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

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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 $\text{NaxWO3}$ at 125 K, and in $\text{LixWO3-y}$ at 132K

• Prospects: curved HTS and extra “excitonic pairing glue” across the interface in nanostructured SCs
Ijima 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


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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…

(N,M) indices

- 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.
NanoTemplates for Superconductors

Carbon Nanotubes

Can we create HTS materials at nanometer scale with Increased Tc, Hc, Isc, etc. via huge interface and curvature

Opals

Inverted opals

Multiwall nanotubes

Multi-walled nanotube

Double Layer Charge injection in nanotubes

Transparent metallic nanofoams
Infiltration can either coat the internal surface or fill the internal volume.

Template (SiO2 opal) cannot be infiltrated and then extracted unless \( 1.11 > \frac{d}{D} > 1.15 \),

\( d \) - intersphere separation, \( D \) - sphere diameter
Advantages of nano-space for growing HTS

Huge interface: >100 m²/cm³ 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

There is a range of frequencies (green color) where light cannot propagate.

Huge internal porosity: $> 100 \text{ m}^2/\text{cm}^3$
Inverse Opals Have > 75 % porosity

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 be made of any material:
  - Metals,
  - Semiconductors,
  - Lasing media: Er, Eu.
  - Quantum dots
- Can infiltrate easily various materials with large change of \( 1 - ff \)
- 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
- Can change \( n \) by filling with transparent liquids
LTS in nanostructure: Pb-in-opal. Will Tc, Hc, change for Pb clusters network
Fabrication of LTS: Pb Inverse Opal

1. POROUS SILICA OPAL

2. METAL-SILICA NANOCOMPOSITE

HIGH-PRESSURE MELT-INFILTRATION

3. METALLIC INVERSE OPAL

REMOVAL OF SILICA WITH HF
Structure of Pb-clusters network in pores of opal: Spheres connected via cylindrical channels

Fig. 1. SEM image of the (1 1 1) 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 channnels \( r_{ch} = 0.155 \cdot r \).

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

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)
Tc increase from 7.1 K to 7.3 K, ΔTc = 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 Tc.

Fig. 4. Magnetization vs. external field for different temperatures. Two well-distinguished peaks have different behavior. Below 5 K the second maximum is dampened by the oscillation of the magnetic moment which disappears again at higher fields, H > 0.8Hc2. The inset shows the whole
4-times Increase of critical $H_{c2}$ 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. $H_{\text{Max1}}$ and $H_{\text{Max2}}$ correspond to the two maximum on $M(H)$. $H_{cl}$ 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 $H_{cl}$. 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 Tc

Microwave absorption studies of MgB$_2$ superconductor

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Figure 1. The temperature dependence of low field signal (LFS) recorded for (a) polycrystalline and (b) single-grain MgB$_2$ samples.
LFS below Tc in Pb in red Opal

Pb in Red Opal

Magnetic Field

MMMA (ARB UNITS)
LFS below TC for Pb in Green Opal

\[ \Delta H = 0.2 \text{ G} \]

Magnetic field (Gauss)

Pb in Green Opal

MMMA (arb.units)
LFS in Pb in blue opal

Magnetic Field vs. MMM (ARB UNITS) for different magnetic field ranges.
Comparison of discrete LFS in Pb-opals

Pb in Green Opal
$\Delta H = 0.2$ G

Pb in Blue Opal
$\Delta H = 0.24$ G

Pb in Red Opal
$\Delta H = 0.35$ G
Low-field microwave absorption in single-crystal superconducting YBa$_2$Cu$_3$O$_{7-\delta}$

A segment of the 9.44 GHz microwave absorption line spectrum of a YBa$_2$Cu$_3$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

Microwave absorption (arb. units)

H, Gauss

Pb foil (~50 μm)
Conclusion to Part 1:
LTS in Nano-space

• Tc increase only slightly: from Tc=7.1 to 7.32
• Critical field Hc2 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 Tc 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 \( \text{Na}_x \text{WO}_3-y \) 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 Tc ~ 91-100 K in Na_xWO_3: is it USO

• Inverse carbon opals: matrices for sol-gel growth of 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 WO$_3$ single crystals surface doped with Na$^+$

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![Graph](image)

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.

![Graph](image)

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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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

B. Calorimetric study of the order-disorder transformation

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

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

FIG. 2. DSC thermograms observed on a powder sample of $\text{Rb}_{0.25}\text{WO}_3$ (≈50 mg) on heating and on cooling at ±10 K/min.
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 $^3$He-$^4$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 Tc

superconductivity also develops on the surface of WO$_3$ crystals that have been subjected to a slight superficial enrichment of sodium.$^5$ 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 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
NaxWO₃ in Inverted Carbon Opals:

1. Porous matrix for WO₃ growth by sol gel
2. WO₃ coated nano-carbon: good electrode for electrochemical Na doping
**BACKGROUND:** Charge injection could enable performance optimization for superconducting materials enhancing Tc.

*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 WO3-inv. opal

**Examples:** NaₓWO₃ 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!**

\[ C = \frac{\text{charge/voltage}}{\text{area} \times \text{dielectric constant /d}} \]
Our Strategies for Obtaining Frozen Interfacial Charge Transfer

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

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-immersse 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 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

- Electronic connections
- Four-probe connection at working electrode
- Working electrode
- Counter electrode

Graph showing the change in conductivity before and after dipping in electrolyte for initial few cycles and after many cycles. The x-axis represents the change in charge carriers per carbon atom, and the y-axis represents the conductivity in S/cm.
Ion-containing Interface Water
Solvated (right) or Unsolvated (left)?

Atom designations: Cl⁻ (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\textsuperscript{1,2} that metals will work just like nanotubes:

Double-layer charge injection increases unit cell volume of Pt by \(\sim 0.4\%\).

Preparation of Na$_x$WO$_3$ Inverted Opal

- We used a sol-gel technology for preparation 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 WO$_3$ into nanoporous material with high surface area and then electrochemically doped to obtain double layer with alkali ions (Li+, Na+, K+).
The temperature dependence of ZFC magnetization for Na$_x$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.
Comparison of FC and ZFC measurements in Na$_x$WO$_{3-y}$ compound with subtracted paramagnetic contribution. Inset shows the measured data. Curie paramagnetic contribution was subtracted using following fitting parameters:

$$M = M_o + C/T,$$

$M_o = 1.35 \times 10^{-6}$ emu,

$C = 12.64 \times 10^{-6}$ emu·K.
Effect of H$_2$O on M(T) of Na$_x$WO$_3$

- Temperature dependences of magnetization measured separately in bulk WO$_3$-y, pure carbon inverse opal matrix, carbon inverse opal infiltrated with WO$_3$-y 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$_3$-y 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 Li$_x$WO$_{3-y}$: Diamagnetism at 132 K

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

$T_c = 132$ K

Temperature, K

Magnetization, emu

50 Oe
Resistivity measurements drop at T_c

Temperature dependence of resistance in ceramic based Na_xWO_{3-y}. Applied current was 1μA.

The direct evidence of polaron formation from temperature dependence of photoemission spectra and formation of bipolarons in weakly reduced to 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 WO_{3-x}. 
Very weak and noisy LFS in NaxWO$_3$ at very low T $\sim$ 5 K
Other Nano-Matrices for NaxWO3

• 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 NaxWO3-y on carbon inverse opal host matrix at Tc=125 K.
Conclusion to NaxWO3

- 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 NaxWO3-y structures are amorphous and only samples sintered at $T_s>300\,\text{oC}$ 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 MgB$_2$) can be tailored into 0-D Dots, 1-D tubes or 3-D networks of inverted f.c.c. MgB$_2$
Frenkel Excitons in Molecular SAM provide pairing glue
Excitons in Semiconducting Single Wall Nanotubes in bundles provide pairing glue for charges in metallic tubes.
Suggestion for MgB\textsubscript{2} nanotubes growth

If highly porous carbon, i.e. CNT forest is used for electrode, then MgB\textsubscript{2} will grow in the form of nanotubes:

Two-walled MgB\textsubscript{2} tubes

SEM image of MgB\textsubscript{2} thin film fabricated by Galvanization method
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 Tc in nano-SC.

• Coating interfaces with organic dyes, will allow to study the possibility of Tc increase via Excitonic extra “pairing glue”
Ready for RTS in UTD

CNT Yarns and Sheets for RTS nanocables

*Science*


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
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\(_2\) nanotube.
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.

Figure 10.7. Intercalation of graphene sheets by C$_{80}$ molecules.
Possible explanation of $T_c > 100$ K

An explanation of such enhancements of $T_c$ was proposed, twenty five years ago, by Lefkowitz,\textsuperscript{19} 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 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.

\textsuperscript{19}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