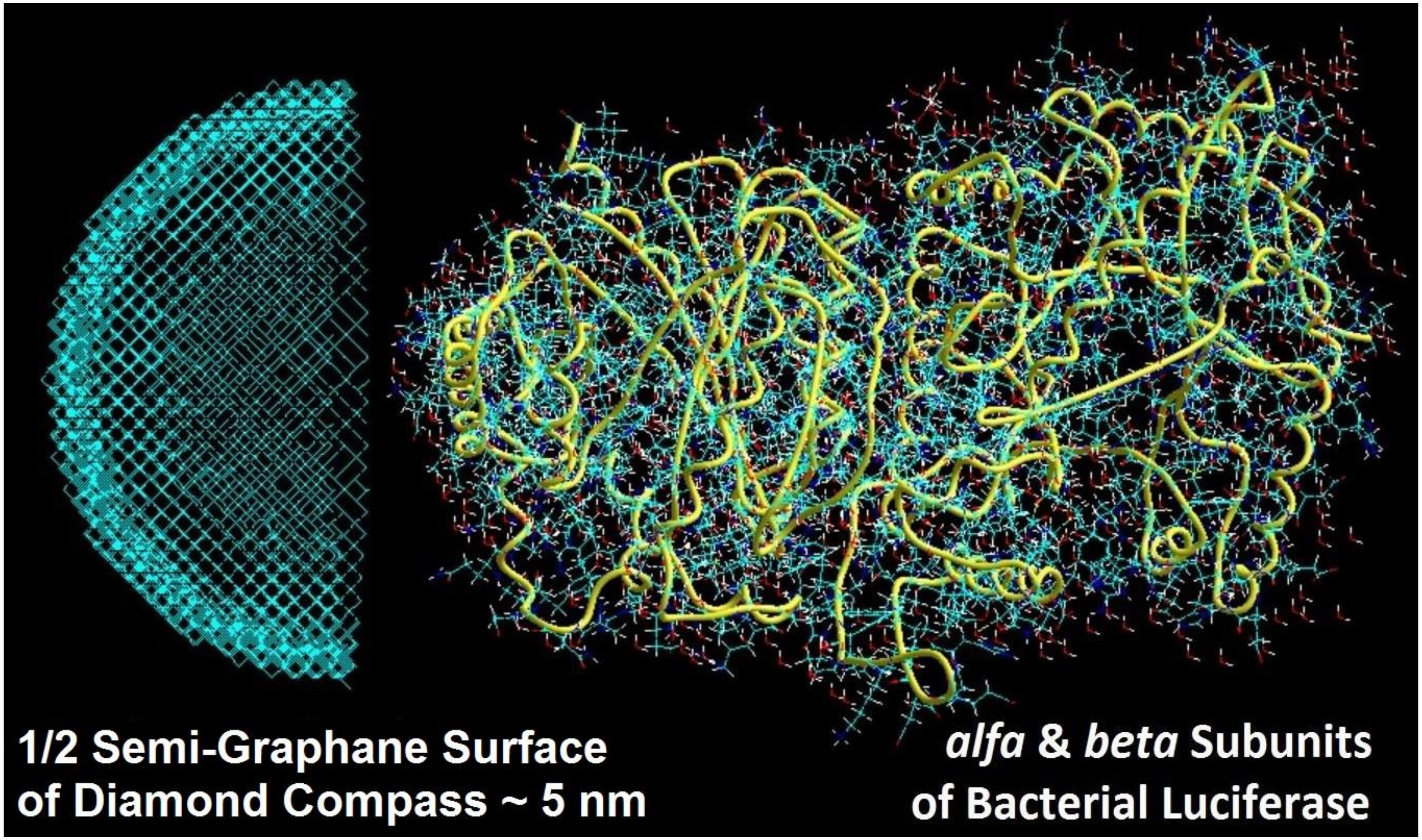


IR band gap from base line

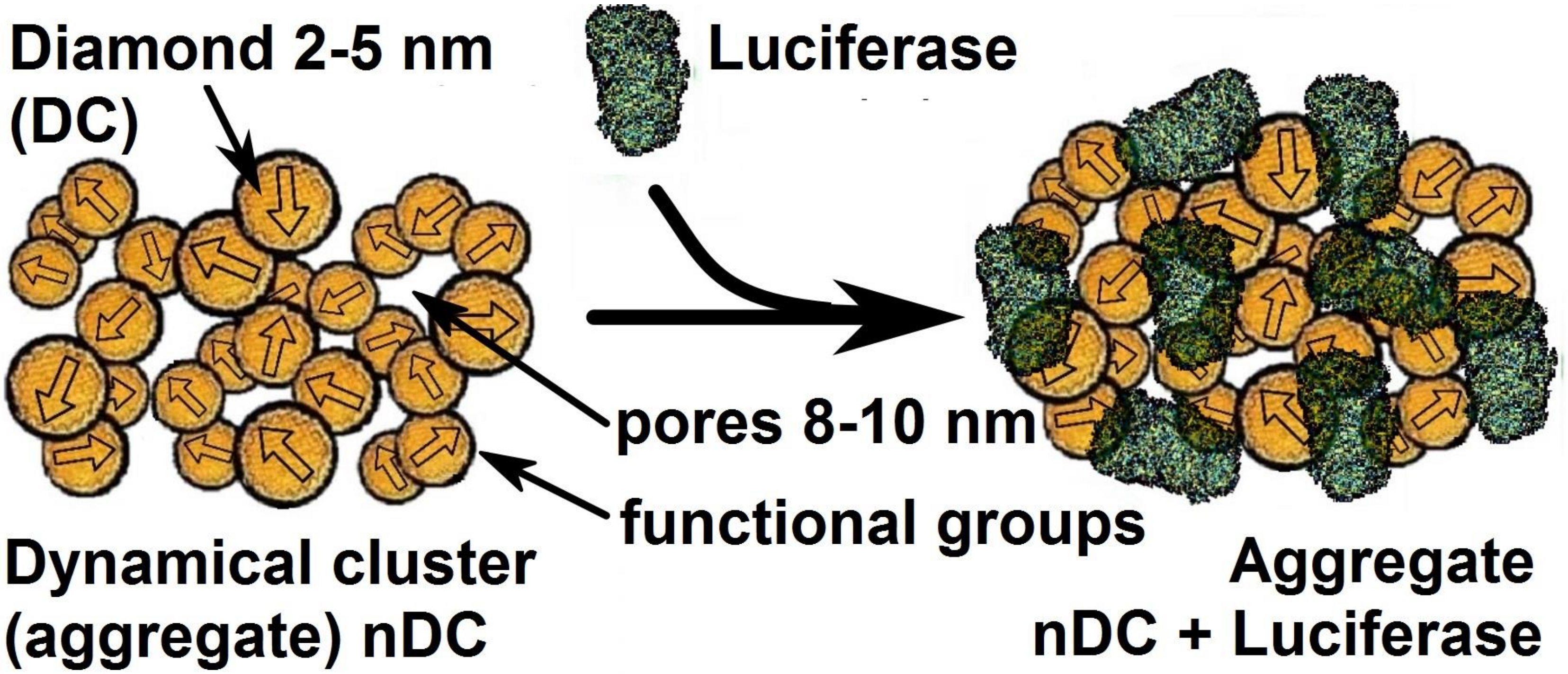


Semiconducting properties

Diamond 2-5 nm & Luciferase



Soluble aggregates nDC (n ~ 10^5)



Conclusions

- The **DC** 2 – 5 nm has **T_S** surface
- DC is Diamond Compass is introduced by us
- The diamond – pyrocarbon composite **NDC** has
  - 3D skeleton with fractal dimension 1.95 – 2.14.
  - **NDC** is solid bulk semiconductor with porous structure
  - all **NDC** properties depend from **γ = mass ratio of** (**T_S/DC**)
- The model **T_S** explains of the spin stability, magnetic, optical and transport properties of **NDC**.
- The agreement of experiments and theory for **NDC**:
  - new carbon semiconductors with controlled band structure
  - novel member of topological materials family

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  - Andrew Flewitt

DC ↔ CD, T-spin …

My Boss & Seasons

- Photo &
- Hunt
  - The Passion

Boss helped me to grasp:

The Silence is Freedom

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