Smart Materials

Graphene and Graphane Flakes into Nanodiamond - Pyrocarbon Composites

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The diamond – pyrocarbon composites

have been created and studied in close cooperation with the colleagues:

- S K Gordeev, S B Korchagina
  - Central Research Institute of Material, St. Petersburg, Russia
- N I Kiselev, E A Petrakovskaya, D A Balaev, B A Belyaev, E V Eremin, N V Volkov, D A Velikanov, A S Krylov, K A Shaikhutdinov, N P Shestakov et al.
  - Kirensky Institute of Physics SB RAS, Krasnoyarsk, Russia
- I A Denisov, A A Zimin, A S Yakimov et al.
  - Siberian Federal University, MOLPIT, Krasnoyarsk, Russia

Outlook

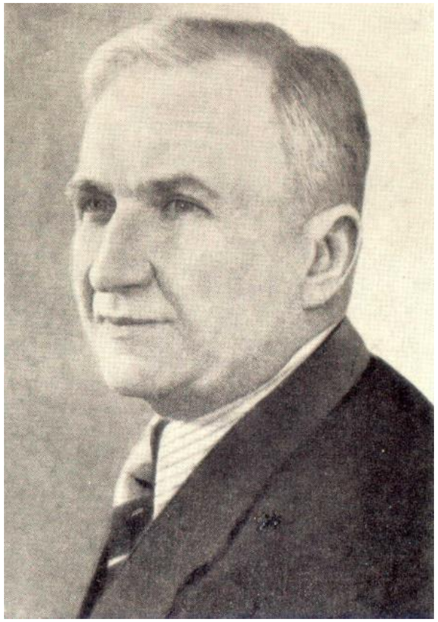
- The mist of graphene & graphane flakes (T_S) relationship in pyrocarbon at diamond surface of ~ 2 ÷ 5 nm **DC**
- **NDC** is solid bulk porous semiconductor
  - structure, electrical conductivity, band structure, X-ray diffraction pattern, Raman, IR, Auger, XPS etc.
- **NDC** properties depend from γ = mass ratio of (T_S/**DC**) phases
  - OLD (incorrect!) γ = mass ratio of (~~sp^2~~/sp^3) phases
- The exact model for low-dimensional pyrocarbon of **NDC**.
- The agreement of experiments and theory allows us to conclude that **NDC** is
  - new pure carbon semiconductors with controlled band structure
  - novel member of topological materials family.
- We will discuss our solution of the T_S below

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 patented 2 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**).

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) ⇒ *Idea of quantum of sound at DC*
- 1933 – «**Tamm levels**» - certain electron states were due to the existence of the surface ⇒ *1D & 2D ё states at DC*
- 1934 – Any system with **virtual separated charges** should have **magnetic moment** ⇒ *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.



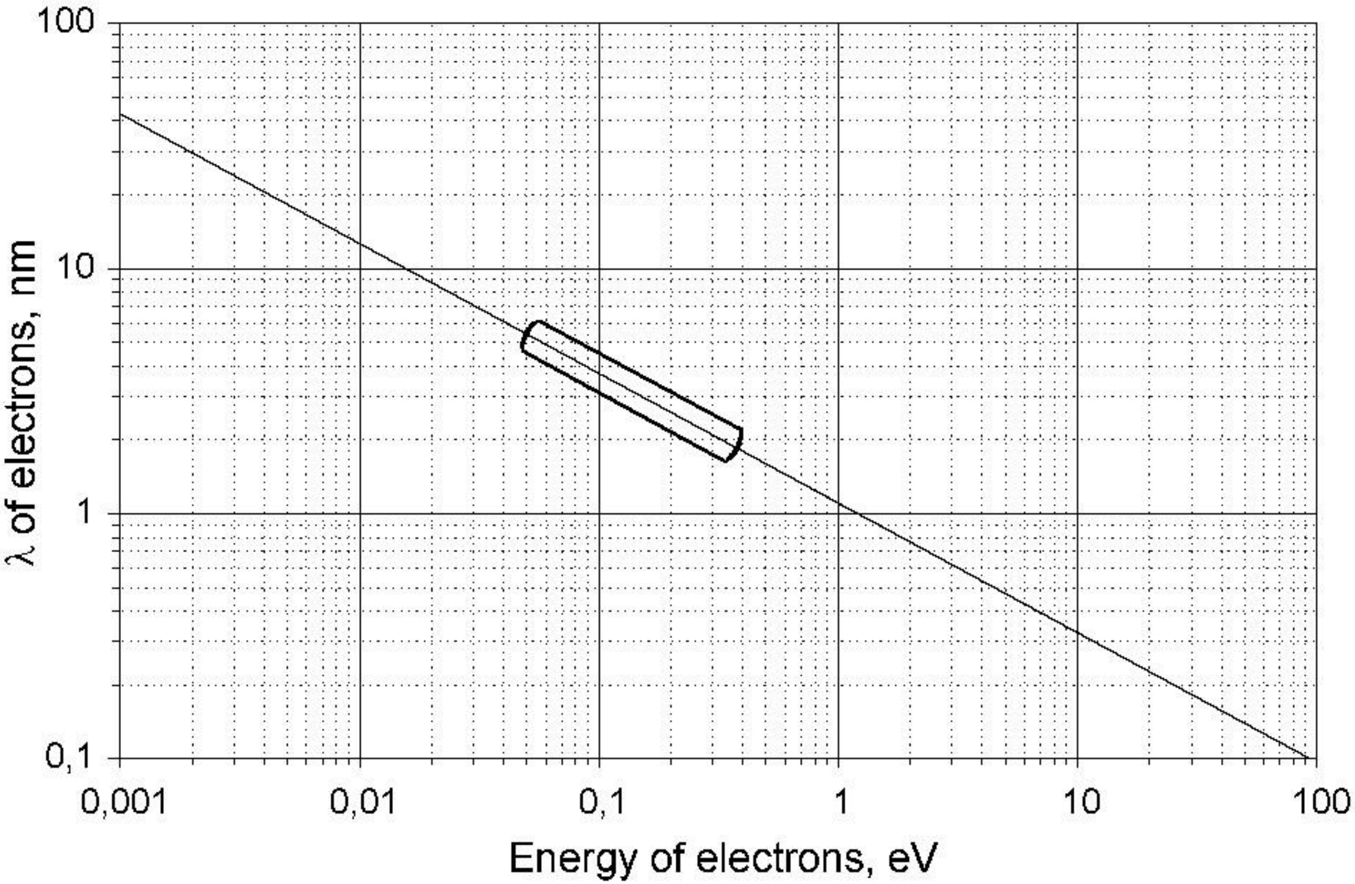
Igor Evgen'evich **Tamm**
(8/07/1895 – 12/04/1971)
1958 – Nobel Prize for the Vavilov-Cherenkov effect

Classical papers of Tamm

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

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

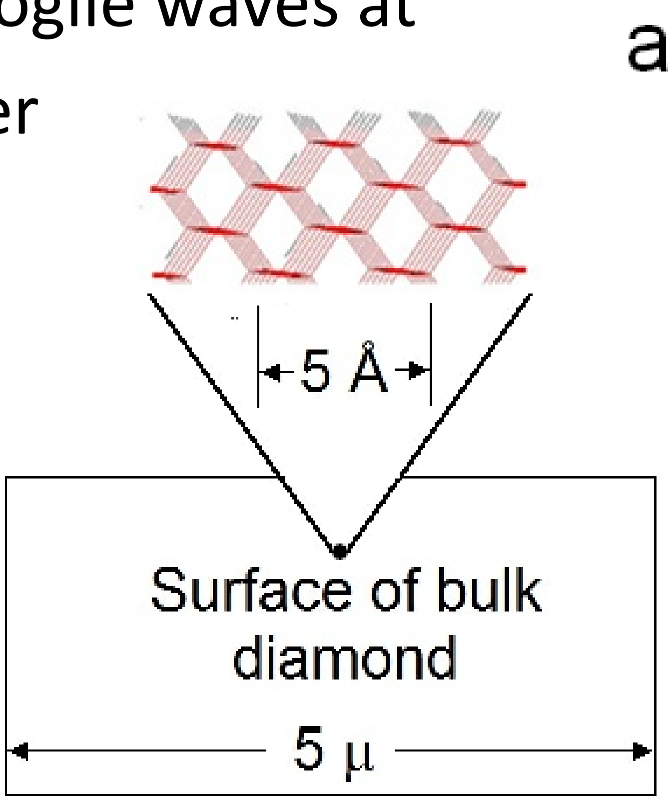
- 1.9-5.2 nm
- λ ~ 4 nm
- E ~ 0.1 eV
- E, p; $\nu = E/h$.

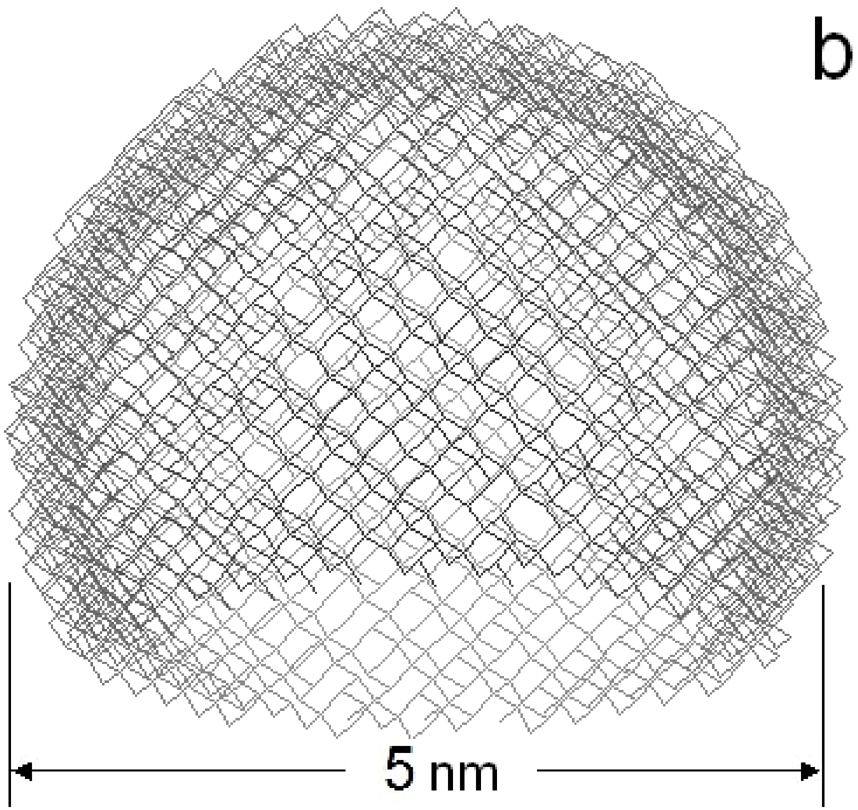
Carbon in Nature: ^{12}C 98,93 % & ^{13}C 1,07 %.

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

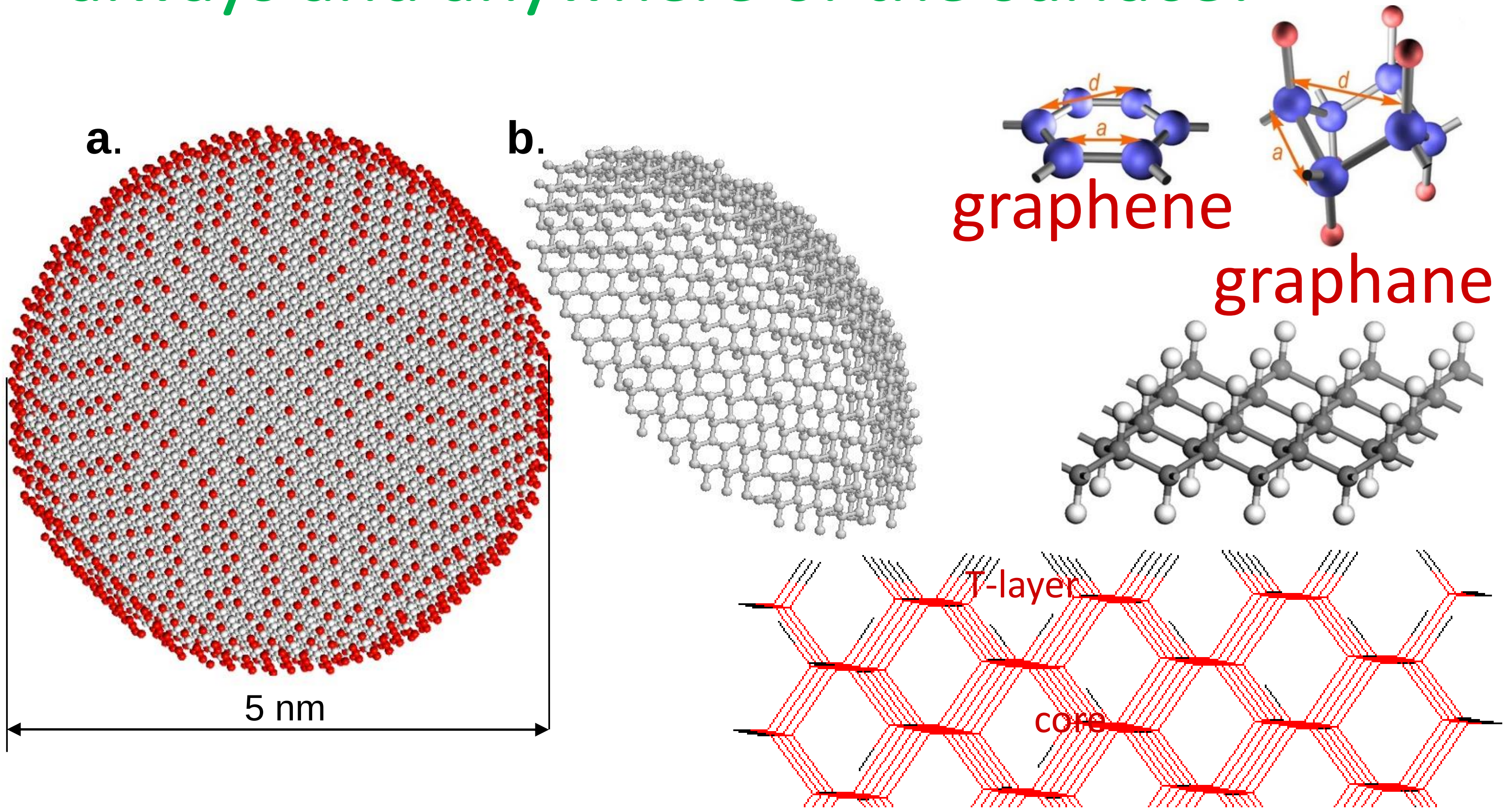
de Broglie waves at

T-layer





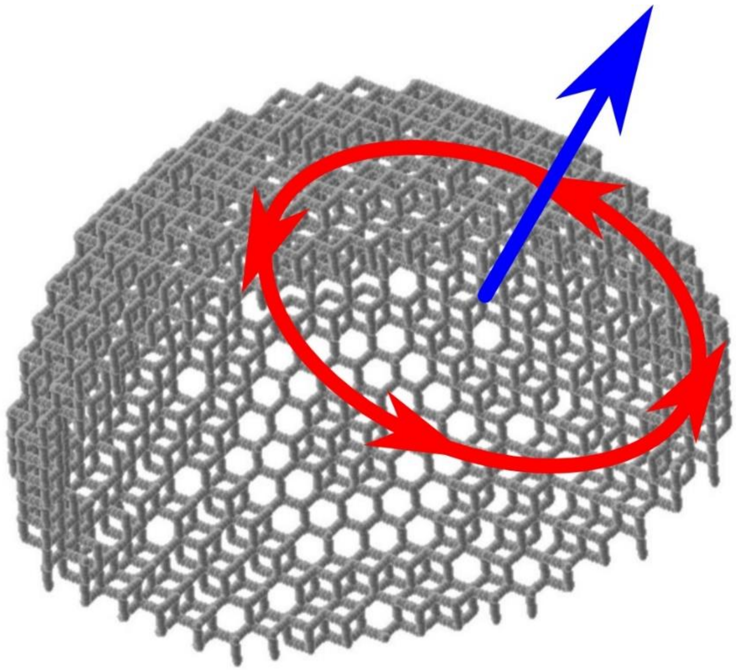
Any diamond encrusted by T-layer always and anywhere of the surface!

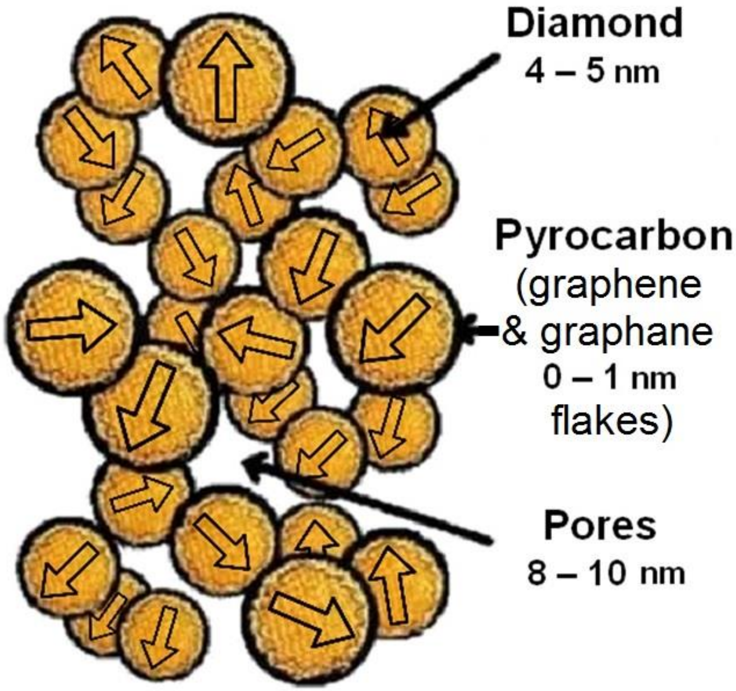


a. Diamond ball 5 nm, terminal atoms marked.

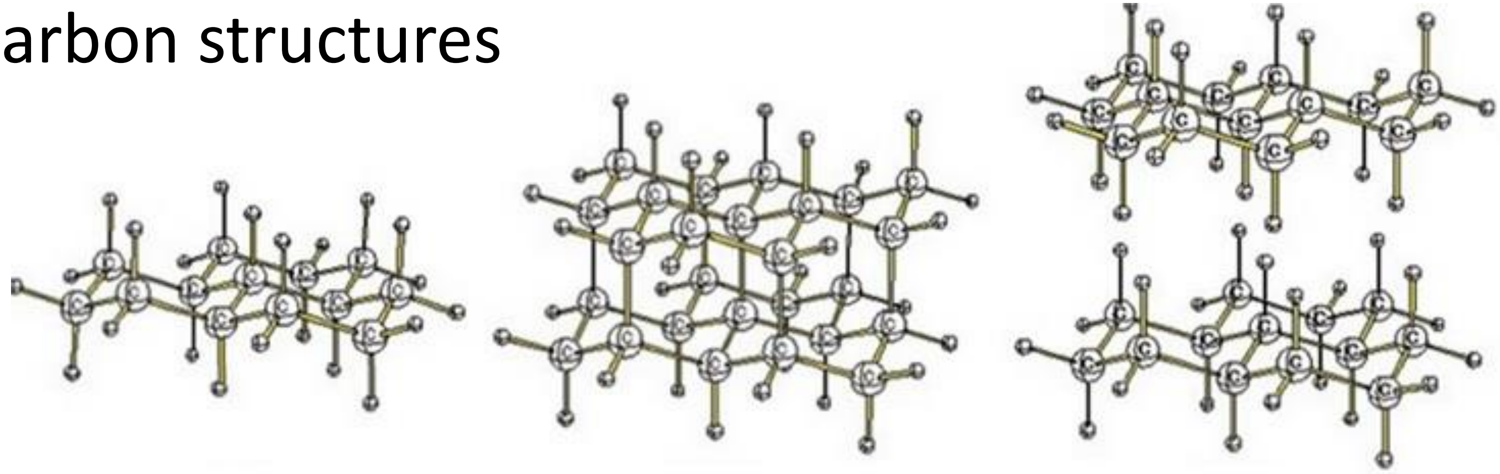
b. T-layer incrustation (extracted from **a**) = sheet from cyclohexanes

Fractional dimensions of electron density

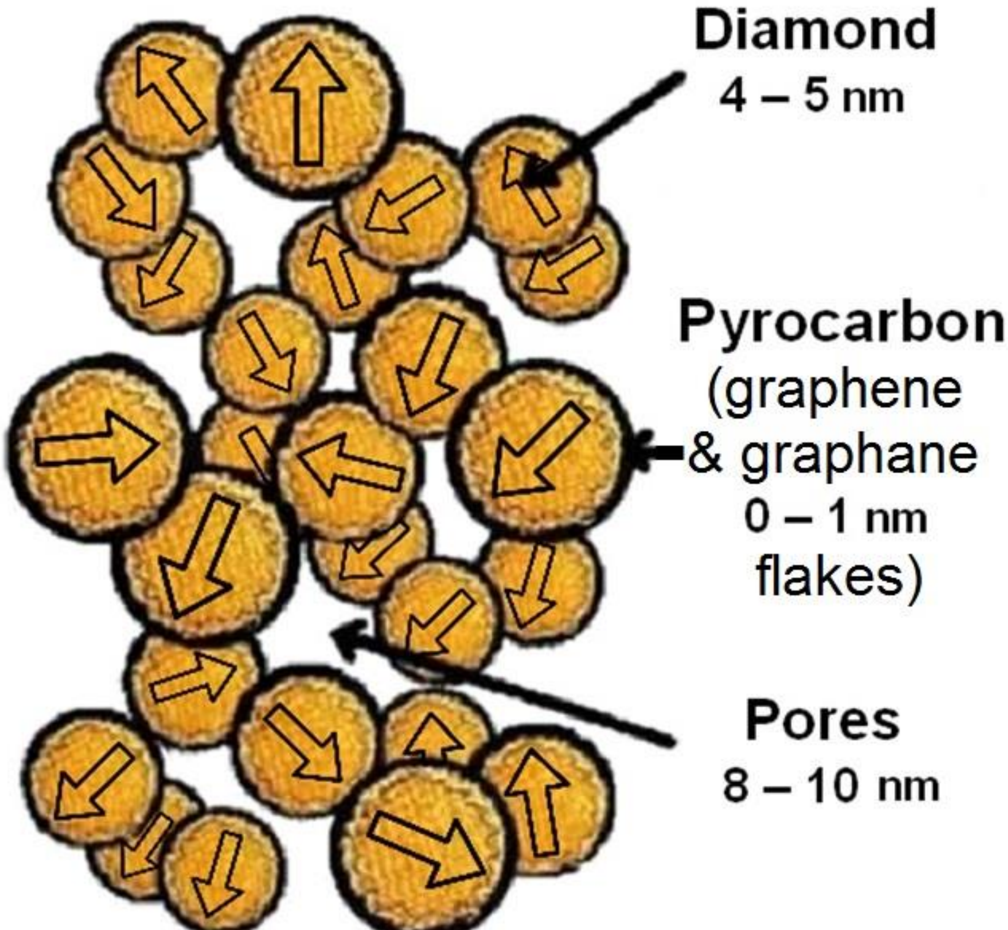




Strong curvature & incommensurate of nearest layers in carbon structures



3 phases: Diamond, Graphane, Pores

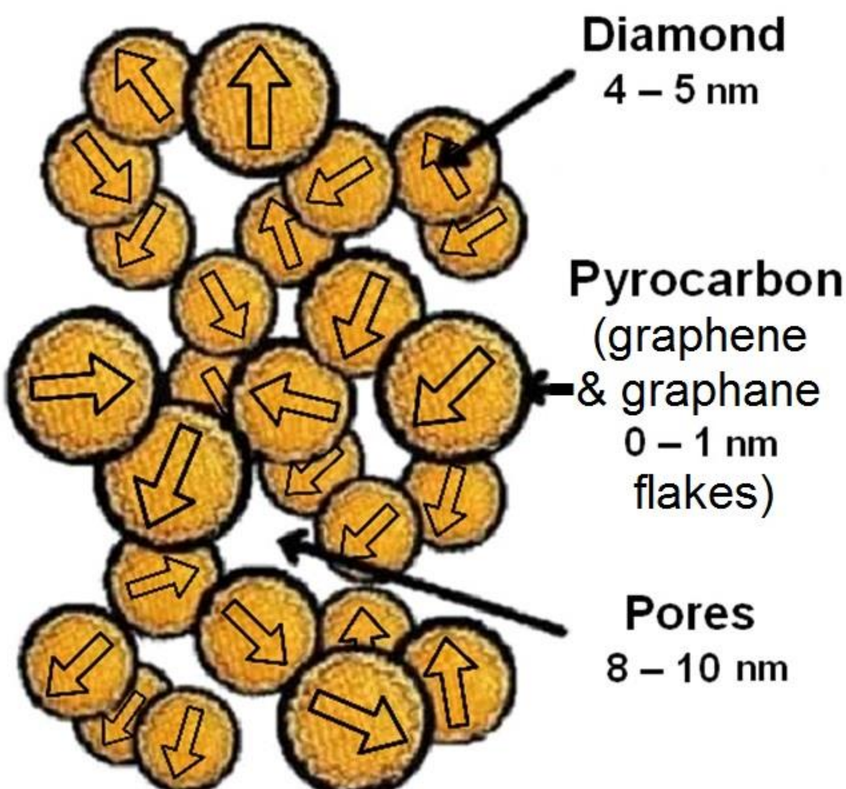


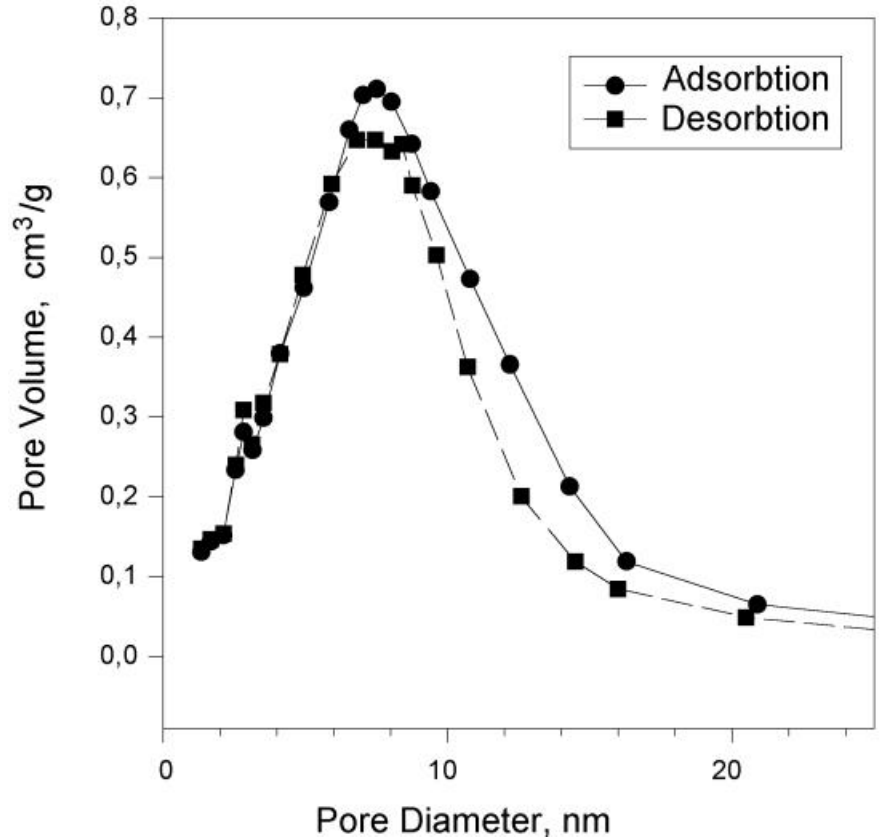
- *All three phases have equal rights and self-consistent*

T-spins into NDC

Structure of NDC composite

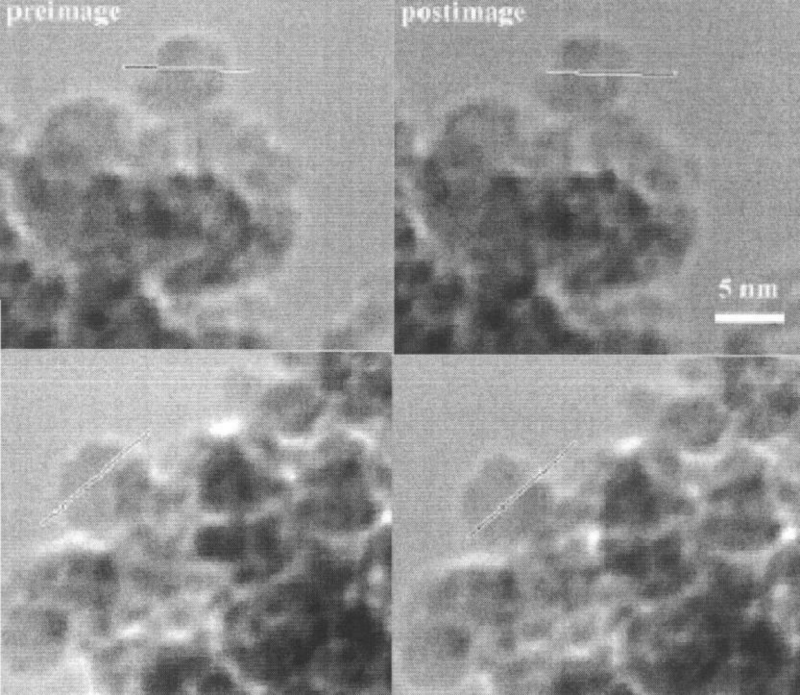
- New family of smart bulk nanomaterials
- High level of properties





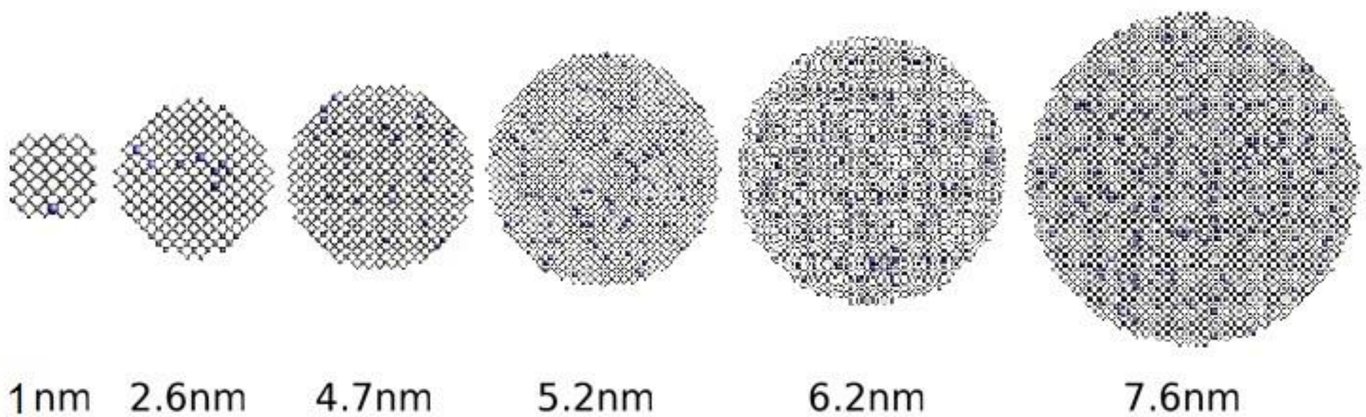
Pore size distribution

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

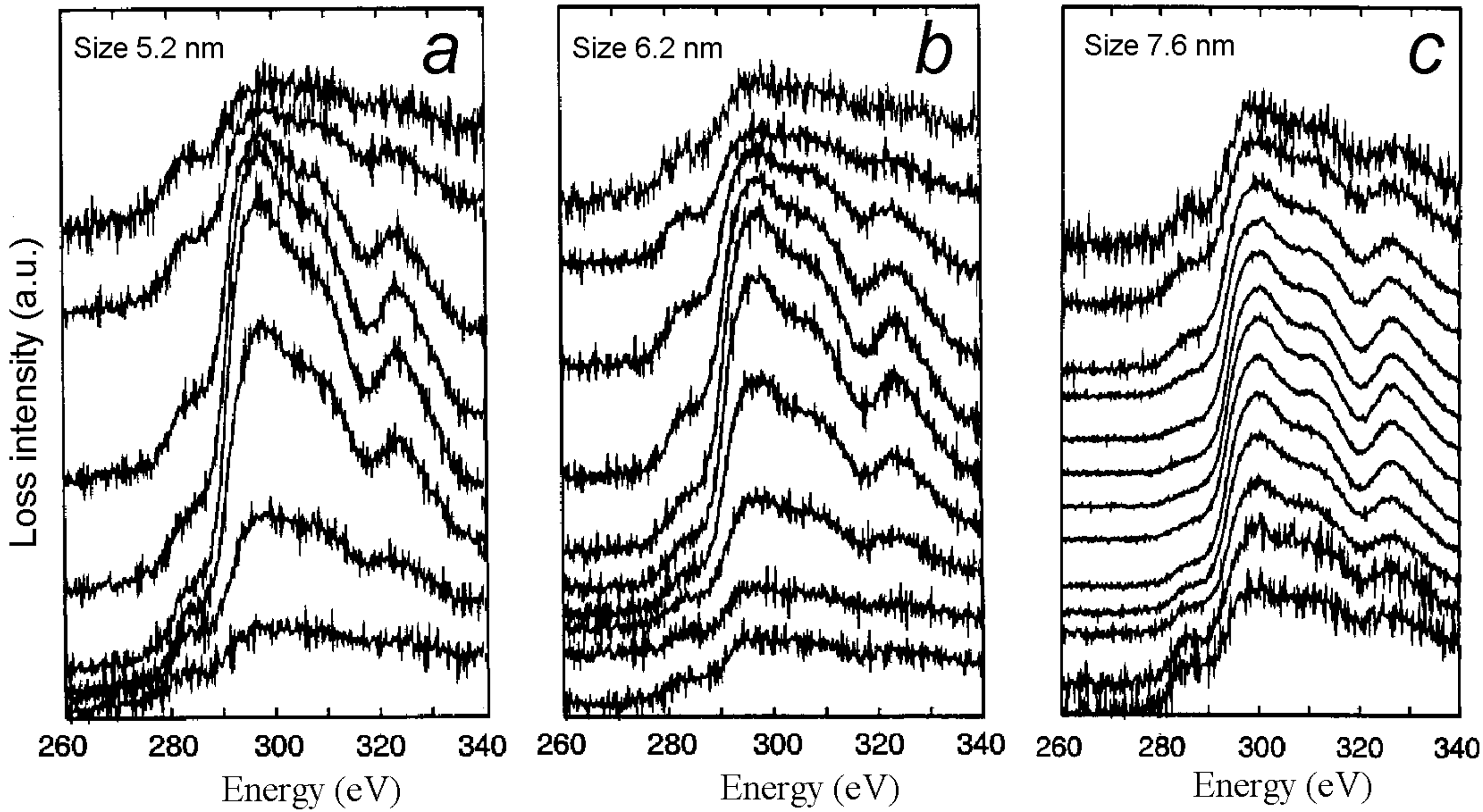


At the low-loss range surface (12–24 eV) & bulk (30–33 eV) plasmons depend on a size of DC.

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).

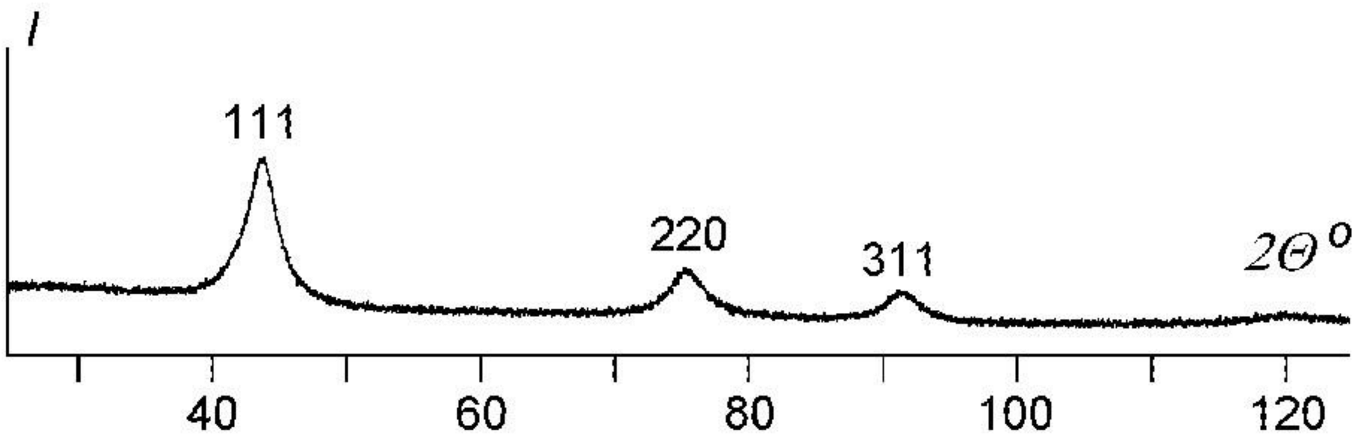
Pre K-edge signal – the property of DC



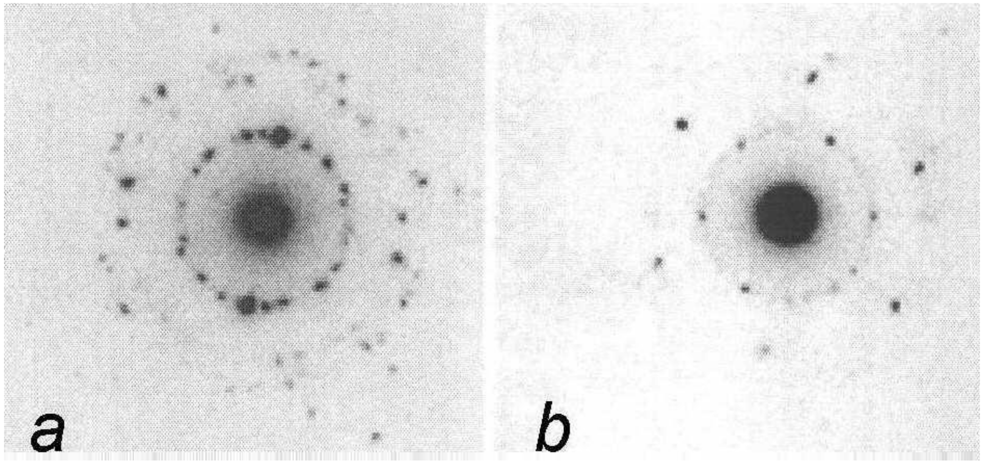
Line scan parallel electron energy loss spectrum for core-loss energy ranges for three DC particles of diameter (a) 5.2, (b) 6.2 and (c) 7.6 nm. Pre-peak (280–295 eV) characterises DC at the core-loss range

L A Bursill at al. *Int.J.Mod.Phys.***15**, 4071 (2001)

X-ray and electronic diffraction of DC

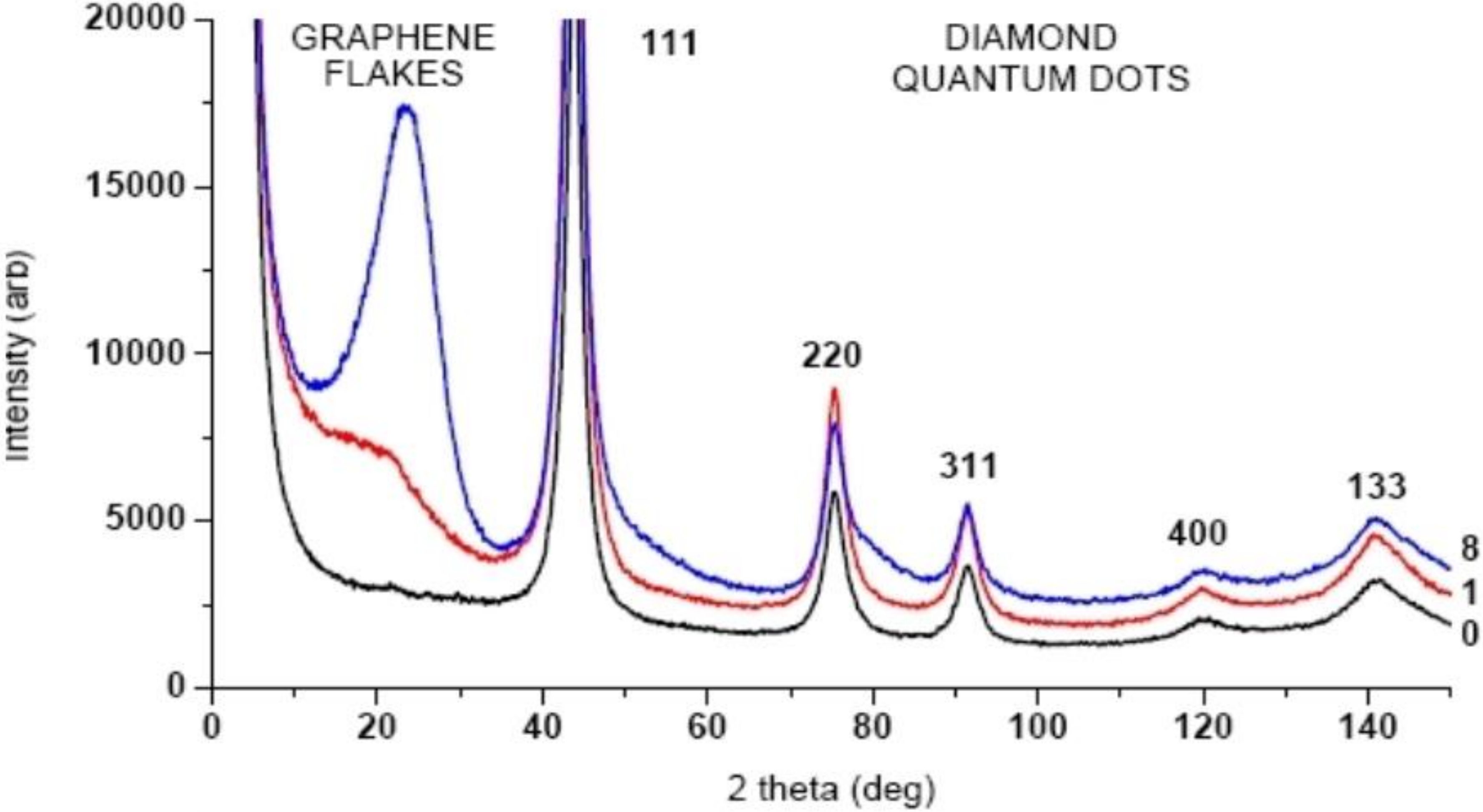


- Nano-diffraction from
- a) several particles
- b) structure of DC ?
  - two DC particles
  - twinning
  - quasicrystal

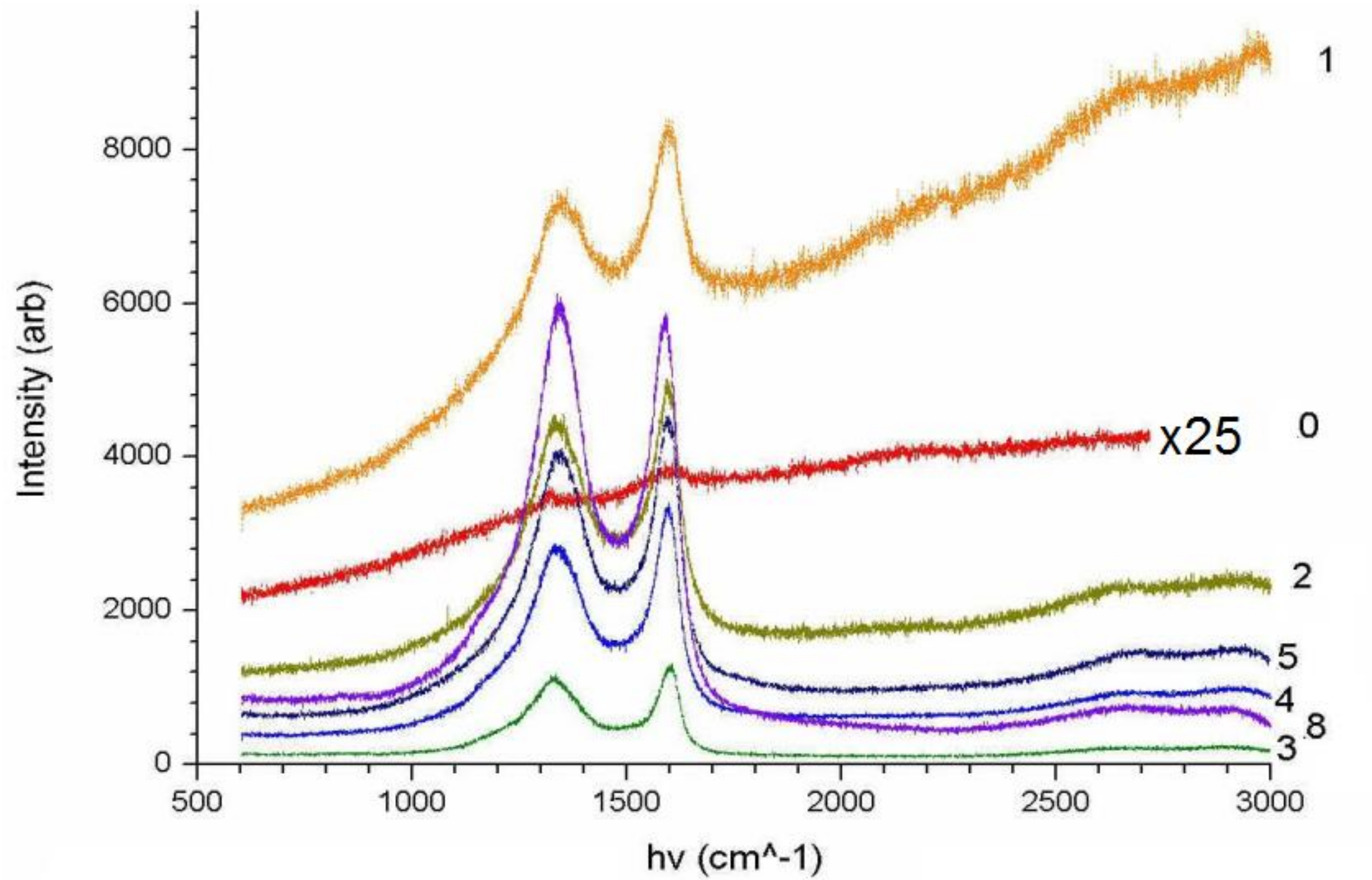


L A Bursill at al. *Int.J.Mod.Phys.***15**, 4071 (2001)

X-ray diffraction of NDC



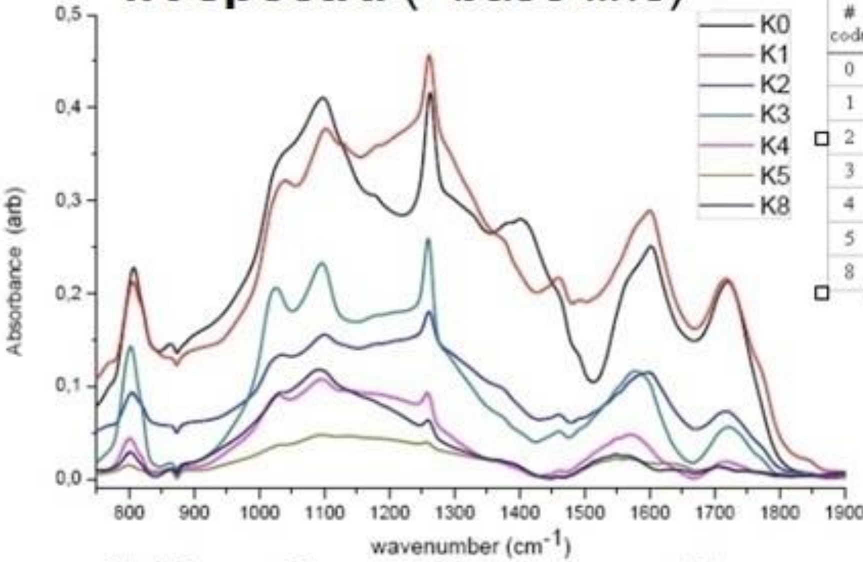
Raman of NDC



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

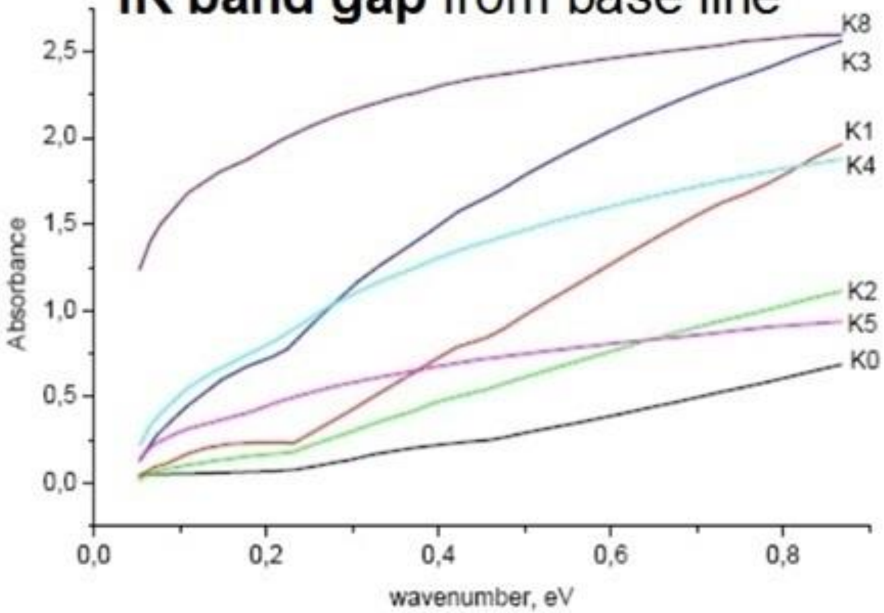
The proof: NDC is semiconductor

IR spectra (- base line)

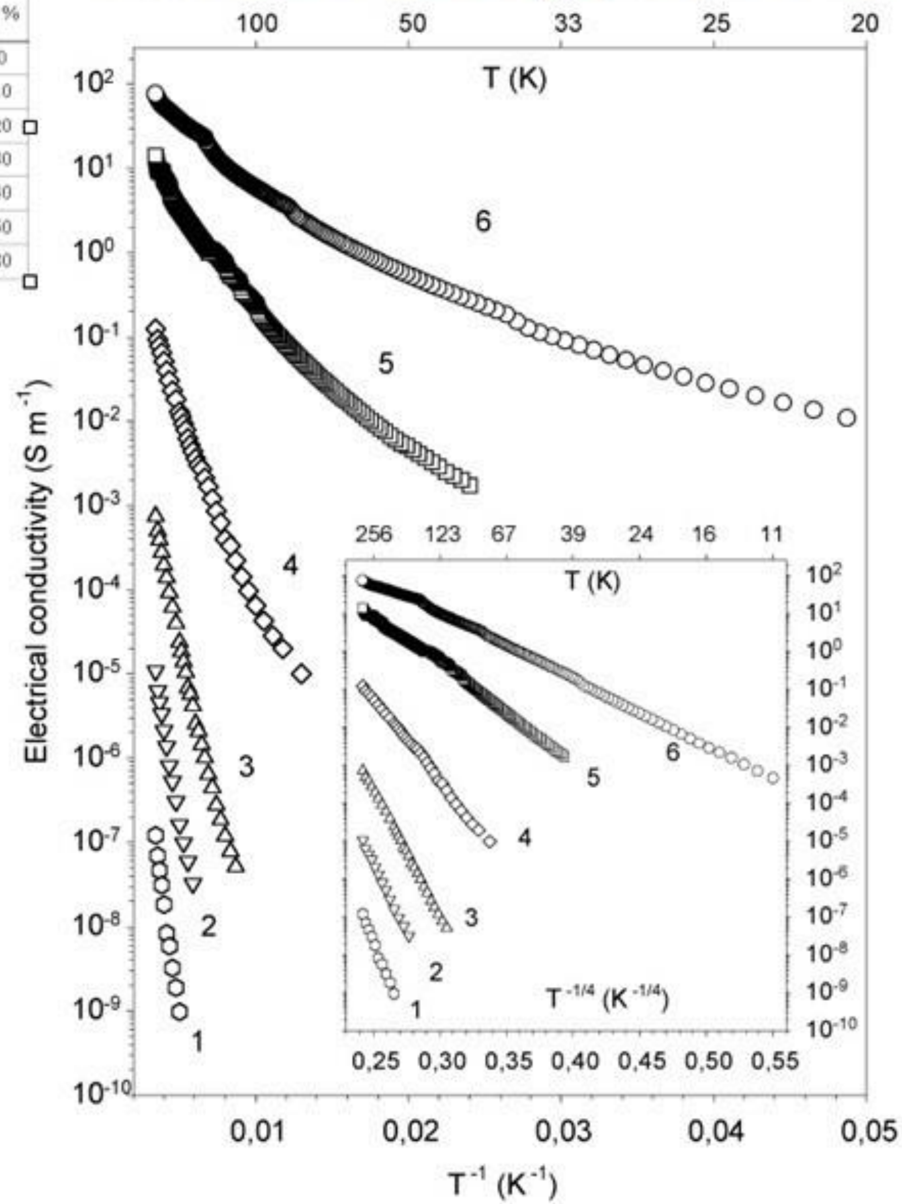


# code	γ, %
0	0
1	10
2	20
3	30
4	40
5	50
8	80

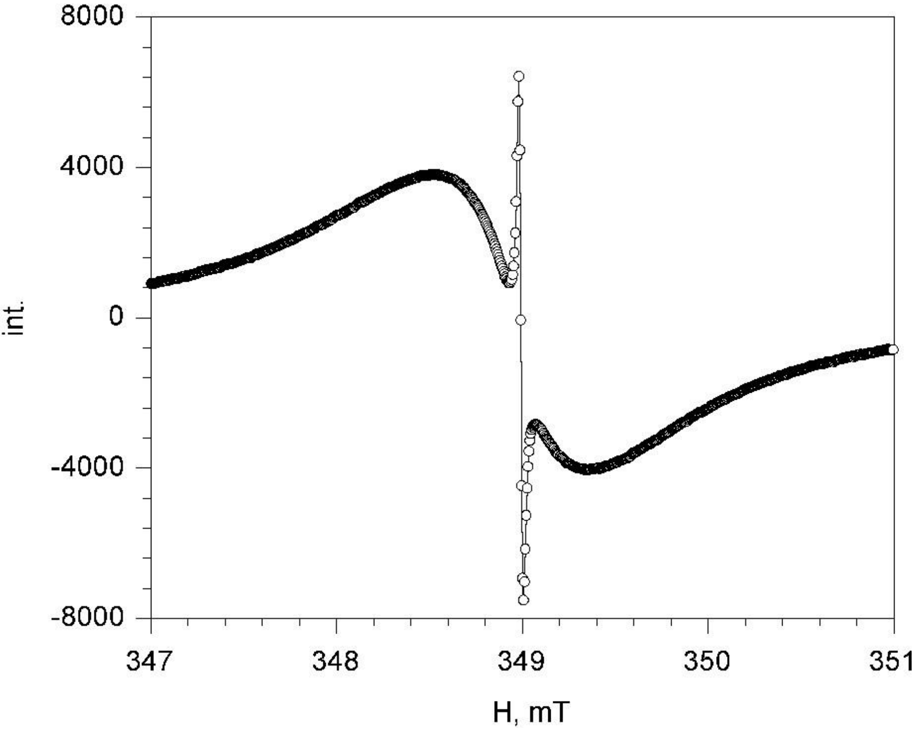
IR band gap from base line



Semiconducting properties



Paramagnetic invariant of DC & NDC



EPR spectrum of DC (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**).

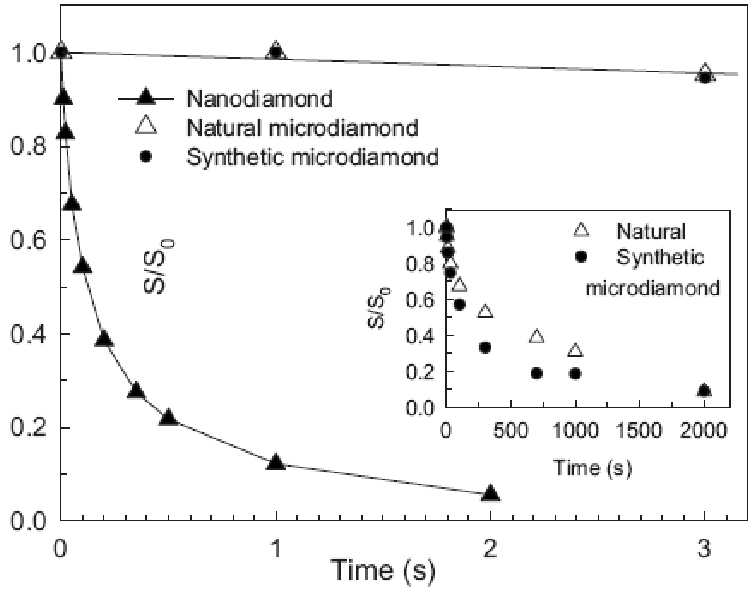
DC & NDC have true Paramagnetic Invariant

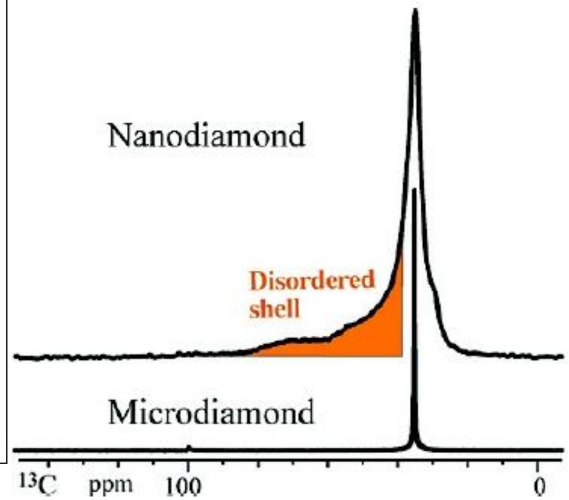
Table 1

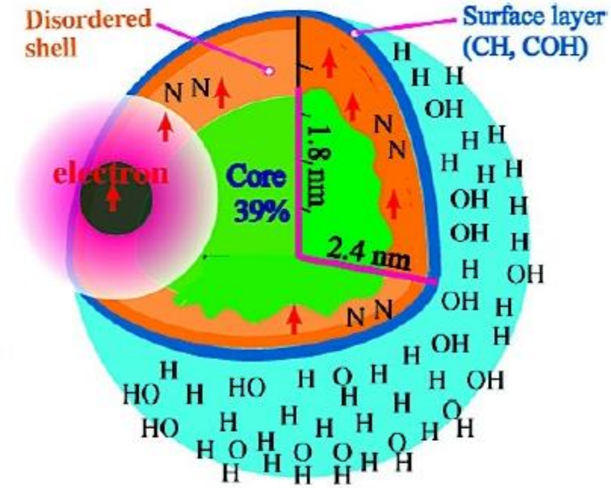
Item	Description of samples	*g*-value	ΔH, mT
1	Preparation [1], purification [7], 4% ash	2.0030(4)	0.85(7)
2	Sample no. 1, modification of the surface by chlorine	2.0028(7)	0.88(8)
3	Sample no.1, modification of the surface by CH_3	2.0029(6)	0.84(9)
4	Preparation and purification [3], 2% ash	2.0022(3)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

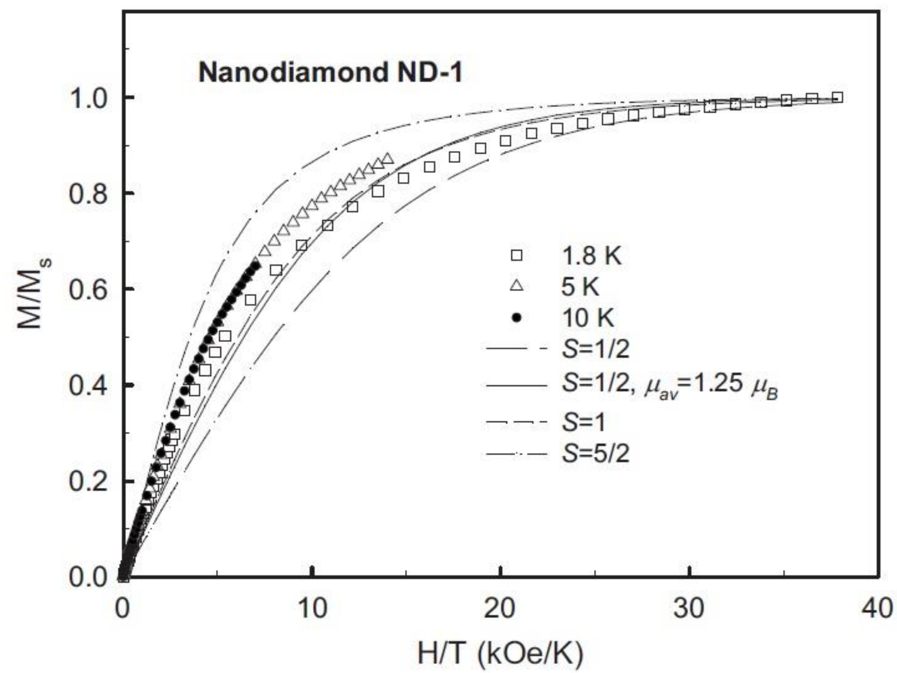




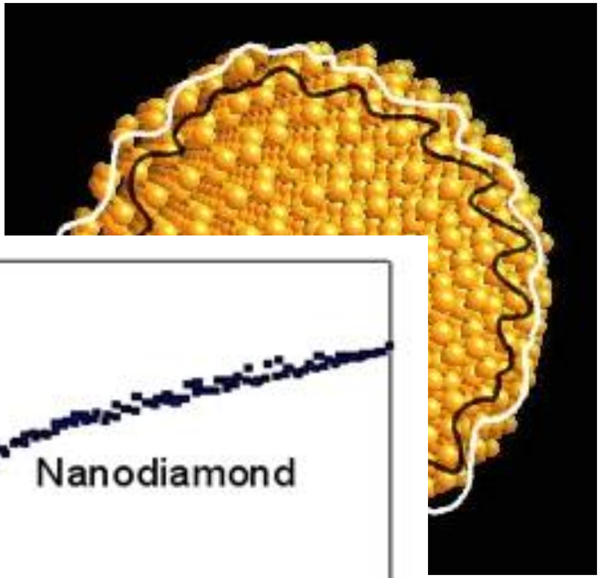


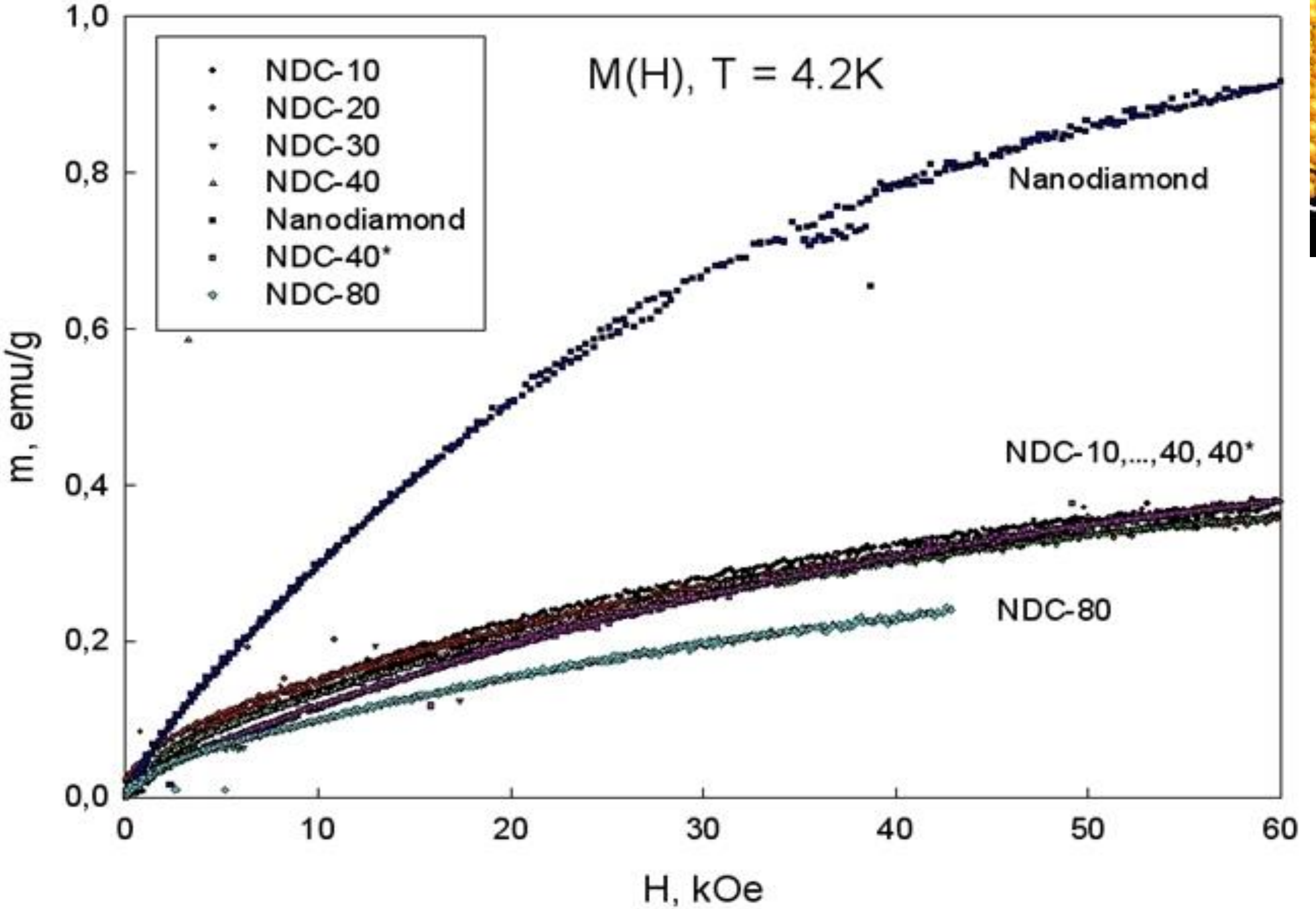
E. M. Levin at al. Magnetization and ^{13}C NMR spin-lattice relaxation of nanodiamond powder. *Phys. Rev. B.* **77**, 054418 (2008).

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





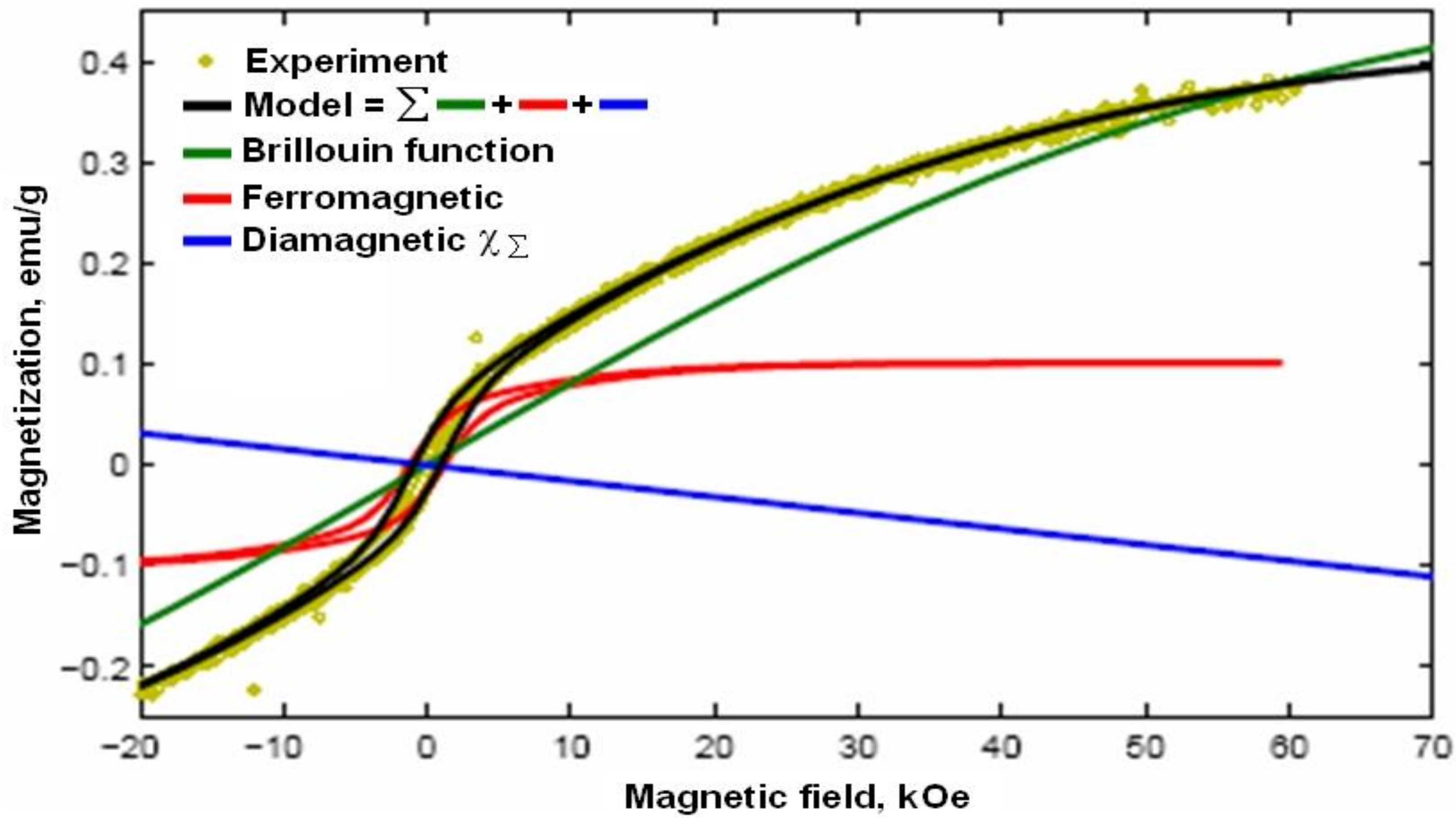
Magnetic susceptibility

Table 1 – The results of magnetic measurement of diamond-graphane flakes composites

#	γ, %	H, Oe	T, K	Doped by	M_{ferro}, emu/g	N, spin/g	N/N_m	g	spin	χ_Σ
1	0	var	4,2	Fe*	0,05	3,00E+19	1600	4,4	0,5	4,37E-06
2	10	var	4,2	Fe	0,1	5,46E+19	835,16	2	0,5	-1,58E-06
3	20	var	4,2	Fe	0,1	5,81E+19	719,80	2	0,5	-2,14E-06
4	20	500	var	Cr		4,50E+19	261,38	2	0,5	2,40E-06
5	30	var	4,2	Fe	0,08	5,46E+19	706,67	2	0,5	-1,55E-06
6	40	var	4,2	Fe	0,07	6,60E+19	543,12	2	0,5	-2,00E-06
7	40	var	4,2	Fe	0,04	6,95E+19	515,77	2	0,5	-2,33E-06
8	40	500	var	S		3,60E+19	995,72	2	0,5	-1,20E-07
9	50	var	2	Fe	-	2,00E+20	167,28	2	0,5	1,52E-05
10	60	500	var	SiO_2**		9,26E+18	3388,28	2	0,5	4,30E-07
11	80	var	4,2	Fe	0,04	6,58E+19	423,85	2	0,5	-3,85E-06

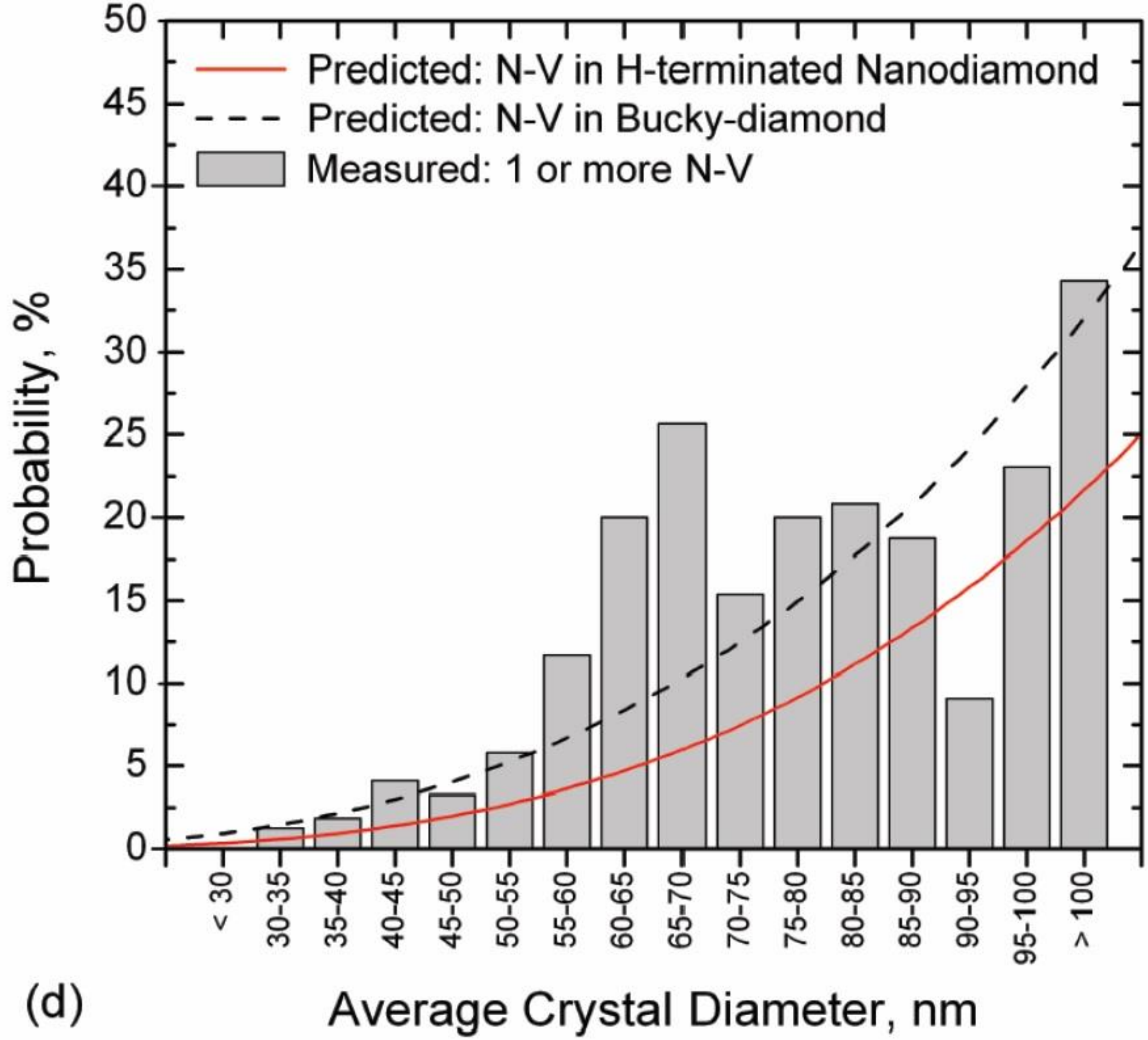
Notes: *There are Fe < 0.4% in all samples except #1 where Fe < 4.3 mass %.
**NDC where nanodiamond was substituted by SiO_2 completely.

NDC = 10^{19} DCs. Paramagnetic DC dislikes Ferromagnetic Impurities. Why?



E.g. note to: J Narayan, A Bhaumik. *J Appl Phys* **118**, 215303 (2015). We think that Ferromagnetism (20 emu/g at 2 Oe) of Q-Carbon Impossible for any carbon!

Why DC dislikes NV-centers?



C Bradac at al. *Nano letters* **9** (10), 3555-3564 (2009).

ND (> 20 nm) ≠ DC (2 ÷ 5 nm)

- Crystal field (> 20 nm) ≠ close packing DC (2 ÷ 5 nm)
- Nobody can take into account,
  - that crystal field ≠ field of close packing structure
  - **50 nm ND & 2-5 nm DC with T_S 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.
- ND dot diameter and height
- 735 nm ± 27 nm and 61 nm ± 3 nm
- 820 nm ± 20 nm and, 245 nm ± 23 nm

A model of T-spin – Hopf Soliton

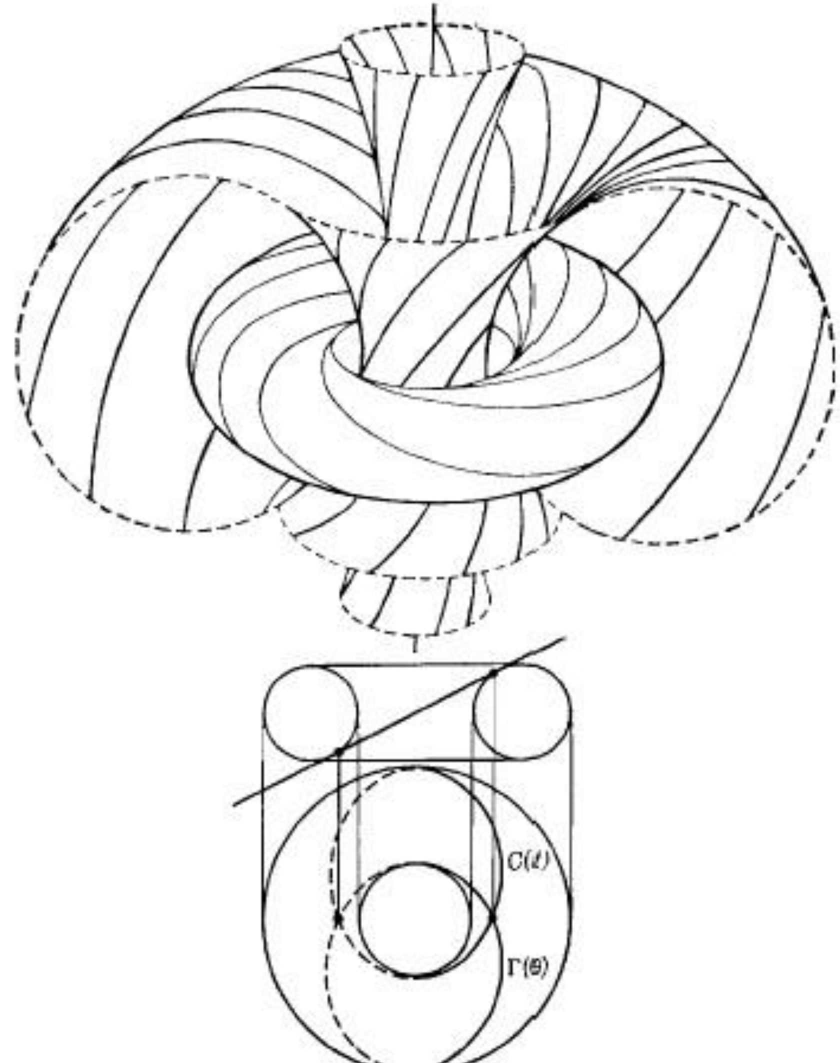
$$\boldsymbol{m}(x,y,z)$$

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

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

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

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



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.

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 Diamond Compass!**

Hausdorff' measure, Tamm & Hopf

- Théorème sur le tore de M. Villarceau (Yvon). Nouvelles annales de mathématiques, journal des candidats aux écoles polytechnique et normale, Sér. 1, 7 (1848), p. 345-347.
- Felix Hausdorff. Dimension und äußeres Maß // Mathematische Annalen 79 (1-2), 157-179 (1918).
- Ig. Tamm. Zur Quantentheorie des Paramagnetismus // Zeitschrift für Physik 32 (1), 582-595 (1925).
- Ig. Tamm. Über die Quantentheorie der molekularen Lichtzerstreuung in festen Körpern. Z. Phys. 60(5-6), 345-363 (1930).
- Heinz Hopf. Über die Abbildungen der dreidimensionalen Sphäre auf die Kugelfläche // Mathematische Annalen 104 (1), 637-665 (1931).
- Ig. Tamm. Über eine mögliche Art der Elektronenbindung an Kristalloberflächen // Zeitschrift für Physik 76 (11), 849-850 (1932).

Лето

From 2D compass to 3D Compass

- Z Nussinov, J van den Brink. **Compass models**: Theory and physical motivations // Rev. Mod. Phys. 87 (1), 1 (2015).
- O A Starykh. **Unusual ordered phases** of highly frustrated magnets: a review // Reports on Progress in Physics 78 (5), 052502 (2015).
- J Maciejko, G A Fiete. **Fractionalized topological insulators** // Nature Physics 11 (5), 385-388 (2015).
- N Seiberg, E Witten. **Gapped Boundary Phases** of Topological Insulators via Weak Coupling // Preprint arXiv:1602.04251 (12 Feb 2016).
- T Chern. Simple Models for **All Topological Phases** // Preprint arXiv:1602.05188 (16 Feb 2016).
- K Hashimoto, T Kimura. Topological Number of **Edge States** // Preprint arXiv:1602.05577 (17 Feb 2016).

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

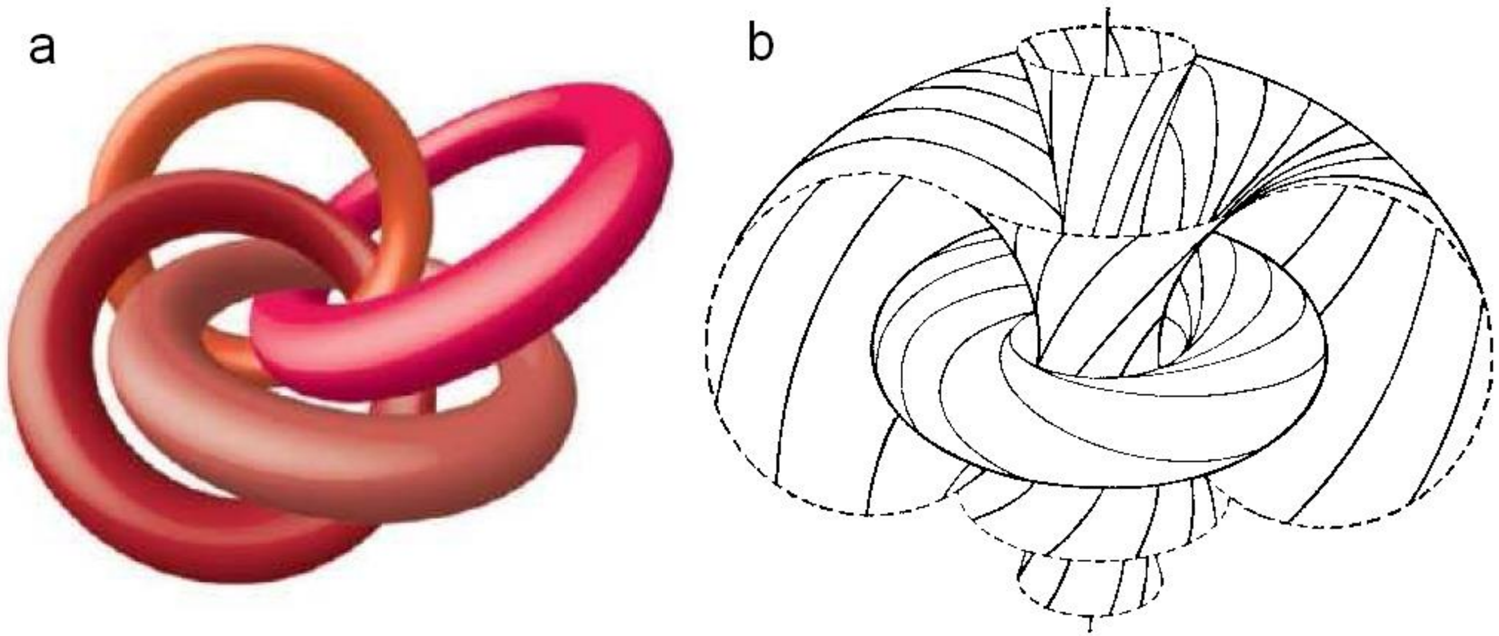
«Surface electronic states of insulator can be metallic» *I E Tamm* ***1932***

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

J Moore ***2010***

Topological insulators

Topological insulators – insulator inside, conducting on the surface.



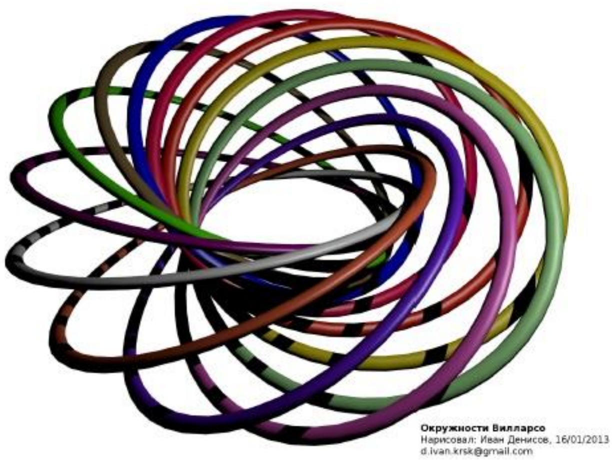
Hopf map $R^3 \subset S^3 \rightarrow S^2$

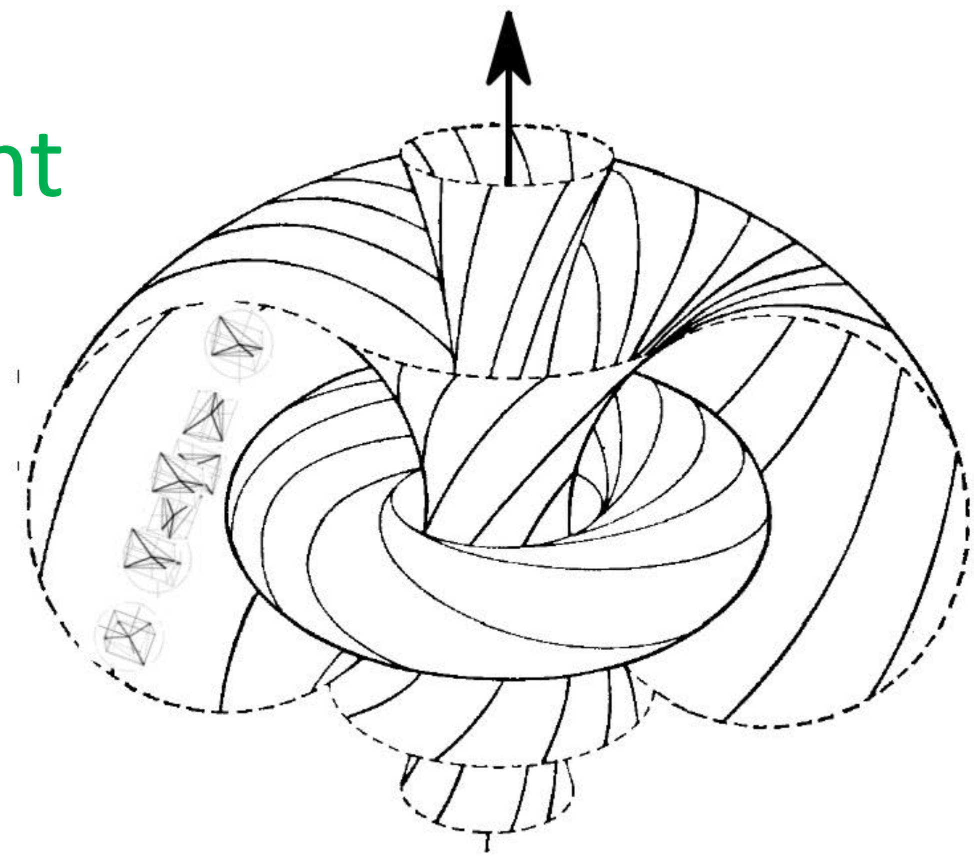
a) J E Moore (2010) The birth of topological insulators. Nature, 464 (7286), 194-8.

b) P I 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!**

Paramagnetic nature of diamond compass is Feynman trajectories

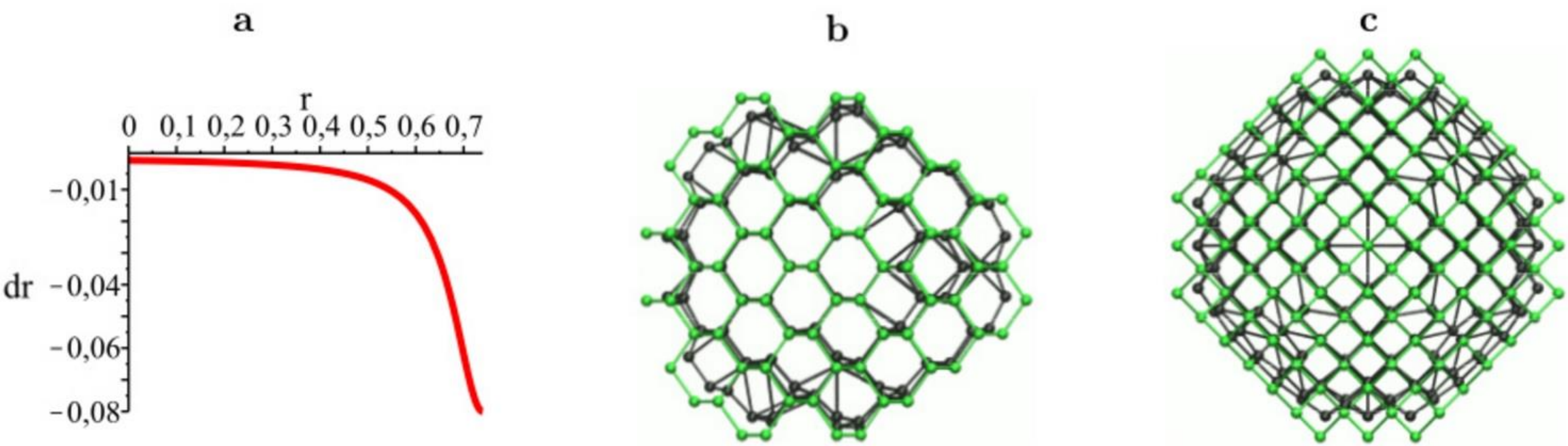
Pauli spin current





Quantum Nonlocal Polarizability of Diamond Compass?

Quantum size effects in DC



(a) Magnitude of the atom position shift to the origin vs. coordinate (fitted to the function (1) with parameters s = 10, a = 0.08). (b, c) Compression of the C_{302} diamond ball according to the function (1). Initial diamond ball (green) and deformed (black)

$$dr(r) = -\frac{a}{(s - rs/R) + 1} \qquad (1)$$

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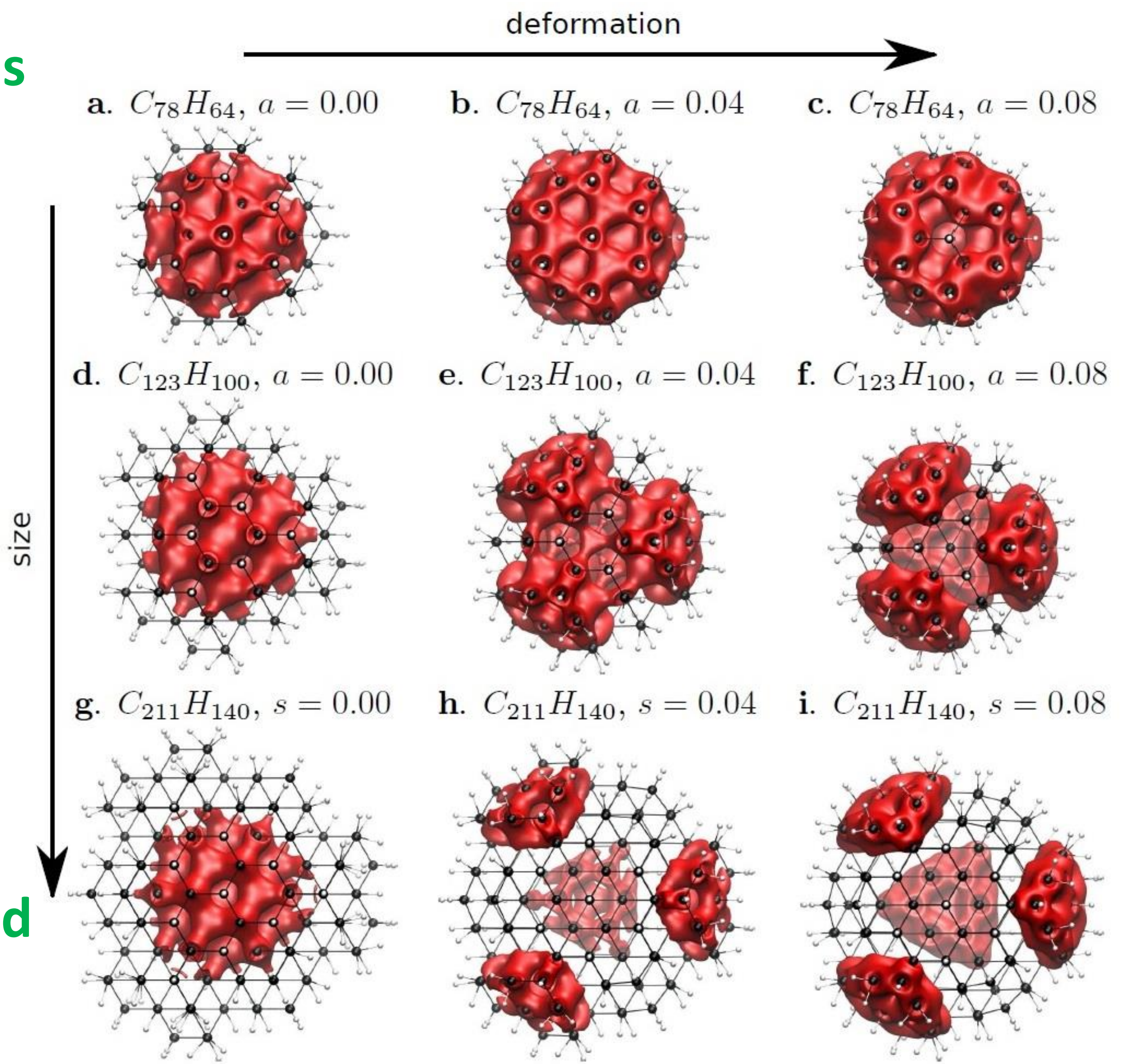
Wavefunctions isosurfaces (0.02 a.u.) for the lowest bonding orbital of diamond compass of three sizes:

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

and three fixed compressions



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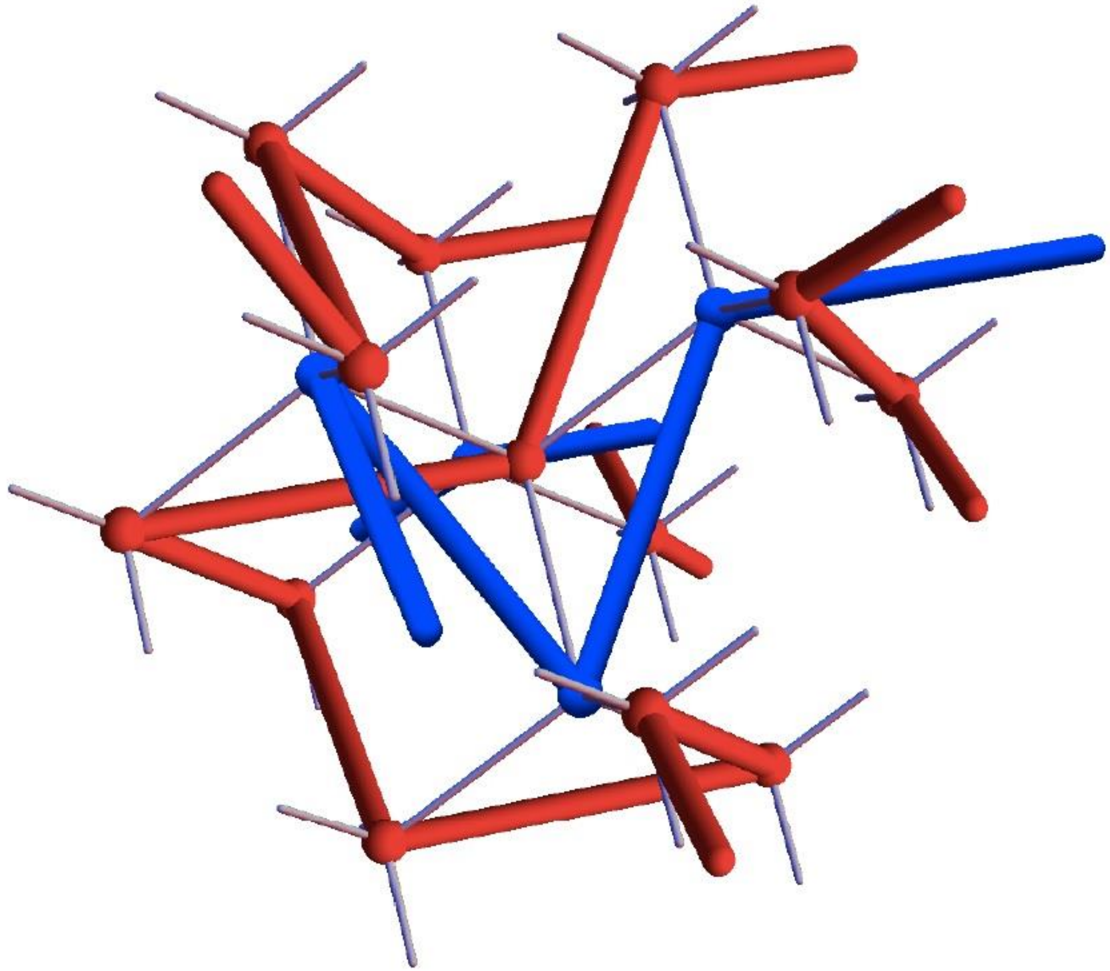

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Conclusions

- The **DC** ~ 2 – 5 nm has $\mathbf{T_S}$ pyrocarbon surface from distorted graphane-like flakes
- 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** ($\mathbf{T_S}$/**DC**)
- The model $\mathbf{T_S}$ 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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DC ↔ CD, T-spin …

My Boss & Seasons

- Photo &
- Hunt
  - The Passion

Boss helped me to grasp:

The Silence is Freedom