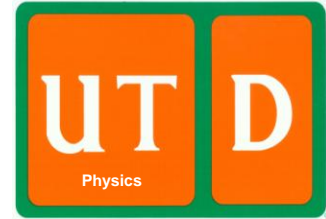




“Road to Room Temperature Superconductivity”,  
Loen, Norway, June 17-23, 2007



## **Nanotechnology for Promise of RTS: Search for Excitonic SC by combined SQUID/LFMA**

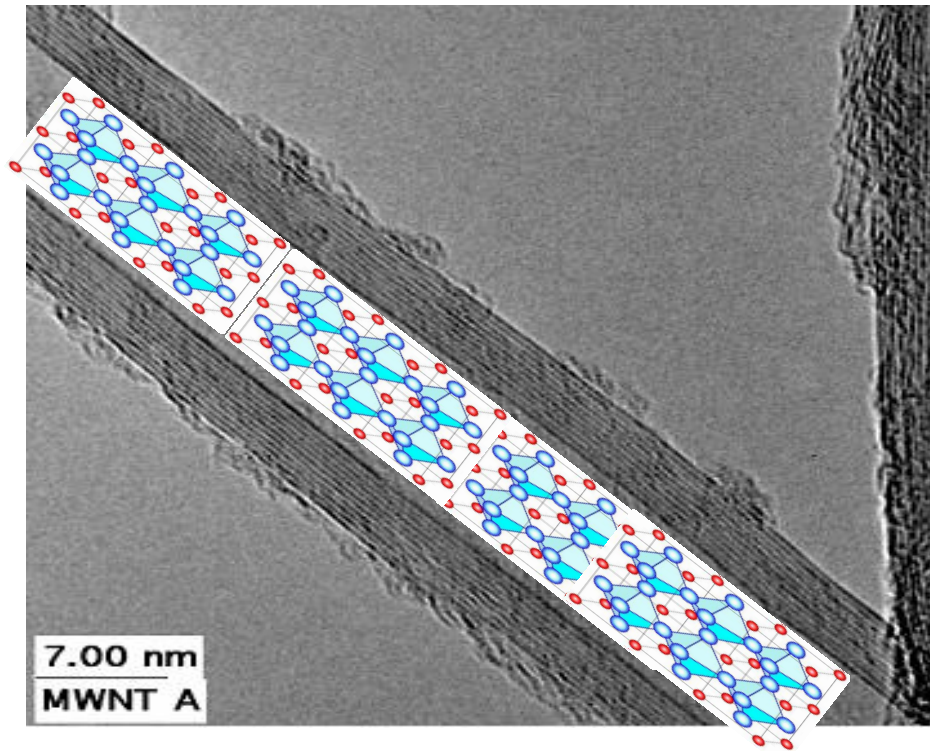
Ali Aliev, Ray Baughman and  
Anvar Zakhidov

*Nanotech Institute*  
*The University of Texas at Dallas*

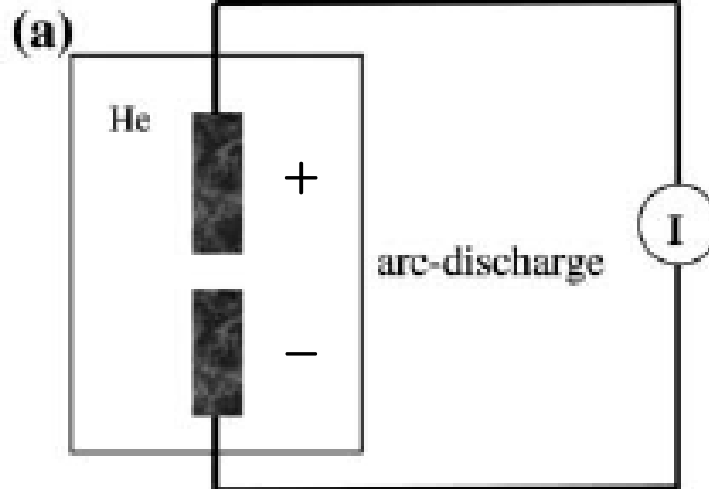
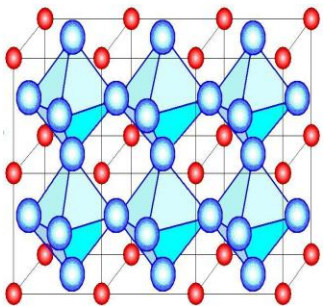
# Outline

- Nanotechnology gain from HTS: discovery of single wall carbon nanotube by arc-synthesis
- Nano-system Zoo for RTS: dots, tubes, opals, inverted opals.
- Conventional LTS in nano-space: Pb inverted opal
- Inverse carbon opals: diamagnetism in  $\text{Na}_x\text{WO}_3$  at 125 K , and in  $\text{Li}_x\text{WO}_3$ -y at 132K
- Prospects: curved HTS and extra“excitonic pairing glue” across the interface in nanostructured SCs

Multi-walled



MWNT Cross-sectional view



Iijima found MWCNTs at the cathode of arc discharge system. For C60 synthesis No catalyst was used

# Large-scale production of single-walled carbon nanotubes by the electric-arc technique

C. Journet\*, W. K. Maser\*†, P. Bernier\*, A. Loiseau‡, M. Lamy de la Chapelle§, S. Lefrant§, P. Deniard§, R. Lee|| & J. E. Fischer||

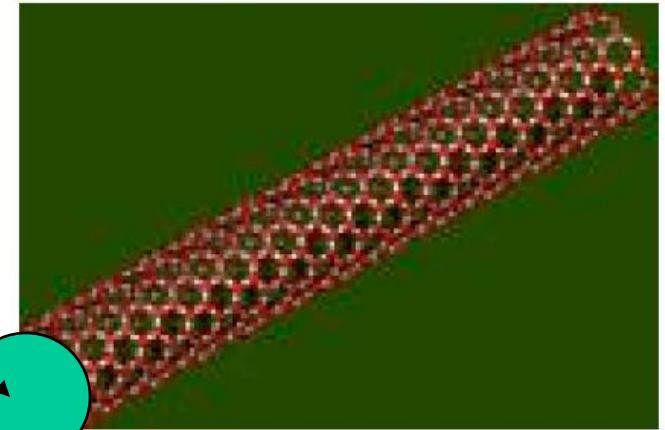
\*Groupe de Dynamique des Phases Condensées, Université de Montpellier II, 34095 Montpellier cedex 5, France

†LPS, ONERA, BP 72, 92322 Châtillon cedex, France

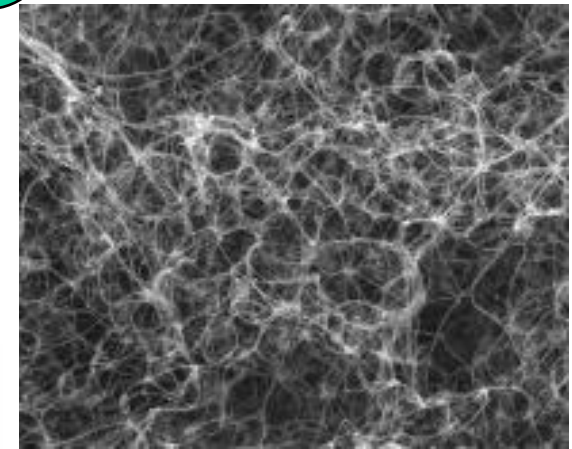
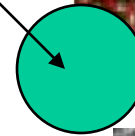
§IMN, Université de Nantes, BP 32229, 44322 Nantes cedex 3, France

||LRSM, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6272, USA

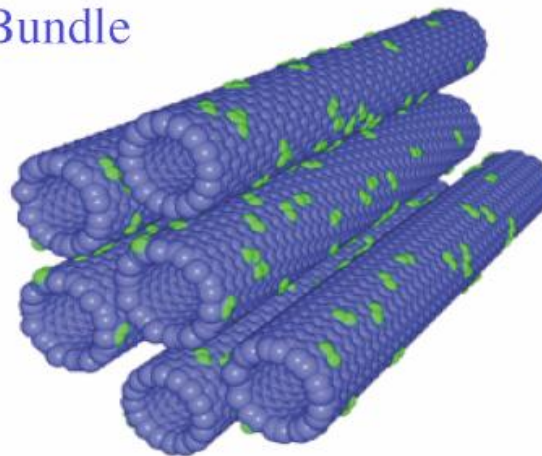
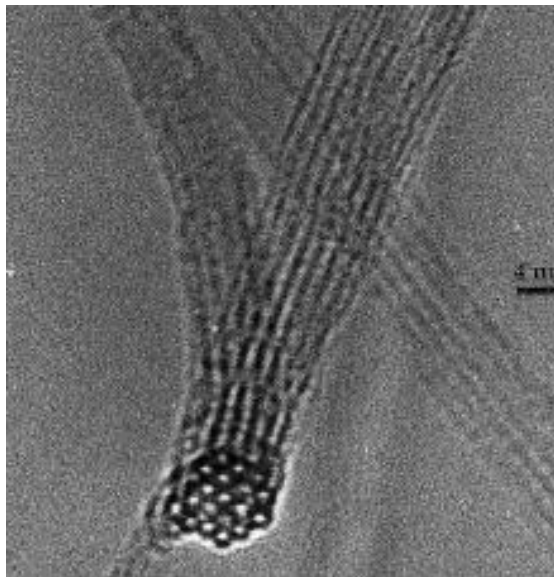
Single-walled



Y-catalyst cluster



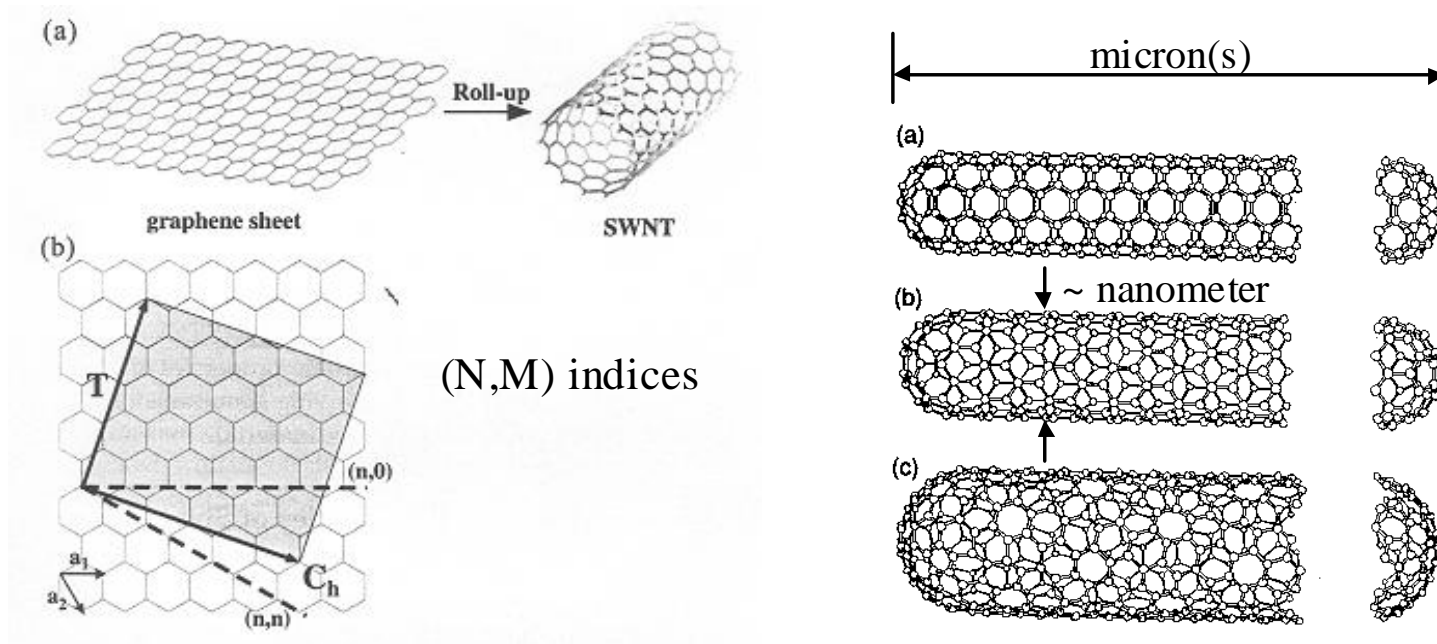
Bundle



Used Y, Ba, Cu, O  
In anode carbon rod  
with a hope to obtain  
MWCTS filled with 123  
HTS

# Description of CNT Tubes

Carbon nanotubes – quasi 1d structures with unique properties



- Single wall NT
- Multiwall NT
- NT ropes
- NT mats...
- Armchair (5,5) tube - metal
- Zig-zag (9,0) tube – very small gap semiconductor (curvature effect)
- Chiral (10,5) tube - semiconductor

2-D layers of graphene at nanoscale self-curve into 0-D Dots, 1-D nanotubes, 3-D networks of inverted f.c.c.

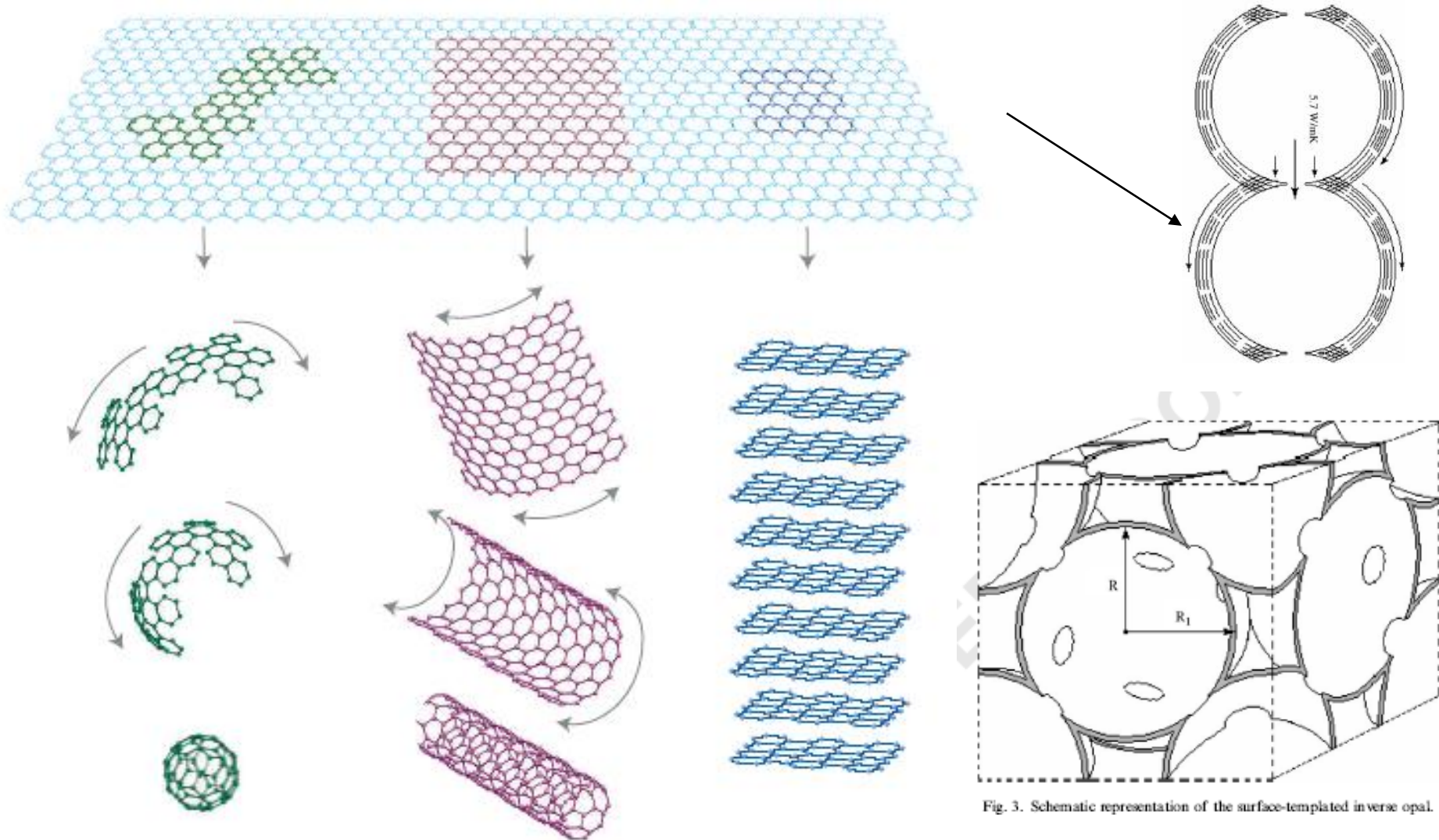


Fig. 3. Schematic representation of the surface-templated inverse opal.

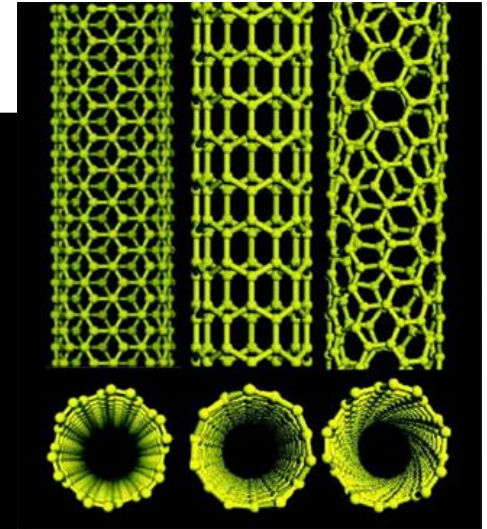
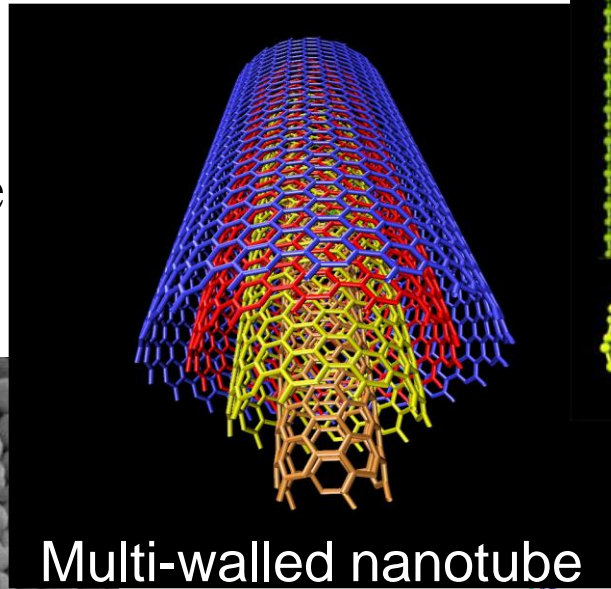
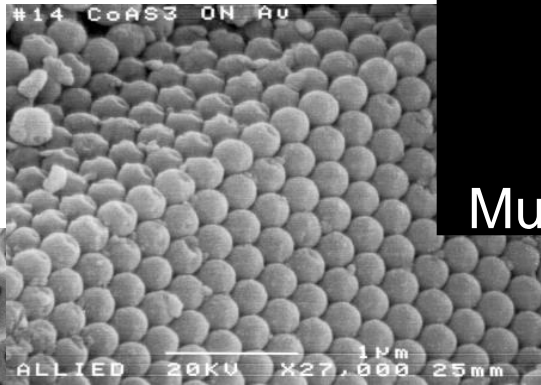
# NanoTemplates for Superconductors

## Carbon Nanotubes

Can we create HTS materials at nanometer scale with Increased  $T_c$ ,  $H_c$ ,  $I_{sc}$ , etc. via huge interface and curvature

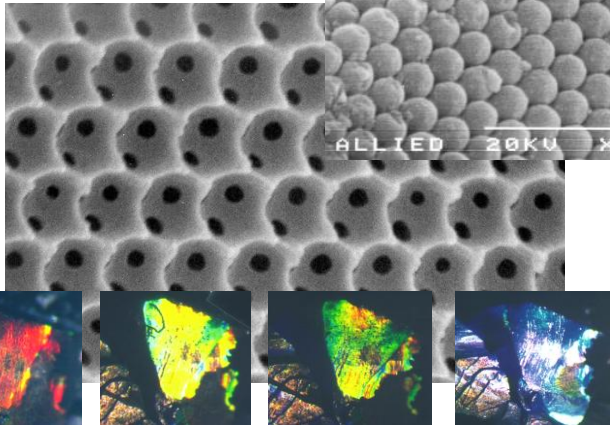
## Multiwall nanotubes

## Opals

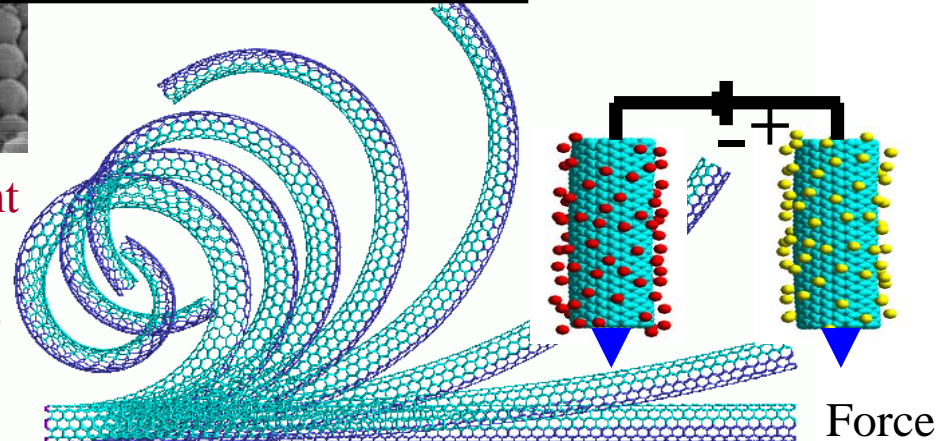


Double Layer Charge injection in nanotubes

## Inverted opals



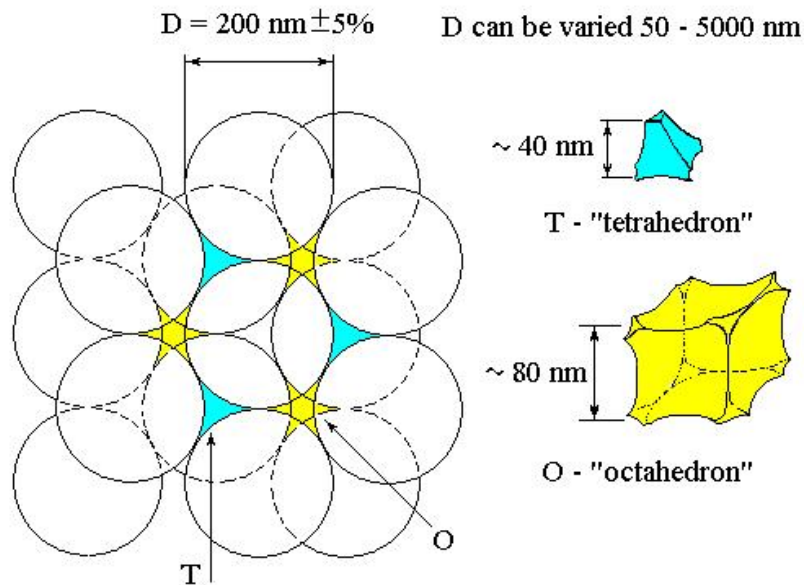
Transparent metallic nanofoams



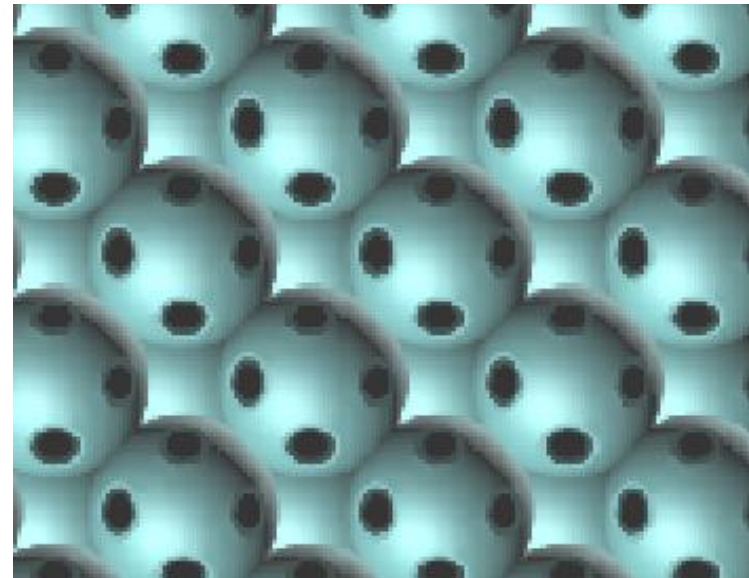
Force

# Geometry for Opal-Derived FCC Structures

## (111) Plane for Direct Opal



## (100) Plane for Surface-Templated Inverse Opal



- Infiltration can either coat the internal surface or fill the internal volume.
- Template (SiO<sub>2</sub> opal) cannot be infiltrated and then extracted unless  $1.11 > d/D > 1.15$ ,  
d - intersphere separation, D - sphere diameter



# Advantages of nano-space for growing HTS

Huge interface:  $>100 \text{ m}^2/\text{cm}^3$  accessible for SC growth.

Possibility to dope by “double layer charge” of ions at the surface

Possibility to self-assembled (SAM) layers of excitonic molecules

Curved surfaces: new phonon spectra

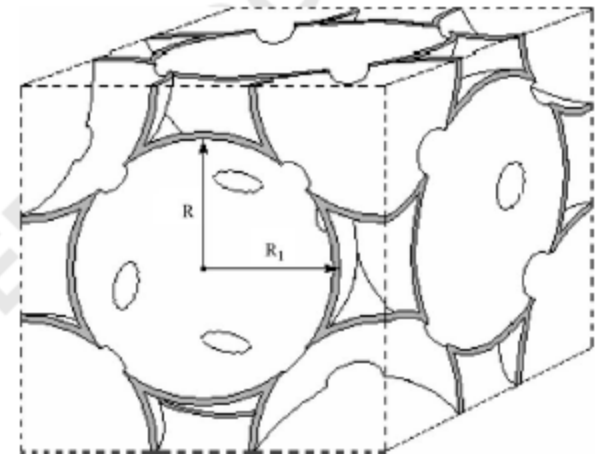
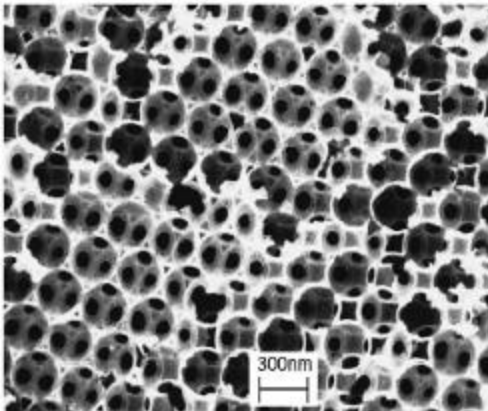
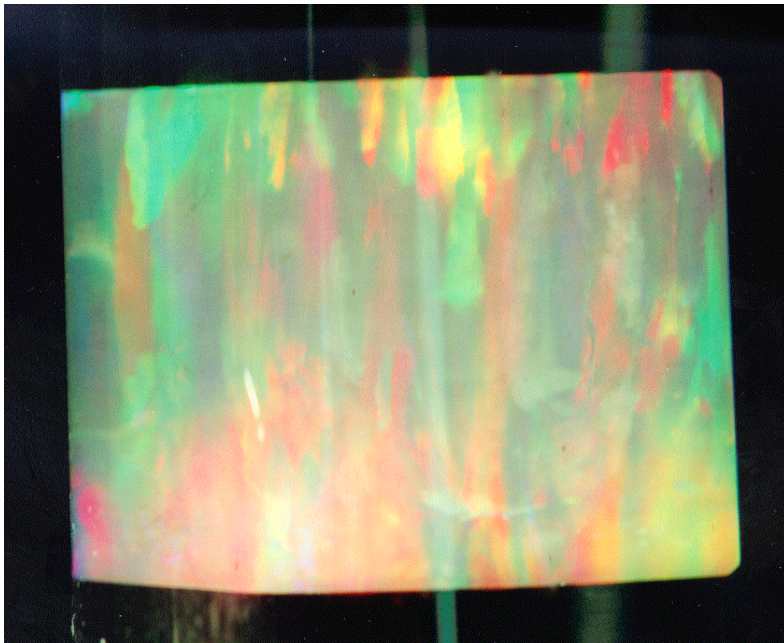


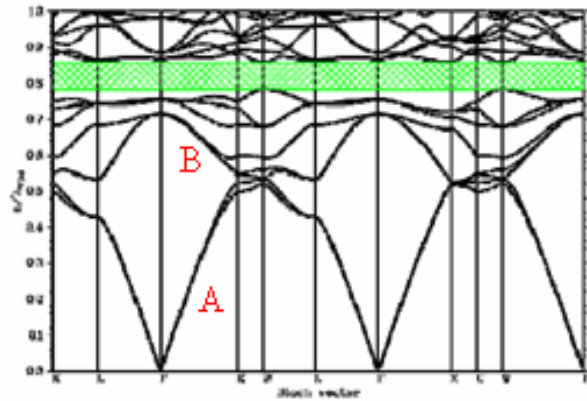
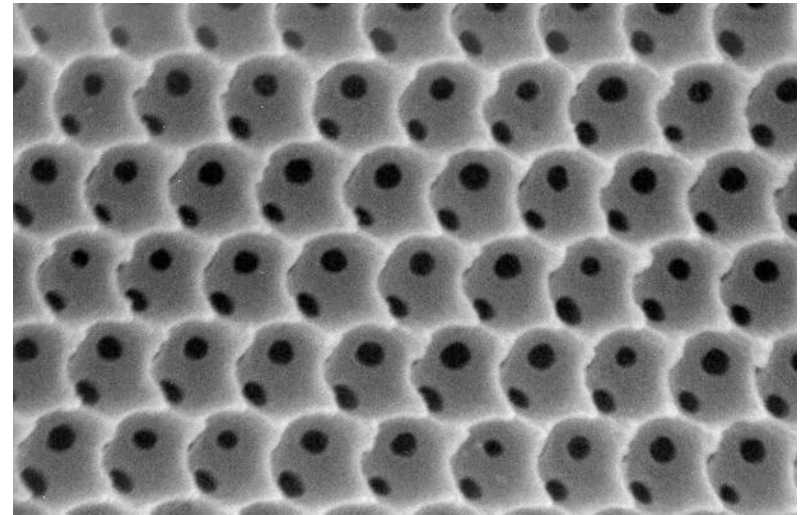
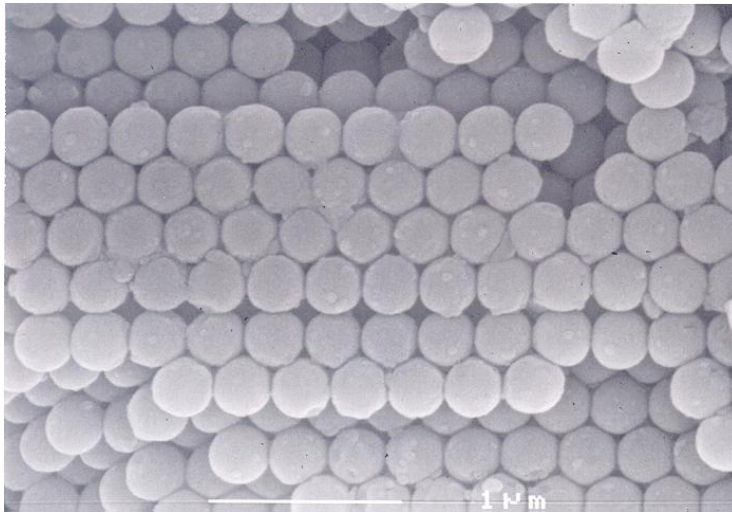
Fig. 3. Schematic representation of the surface-templated inverse opal.

# Synthetic Opal: Porous Silica Filled with Chloroform



However the colors are not very bright, meaning PBG is not wide, since filling factor for air is small

# Porous Opal Photonic Crystals



Huge internal porosity:  
> 100 m<sup>2</sup>/cm<sup>3</sup>

There is a range of frequencies (green color) where light can not propagate

# Inverse Opals Have $> 75\%$ porosity

*Science*,  
Vol. 282,  
(1998),  
p. 833



This inverted opal material is a transparent polymer

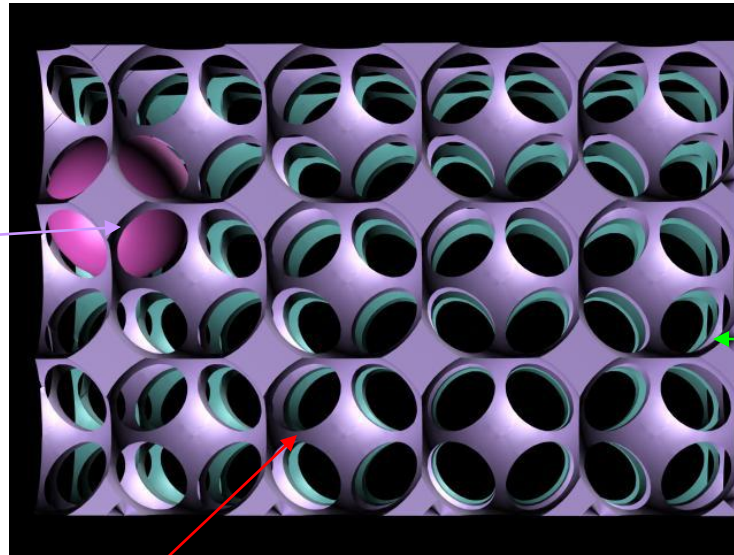
Any material can be Used for making Inverted opals:

- Gold
- Diamond
- Carbon (conductive)
- Metals,
- semiconductors
- superconductors

# Inverse Opals: Advantages for Templating of different materials

- Low filling factor  
 $ff < 0.24$

- Can infiltrate easily various materials with large change of  $(1-ff)$



- Can be made of any material:

- Metals,
- semiconductors,
- Lasing media: Er, Eu.
- Quantum dots

• Can change  $n$  by filling with transparent liquids

Can use electrochemistry, if the matrix is conductive

- Control connectivity between T and O via narrow necks:  
“network-cermet” transition: change of R and T

# LTS in nanostructure: Pb-in-opal. Will $T_c$ , $H_c$ , change for Pb clusters network



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Physica C 453 (2007) 15–23

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**PHYSICA C**

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## Superconductivity in Pb inverse opal

Ali E. Aliev <sup>\*</sup>, Sergey B. Lee, Anvar A. Zakhidov, Ray H. Baughman

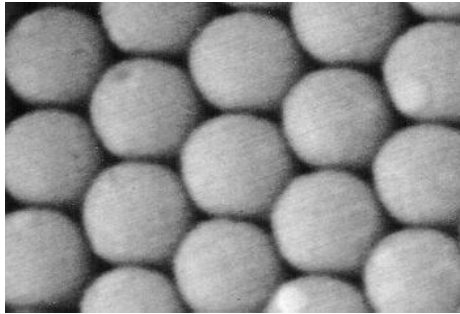
*Nano Tech Institute, University of Texas at Dallas, Richardson, TX 75083-0688, United States*

Received 27 December 2005; received in revised form 14 October 2006; accepted 8 December 2006

Available online 22 December 2006

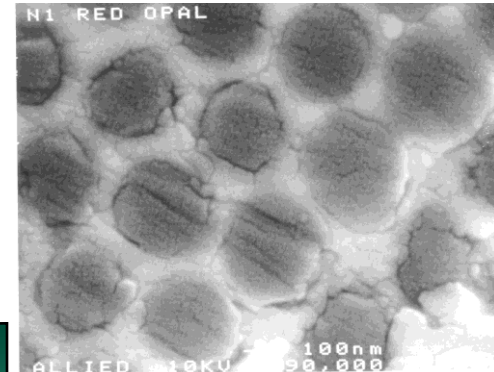
# Fabrication of LTS: Pb Inverse Opal

## 1. POROUS SILICA OPAL



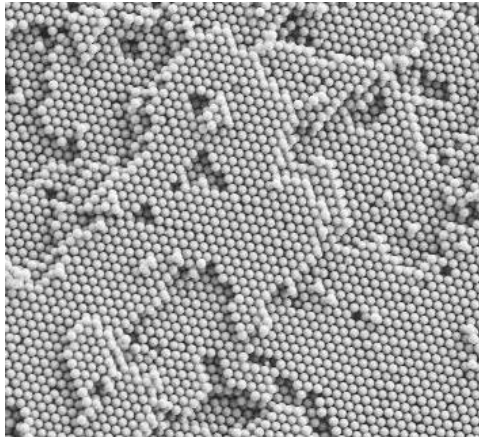
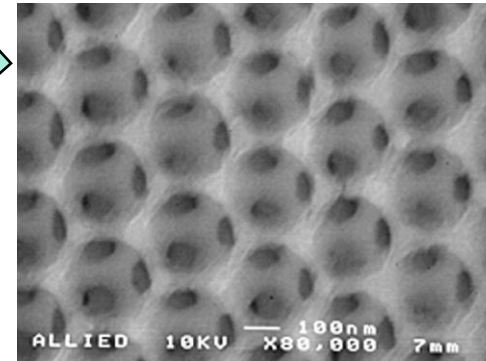
HIGH-PRESSURE  
MELT-INFILTRATION

## 2. METAL-SILICA NANOCOMPOSITE



REMOVAL OF  
SILICA WITH HF

## 3. METALLIC INVERSE OPAL



# Structure of Pb-clusters network in pores of opal: Spheres connected via cylindrical channels

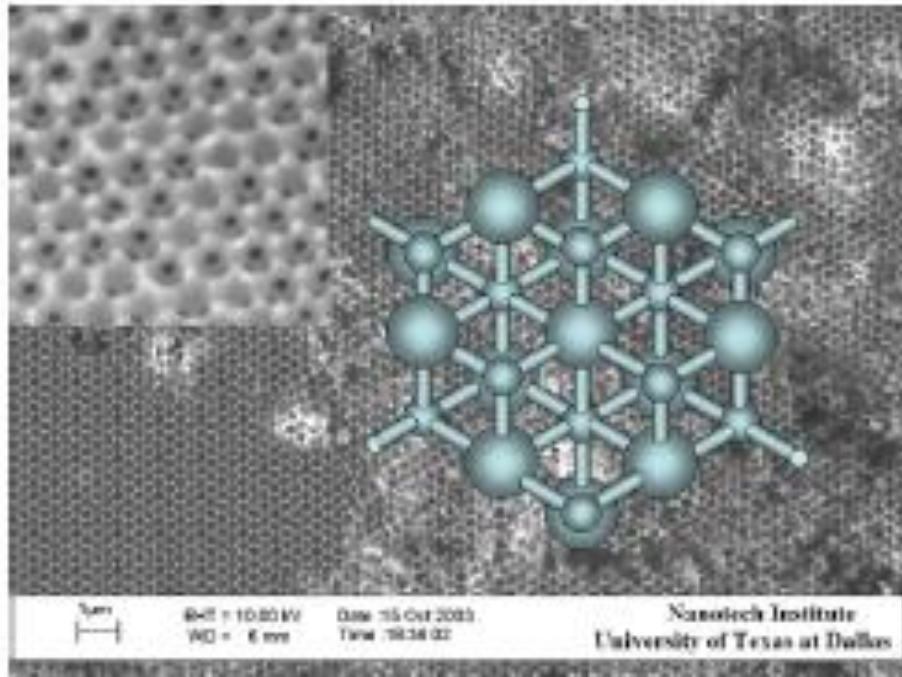


Fig. 1. SEM image of the (111) plane of the cleaved edge of a lead inverse opal. Highly crystalline structure is observable throughout the whole region. The top left corner inset shows a detail where the three channels in each void sphere connect with the spheres in the underlying layer. The void sphere diameter is 300 nm, which correspond to a red opal. The right inset shows a schematic representation of a lead inverse opal: octahedral and tetrahedral pores of fcc opal infiltrated with Pb can be represented as spheres ( $r_o = 0.414 \cdot r$ ,  $r_t = 0.225 \cdot r$ ) connected through cylindrical channels ( $r_{ch} = 0.155 \cdot r$ ).

Table 1  
Sample parameters

Parameter	Red inverse opal	Green inverse opal	Blue inverse opal	Bulk lead, Pb
Octahedral radius, nm	62.1	45.54	33.14	
Tetrahedral radius, nm	33.7	24.75	18.0	
Radius of channel, nm	23.2	17.05	12.4	
Weight, mg	24.8	24.8	24.8	211.88
Volume, mm <sup>3</sup>	8.5	8.5	8.5	18.75
Density, g/cm <sup>3</sup>	2.92	2.92	2.92	11.3

The radius of the lead infiltrated octahedral pores represented by big spheres in right inset to Fig. 1 is  $r_o = R(\sqrt{2} - 1)$ , the radius of tetrahedral pores is  $r_t = R(\sqrt{3}/2 - 1)$ , and the radius of the interconnected channels is  $r_{ch} = R(2/\sqrt{3} - 1)$ .  $R$  is the radius of void spheres remaining after chemical extraction of silica spheres of direct opal.



# Magnetization in red Pb opal ( $D=300$ nm)

$T_c$  increase from 7.1 K to 7.3 K,  $\Delta T_c = 0.3$  K

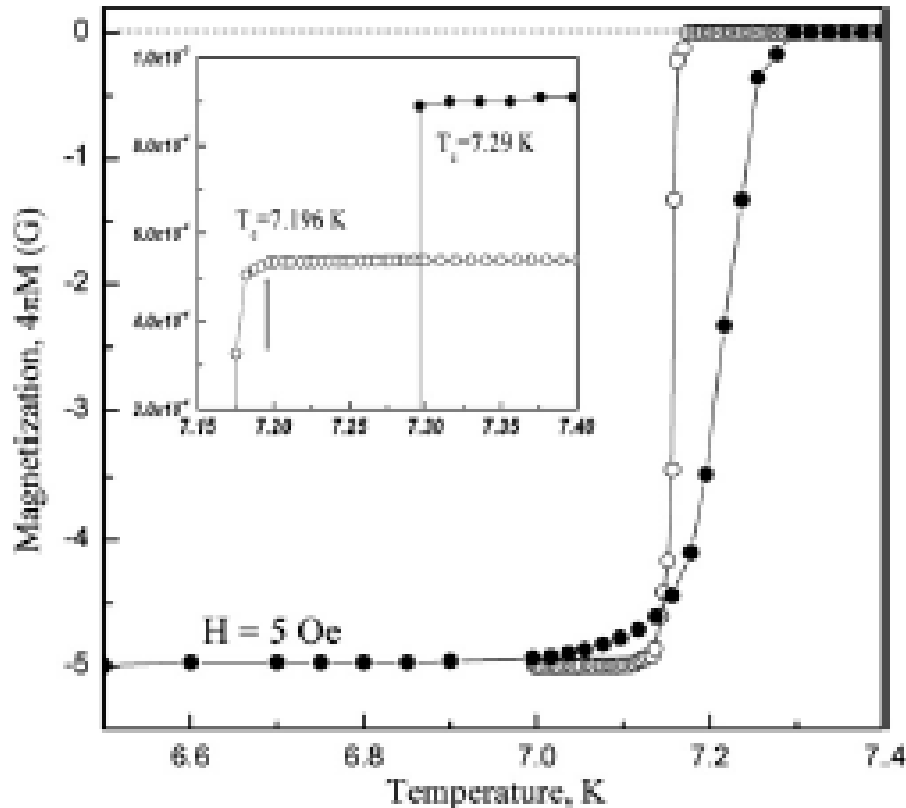


Fig. 2. The temperature dependences of ZFC magnetization for red Pb inverse opal (solid circles) and bulk Pb (open circles) at 5 Oe. The inset shows the ZFC magnetization near  $T_c$ .

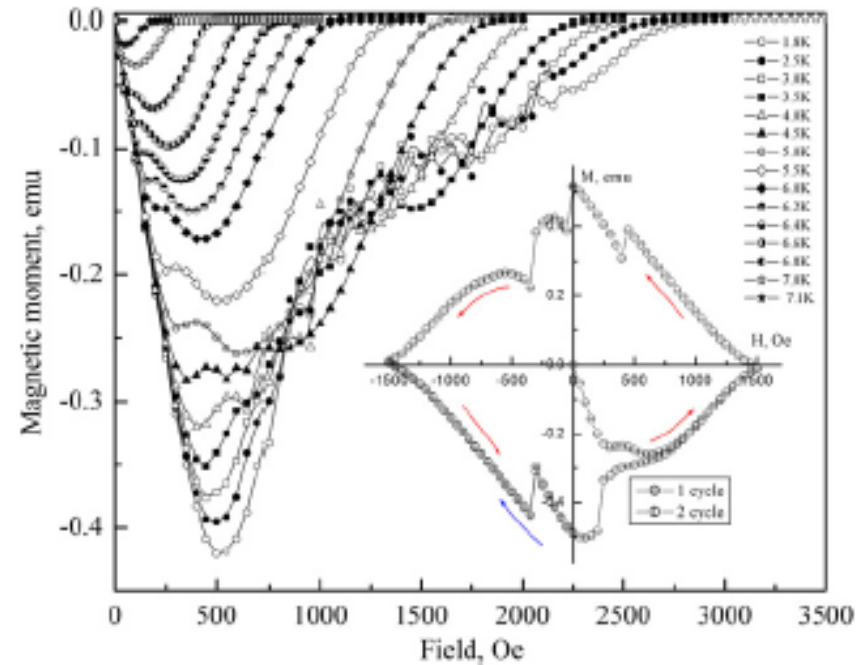


Fig. 4. Magnetization vs. external field for different temperatures. Two well-distinguished peaks have different behavior. Below 5 K the second maximum is damped by the oscillation of the magnetic moment which disappears again at higher fields,  $H > 0.8H_{c2}$ . The inset shows the whole

# 4-times Increase of critical Hc2 in Pb- opal

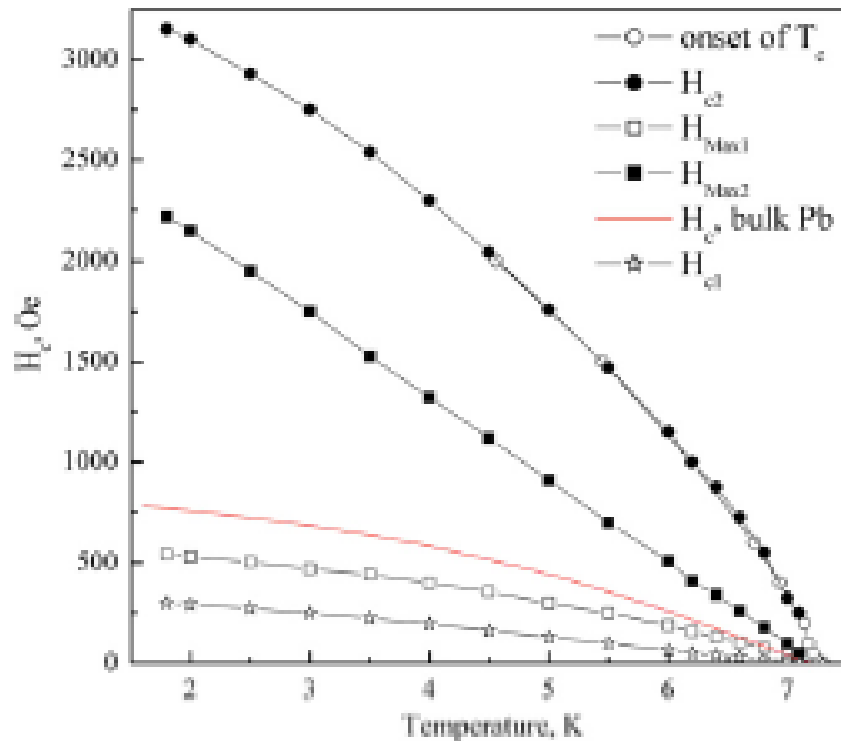


Fig. 6. Temperature dependence of various characteristic fields for lead inverse opal. The open circles are  $T_c(H)$ , the temperature of the onset of superconductivity. The solid circles correspond to the upper critical field  $H_{c2}$  at which a tangent to the rising branch of magnetization intersect the  $H = 0$  line.  $H_{c1max1}$  and  $H_{c1max2}$  correspond to the two maximum on  $M(H)$ .  $H_{c1}$  is the lower critical field. The solid line is the  $H_c(T)$  for the bulk Pb sample [32].

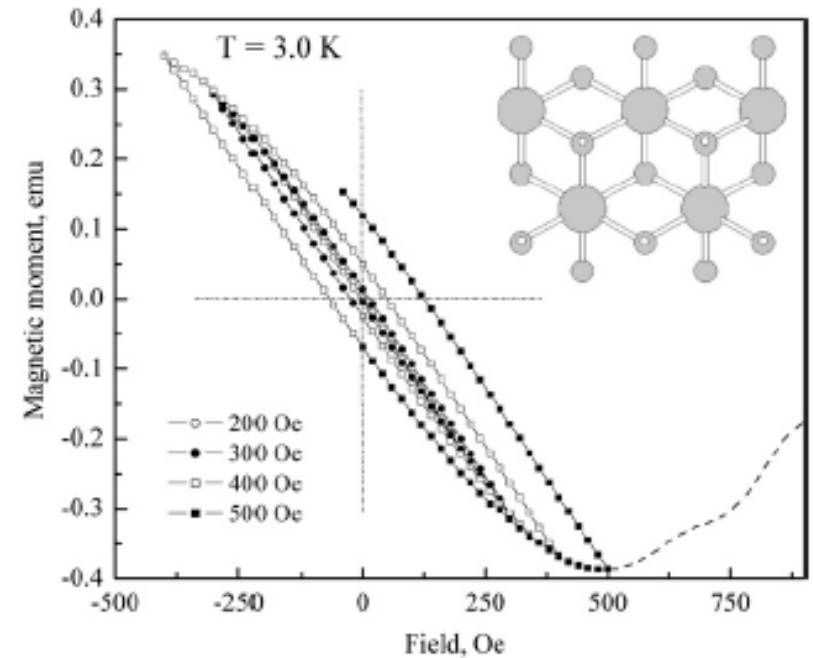
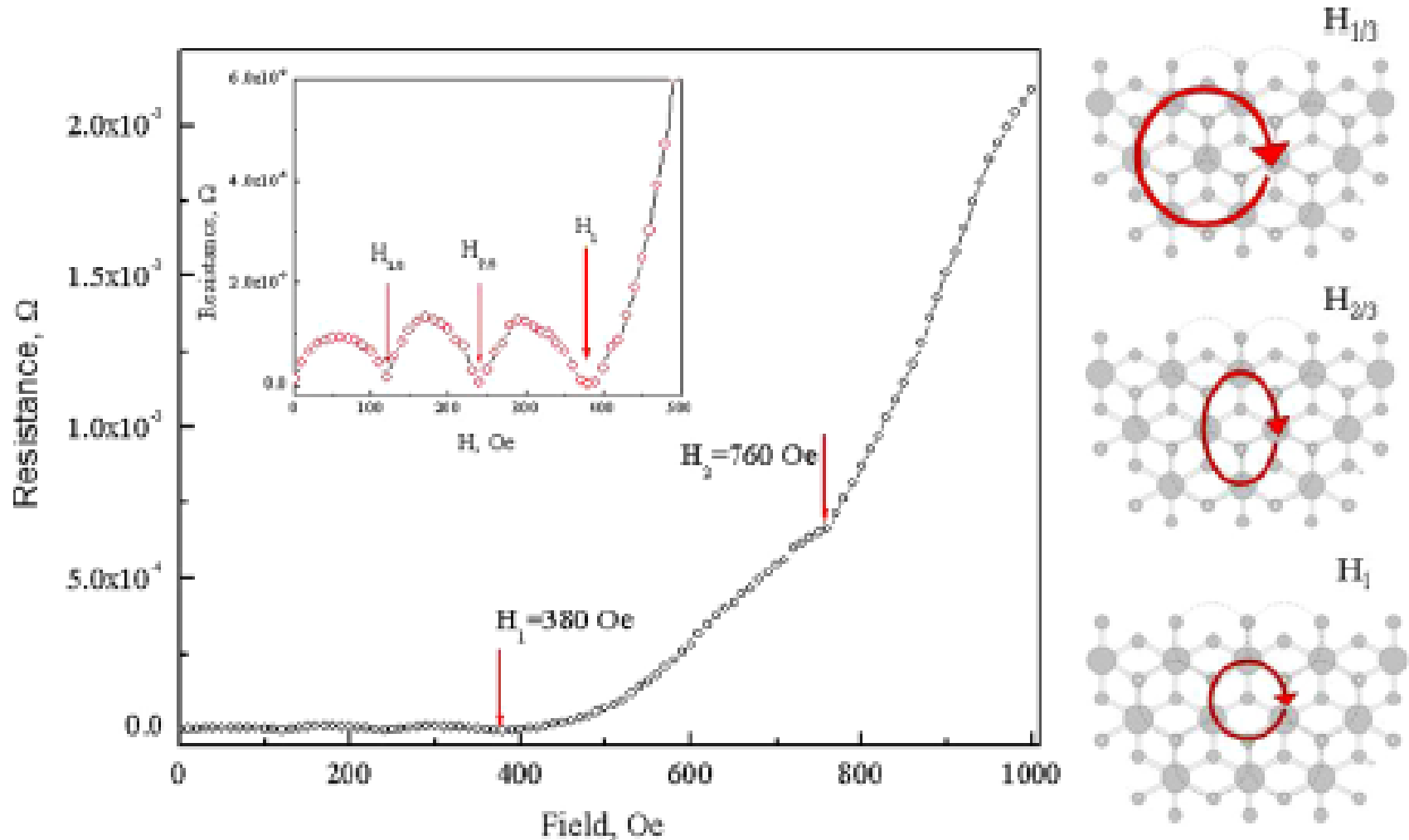


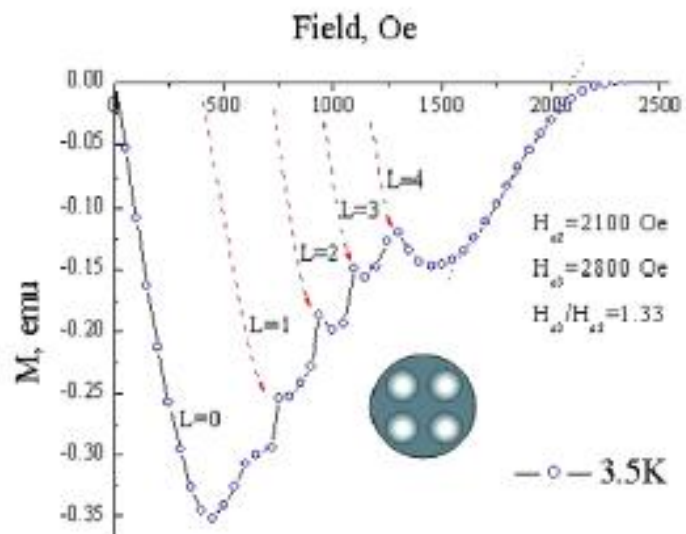
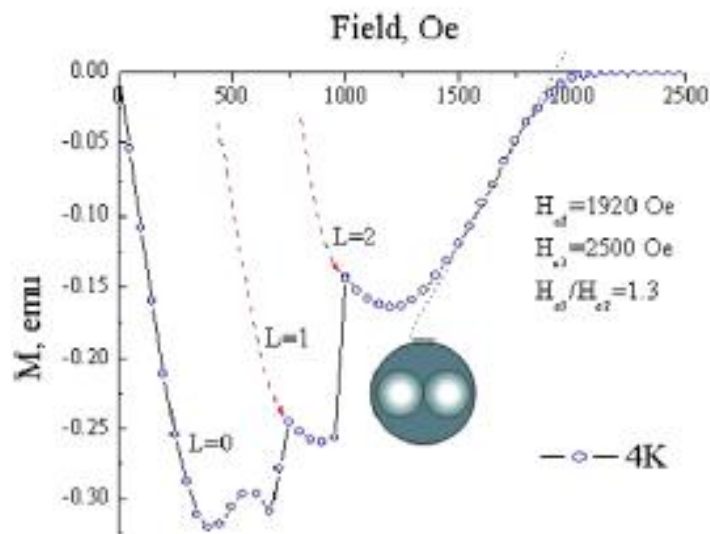
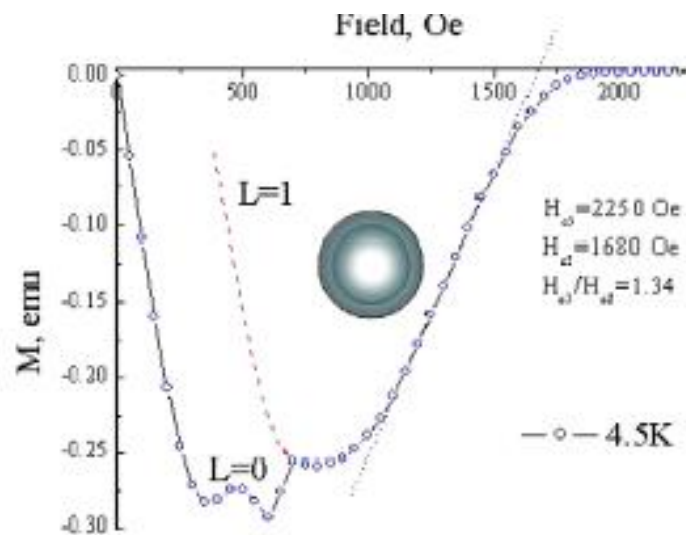
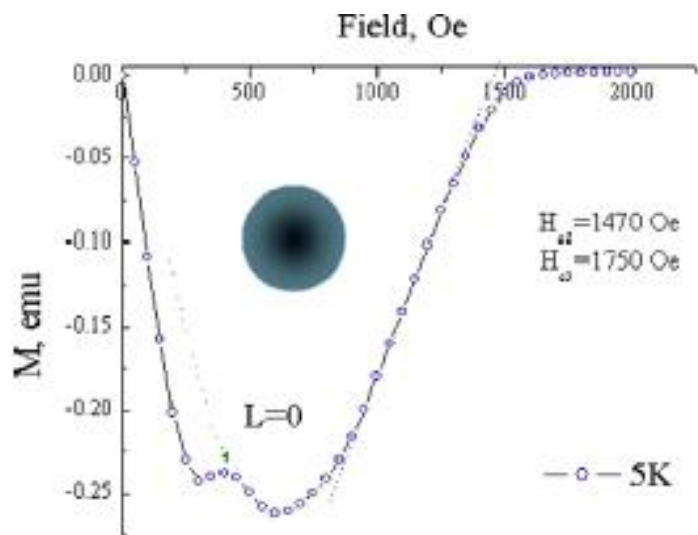
Fig. 5. Low-field hysteresis loop at the temperature 3 K. The loop closes at the lower critical field  $H_{c1}$ . Inset shows the fcc structure of opal pores infiltrated with Pb. Large spheres are octahedral pores ( $r_{oct} = 62.1$  nm), and small spheres are tetrahedral pores ( $r_{tet} = 33.7$  nm).

# Magnetoresistance in green Pb opal

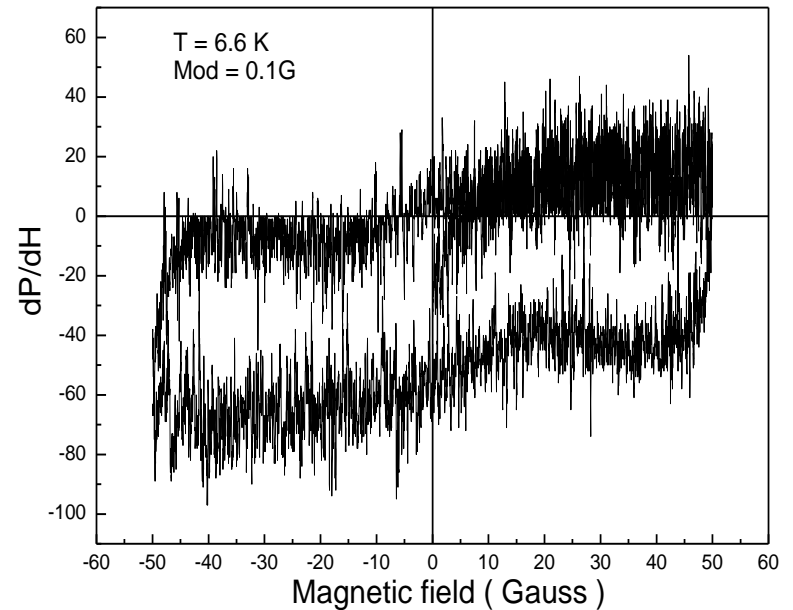
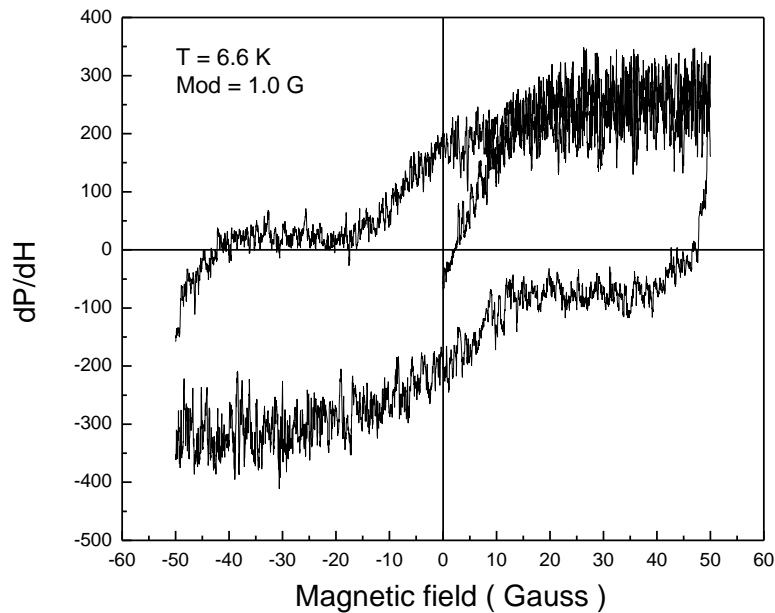
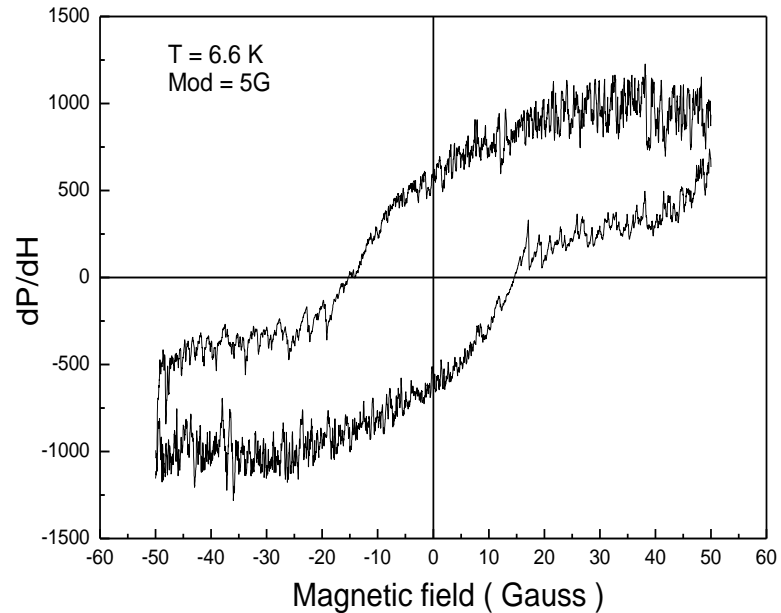
$T = 7.1$  K,  $I = 0.5$  mA,  $H$  along  $[111]$ ,  $I$  along  $[100]$



# Appearance of new fluxoid phases in M with lowering T in blue Pb-Opal



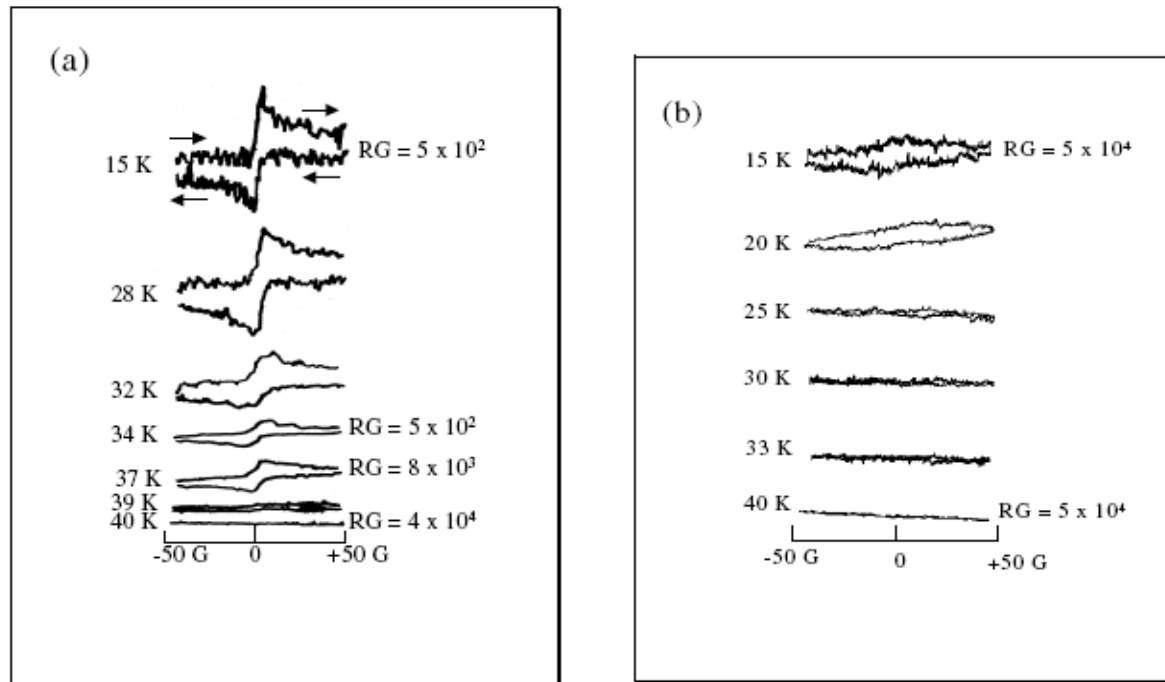
# Low Field signal of MW absorption in Pb in Blue Opal (160 nm spheres)



# Low Field Signal of MW absorption on fluxons or weak link vortices always appear in SC below $T_c$

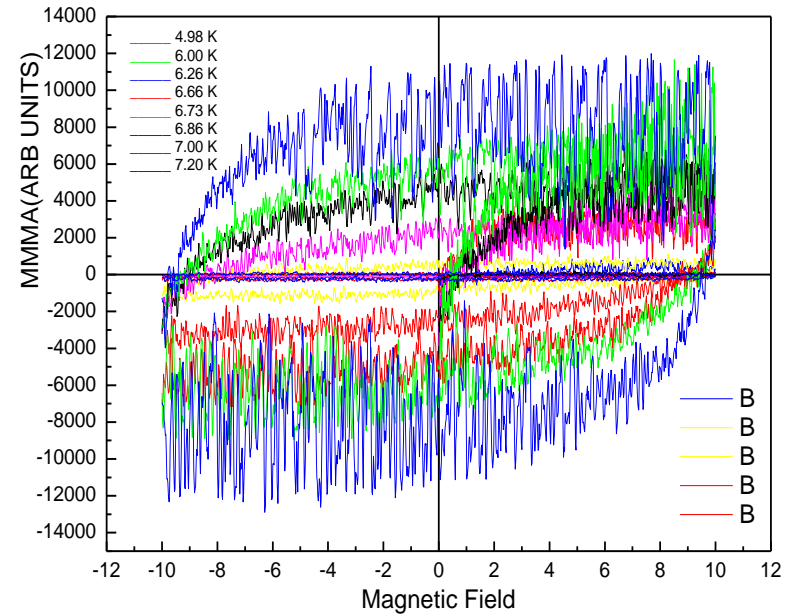
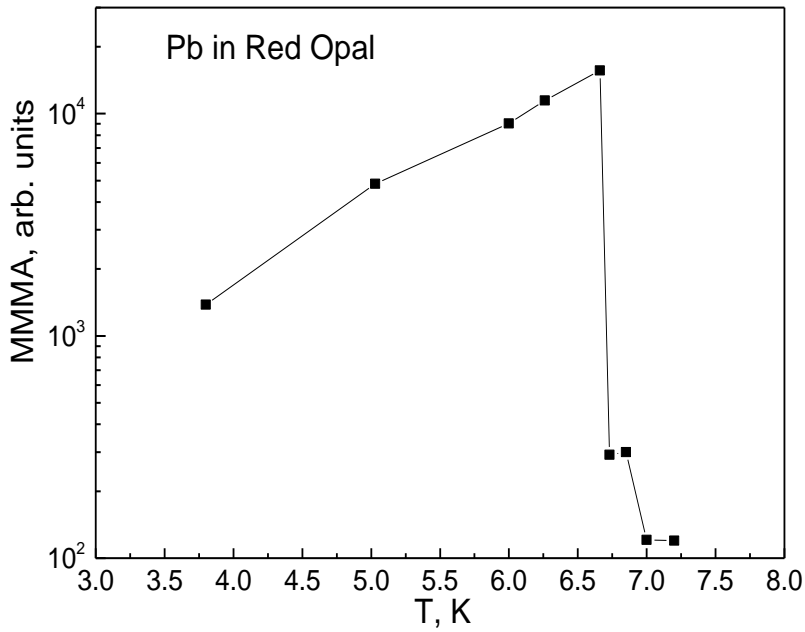
## Microwave absorption studies of $MgB_2$ superconductor

M K BHIDE<sup>1,\*</sup>, R M KADAM<sup>1</sup>, M D SASTRY<sup>1</sup>, AJAY SINGH<sup>2</sup>,  
SHASHWATI SEN<sup>2</sup>, MANMEET KAUR<sup>2</sup>, D K ASWAL<sup>2</sup>, S K GUPTA<sup>2</sup>  
and V C SAHNI<sup>2</sup>

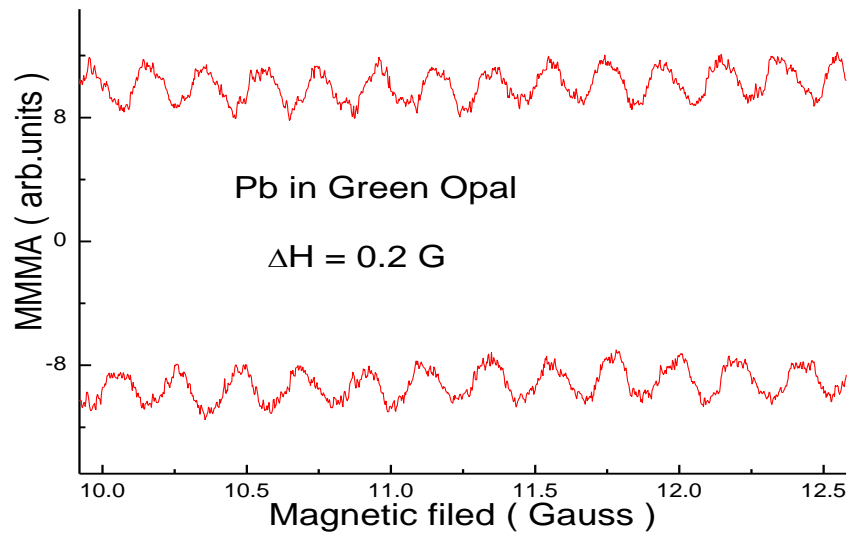
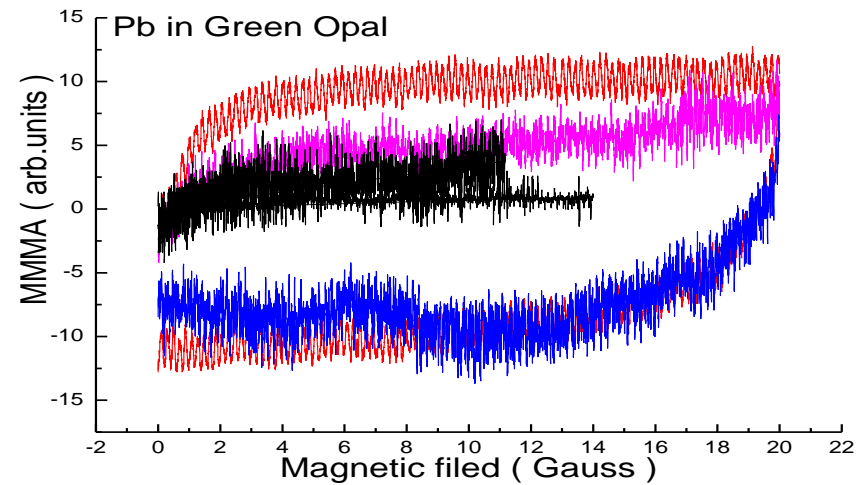
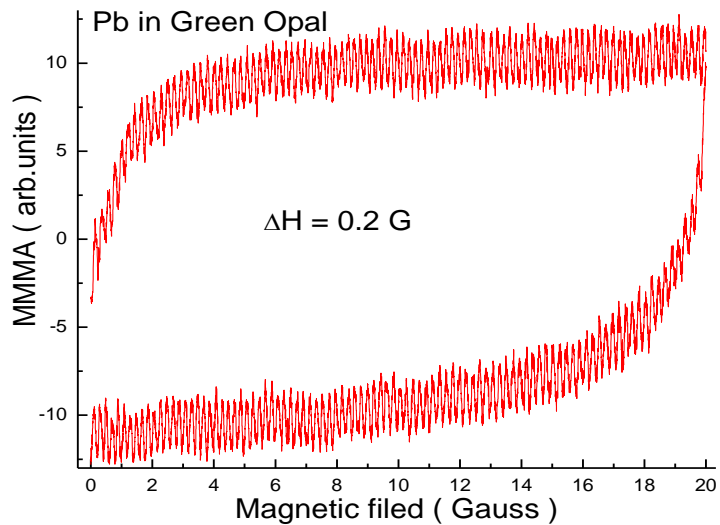


**Figure 1.** The temperature dependence of low field signal (LFS) recorded for (a) polycrystalline and (b) single-grain  $MgB_2$  samples.

# LFS below $T_c$ in Pb in red Opal

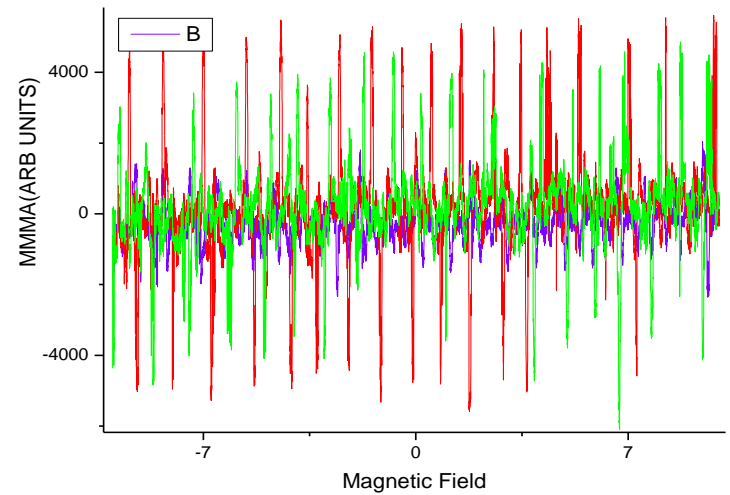
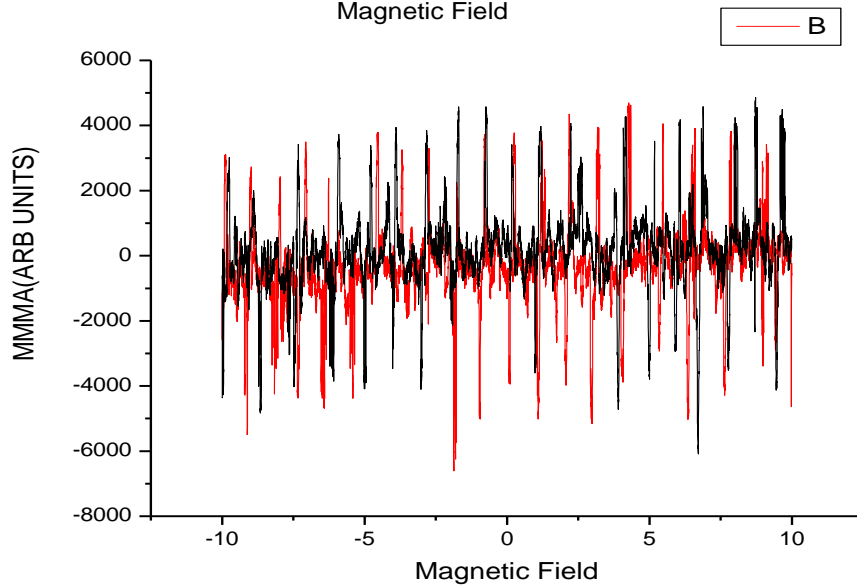
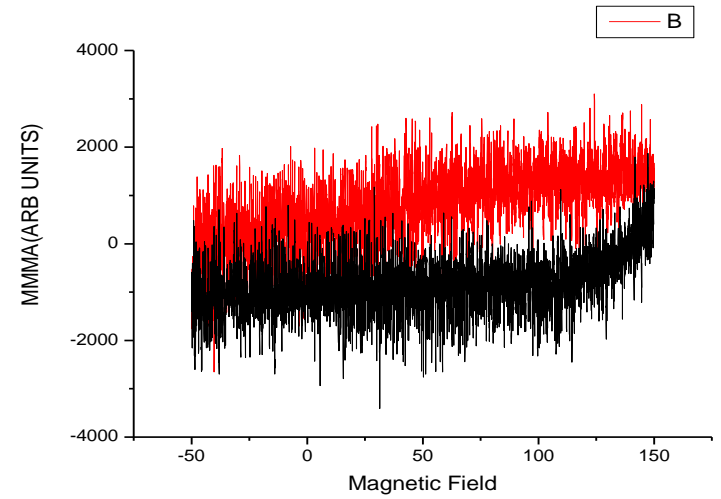
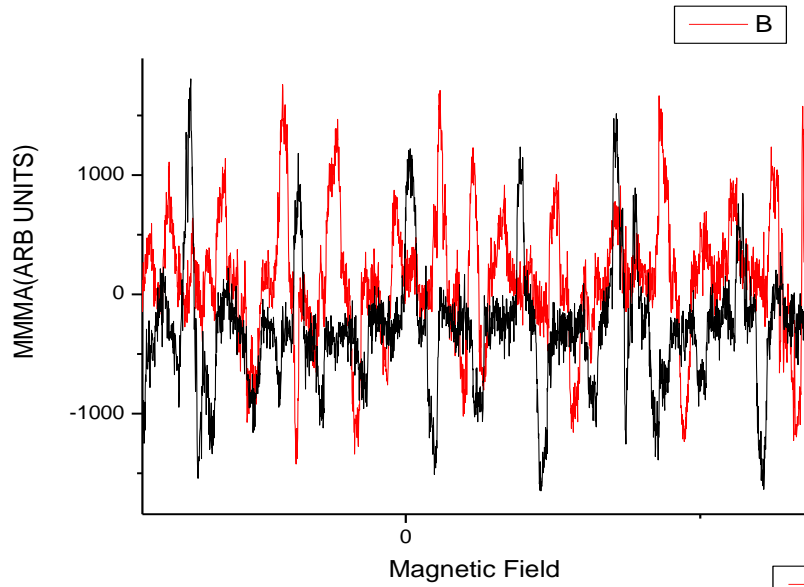


# LFS below TC for Pb in Green Opal

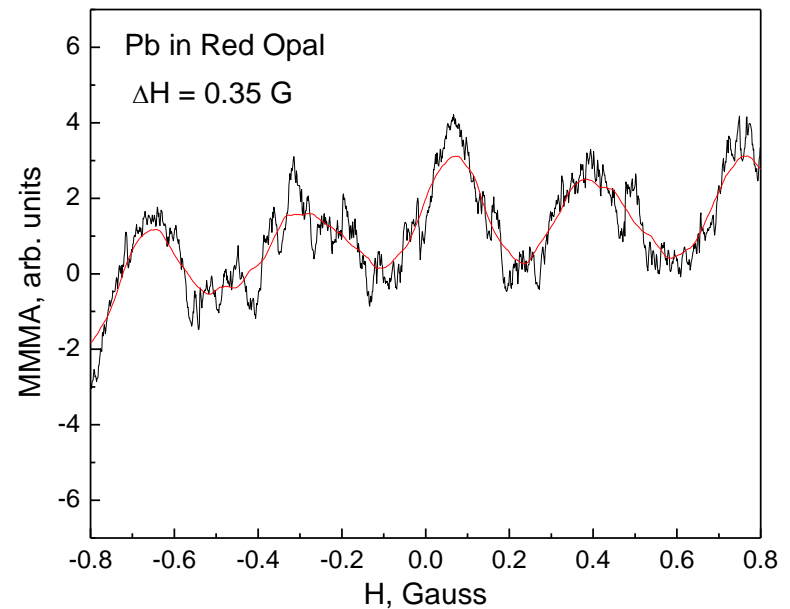
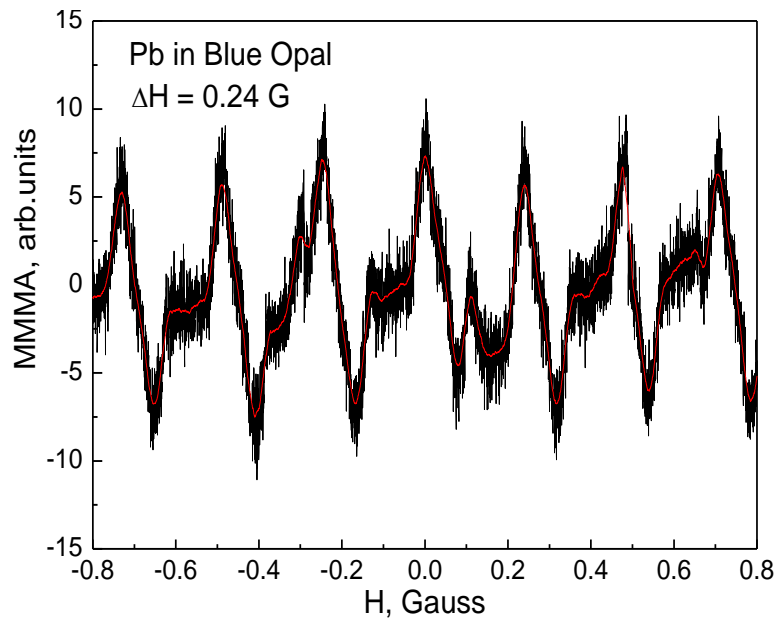
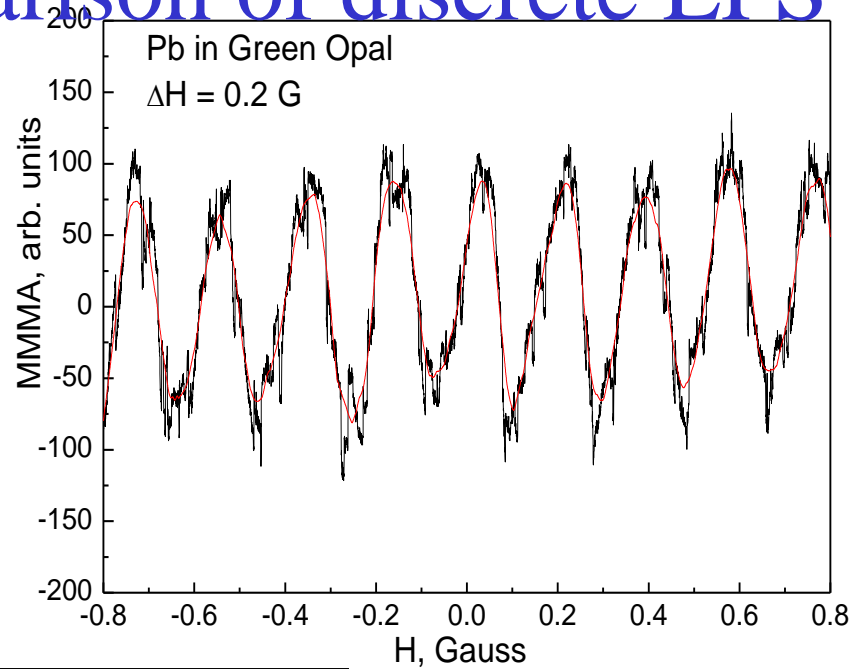




# LFS in Pb in blue opal

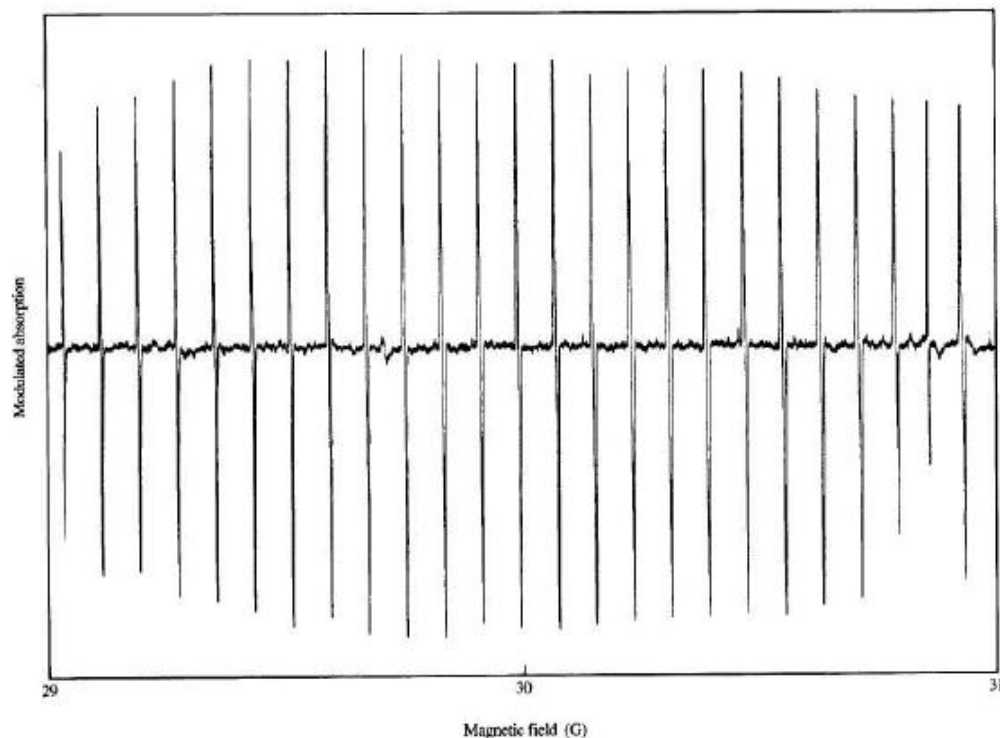


# Comparison of discrete LFS in Pb-opals



# Low-field microwave absorption in single-crystal superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

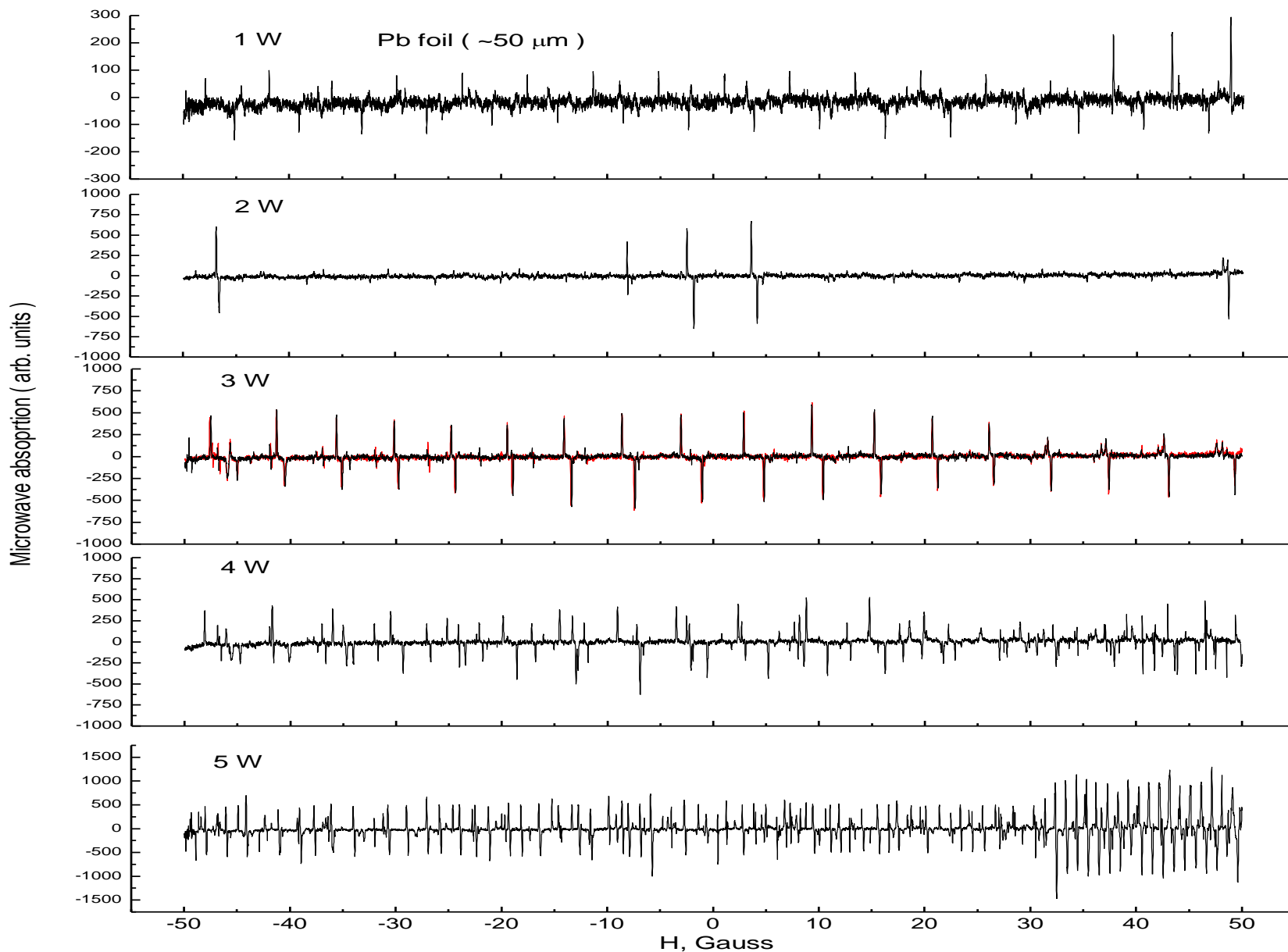
by K. W. Blazey  
F. H. Holtzberg



**Figure 1**

A segment of the 9.44 GHz microwave absorption line spectrum of a  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  single crystal between 29 and 31 gauss at 4.3 K. The applied magnetic field is  $\perp$  ( $c$ ) and  $\parallel$  (110), and the microwave field  $\parallel$  ( $c$ ).

# LFS in Pb FOIL: origin is the fluxons in grain boundaries



## Conclusion to Part 1: LTS in Nano-space

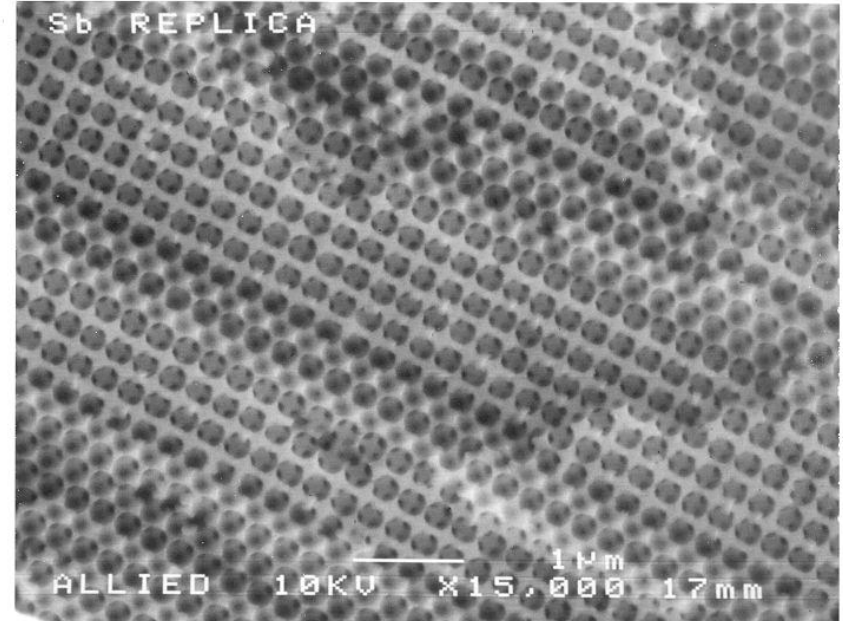
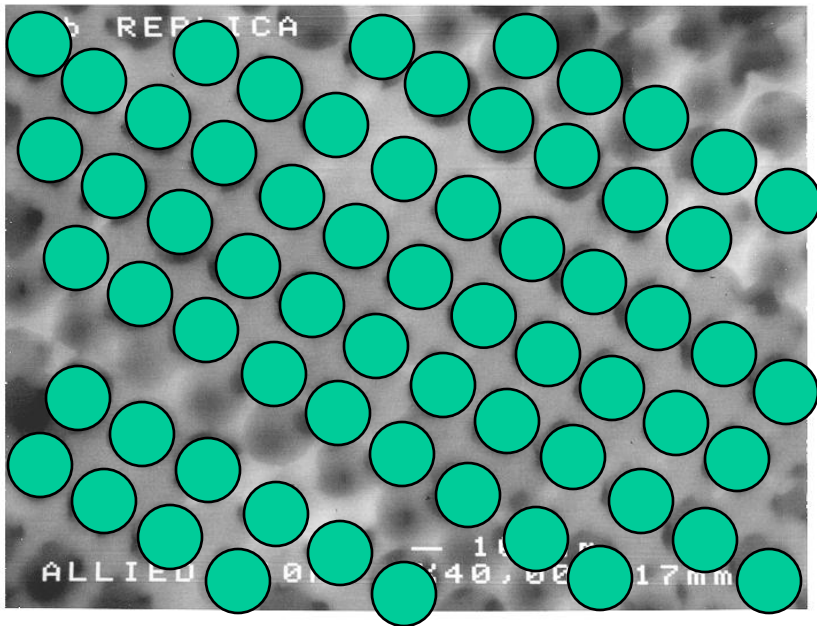
- $T_c$  increase only slightly: from  $T_c=7.1$  to  $7.32$
- Critical field  $H_{c2}$  increased 4-fold.
- Oscillations of  $M$  and  $R(M)$  demonstrate different fluxon phases.
- Huge interface of nanostructured SC can be used for tuning its properties

# What next with Pb and other nano-LTS with extended interface?

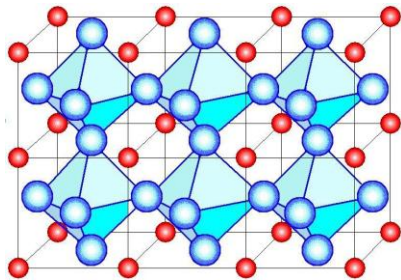
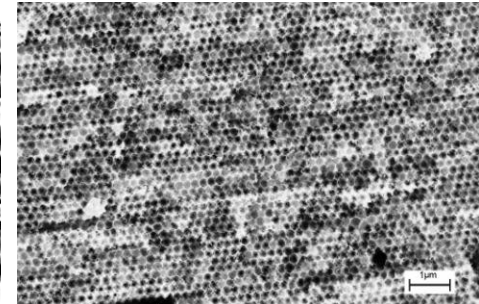
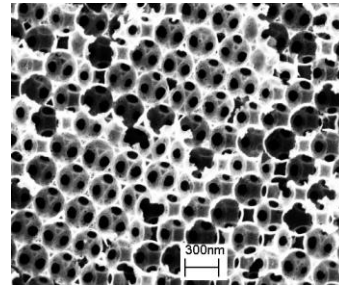
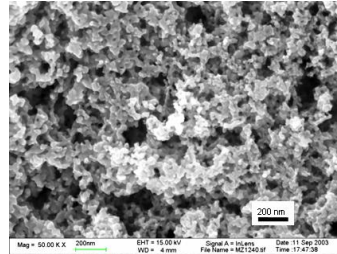
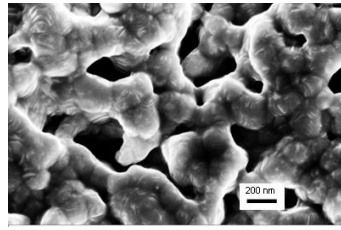
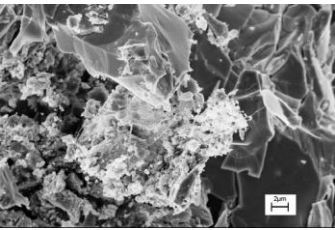
- Try to self-assemble organic molecules with intensive Frenkel exciton transitions for extra “pairing glue” across the interface
- Can change  $T_c$  by changing concentration of carriers by “double layer charge injection”

# Pb-Inverse Opal :

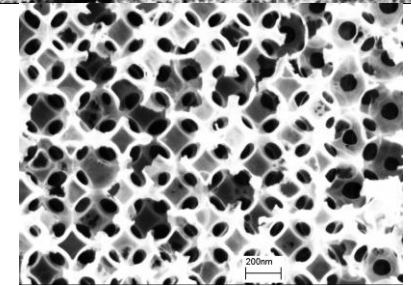
Internal surface can be filled with “excitonic organic matter”



# Part 2: Search for High Temperature Superconductivity in $\text{Na}_x\text{WO}_3$ grown by Sol-Gel Route in Inverted Carbon opal



**Motivation:**



**Confirm Diamagnetism around 91-100 K**  
**Prove SC Tc by Low Field Signal of MW absorption**  
**Try to understand the origin of High Tc**



## Outline for Part 2

- High  $T_c \sim 91-100$  K in  $\text{Na}_x\text{WO}_3$ : is it USO
- Inverse carbon opals: matrices for sol-gel growth of  $\text{WO}_3$
- Double layer electrochemical doping of Na by new “dry charging” method
- Magnetization results.
- Absence of LFMA: No SC ?

*Rapid Note***Possible nucleation of a 2D superconducting phase on  $\text{WO}_3$  single crystals surface doped with  $\text{Na}^+$** 

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Department of Materials and Interfaces, The Weizmann Institute of Science, Rehovot 76100, Israel

Received 26 January 1999

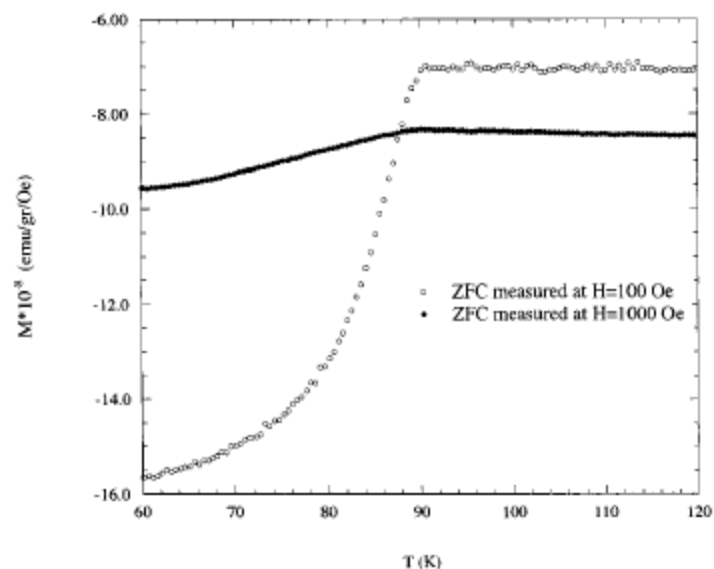


Fig. 3. Zero field cooled magnetic moment vs. temperature curves normalized by the magnetic field: (○) measured at 100 Oe; (●) measured at 1000 Oe in a heating cycle.

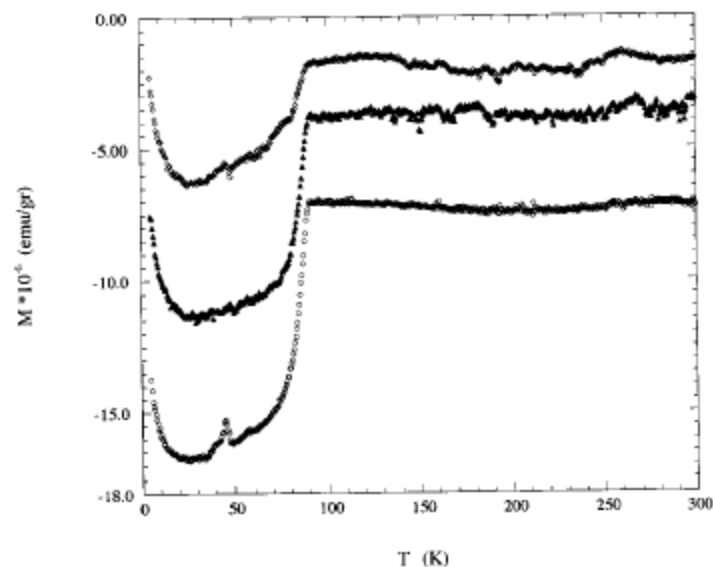


Fig. 7. Magnetic moment vs. temperature (ZFC) measured at 100 Oe in a heating cycle. (○) Bare crystals, (▲) crystals coated with gold after first sputtering process, (◊) after second sputtering process.

# Concentration dependence of superconductivity and the order-disorder transition in the hexagonal rubidium tungsten bronze $\text{Rb}_x\text{WO}_3$ : Interfacial and bulk properties

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(Received 10 October 2001; published 4 April 2002)

We revisited the problem of the stability of the superconducting state in  $\text{Rb}_x\text{WO}_3$  and identified the main causes of the contradictory data previously published. We have shown that the ordering of the Rb vacancies in the nonstoichiometric compounds have a major detrimental effect on the superconducting temperature  $T_c$ . The

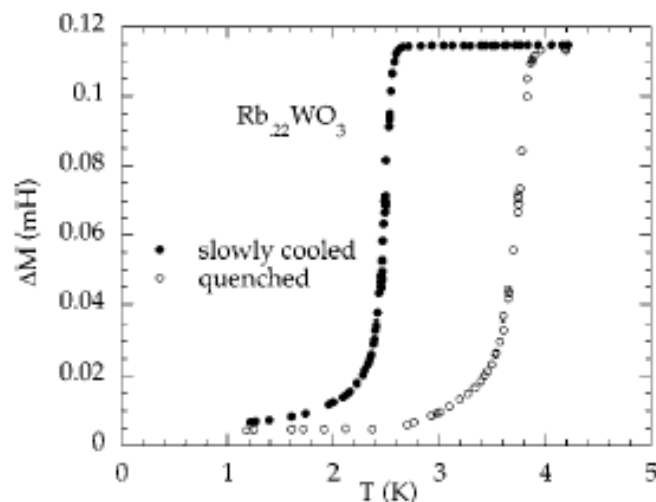


FIG. 1. Superconducting transitions (mutual-inductance variations) of a powder sample of  $\text{Rb}_{0.22}\text{WO}_3$  after different cooling rates.

## B. Calorimetric study of the order-disorder transformation

After several unsuccessful attempts, we finally observed the enthalpy anomaly accompanying this transformation, but

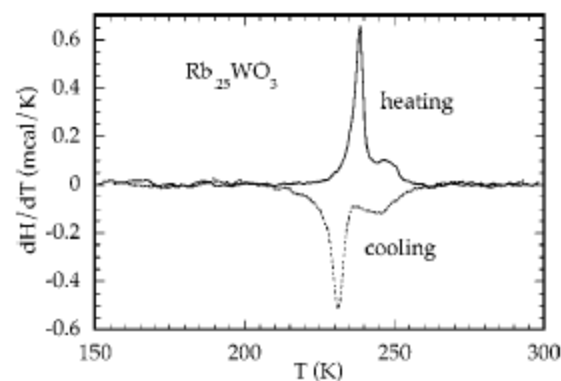


FIG. 2. DSC thermograms observed on a powder sample of  $\text{Rb}_{0.25}\text{WO}_3$  ( $\approx 50$  mg) on heating and on cooling at  $\pm 10$  K/min.

# $T_c$ dependence on $x$ : disorder driven SC in $\text{Rb}_x\text{WO}_3$

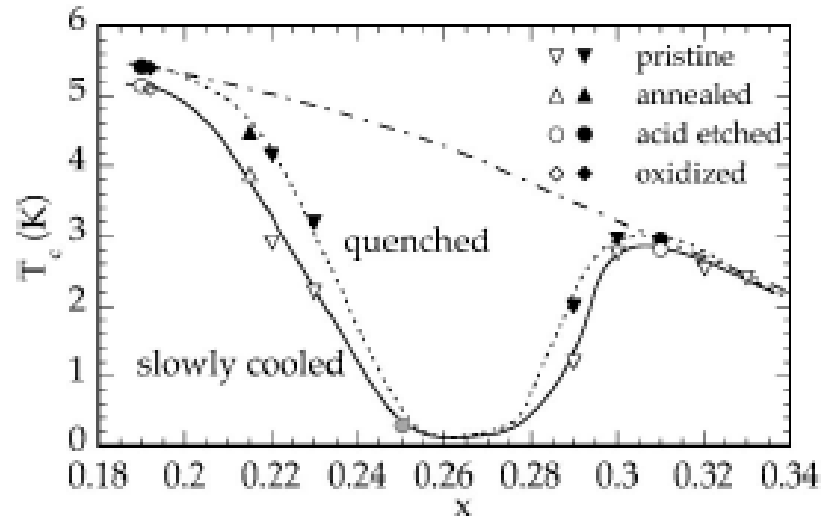
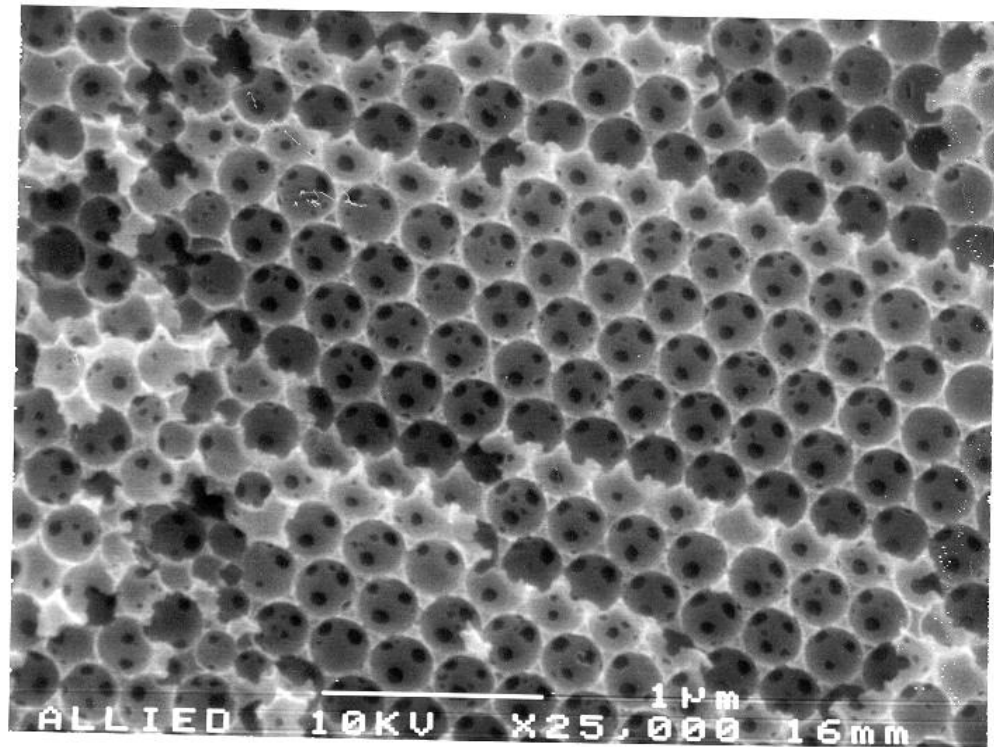
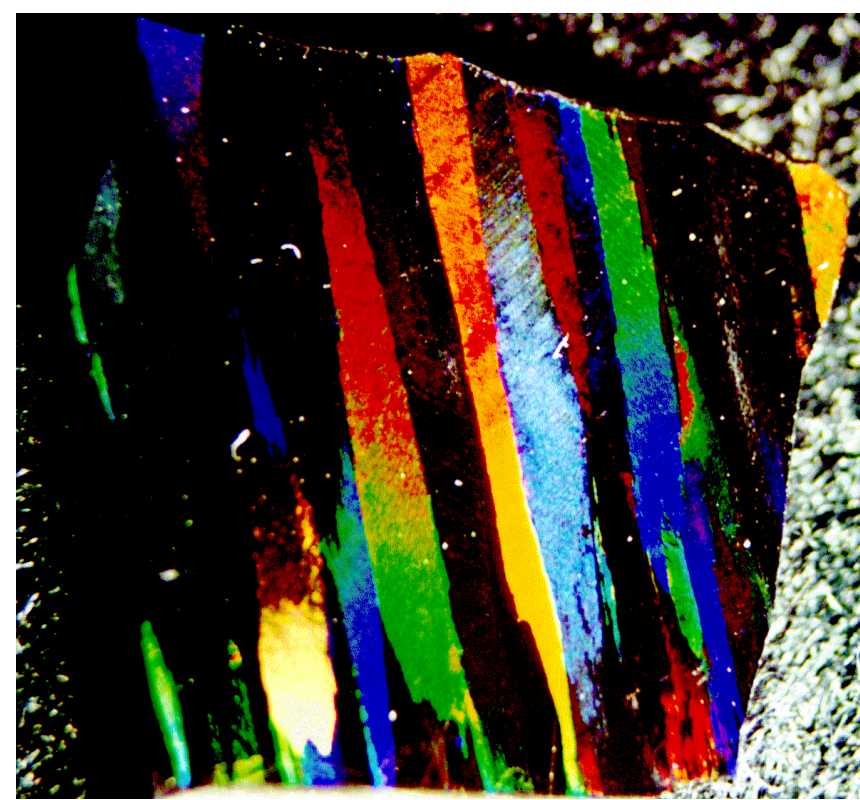


FIG. 9. The superconducting transition  $T_c$  as a function of the rubidium content  $x$ . Empty or full markers refer to measurements after slow cooling or quenching from  $\approx 300$  K, respectively. The grey marker corresponds to an intermediary cooling in a  $^3\text{He}$ - $^4\text{He}$  dilution refrigerator. The curves are only guides to the eye and the monotonous one extrapolates what we think would be the  $T_c(x)$  dependence if the vacancy ordering could be prevented.

## Interfacial SC with high $T_c$

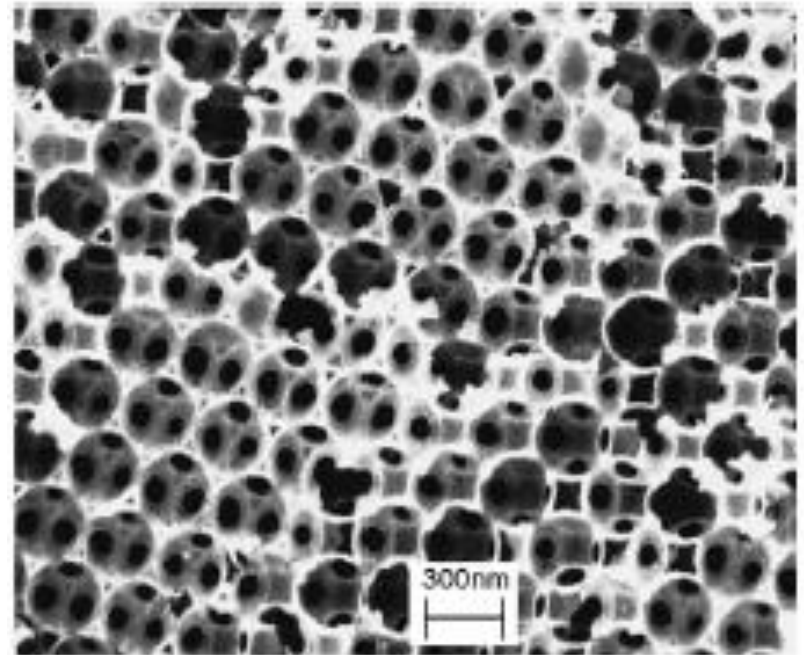
superconductivity also develops on the surface of  $\text{WO}_3$  crystals that have been subjected to a slight superficial enrichment of sodium.<sup>5</sup> The very high  $T_c$ 's observed in the latter case (up to 91 K) is evidently far from being explained but indicates how much the interfacial properties of these materials could be promising. The great versatility of the  $\text{WO}_6$  octahedra we discussed above, certainly plays a part in these superficial or interfacial properties.

# Carbon Inverted Opal: Intensely Colorful and Highly Conductive



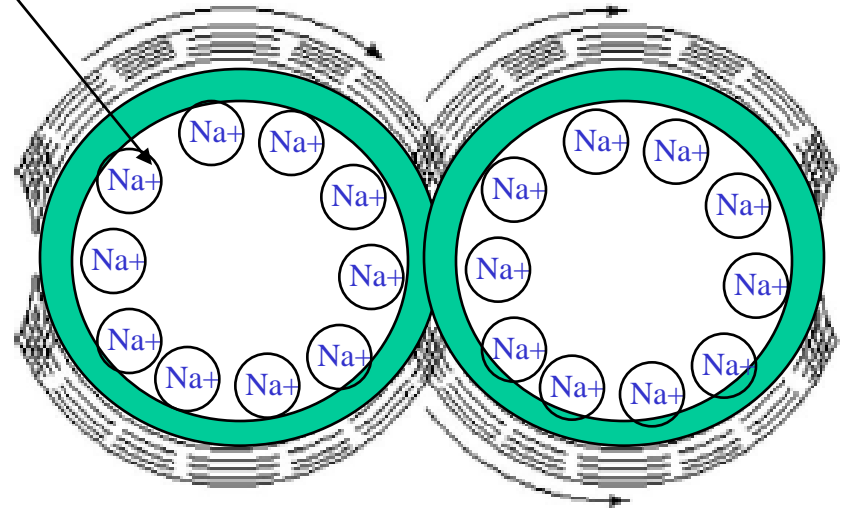
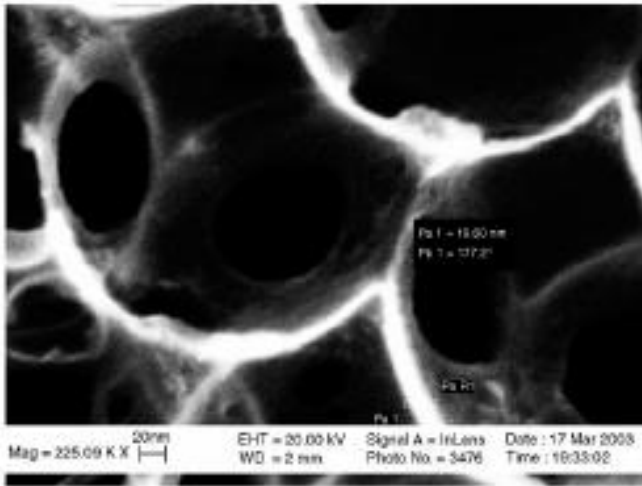
# What we need to make a good $\text{Na}_x\text{WO}_3$

1. Huge Interface
2. Synthesize  $\text{WO}_3$  at interface of nanocarbon
1. Coat it with:
  - with Na ions layer by electrochemistry



# $\text{Na}_x\text{WO}_3$ in Inverted Carbon Opals:

1. Porous matrix for  $\text{WO}_3$  growth by sol gel
2.  $\text{WO}_3$  coated nano-carbon: good electrode for electrochemical Na doping





# Search for Superconducting Materials Using Frozen Giant Interfacial Charge Injection

***BACKGROUND:*** Charge injection could enable performance optimization for superconducting materials enhancing  $T_c$ .

*However,* dielectric charge injection in FETs is normally not in the bulk and is normally small and short-lived.

***GOAL:*** Tune Superconducting material properties using giant frozen charge transfer at huge interfaces in  $\text{WO}_3$ -inv. opal

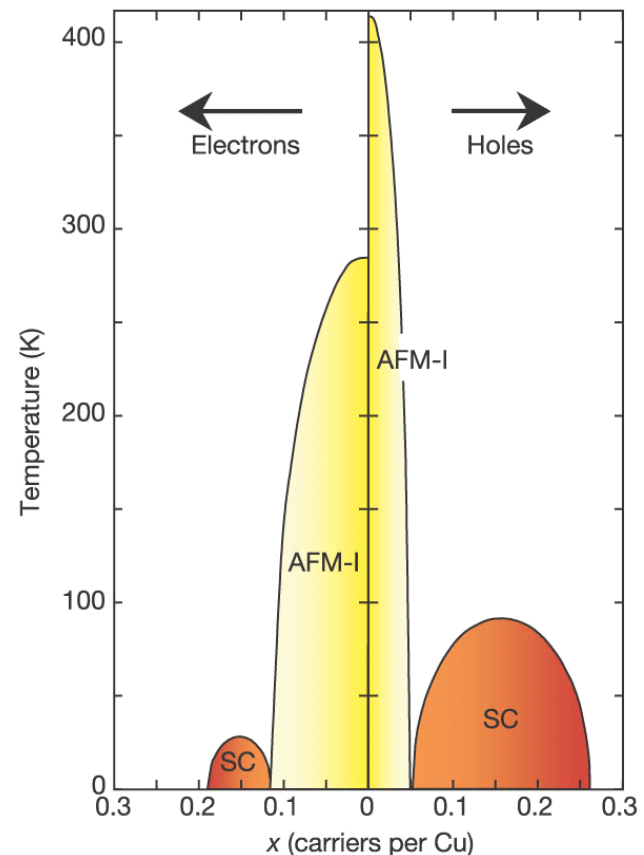
***Examples:***  $\text{Na}_x\text{WO}_3$  created by sol-gel in conductive carbon inverse opals, doped by Na, via charge injection in NaCl: observation of diamagnetic transition at 125 K, but no LFMA (?)

# Properties Changes Possible From Frozen Interfacial Charge Transfer

## *Optimize (or generate)*

- Superconductivity
- Ferromagnetism
- Electrical conductivity
- Optical properties
- Thermal conductivity
- Catalytic activity
- Absorption (sensing)
- Thermoelectric ZT

Transition between anti-ferromagnetic and superconducting behavior as a function of charge concentration for high  $T_c$  superconductors.



# Methods of Charge Injection

- DOPANT INTERCATION CHARGING:

Fundamentally *changes structure*, *adds defects*, requires *slow bulk diffusion*, and is *not fully reversible*.

- ELECTROSTATIC CHARGING:

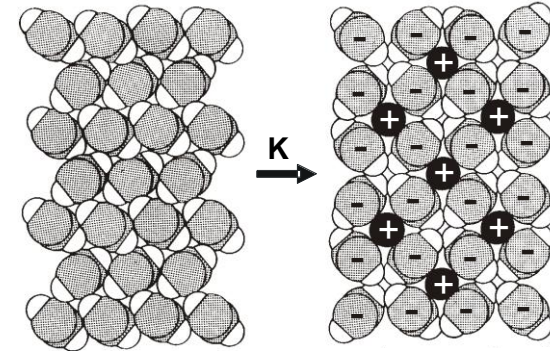
*Stores little charge or requires high voltages and requires electrode proximity.*

- INTERFACIAL DOUBLE-LAYER CHARGING:

*Stores high charge at low voltage, but needs electrolyte.*

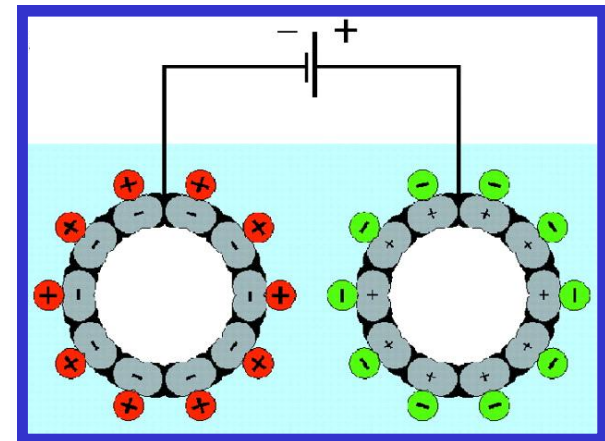
***SURPRISES WILL BE SHOWN!***

Polyacetylene



$C = \text{charge/voltage}$

$C = \text{area} \times \text{dielectric constant} / d$



$d$  is in nms

# Our Strategies for Obtaining Frozen Interfacial Charge Transfer

*All strategies use conducting materials having very large surface areas (above  $100 \text{ m}^2 \text{ gm}^{-1}$ /density)*

Electrochemical double-layer charge injection followed by removal from electrolyte.

***WE SHOW THAT ELECTRODES WITH GIANT CHARGE INJECTION ARE SEPARATABLE WITHOUT LOSING CHARGE!***

**TRICK: COUNTERIONS PREVENT COULOMB EXPLOSION.**

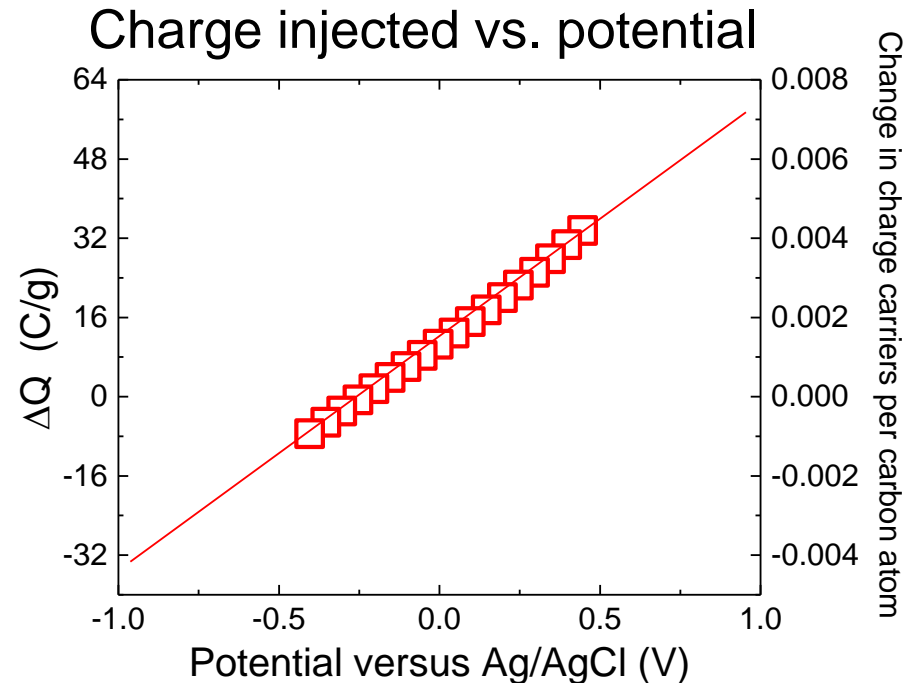
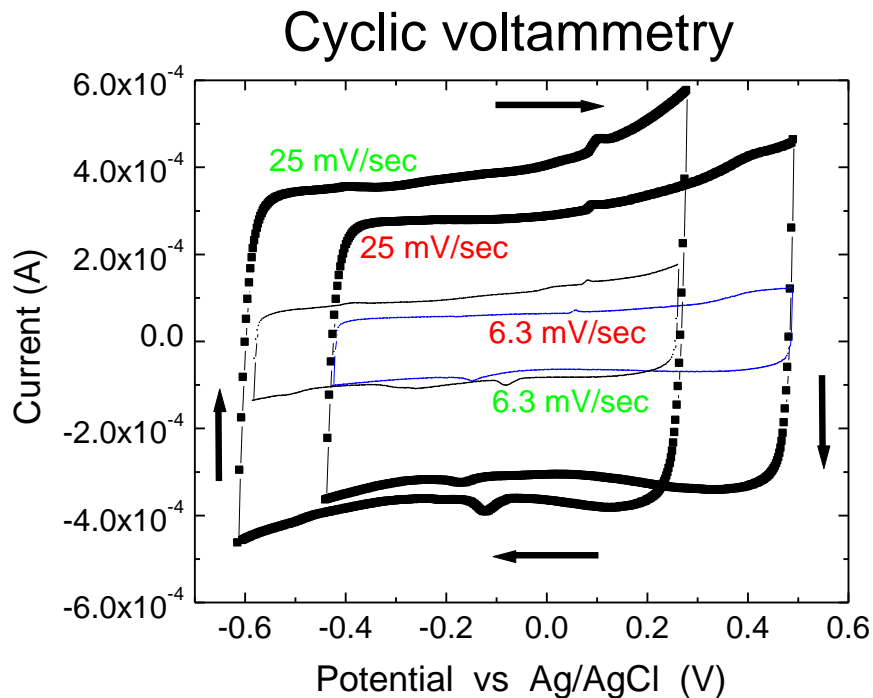
# Prototype High-Surface-Area Material

(We are now doing the same experiments for compacted Pt nanoparticle electrodes)

- Charge SWNT electrodes in 1M NaCl – show CV of classical interfacial double-layer charge injection.
- Demonstrate about 10 fold conductivity increase from hole injection.
- Remove charged-injected electrode from electrolyte – show increased conductivity is maintained even after exposure to dynamic vacuum for 3 hours.
- Re-immerses electrode in electrolyte and show by electrochemical measurements that the charge is maintained.

# Cyclic Voltammetry Indicates Classical Behavior for Double-Layer Charging

(Annealed HiPco SWNTs in 1 M NaCl)

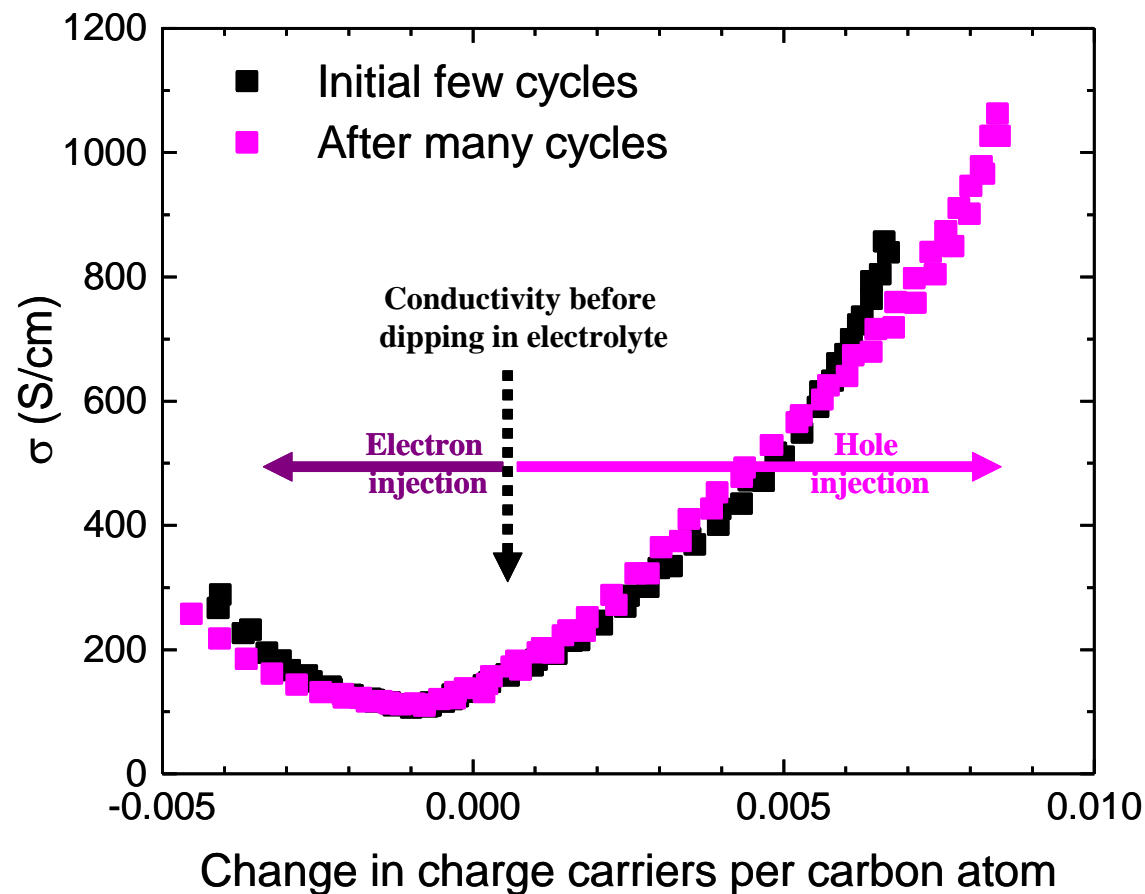
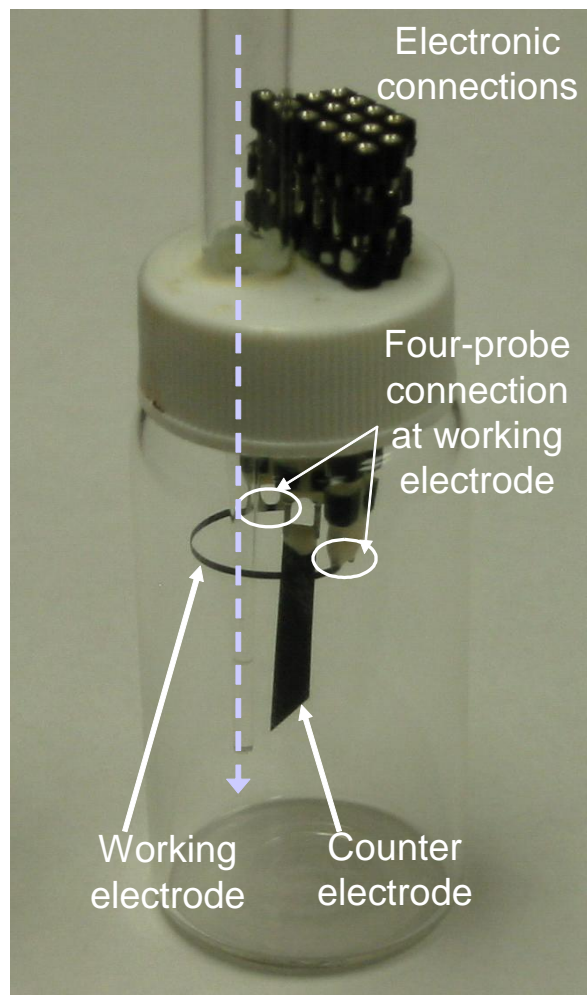


Capacitance of 22 F/g increases slightly (to 28 F/g) with increasing cycling – likely due to increased SWNT wetting.

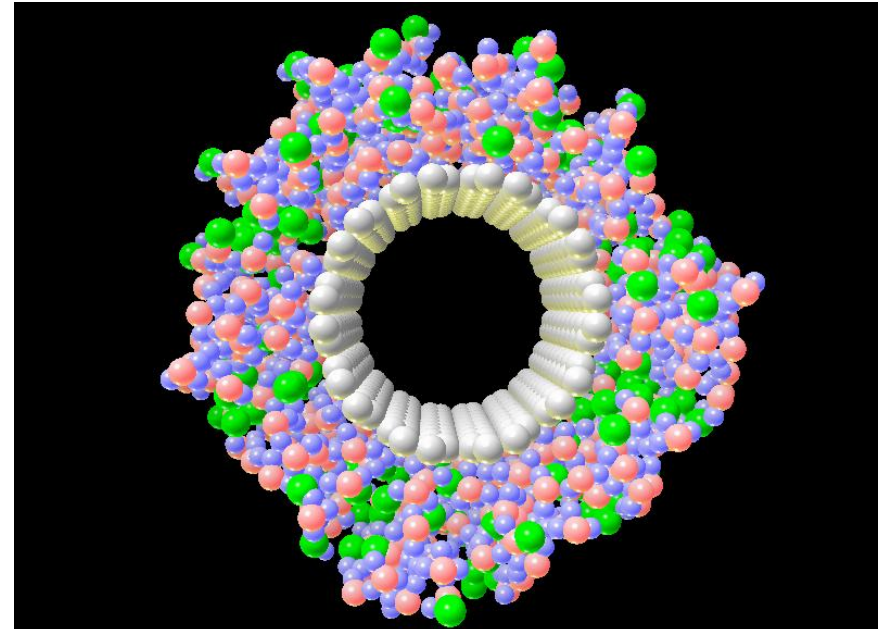
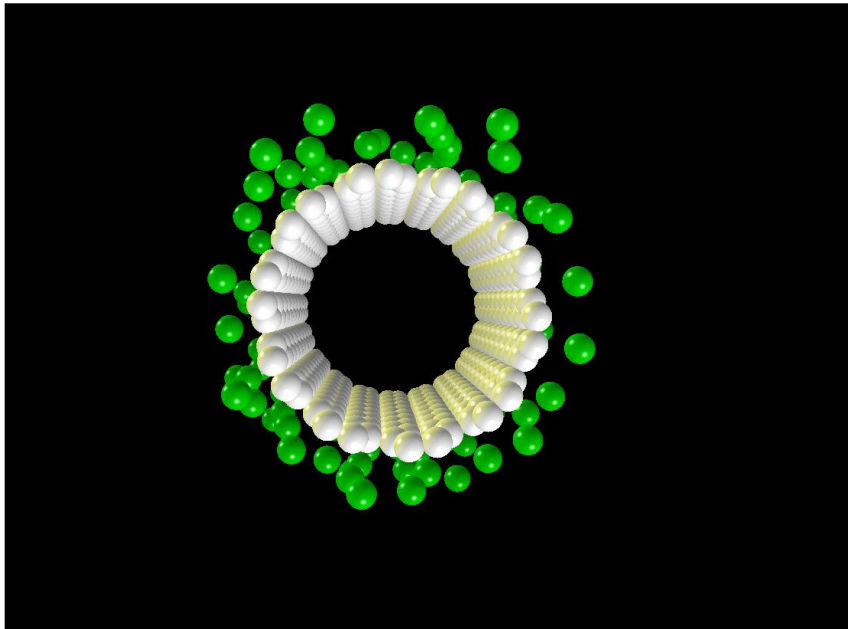
*Injected charge can be increased by increasing the redox stability window of the electrolyte (<2 V TO 5 V).*

*Minor Faradic peaks are a problem, and can be eliminated.*

# Four-Probe Electrical Conductivity Increases About Order of Magnitude Upon Hole Injection



# Ion-containing Interface Water Solvated (right) or Unsolvated (left)?



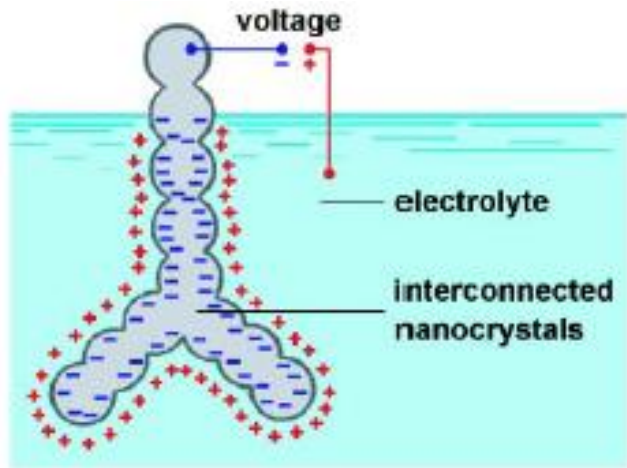
Atom designations: Cl<sup>-</sup> (green) carbon (white), hydrogen (blue), oxygen (red).



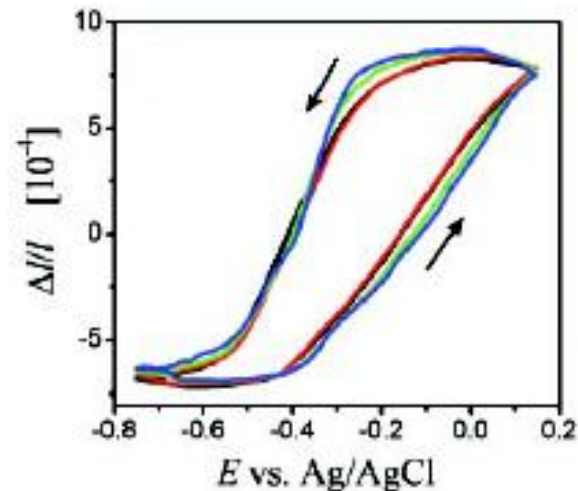
# These Processes Work for Any Nanoscale Conductor

*Example:* Metal nanoparticles molded into shaped articles, molten electrolyte is injected, charge is electrochemically injected, then electrolyte is “frozen”.

*Evidence<sup>1,2</sup> that metals will work just like nanotubes:*



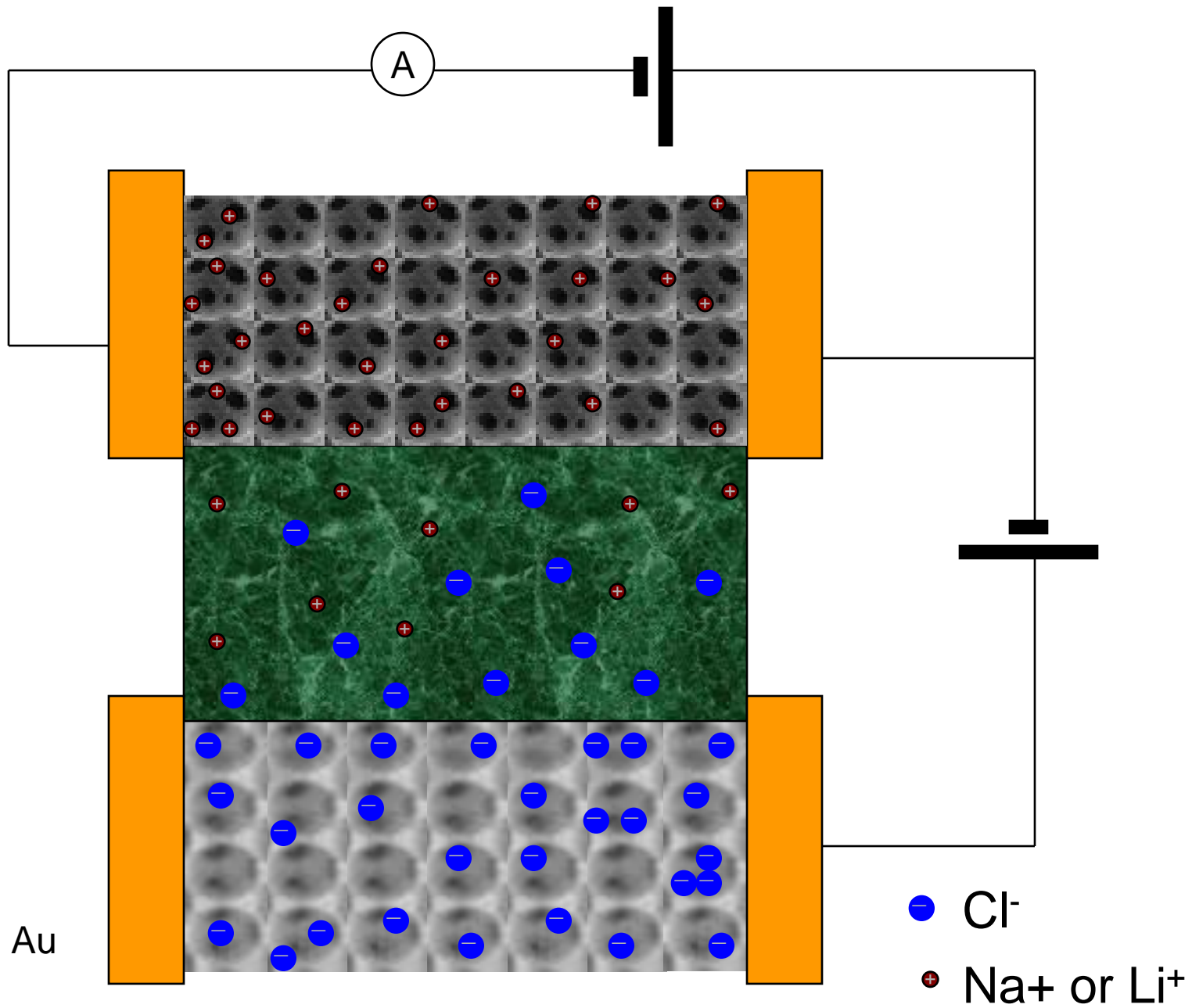
Double-layer charge injection increases unit cell volume of Pt by ~0.4%.



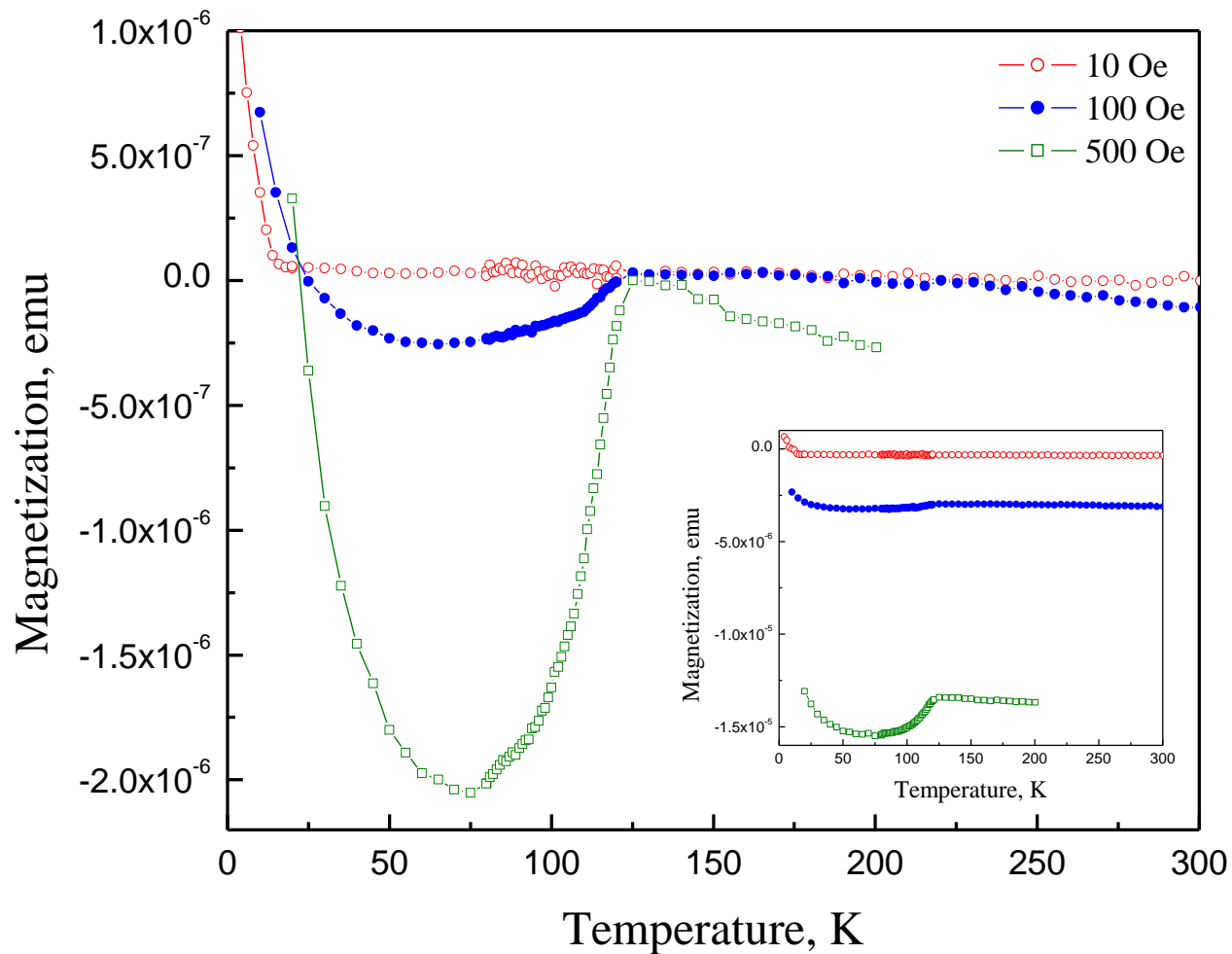
Weissmuller *et. al.* *Science* **300**, 312 (2003)  
Baughman, *Science* **300**, 268 (2003)

# Preparation of $\text{Na}_x\text{WO}_3$ Inverted Opal

- We used a sol-gel technology for preparation  $\text{WO}_3$  film in porous nanostructured host matrices.
- Sol-gel technology allows to vary the structural parameters and concentration of composition in wide range.
- To increase the volume fraction of superconducting phase we infiltrated  $\text{WO}_3$  into nanoporous material with high surface area and then electrochemically doped to obtain double layer with alkali ions ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ).

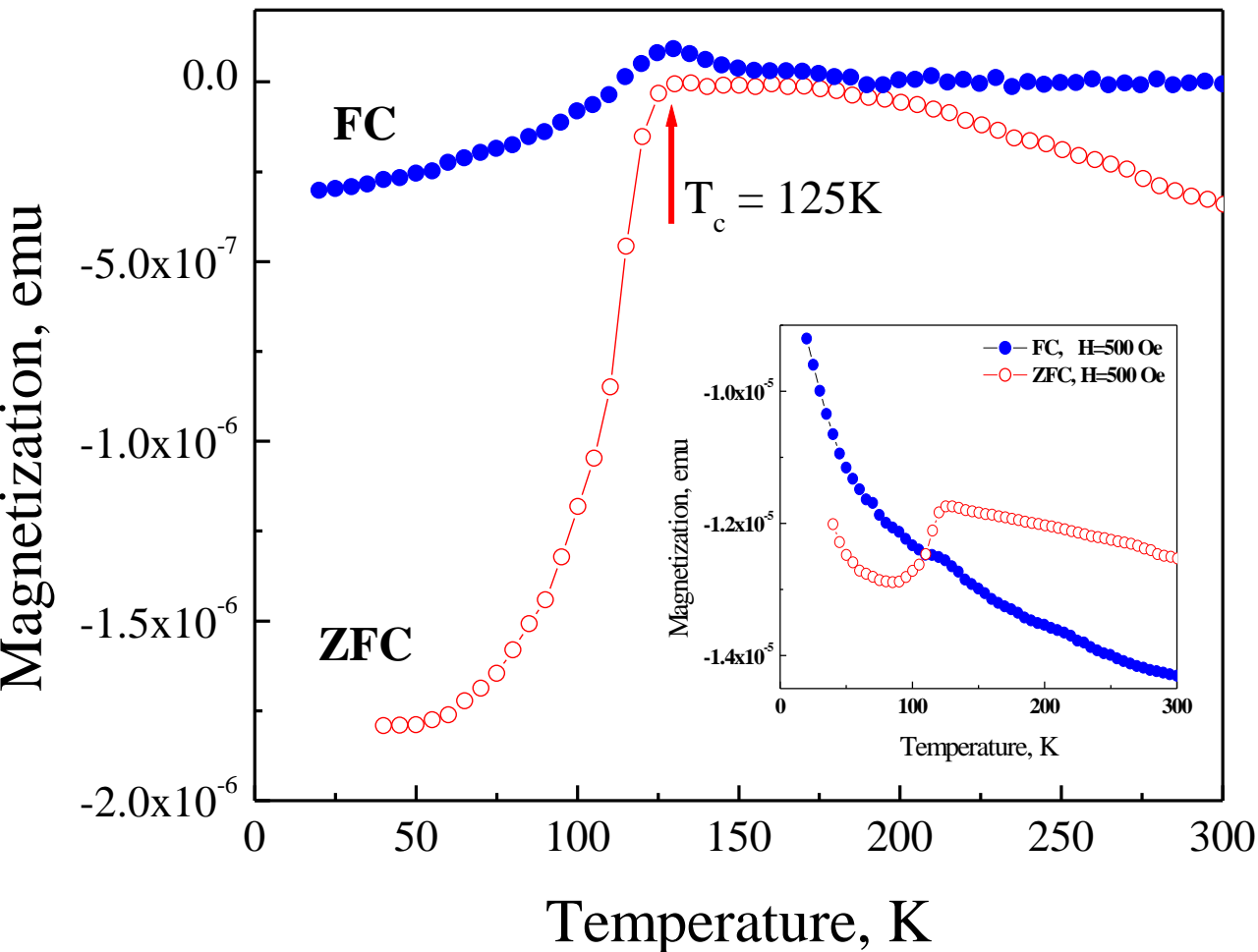


# ZFC magnetization: Diamagnetic drop at T=125-130 K



The temperature dependence of ZFC magnetization for  $\text{Na}_x\text{WO}_{3-y}$  infiltrated into carbon inverted opal at three different applied fields: 10, 100 and 500 Oe. For comparison all three curves were bound to  $M=0$  at  $T=130$  K by subtraction the contribution from host matrix. Inset shows the real distribution of measured magnetization.

# FC and ZFC magnetization



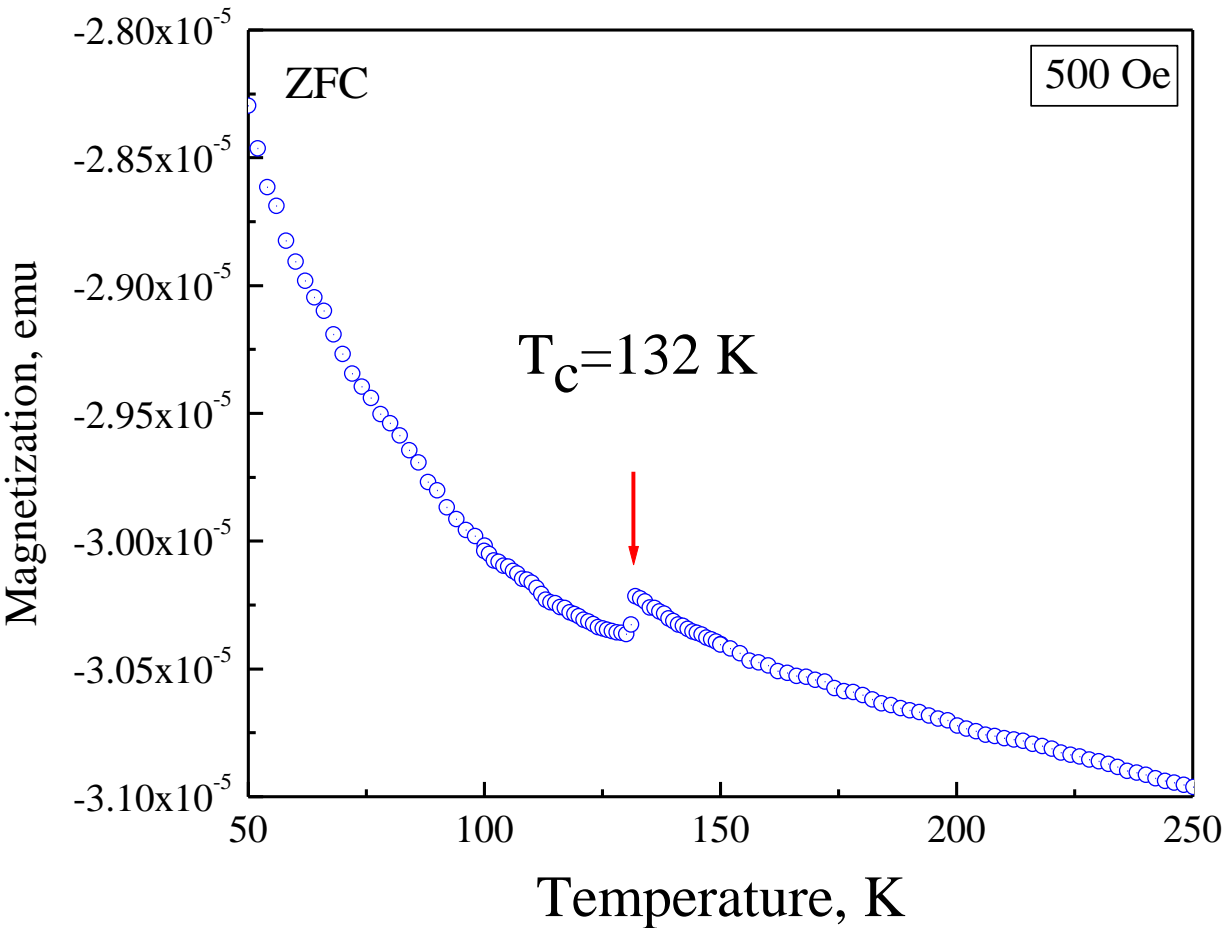
Comparison of FC and ZFC measurements in  $\text{Na}_x\text{WO}_{3-y}$  compound with subtracted paramagnetic contribution. Inset shows the measured data. Curie paramagnetic contribution was subtracted using following fitting parameters:

$$M = M_0 + C/T,$$
$$M_0 = 1.35 \times 10^{-6} \text{ emu},$$
$$C = 12.64 \times 10^{-6} \text{ emu} \cdot \text{K}.$$

# Effect of H<sub>2</sub>O on M(T) of Na<sub>x</sub>WO<sub>3</sub>

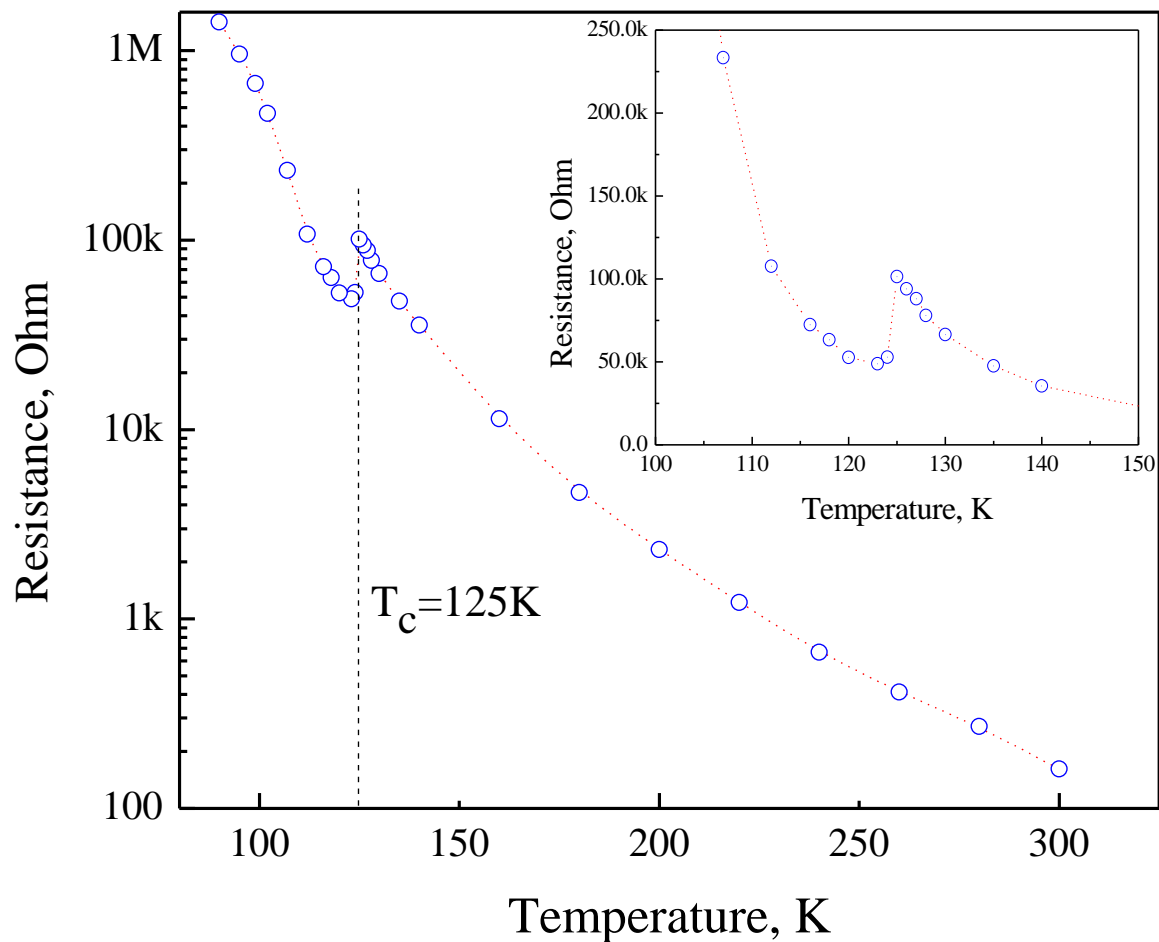
- Temperature dependences of magnetization measured separately in bulk WO<sub>3-y</sub>, pure carbon inverse opal matrix, carbon inverse opal infiltrated with WO<sub>3-y</sub> and last one just dipped in electrolyte without charging, do not show any diamagnetic onset in the studied range of temperatures, 50 K < T < 250 K. However, we observed an intensive fluctuation in magnetization below T ~ 110 - 150 K for as-prepared bulk WO<sub>3-y</sub> having high concentration of residual and physically absorbed water. Perhaps absorbed water or chemically bounded protons play an important role in formation of superconducting phase.

# ZFC in $\text{Li}_x\text{WO}_{3-y}$ : Diamagnetism at 132 K



Temperature dependence of ZFC magnetization for  $\text{Li}_x\text{WO}_{3-y}$  in carbon inverse opal.

# Resistivity measurements drop at $T_c$

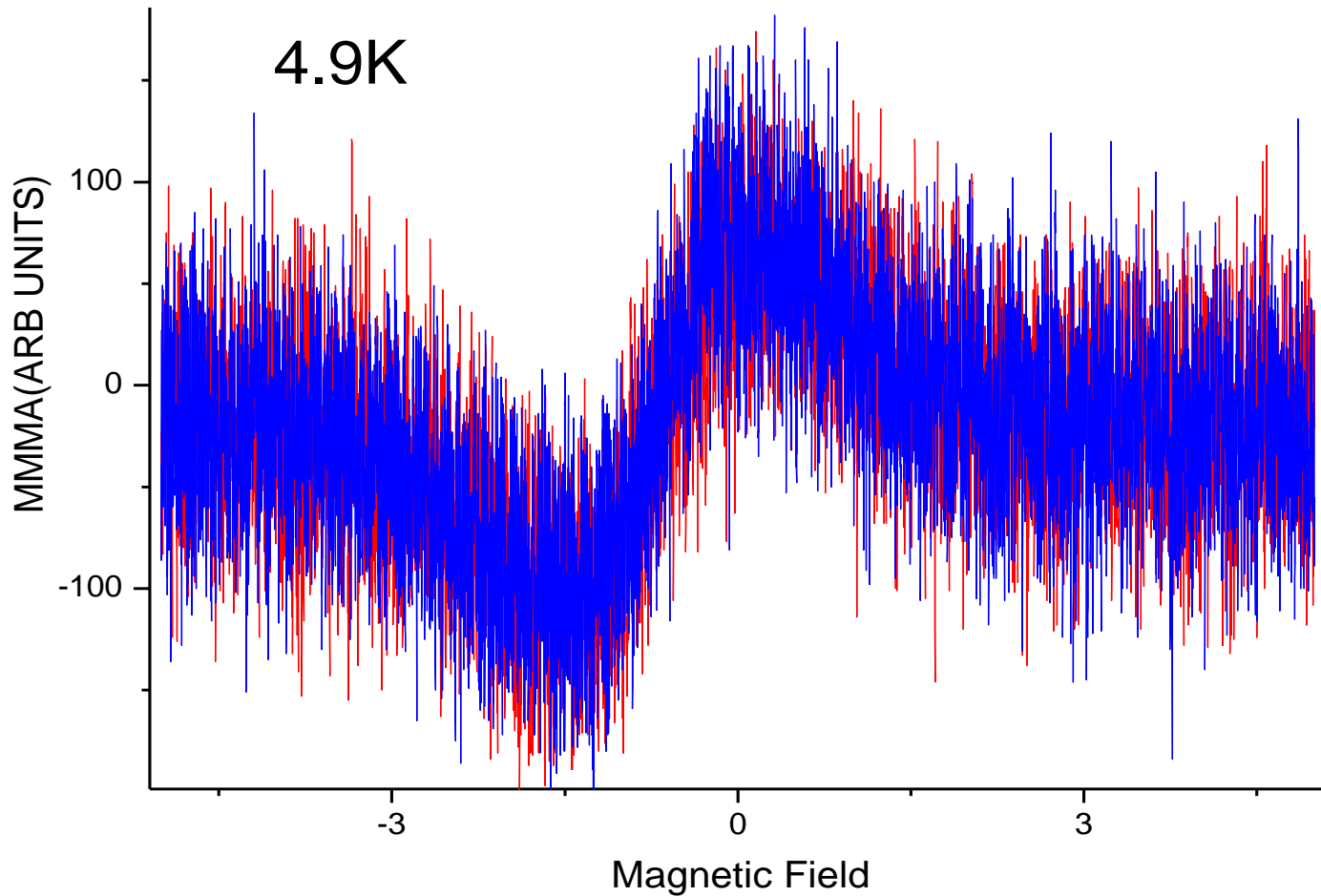


Temperature dependence of resistance in ceramic based  $\text{Na}_x\text{WO}_{3-y}$ . Applied current was  $1\mu\text{A}$ .

The direct evidence of polaron formation from temperature dependence of photoemission spectra and formation of bipolarons in weakly reduced to  $\text{WO}_{3-y}$  with 3-y typically in the order of 2.95 suggest bipolarons mechanism of a Bose-Einstein condensation of trapped electron pairs in highly doped  $\text{WO}_{3-x}$ .



Very weak and noisy LFS  
in  $\text{Na}_x\text{WO}_3$  at very low  $T \sim 5\text{ K}$



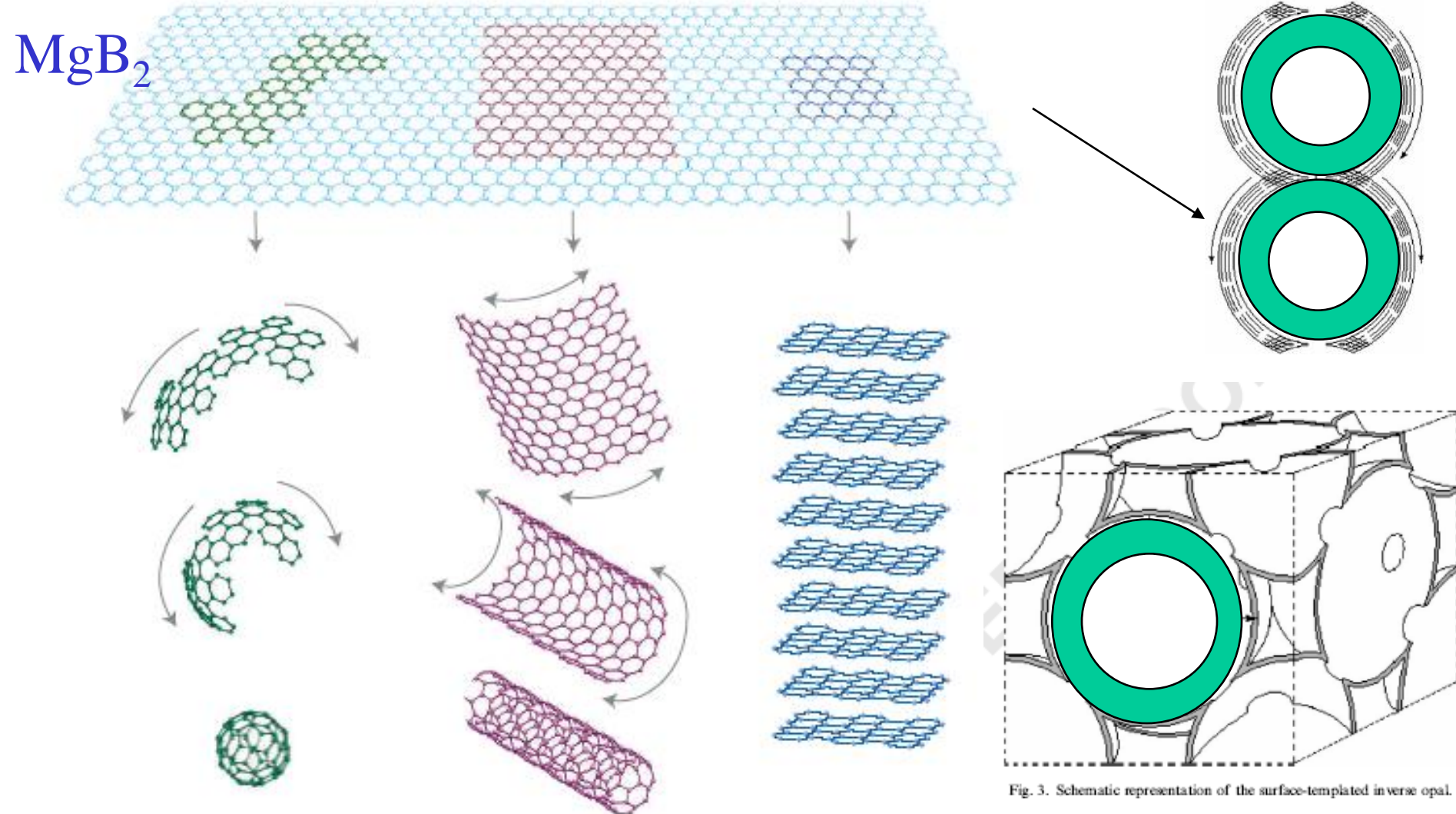
# Other Nano-Matrices for $\text{Na}_x\text{WO}_3$

- As porous host matrices we tested carbon inverse opal, platinum sponge, and CVD grown multiwalled carbon nanotube paper.
- Most pronounced and reproducible onset in magnetization and resistance measurements was found for  $\text{Na}_x\text{WO}_{3-y}$  on carbon inverse opal host matrix at  $T_c=125$  K.

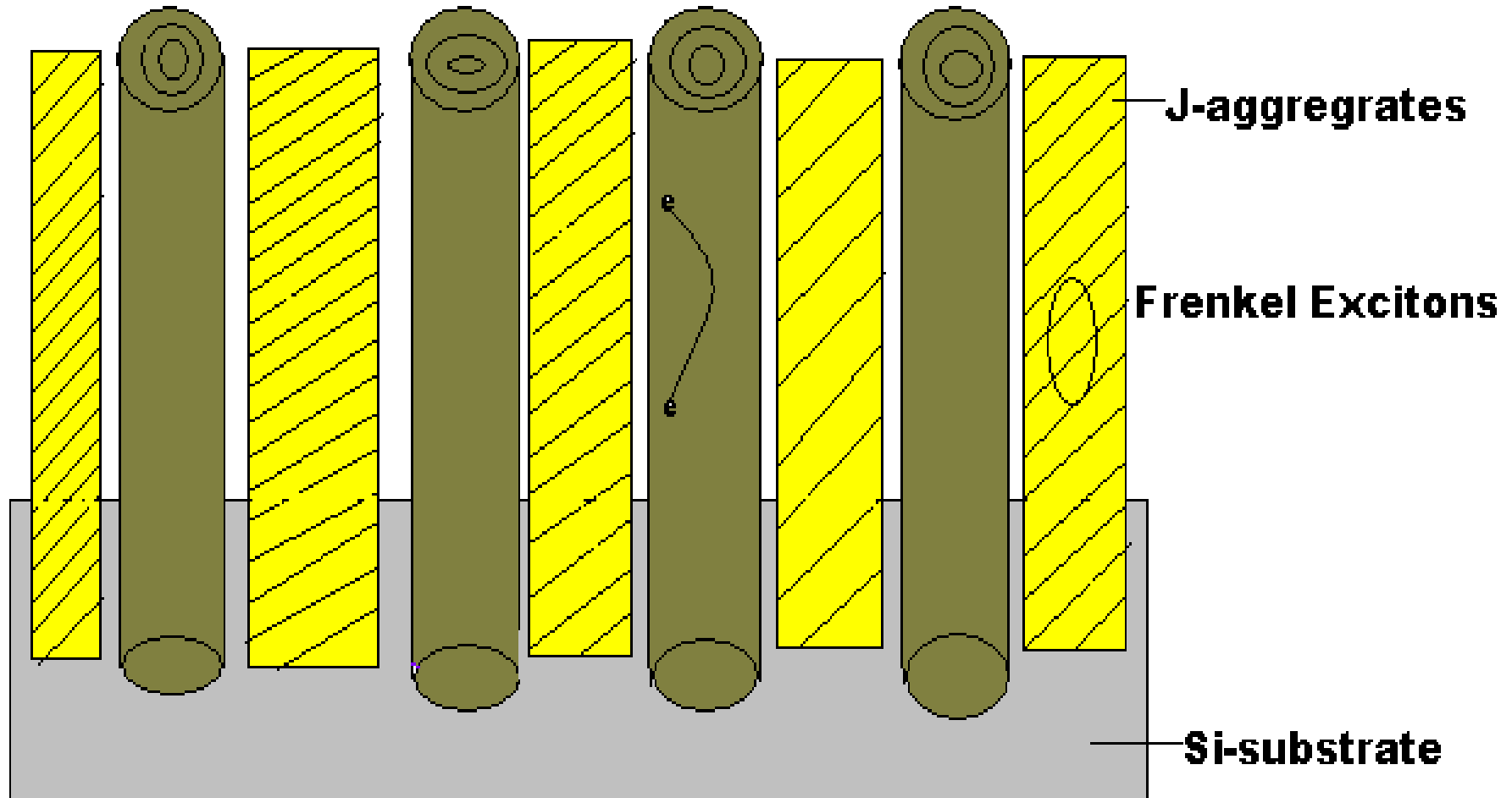
# Conclusion to $\text{Na}_x\text{WO}_3$

- The observed diamagnetism in ZFC and FC magnetization together with temperature behavior of resistance **support the superconductive nature** of obtained anomalies at  $T_c=125\text{ K}$  and  $T_c=132\text{ K}$ .
- Our  $\text{Na}_x\text{WO}_3$ -y structures are amorphous and only samples sintered at  $T_s > 300^\circ\text{C}$  in argon atmosphere had polycrystalline structure.
- The samples sintered in argon had the deficiency of oxygen with 3-y typically in order of 2.95.
- LFS of microwave absorption (known for type 2 SCs) is found only at very low T below, indicated **different nature of superconducting phase (if any)** in Na-tungsten bronze

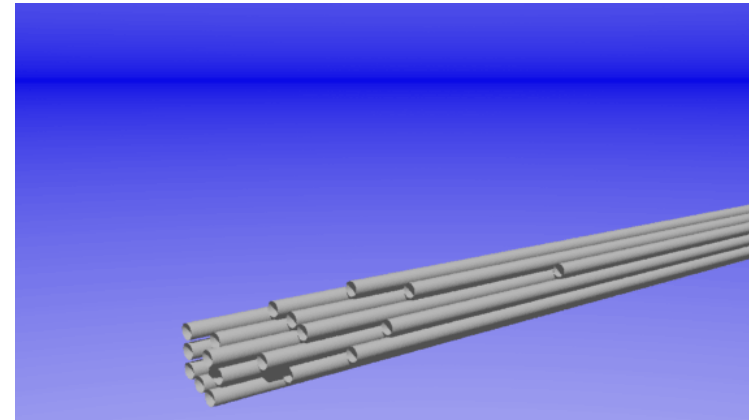
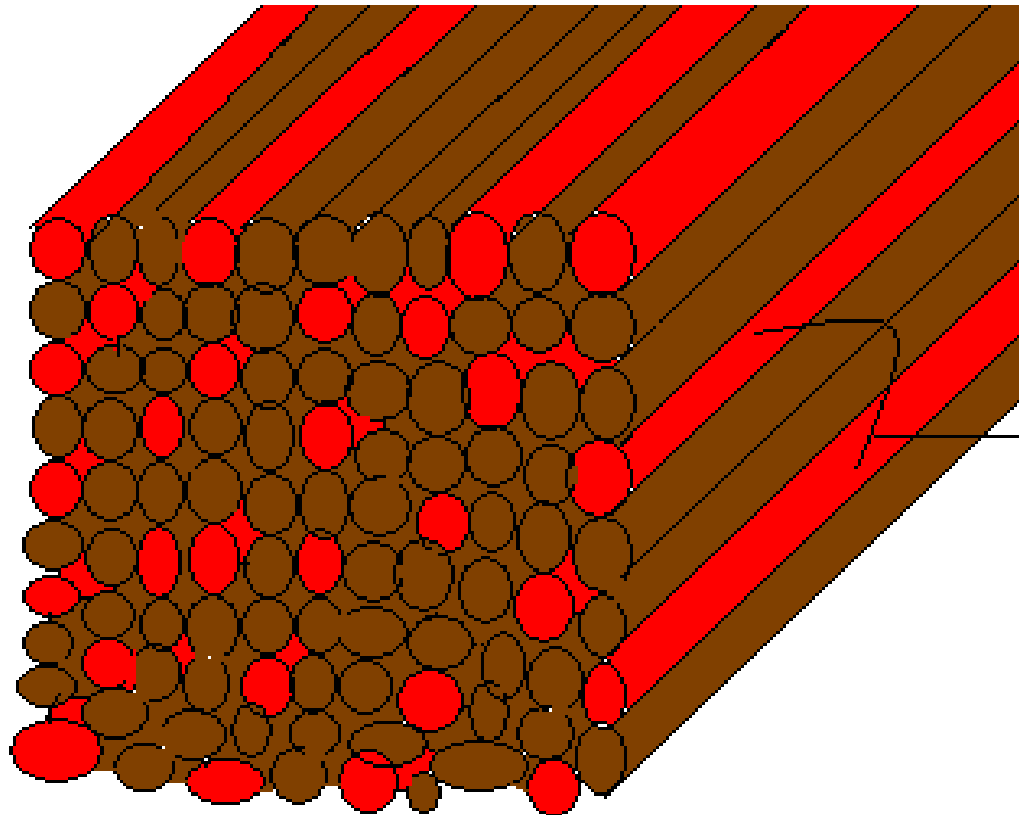
2-D layers of HTS (or  $\text{MgB}_2$ ) can be tailored into 0-D Dots, 1-D tubes or 3-D networks of inverted f.c.c.



# Frenkel Excitons in Molecular SAM provide pairing glue



# Excitons in Semiconducting Single Wall Nanotubes in bundles provide pairing glue for charges in metallic tubes

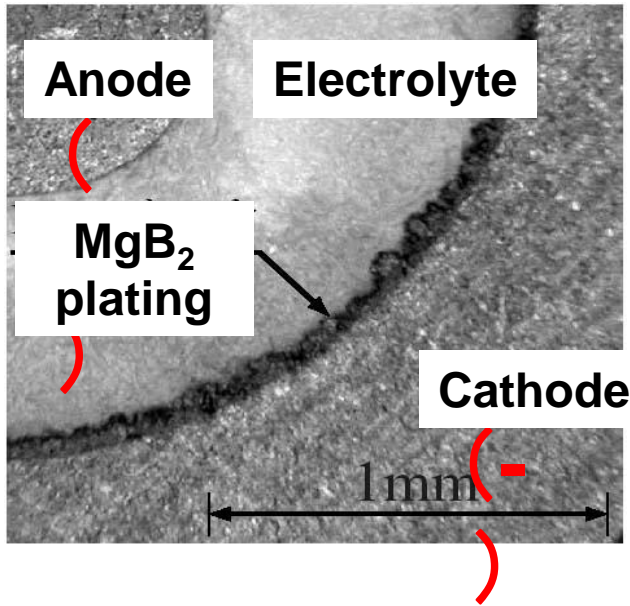
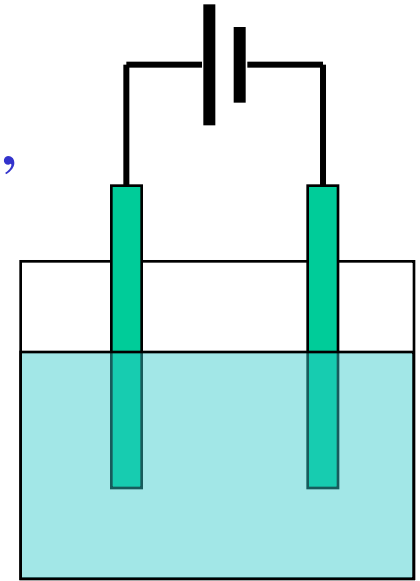


**J-Tunneling  
Coupling**

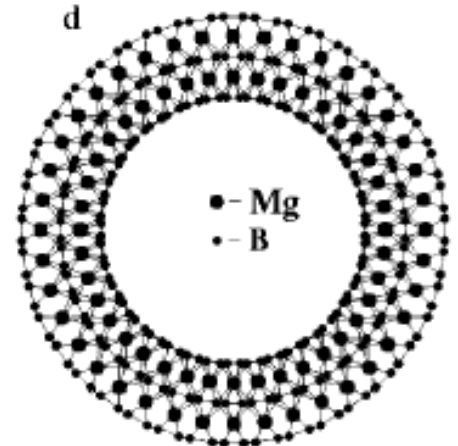
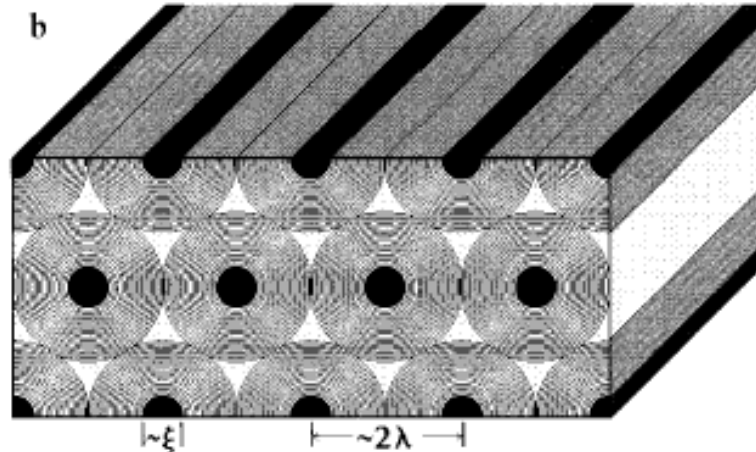
-  **Metallic**
-  **Semiconducting**

# Suggestion for MgB<sub>2</sub> nanotubes growth

If highly porous carbon, i.e. CNT forest is used for electrode, Then MgB<sub>2</sub> will grow In form of nanotubes:



SEM image of MgB<sub>2</sub> thin film fabricated by Galvanization method



Two-walled MgB<sub>2</sub> tubes

# Perspectives for RTS

- HTS which have 2-D planes, can be converted into curved 1-D nanotubes, or into “effectively 3-D” nanosystems e.g. by electrochemical growth.
- Carrier density can be significantly increased by dry double layer doping which may increase  $T_c$  in nano-SC.
- Coating interfaces with organic dyes, will allow to study the possibility of  $T_c$  increase via Excitonic extra “pairing glue”

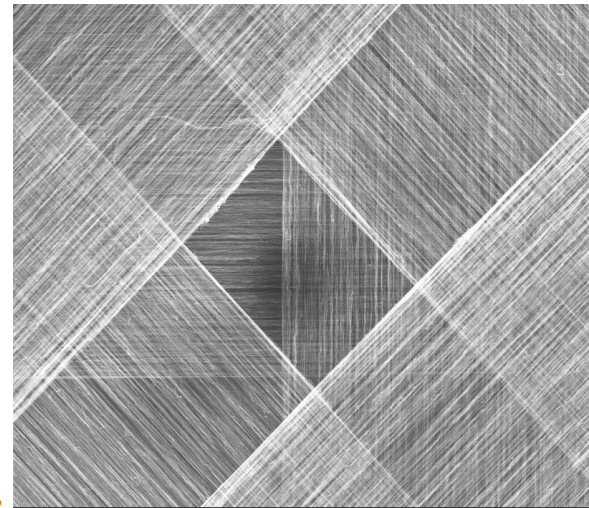
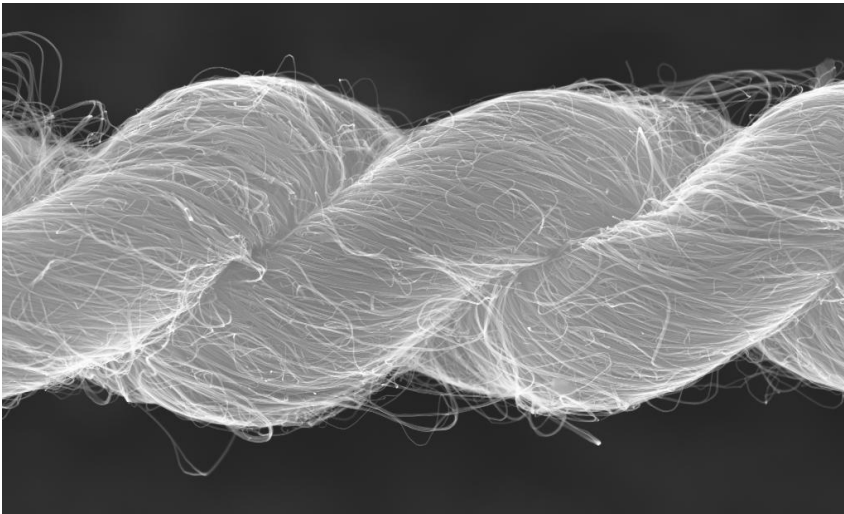




## Ready for RTS in UTD

# CNT Yarns and Sheets for RTS nanocables *Science*

Vol. 306, 2004 and Vol. 309, 2005



Research with RTS applications in mind!

# “Science is People!”

Alan MacDiarmid, 2000 Nobel laureate in Chemistry



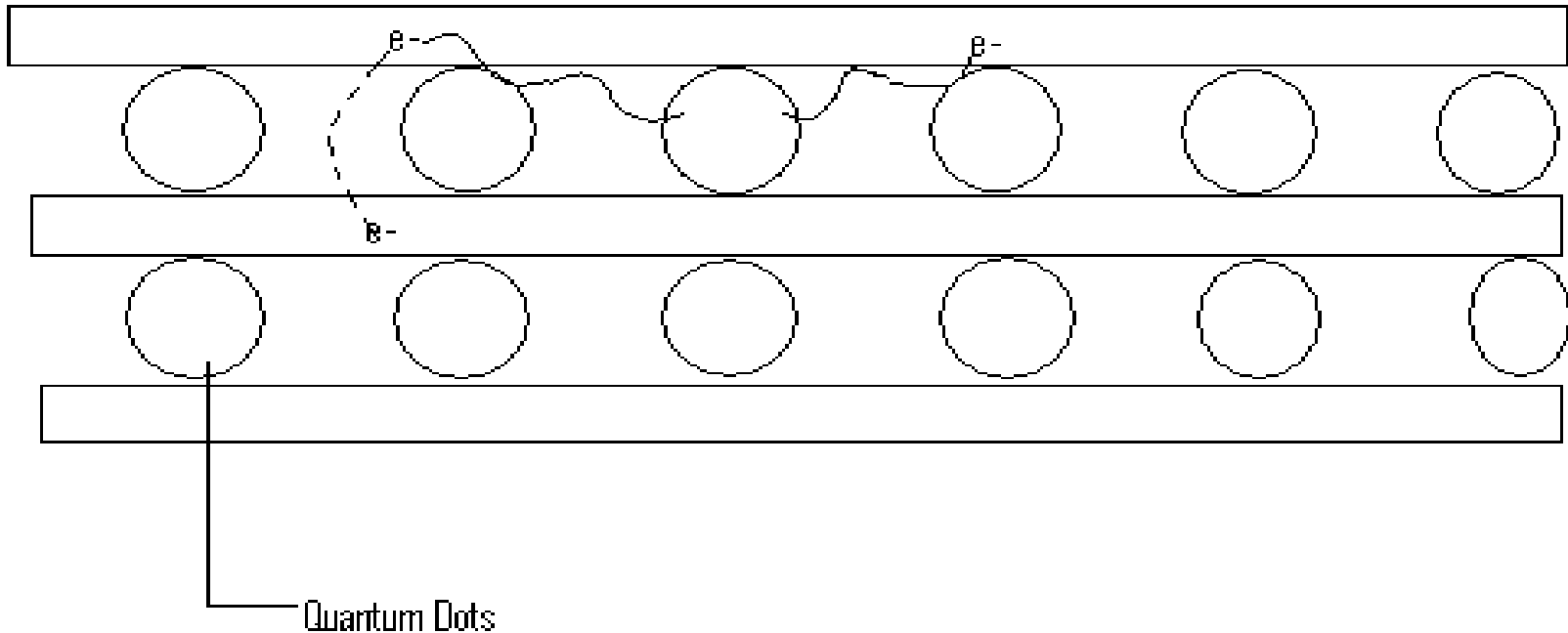
## UTD Superconductivity Team:

Ali Aliev,  
Anvar Zakhidov,  
Ray Baughman

## Funding

- US Air Force via AFOSR programs
- Robert A. Welch Foundation
- Defense Advanced Research Projects Agency
- SPRING (Strategic Partnership for Research in Nanotechnology)

# Excitons in Quantum Dots provide pairing glue in metallic single wall carbon nanotubes



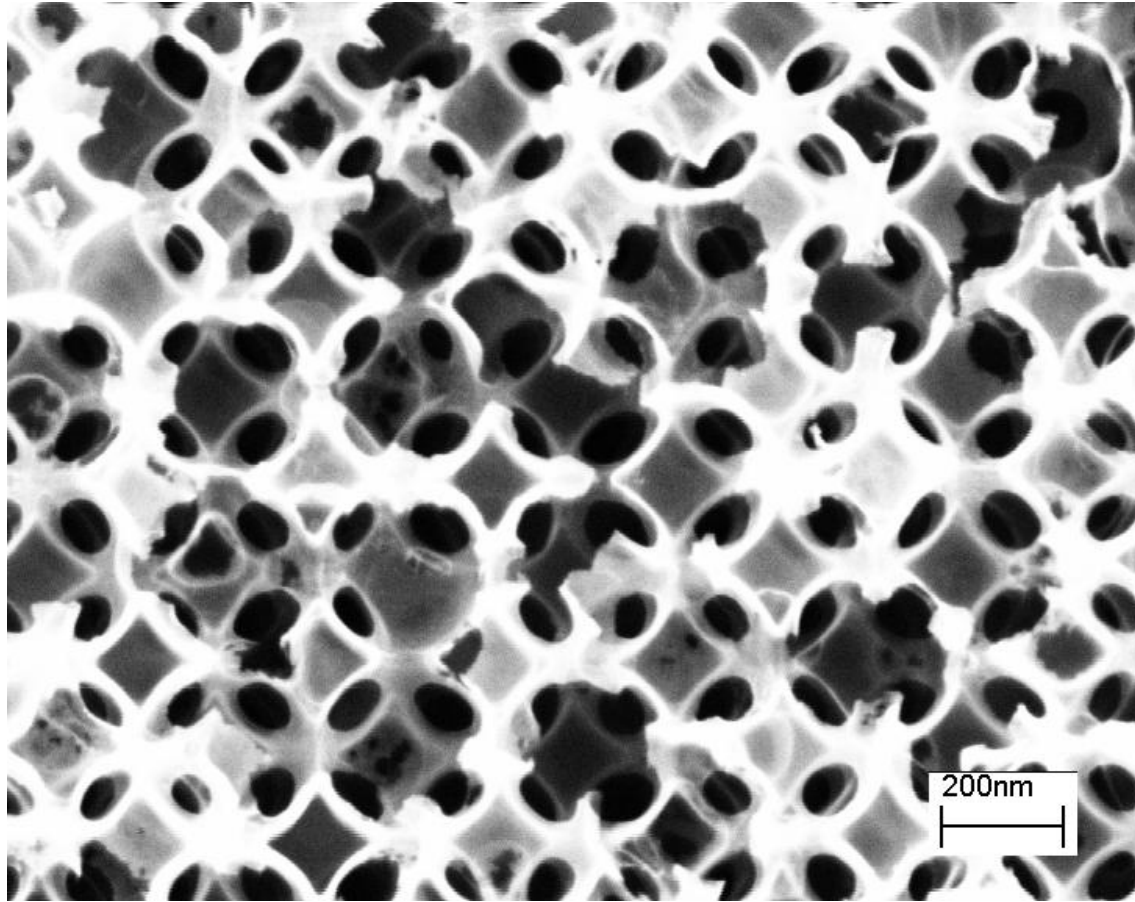
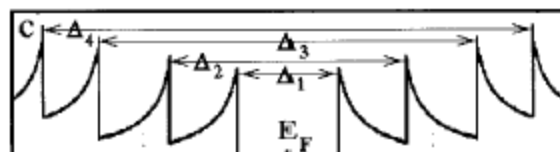
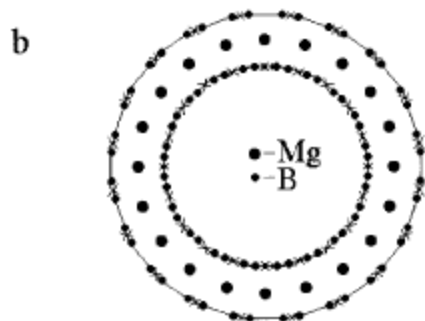
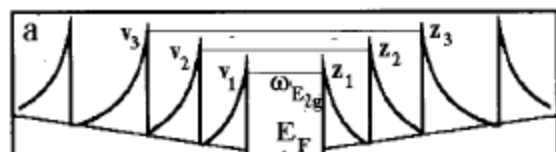


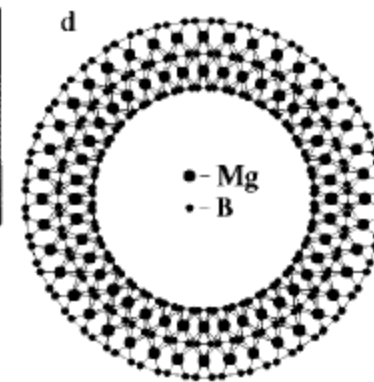
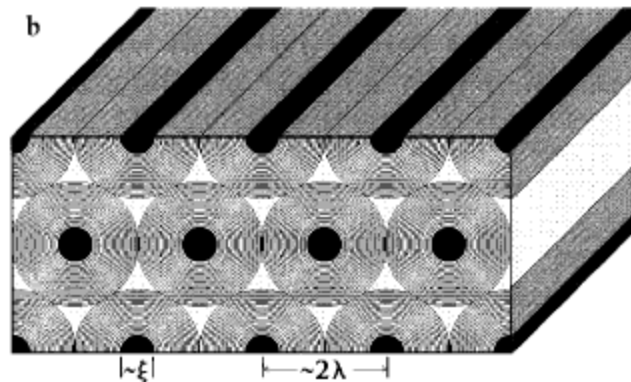
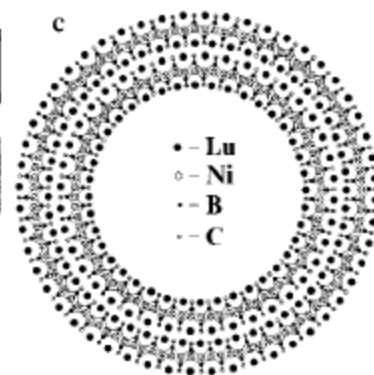
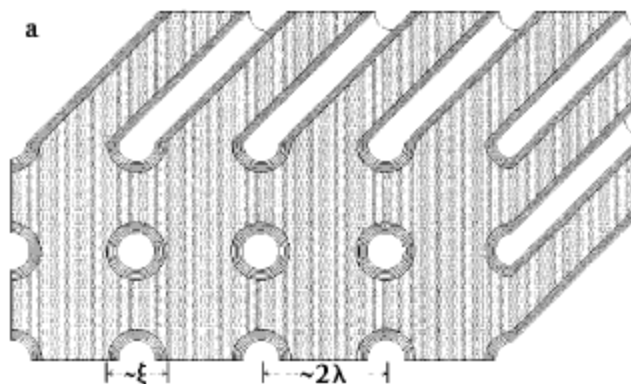
Fig. 8

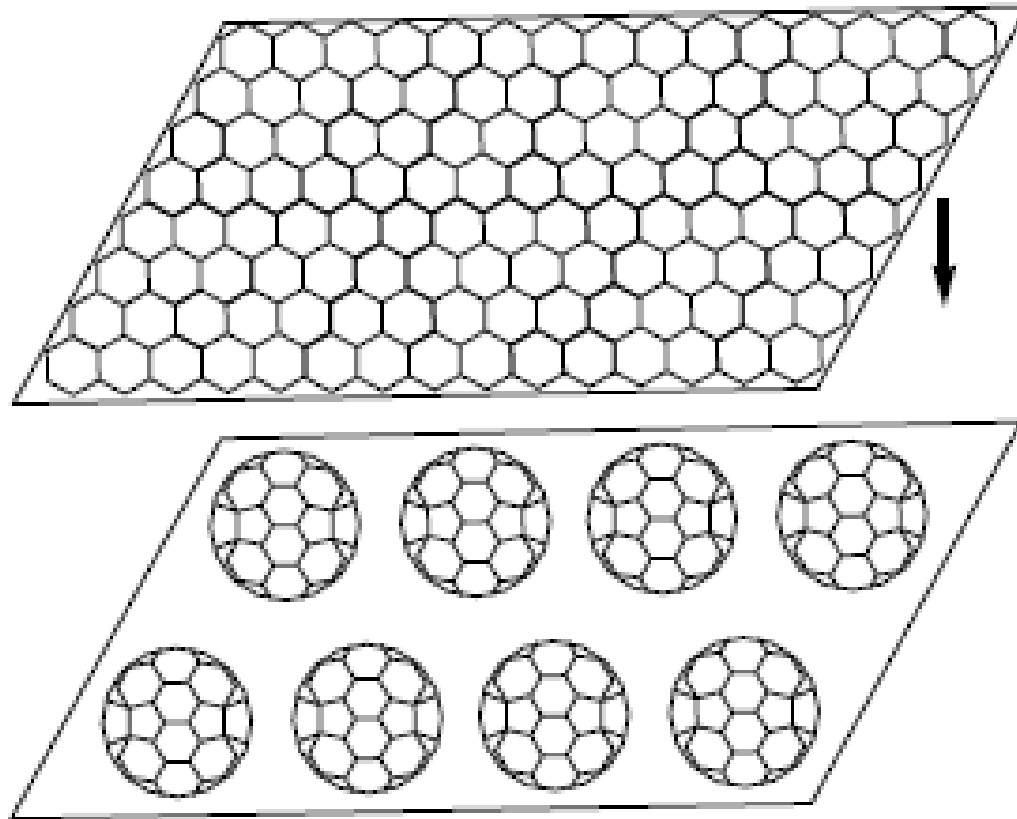
## Nanostructured superconductors: from granular through wire towards high- $T_c$ nanotubular 2D composites

Vladimir Pokropivny



**Figure 3** Two kinds of ideal high- $T_c$ -superconductors on base of membrane 2D crystals (a lattice parameter of which is about the double penetration depth of a magnetic field  $a \sim 2\lambda$ ), built from nanotubes (diameter of which is about the correlation length  $d \sim \xi$ ), wrapped from layered superconducting materials: (a) square lattice of nanotubes deposited on inner walls of nanocylinders of 2D-membrane; (b) triangle lattice of nanotubes deposited on outer walls of nanofibers of 2D brush-like lattice; (c) cross-section of the single-walled LuNiBC nanotube; (d) cross-section of the two-walled MgB<sub>2</sub> nanotube





*Figure 10.7.* Intercalation of graphene sheets by C<sub>60</sub> molecules.

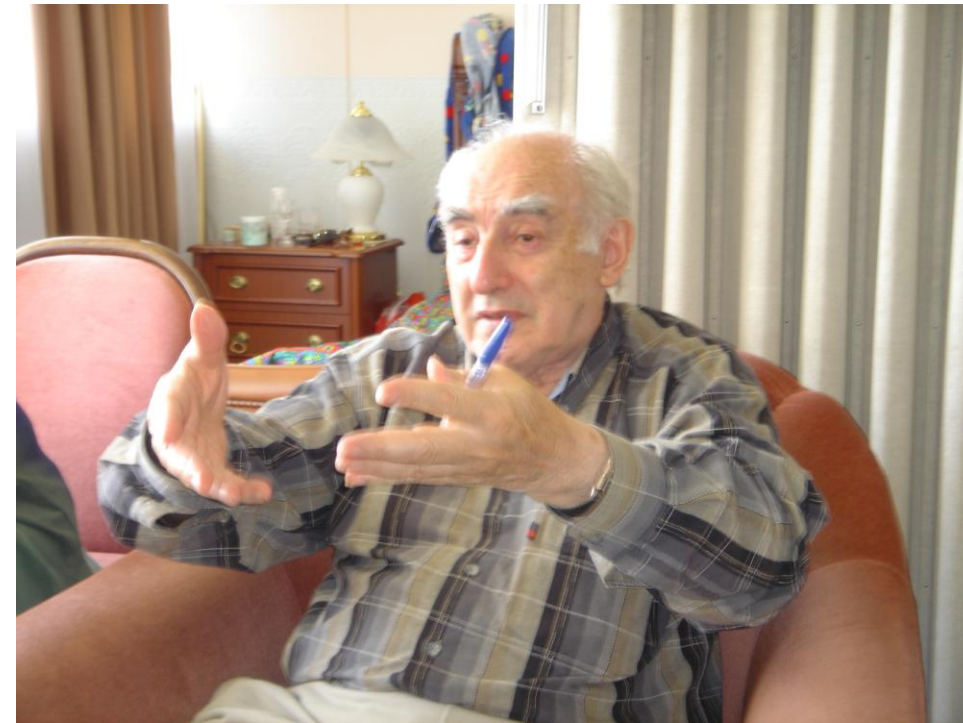
- In addition to experiments on single crystals of pure or polymerized fullerenes, the fullerenes can also be used in a combination with graphite or/and nanotubes. One can intercalate the graphene sheets in graphite by fullerenes

## Possible explanation of $T_c > 100$ K

An explanation of such enhancements of  $T_c$  was proposed, twenty five years ago, by Lefkowitz,<sup>19</sup> who thought that the anomalous  $T_c(x)$  dependence in the tungsten bronzes was a surface effect: he stressed that a ferroelectric instability can condense at low temperatures in  $\text{WO}_3$  and hypothesized that this could lead to high electric fields at the boundary between the insulating material and the doped regions—thus inducing a new electron density of states at the Fermi level. Although we are now quite sure that the increase in  $T_c$  with the reduction of the alkali content in these bronzes is really a bulk property, the Lefkowitz's proposition seems fairly seductive when considering the phenomenon we observed in the vapor-transported samples.

<sup>19</sup>I. Lefkowitz, *Ferroelectrics* **16**, 239 (1977).

**Inspired by Vitaly Ginzburg, my grand-teacher and  
the leader of Russian program on High Tc**





**Vitaly Ginzburg and Vladimir Agranovich**  
**“Krasnaya Polyana”, Chehov, 2004**

