

# Superatom Thermoelectric Materials

## 2cd Multifunctional Materials for Defense Workshop

30 July 2012



Materials & Manufacturing Directorate

AFRL/RXBT

Dr. Douglas Dudis

| Report Documentation Page                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                                    |                                     |                                                           | Form Approved<br>OMB No. 0704-0188                  |                                 |
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## **Team Members / Collaborators**



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**Dr. Nicholas Gothard**

**Dr. Bevan Elliott**

**Prof. Tahir Cagin (Texas A&M University)**

**Prof. Michael Leamy (Georgia Tech)**



# Outline



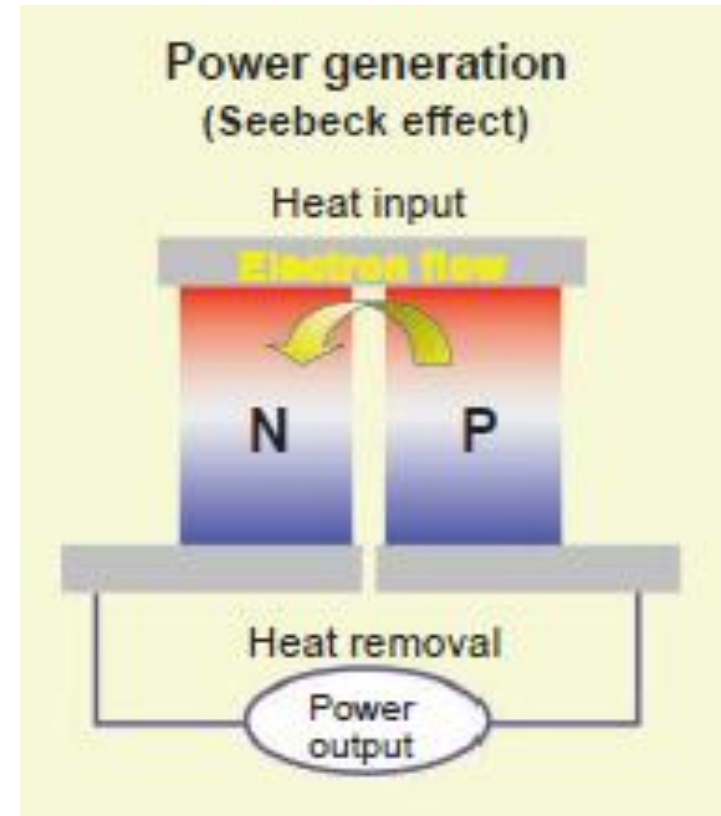
- **Thermoelectrics**
- **Materials Challenges**
- **Advantages of Superatoms**
- **Fullerenes/Fullerides**
- **Progress**
- **Conclusions**



# Thermoelectric Architecture



- Two materials in contact
  - N and P refer to desired direction that the electron wants to travel through the material
    - Examine electrons for P-type and holes for N-type
- Temperature differential allows for electron to be excited and released

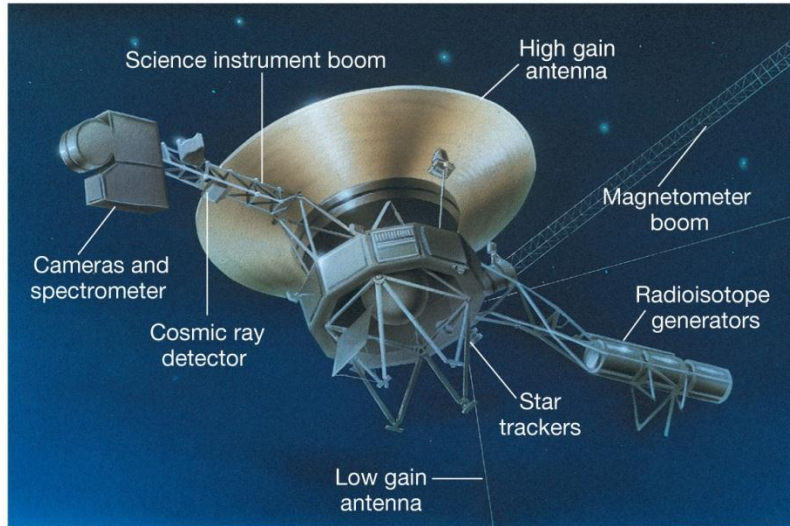


## **ANAOLGIES:**

**Mechanical:** Solid State Heat Pump electrons are working fluid  
**Photovoltaic:** Energy Harvester with thermal excitation instead of light



# Where TE's are used today...



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<http://www.aerospaceweb.org>  
voyager spacecraft



**AMERIGON'S  
GENERATOR**  
positions semiconductors  
between the exhaust stream  
and a cooled outer surface  
to produce electricity.

Amerigon.com



Newsroom.orange.co.uk/



# Thermoelectric Interest & Relevance



## AF Impacts Advantages

|               |                                                               |
|---------------|---------------------------------------------------------------|
| DEW Lasers    | <i>Precision Temp Control</i>                                 |
| Satellites    | <i>Reconfigurable, <u>Long Life</u>, <u>No Vibrations</u></i> |
| Pilot Suits   | <i><u>Independent of Orientation &amp; g-forces</u></i>       |
| UAVs, Sensors | <i>Efficient for small applications</i>                       |
| Electronics   | <i>Solid State, switchable</i>                                |



Refrigeration & Heating  
Heat Lift & Rejection  
Energy Harvesting

## Air Force Research Laboratory TE Interest

Propulsion Directorate (AFRL/RZ)  
Human Effectiveness (AFRL/RZH)  
Directed Energy Directorate (AFRL/RD)  
Air Vehicle Directorate (AFRL/RB)  
Space Vehicles Directorate (AFRL/RV)  
Information Directorate (AFRL/RI)  
Materials & Manufacturing Directorate (AFRL/RX)



# Thermoelectric Efficiencies

**If you want to cool a meat locker, use vapor compression cycle.  
If you want to cool a hot dog, use a thermoelectric.**

Specific Power:

|                                |          |
|--------------------------------|----------|
| High Eff. Stirling 25 kW est.: | 220 W/kg |
| NASA Stirling 5 kW System:     | 140 W/kg |
| Bi-Te Thermoelectric 14.7 W:   | 300 W/kg |

***Similarly, thermoelectric energy harvesting on small scale can be better than other options.***

***UAV ~ 100W generator based on waste heat reutilization.  
Replace mechanically based generator.  
(ongoing program)***

**Notion that thermoelectrics are inefficient is misguided – question of scale.**



# Scramjet Characteristics

## Power and Thermal Challenges



- **X-51 Waverider:**  
**Longest duration**  
**scramjet flight 2+**  
**minutes at Mach 5**
- **High Speed Strike**  
**Weapon**

### **Thermal**

- High temperature heat loads
  - Large surface area
  - $\Delta T$  - array of fuel cooling paths
- Heat capacity of fuel as heat sink
- Air inlet drag limitations
- Altitude - convection

### **Power**

- No rotating shaft
- High electrical power requirements
- Inlet air drag
- Altitude – air breathing technologies

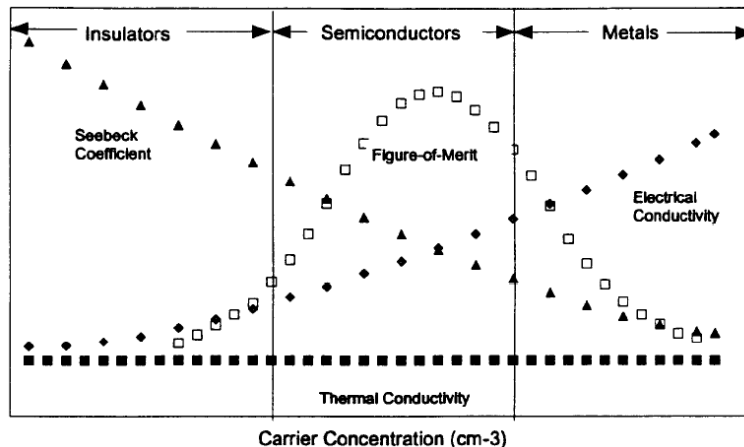


# Relation to Thermoelectric Materials



$$ZT = \frac{(S(T))^2 \cdot \sigma(T)}{\kappa_e(T) + \kappa_l(T)} \cdot T$$

We want a phonon glass,  
electron crystal material.



# Periodic Table of the Elements

|    |    |     |     |     |     |     |     |     |     |     |     |     |    |    |    |    |    |    |    |    |    |    |    |
|----|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|----|----|----|----|----|----|----|----|----|----|----|
| 1  |    |     |     |     |     |     |     |     |     |     |     |     |    |    |    |    | 2  |    |    |    |    |    |    |
| H  |    |     |     |     |     |     |     |     |     |     |     |     |    |    |    |    | He |    |    |    |    |    |    |
| 3  | 4  |     |     |     |     |     |     |     |     |     |     |     |    |    |    |    |    | 5  | 6  | 7  | 8  | 9  | 10 |
| Li | Be |     |     |     |     |     |     |     |     |     |     |     |    |    |    |    |    | B  | C  | N  | O  | F  | Ne |
| 11 | 12 |     |     |     |     |     |     |     |     |     |     |     |    |    |    |    |    | 13 | 14 | 15 | 16 | 17 | 18 |
| Na | Mg |     |     |     |     |     |     |     |     |     |     |     |    |    |    |    |    | Al | Si | P  | S  | Cl | Ar |
| 19 | 20 | 21  | 22  | 23  | 24  | 25  | 26  | 27  | 28  | 29  | 30  | 31  | 32 | 33 | 34 | 35 | 36 |    |    |    |    |    |    |
| K  | Ca | Sc  | Ti  | V   | Cr  | Mn  | Fe  | Co  | Ni  | Cu  | Zn  | Ga  | Ge | As | Se | Br | Kr |    |    |    |    |    |    |
| 37 | 38 | 39  | 40  | 41  | 42  | 43  | 44  | 45  | 46  | 47  | 48  | 49  | 50 | 51 | 52 | 53 | 54 |    |    |    |    |    |    |
| Rb | Sr | Y   | Zr  | Nb  | Mo  | Tc  | Ru  | Rh  | Pd  | Ag  | Cd  | In  | Sn | Sb | Te | I  | Xe |    |    |    |    |    |    |
| 55 | 56 | 57  | 72  | 73  | 74  | 75  | 76  | 77  | 78  | 79  | 80  | 81  | 82 | 83 | 84 | 85 | 86 |    |    |    |    |    |    |
| Cs | Ba | *La | Hf  | Ta  | W   | Re  | Os  | Ir  | Pt  | Au  | Hg  | Tl  | Pb | Bi | Po | At | Rn |    |    |    |    |    |    |
| 87 | 88 | 89  | 104 | 105 | 106 | 107 | 108 | 109 | 110 | 111 | 112 | 113 |    |    |    |    |    |    |    |    |    |    |    |
| Fr | Ra | +Ac | Rf  | Ha  | Sg  | Ns  | Hs  | Mt  | 110 | 111 | 112 | 113 |    |    |    |    |    |    |    |    |    |    |    |

\* Lanthanide Series

|    |    |    |    |    |    |    |    |    |    |    |    |    |    |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| 56 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 |
| Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |

+ Actinide Series

|    |    |    |    |    |    |    |    |    |    |     |     |     |     |
|----|----|----|----|----|----|----|----|----|----|-----|-----|-----|-----|
| 90 | 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 100 | 101 | 102 | 103 |
| Th | Pa | U  | Np | Pu | Am | Cm | Bk | Cf | Es | Fm  | Md  | No  | Lr  |

$\sigma(T)$  is electrical conductivity [S/cm]  
 $\kappa(T)$  is thermal conductivity [W/(m\*K)]  
 $S(T)$  is the Seebeck coefficient/thermopower [ $\mu\text{V/K}$ ]

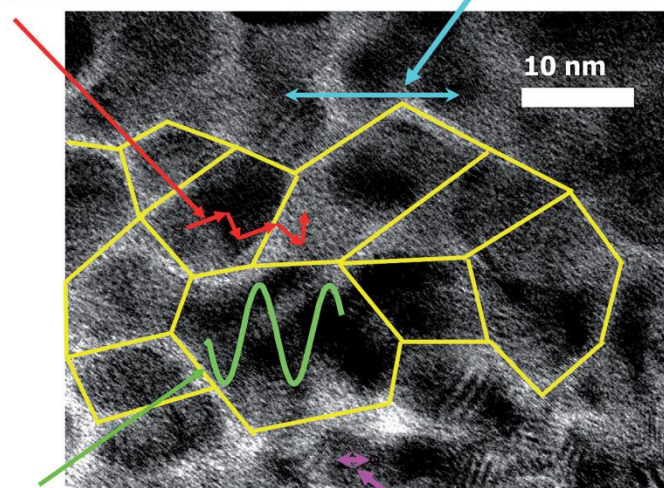


# Current Approaches

- **Decreasing thermal conductivity contribution**
  - Nanostructuring
    - Superlattices (2D), nanowires (1D), and quantum dots (0D)
  - Doping with heavier element
    - Allows for lower sound velocities
    - i.e.  $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ ,  $\text{Si}_{80}\text{Ge}_{20}$

Mean free path:  
2-5 nm

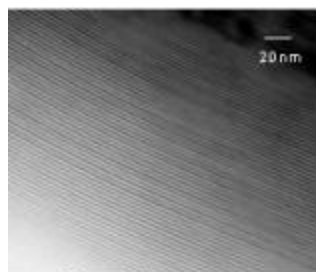
Grain size:  
10-20 nm



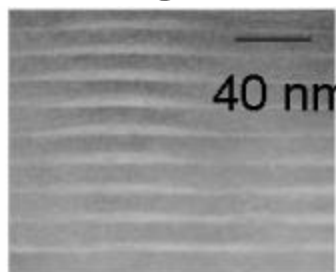
Wavelength:  
5-10 nm

Inter-impurity distance:  
1-2 nm

- **Electron Filtering**



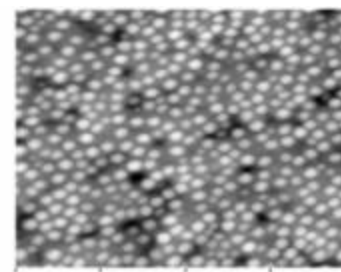
Bulk



Superlattice



Nanowire



Quantum Dots

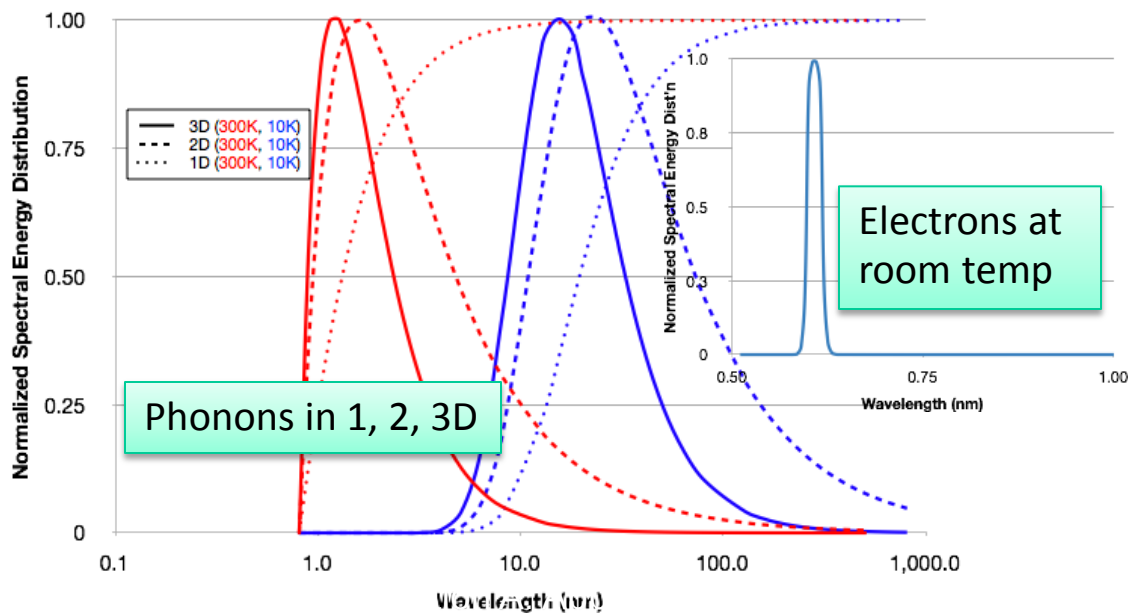


# Phonon Glass Electron Crystals

**PGEC: G. A. Slack, in “CRC Handbook of Thermoelectrics,” edited by D. M Rowe (CRC Press, London), 1995, p. 407.**

***An ideal thermoelectric material will behave like a crystal in terms of electrical conductivity, but will behave like a glass in terms of thermal conductivity.***

**Electron wavelengths and phonon wavelengths are very different : can be decoupled.**

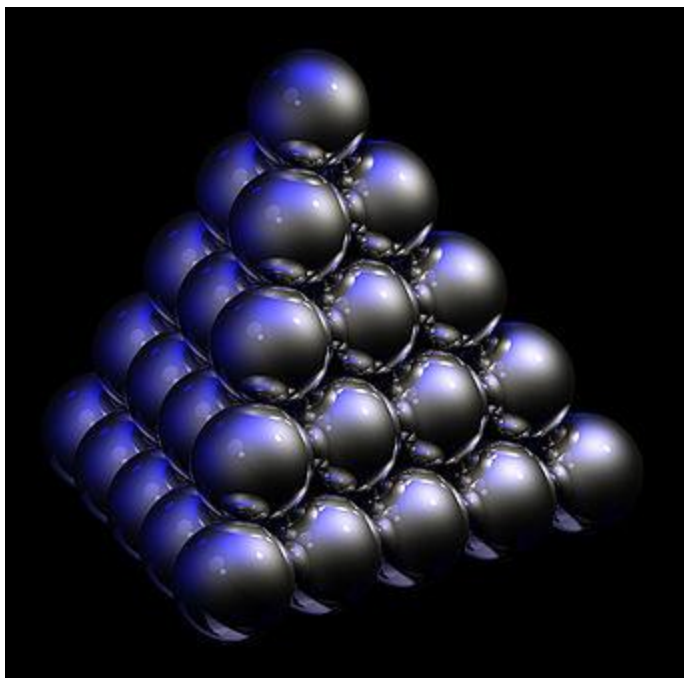


|                                                     |                                                            |
|-----------------------------------------------------|------------------------------------------------------------|
| High $\sigma$ / High $\kappa$<br>Graphite<br>Silver | High $\sigma$ / Low $\kappa$<br>???                        |
| Low $\sigma$ / High $\kappa$<br>Diamond             | Low $\sigma$ / Low $\kappa$<br>Polymers<br>Molecular Matls |

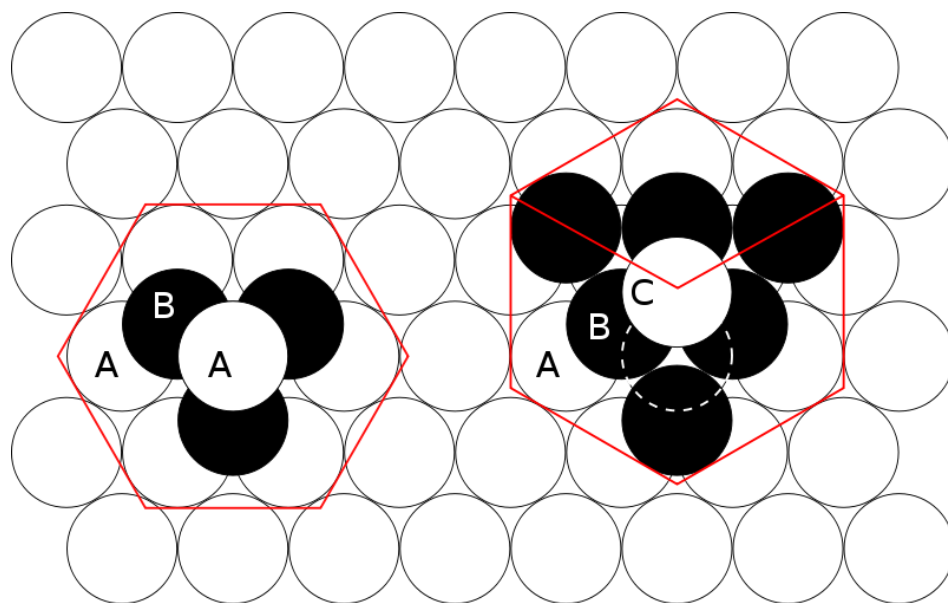
**Fullerides as PGECs**



# Closest Packing Considerations: AgI Fast Ion Conduction



<http://en.wikipedia.org/wiki/Close-packing>



## ***Silver Iodide: Great Example of Size Mismatch in CP Structures***

Room Temperature: Wurtzite Structure

$\text{Ag}^+$  1.15 Å (115 pm)

Above 147 °C, NaCl Structure

$\text{I}^-$  2.20 Å (220 pm)

Becomes Fast Ion Conductor (the silver sub-lattice melts)



# Diminished Thermal Conductivity in Nanowires

## Importance of Interfaces

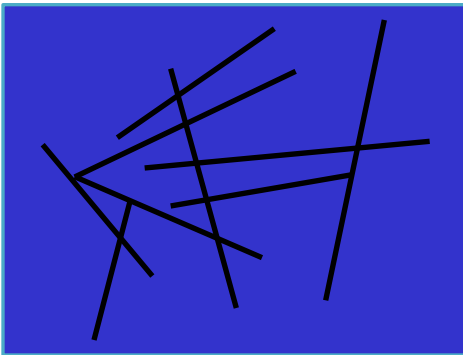


### Silicon Nanowires as Efficient Thermoelectric Materials

A. I. Bouka, Y. Bunimovich, J. Tahir-Kheli, J.-K. Yu, W. A. Goddard, J. R. Heath, **Nature Letters**, **451**, 2008, 168-171.

### Enhanced Thermoelectric Performance of Rough Silicon Nanowires

A. I. Hochbaum, R. Chen, R. D. Delgado, W. Liang, E. C. Garnett, M. Najarian, A. Majumdar, and P. Yang, **Nature Letters**, **451**, 2008, 163-168.



- Diameter of nanowire  $<$  phonon mean free path
- Charge can hop (real particle); phonon can't

***“While nanostructured thermoelectric materials can increase  $ZT > 1$ , the materials (Bi, Te, Pb, Sb and Ag) and processes used are not often easy to scale to practically useful dimensions.”***



# Build Thermoelectric Materials Incorporating Superatoms



**Superatoms ~ cluster than can behave as a unit / have characteristics similar to an atom.**

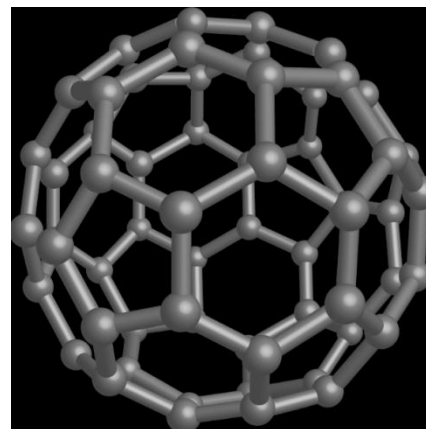
**Diamond  
CNTs (Parallel)**

**~ 2000+ W/mK**



**CNTs (vdW)**

**~ 10 W/mK**



**Buckyball**

**~ 0.5 W/mK**

While fullerenes can be thought of as closest packing like atomic closest packing, there is a size mismatch relative to thermal energy transport. Within a buckyball, coupling length ~ 0.14 nm, but from inter-buckyball length ~ 1.5 nm.



# $C_{60}$ Characteristics

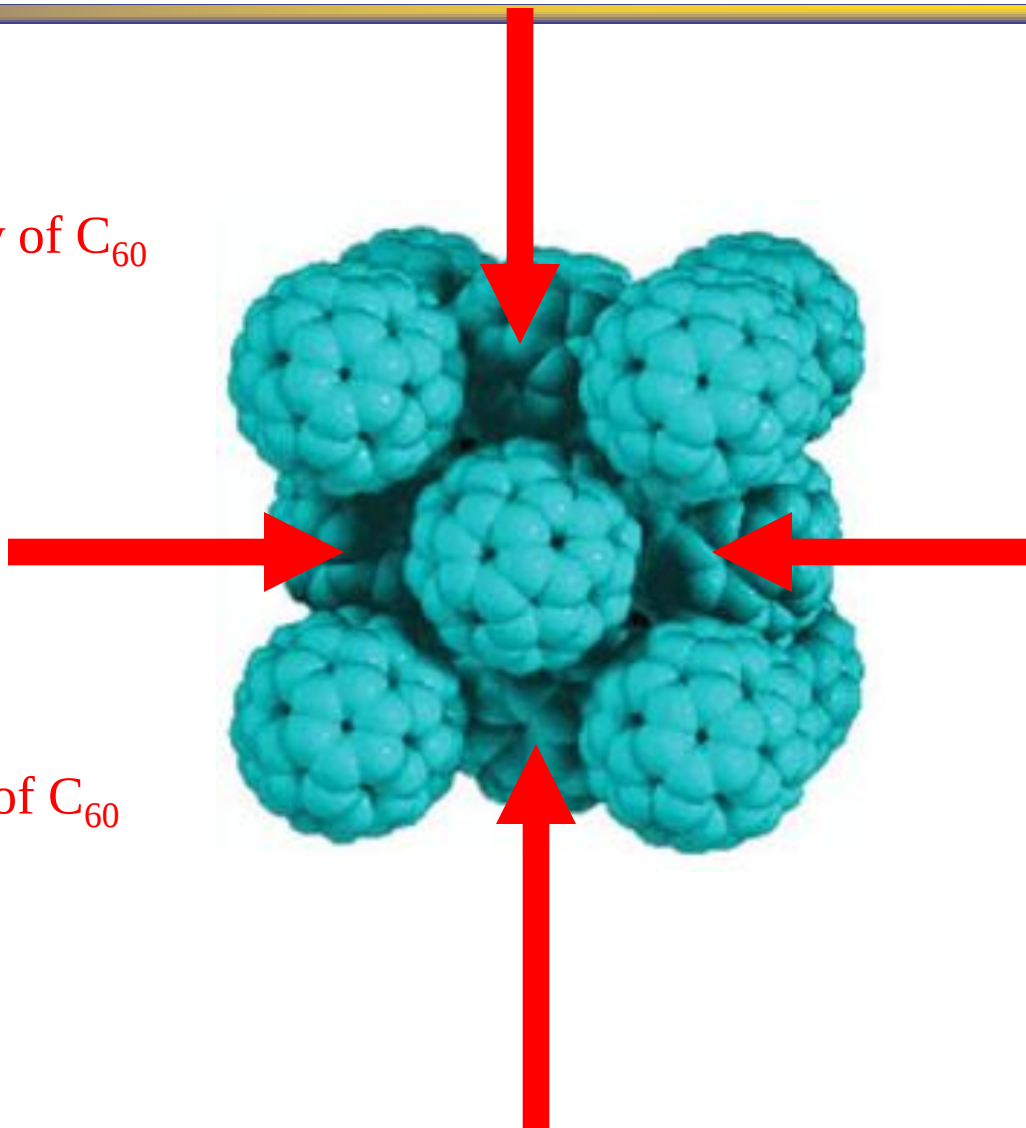


Goal: Increase electrical conductivity of  $C_{60}$

How? **Fulleride formation**

Goal: Decrease thermal conductivity of  $C_{60}$

How? **Fulleride formation**

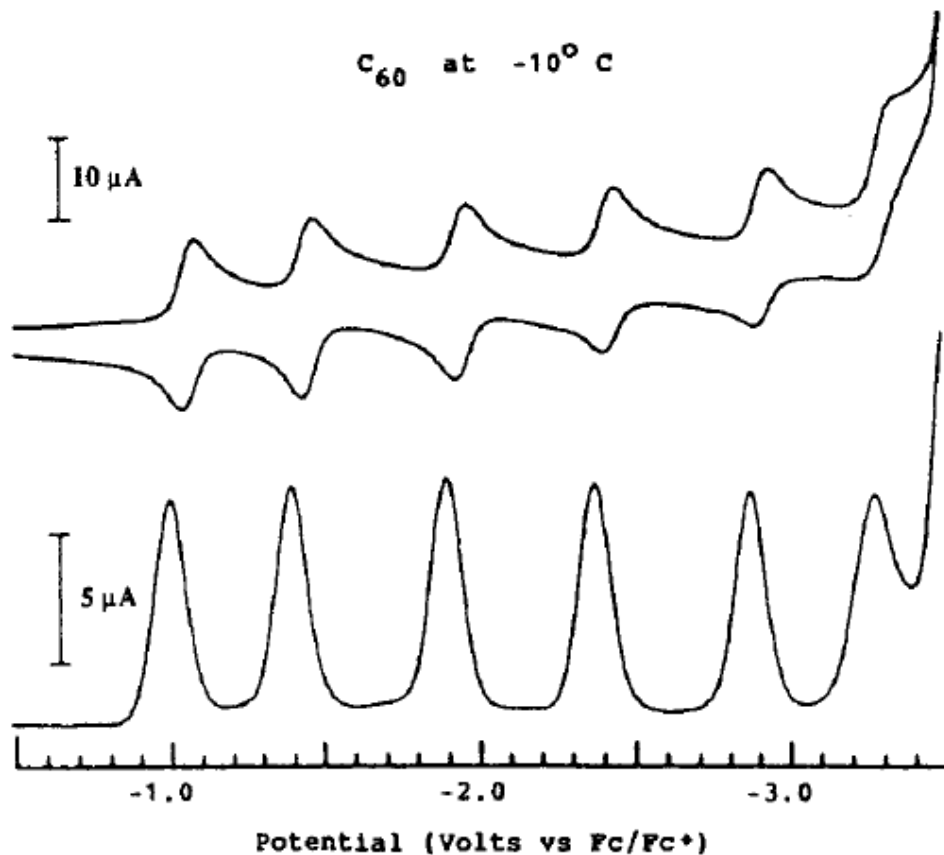
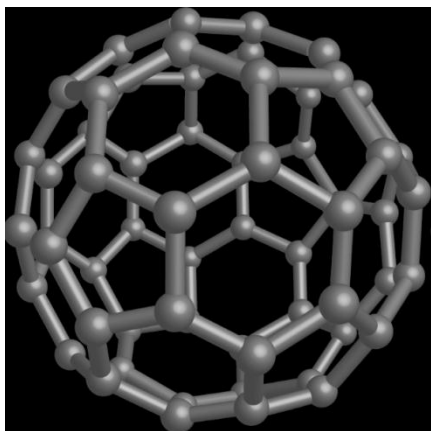


**Fullerides as PGECs**



# Why $C_{60}$ ?

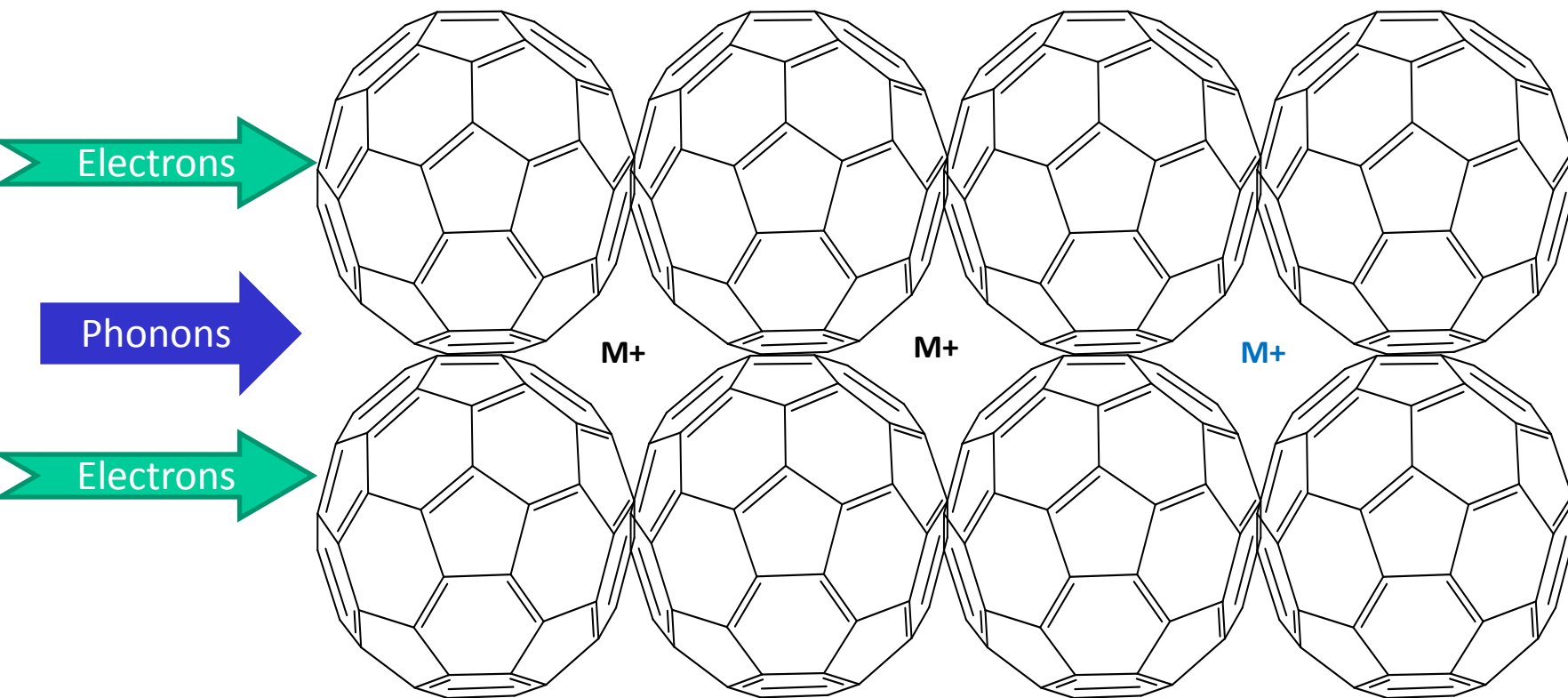
- Inherently low thermal conductivity
- Similar to skutterudites
- Multiple charge/spin states



Potential for Jahn-Teller Distortion:  
“Selective e-phonon coupling” ?



# Rattler Effect in Fullerides



- Gigantic Rattler Effect?
- Alloying Enhancements (Lowering) of  $\kappa$
- Uncouples electron and & phonon transport

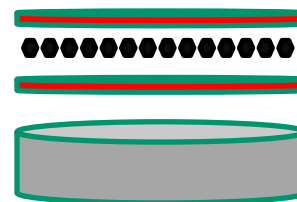


# Synthesis of Materials



## •Thin Film

- Performed in a deep vacuum deposition chamber
- Used magnetron sputtering to deposit zinc and thermal evaporator to deposit  $C_{60}$

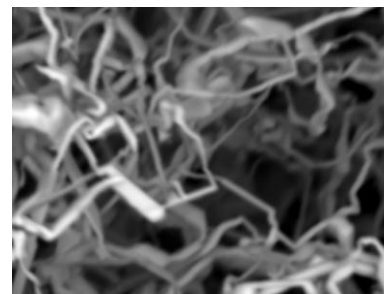


## •Wet Synthesis

- Based on redox potentials of transition metals

## •Chemical Vapor Deposition

- Grown in a process using a zoned furnace system and vacuum system



2012/01/24 13:50 H D4.6 x10k 10 um



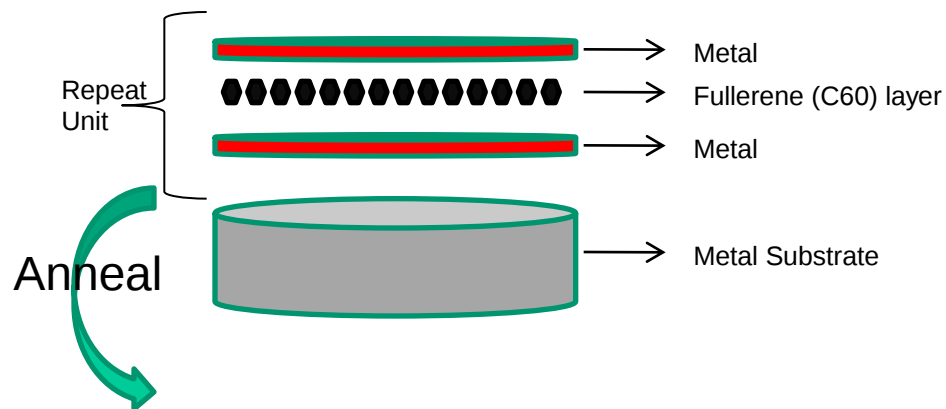
det spot HV WD mag  
BSED 4.0 10.00 kV 10.1 mm 13.000 x



# High Electrical Conductivity Phonon Blocking Layers

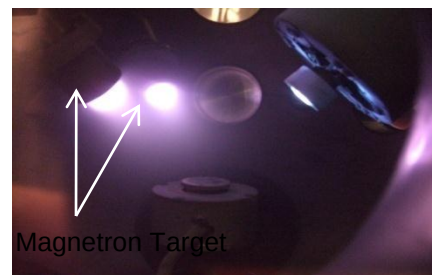
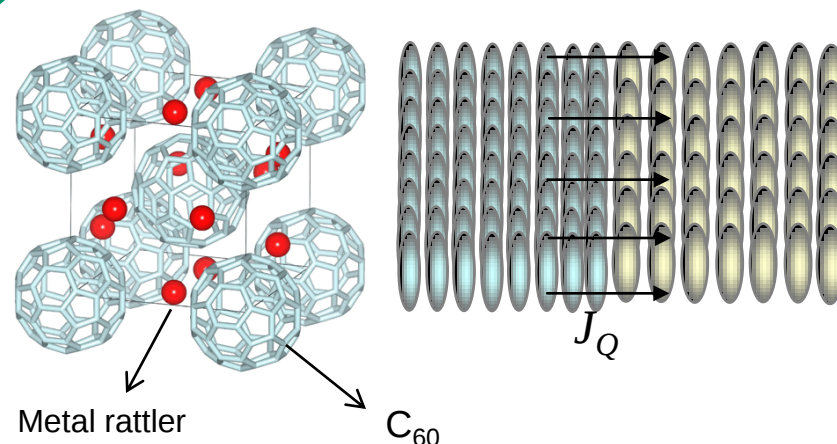


**Objective:** Demonstration of high electrical conductivity, low thermal conductivity phonon-blocking layer (PBL) formation through novel deposition and annealing techniques



## Novel concepts addressed :

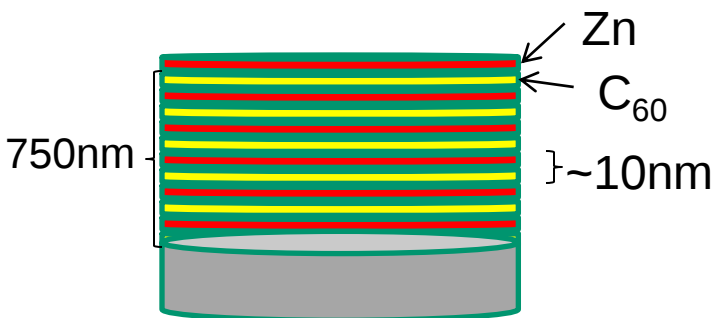
- Incorporation of nanoparticle scattering sites inside a thin film structure
- Demonstration of an air stable metal fulleride ( $\text{Zn C}_{60}$ )
- Demonstration of low thermal conductivity and high electrical conductivity of fulleride (rattlers)
- Demonstrate the use of thin film deposition technique for use in combinatorial analysis.



$$Z = \frac{S(T)^2 \sigma(T)}{\kappa(T)}$$

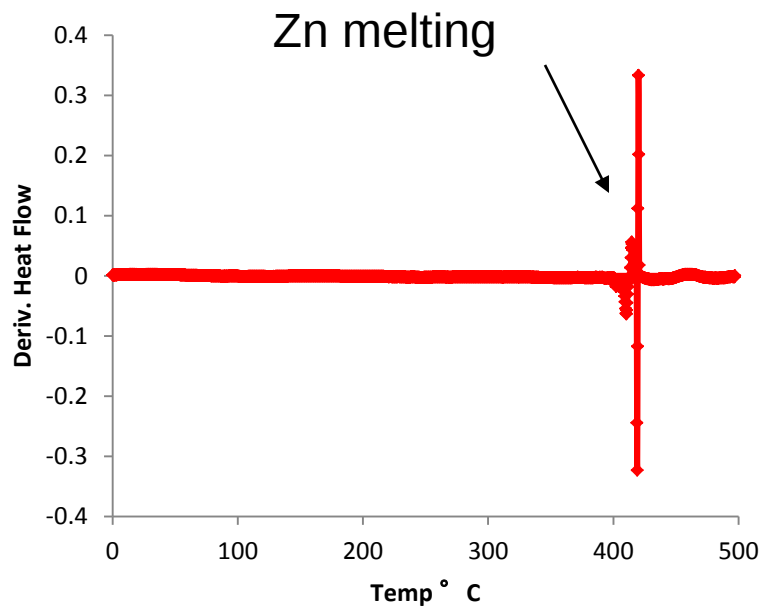


# DSC of Zn C<sub>60</sub> layers

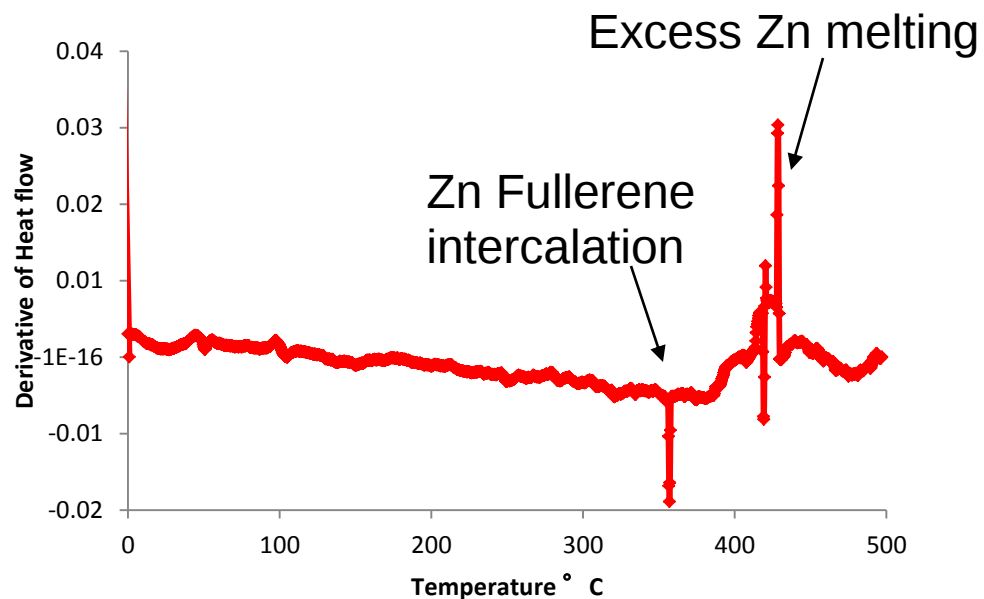


- Sample made with 75 layers. Each layer was ~10nm thick with alternating Zn/C<sub>60</sub>
- Looking for exotherms and endotherms on DSC to confirm Zn intercalation into the C<sub>60</sub>

Deriv. Heat Flow Pure Zn

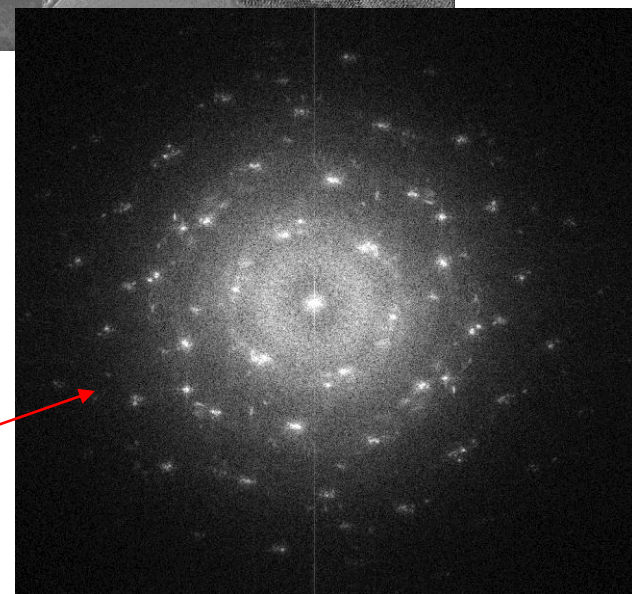
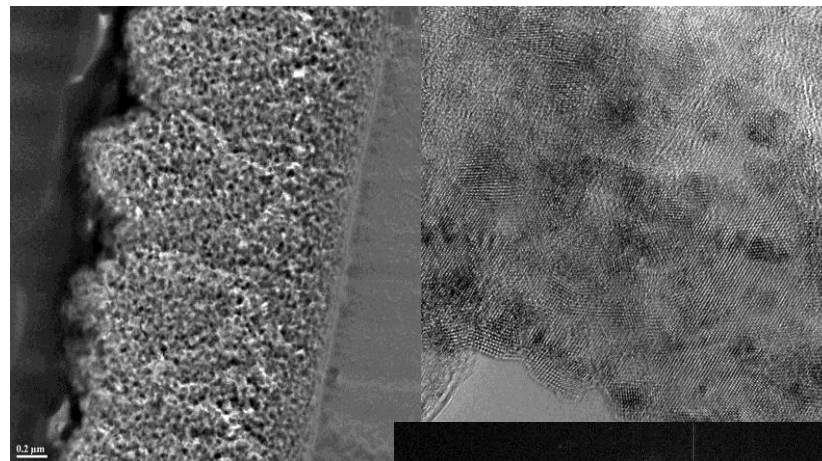
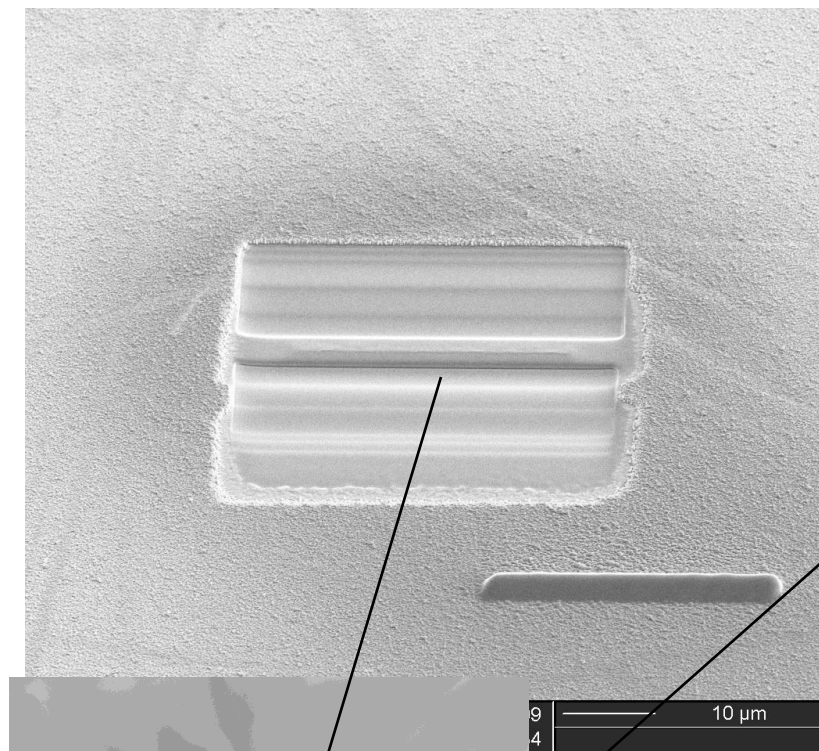


75 Layers Zn-C60 DSC (Derivative of Heat Flow)





# TEM and e<sup>-</sup> Diffraction

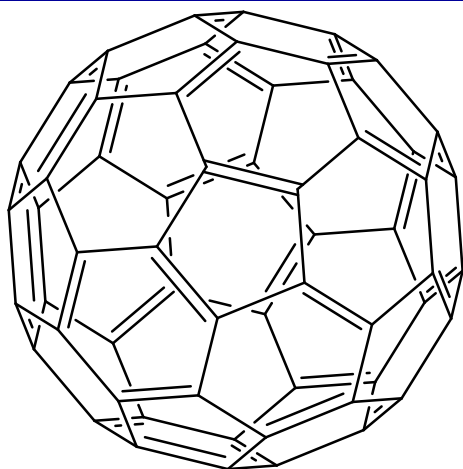


Does not show a  
separate phase for  
Zn



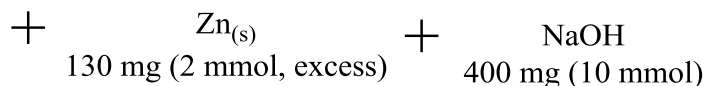


# Wet Chemical Approaches



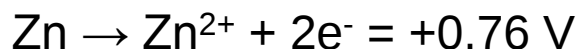
$C_{60}$   
34 mg (0.047 mmol)

Reactants and solvent was mixed together  
in glove box to remove all oxygen



20 mL of THF

Reactants do not dissolve in THF, vial is  
sealed with a septum and removed from  
glove box

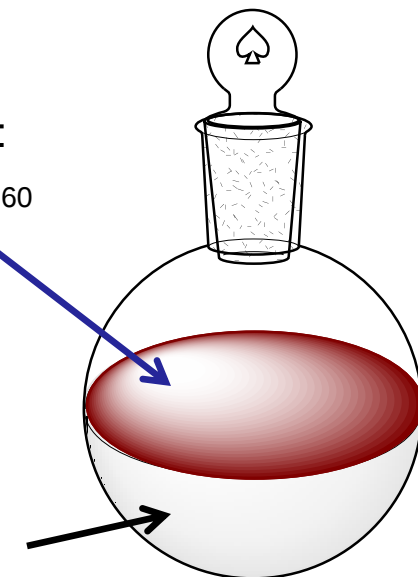


**5 mL of de-oxygenated water is added via  
syringe**

- Water was boiled for 20 minutes to removed non-  
condensed gases, then cooled and mineral oil was  
added to the surface, then nitrogen was bubbled through  
water for 30 minutes

Rapid reaction occurred,  $H_2$  gas evolved, two layers produced

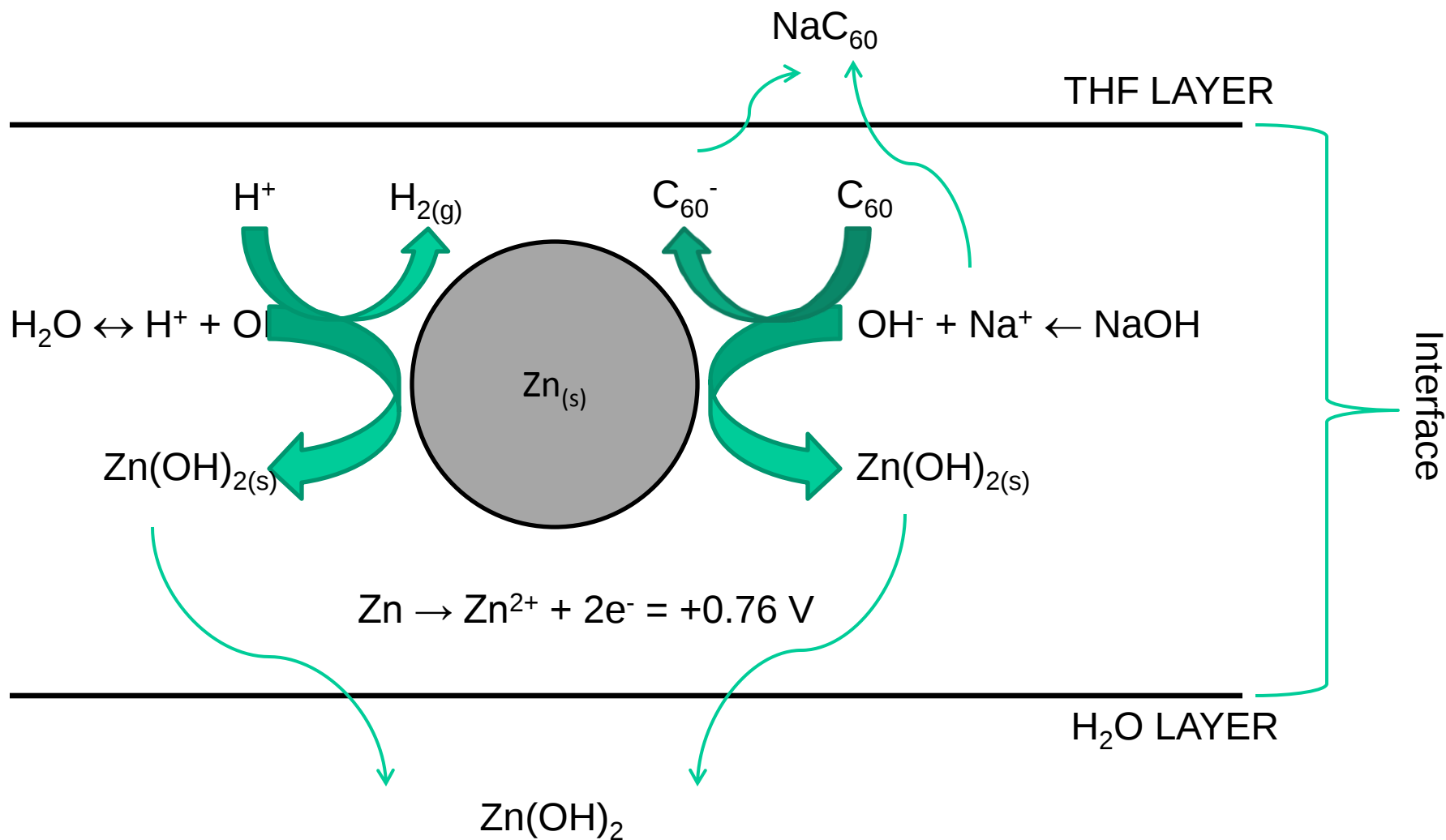
Top Layer:  
THF +  $\text{NaC}_{60}$



Bottom Layer:  
 $H_2O + \text{Zn}(\text{OH})_2$  + unreacted starting material



# Proposed Mechanism of Reaction





# Synthetic Protocol for Metal Fullerides



Procedure: Based on Redox Potentials of Starting Materials and Solvents and Activity Series of Metals Involved

Reactants and solvent was mixed together  
in glove box to remove all oxygen

$C_{60}$   
34 mg (0.047 mmol)

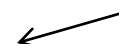
+

$Zn_{(s)}$   
130 mg (2 mmol, excess)

+

$Zn(OH)_2$   
1 g (10 mmol)

$Zn(NO_3)_2 + NaOH$



20 mL of THF

Reactants do not dissolve in THF, vial is  
sealed with a septum and removed from  
glove box

5 mL of de-oxygenated water is added via  
syringe

- Water was boiled for 20 minutes to removed non-  
condensed gases, then cooled and mineral oil was added to  
the surface, then nitrogen was bubbled through water for 30  
minutes

Reaction occurred much slower,  $H_2$  gas evolved, two layers produced to an extent  
**Sodium Nitrate Contaminants!**

Top Layer = THF +  $Zn_x(C_{60})_y$

Bottom Layer =  $H_2O + Zn(OH)_2$  + unreacted starting materials



# Standard Reduction Potentials for Fullerene



## $E_{1/2}$ of various $C_{60}$ anions in solvents in 0.1 M (TBA)ClO<sub>4</sub>

| Solvent | $C_{60}^0/C_{60}^-$ | $C_{60}^-/C_{60}^{2-}$ | $C_{60}^{2-}/C_{60}^{3-}$ | $C_{60}^{3-}/C_{60}^{4-}$ |
|---------|---------------------|------------------------|---------------------------|---------------------------|
| THF     | -0.33               | -0.92                  | -1.49                     | -1.99                     |
| THF     | -0.35               | -0.93                  | -1.43                     | -2.01                     |
| DMF     | -0.26               | -0.72                  | -1.31                     | -1.85                     |
| DMSO    | -0.16               | -0.66                  | ---                       | ---                       |

## Reduction Potentials of $C_{60}$

| Solvent     | $C_{60}^0/C_{60}^-$ | $C_{60}^-/C_{60}^{2-}$ | $C_{60}^{2-}/C_{60}^{3-}$ | $C_{60}^{3-}/C_{60}^{4-}$ |
|-------------|---------------------|------------------------|---------------------------|---------------------------|
| ACN         | ---                 | -0.735                 | -1.225                    | -1.685                    |
| DMF         | -0.312              | -0.772                 | -1.362                    | -1.902                    |
| Aniline     | -0.396              | -0.693                 | -1.158                    | -1.626                    |
| Benzonitr.  | -0.397              | -0.817                 | -1.297                    | -1.807                    |
| DCM         | -0.468              | -0.858                 | -1.308                    | -1.758                    |
| THF         | -0.473              | -1.063                 | -1.633                    | -2.133                    |
| Chloroform. | -0.554              | -0.908                 | ---                       | ---                       |

## Aprotic Polar Solvents

Dichloromethane

Tetrahydrofuran

Ethyl Acetate

Acetone

DMF

Acetonitrile

DMSO

Reaction seems to prefer certain aprotic polar solvents

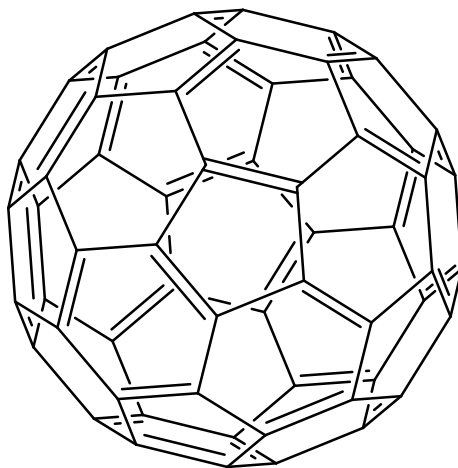


# Standard Reduction Potentials for Viable Metals



## Reduction Potential for Metals in Water

| Half-Reaction                                                                   | $E^\circ$ (V) |
|---------------------------------------------------------------------------------|---------------|
| $\text{Fe}^{2+}_{(\text{aq})} + 2\text{e}^- \rightarrow \text{Fe}_{(\text{s})}$ | -0.44         |
| $\text{Cr}^{3+}_{(\text{aq})} + 3\text{e}^- \rightarrow \text{Cr}_{(\text{s})}$ | -0.74         |
| $\text{Zn}^{2+}_{(\text{aq})} + 2\text{e}^- \rightarrow \text{Zn}_{(\text{s})}$ | -0.76         |
| $\text{Mn}^{2+}_{(\text{aq})} + 2\text{e}^- \rightarrow \text{Mn}_{(\text{s})}$ | -1.18         |
| $\text{Al}^{3+}_{(\text{aq})} + 3\text{e}^- \rightarrow \text{Al}_{(\text{s})}$ | -1.66         |



$\text{C}_{60}$   
0.047 mmol

+

$\text{M}_{(\text{s})}$   
2 mmol, excess

+

$\text{M}(\text{OH})_x$   
10 mmol



# Synthetic Protocol for Metal Fullerides



5.00 g  $C_{60}$   
19.1 g  $Zn_{(s)}$  granular  
1 L THF

Placed into a 2 L round bottom flask,  
sealed with a septum, and removed  
from the glove box

150 g of freshly made  $Zn(OH)_2$   
needs to be synthesized

Re-dissolved in 1 L ammonium  
hydroxide

$[Zn(NH_3)_4](OH)_2$

Syringed into 2 L round bottom  
React at 45 °C for 5 days

**Zinc Fulleride (+ 7 grams of product, brown powder)**

270.75 g of  $Zn(SO_4) \cdot H_2O$  dissolved into 2 L  
of water

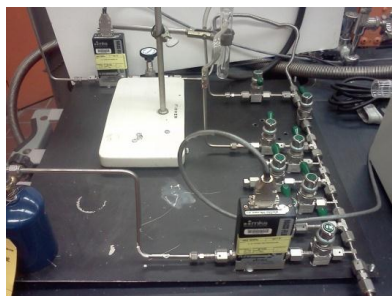
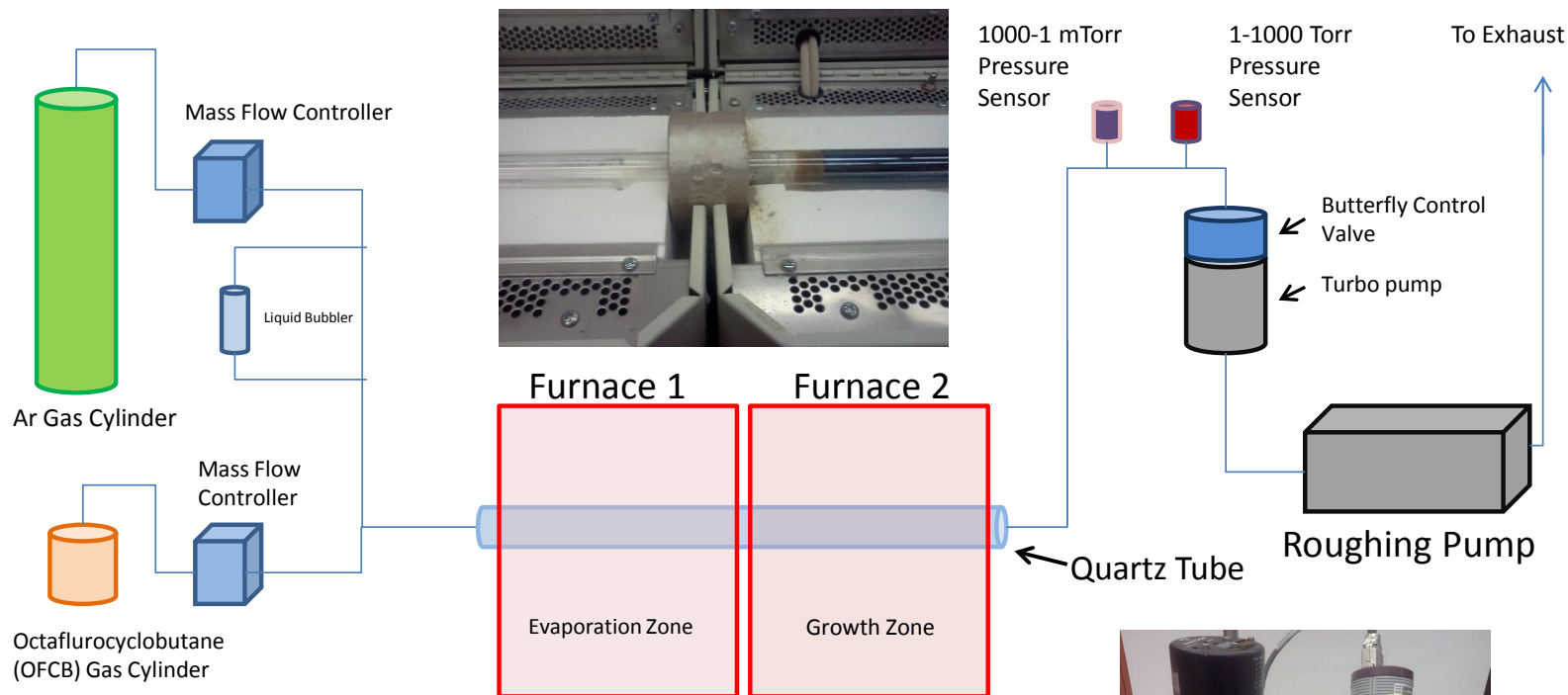
Add 203.75 mL of  $NH_4OH$

$Zn(OH)_2$



# Zn Nanowires +

## Schematic Layout of CVD system





## Zn wires with C60 coating

Hold Zn boat at 950° C/325° C for 15 hr

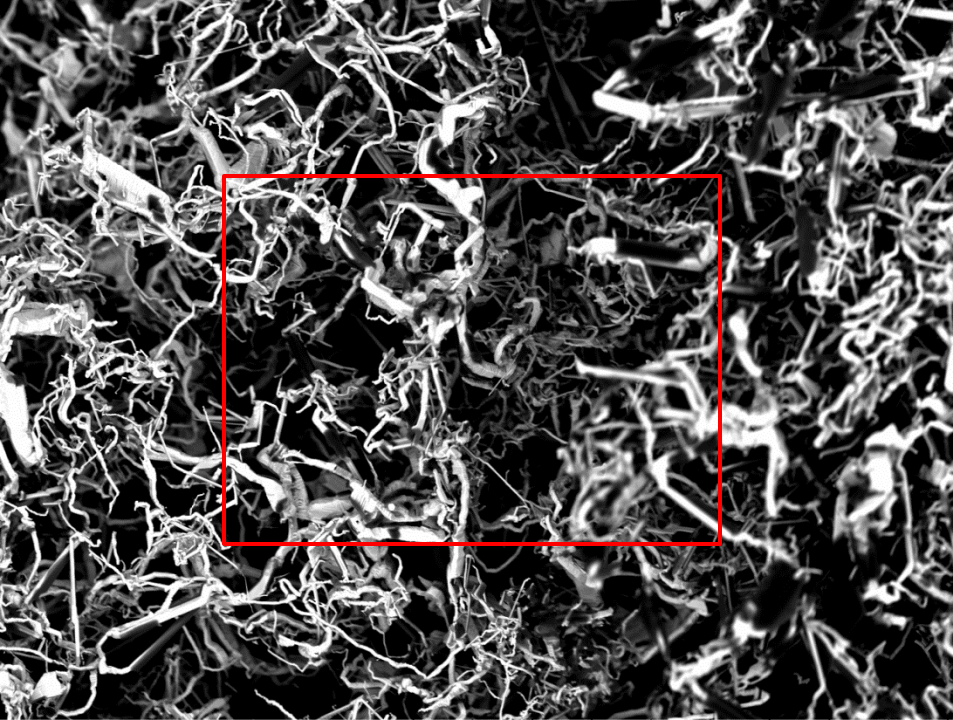
Maintain constant 3 Torr and 50 SCCM Ar

Cool to RT and swap out empty boat for C60 boat

Hold at 1000° C/350° C for 15 hr

Maintain constant 3 Torr and 100 SCCM Ar

Note: All pictures can be enlarged while keeping good picture quality.

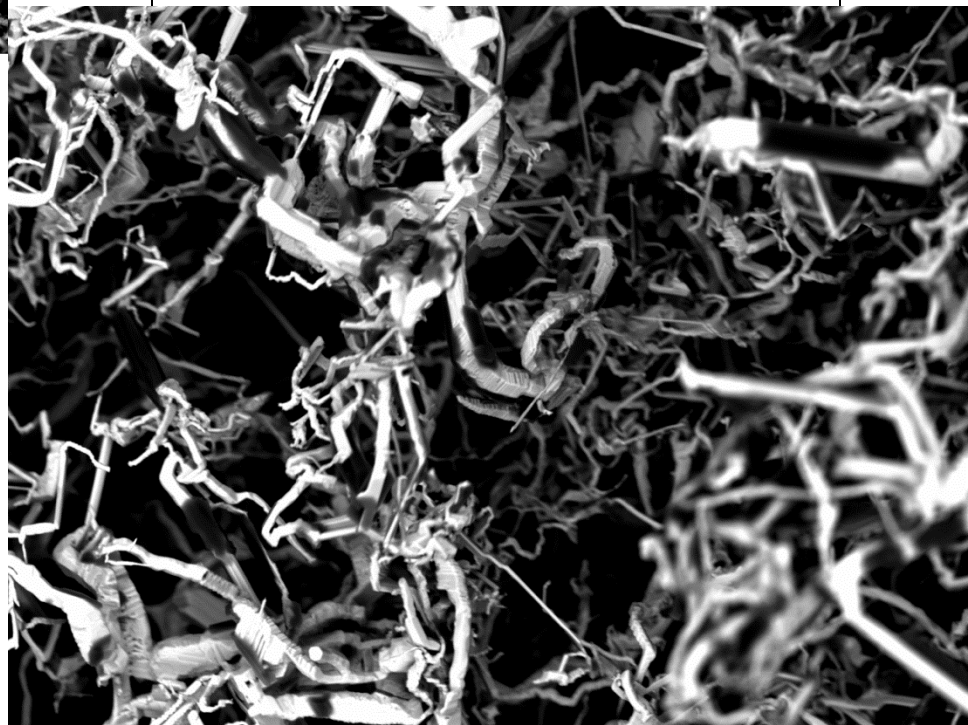


2012/02/03 09:18 H D4.8 x500 200 um



Region 1 (x500)

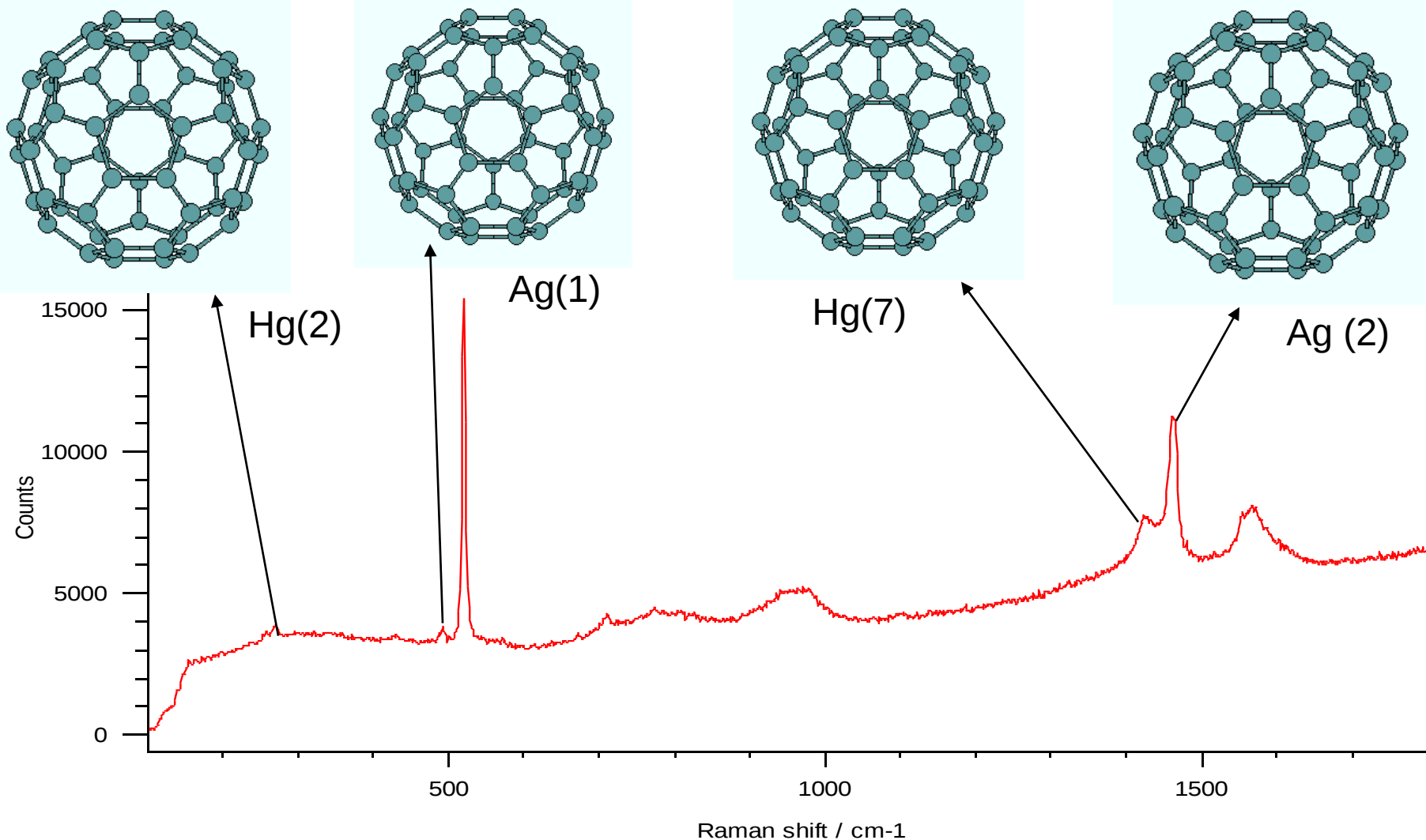
Region 1 (x1000)



2012/02/03 09:20 H D4.8 x1.0k 100 um



# Raman Modes in Neutral $C_{60}$





# Raman Spectroscopy of $\text{Zn}_x\text{C}_{60}$



## Landau damping and lifting of vibrational degeneracy in metallic potassium fulleride

J. Winter and H. Kuzmany

Universität Wien, Institut für Festkörperphysik, Strudlhofgasse 4, A-1090 Wien, Austria

(Received 21 July 1995)

- A rather strong shift of vibrational modes as a consequence of charge transfer
- The electron-phonon interaction may well be considered in case as the reason for the broadening and for the shift of the lines and electron-phonon coupling constants may be deduced
- For the description of the relation between phonon linewidth and electron-phonon coupling constants for a single particle excitation Allen's formula may be used

$$\gamma_i = \frac{1}{g_i} \frac{\pi}{2} N(0) \lambda_i \omega_{bi}^2$$

$\gamma_i$  Is the full width at half max of the line

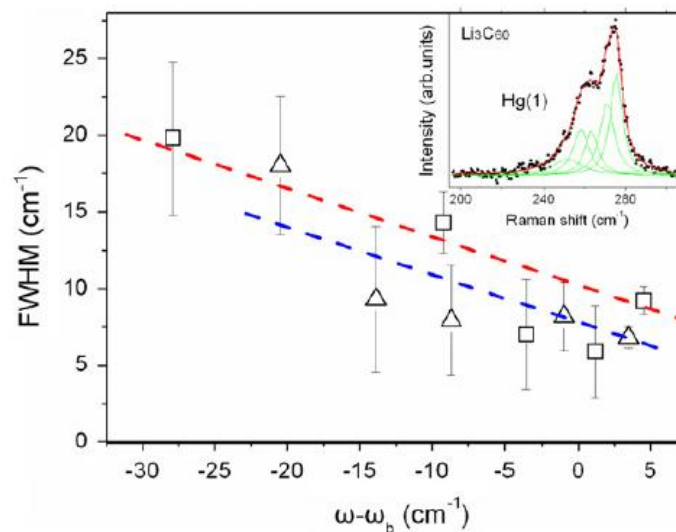
$N(0)$  Density of States at the Fermi level per spin and molecule

$\lambda_i$  and  $g_i$  Dimensionless electron phonon coupling constants

$\omega_{bi}$  Bare phonon frequency before coupling to the electrons

## Raman study of the electron–phonon interaction in light alkali metal intercalated metallic fullerenes

Mingguang Yao<sup>1,2</sup>, Vittoria Pischedda<sup>1</sup> and Alfonso San Miguel<sup>1</sup>

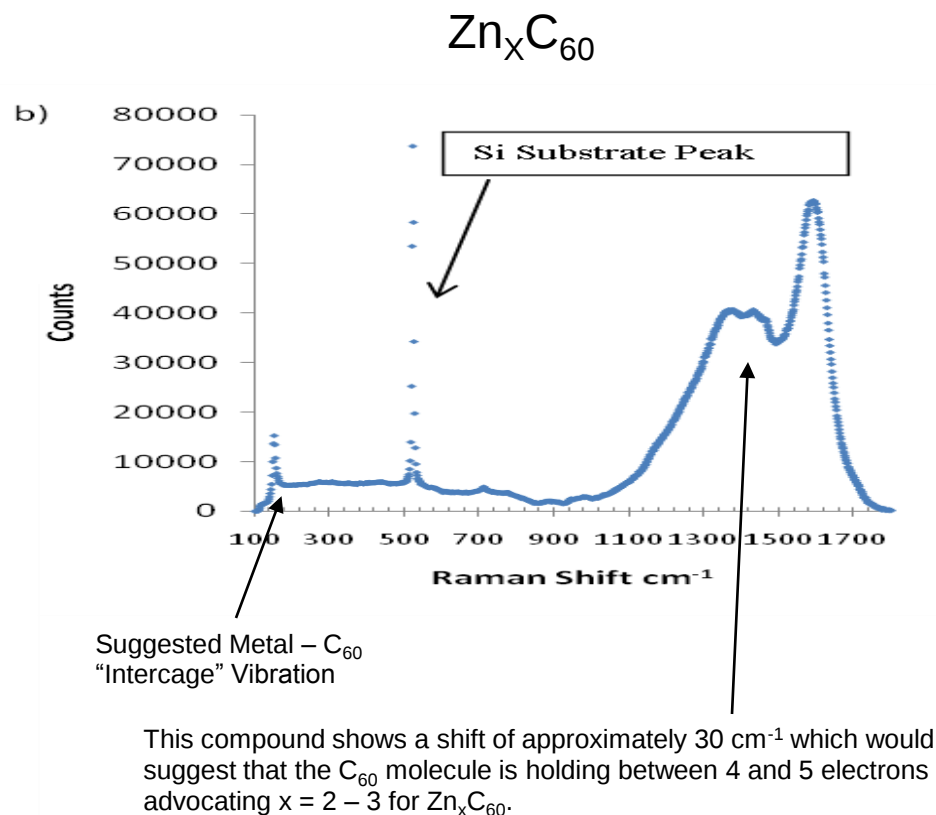
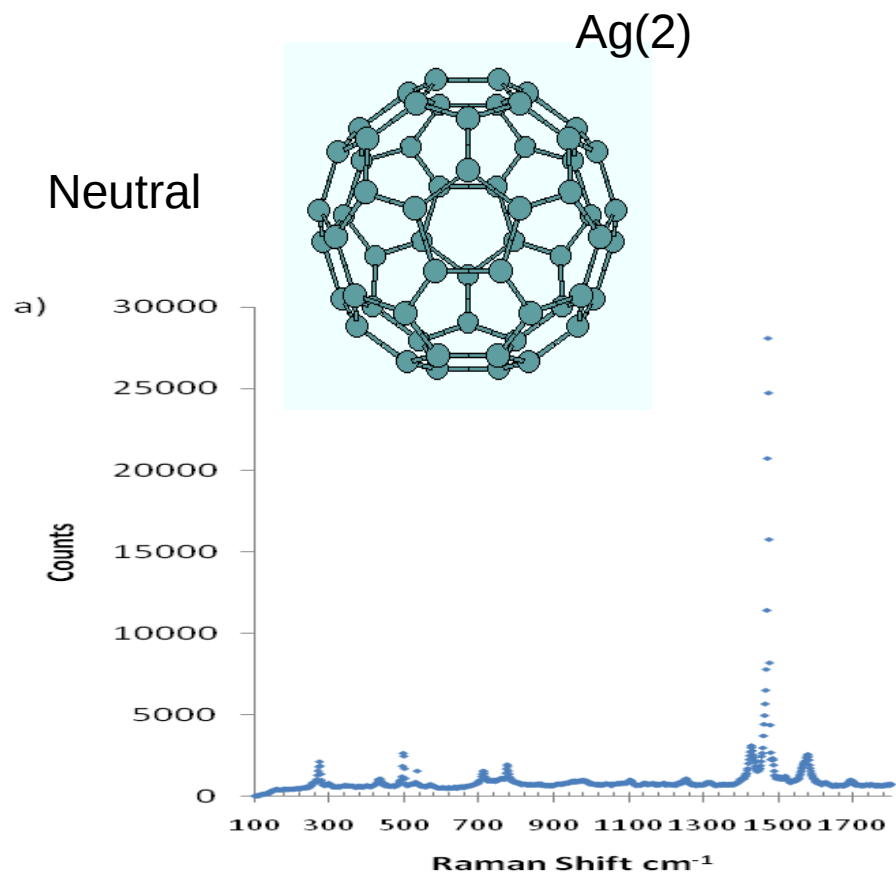


Electron-phonon coupling uses the phonon widths measured in Raman scattering. In metallic systems a phonon can decay in an electron-hole pair excitation. The extra width due to this decay is a measure of the coupling.



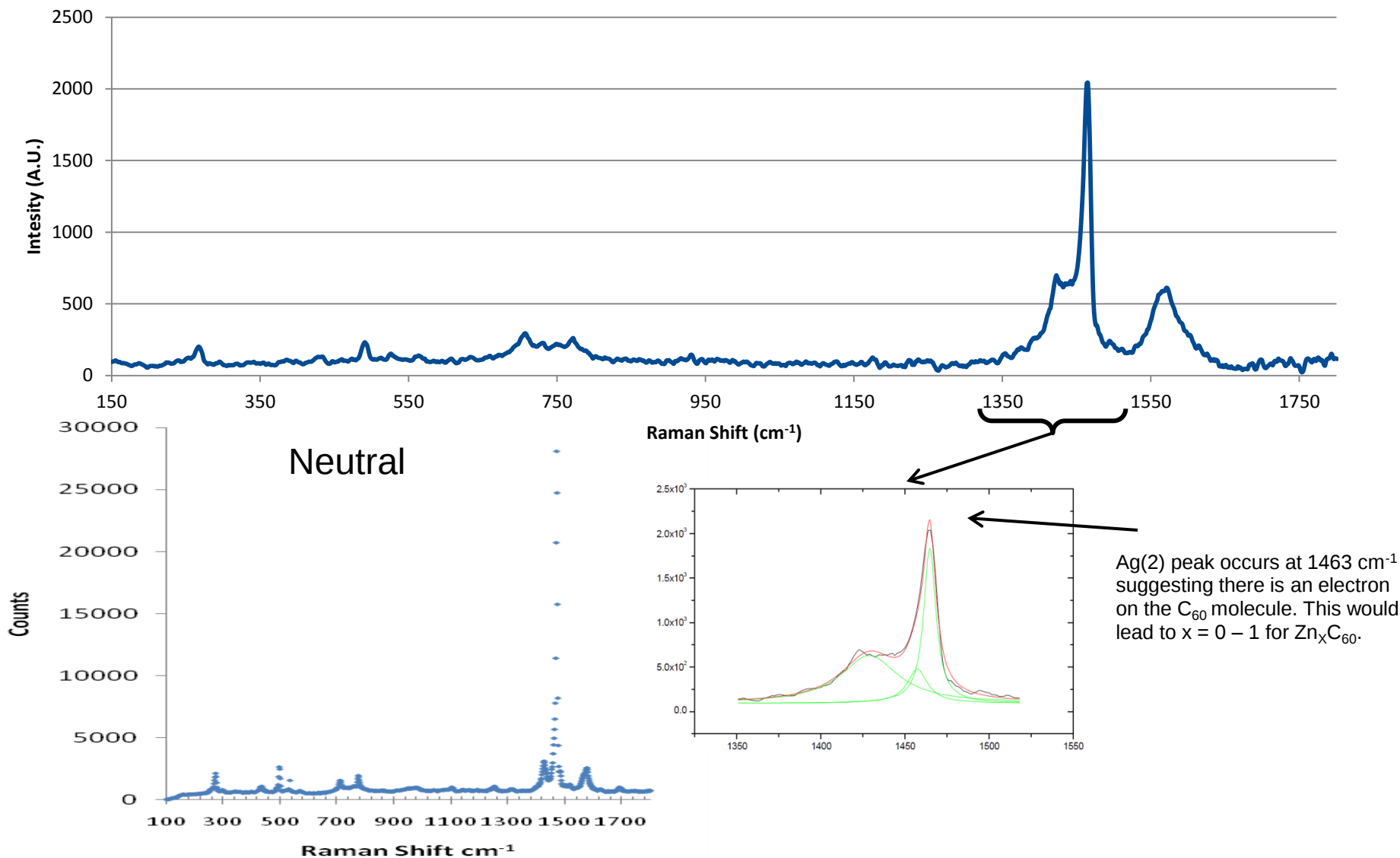
# Raman Spectroscopy of $\text{Zn}_x\text{C}_{60}$ thin film

Sample is 75 Layers of  $\text{C}_{60}$  and Zn ( $\text{C}_{60}$  and Zn Layers are 10nm thick) After Annealing in furnace at  $400^\circ\text{C}$



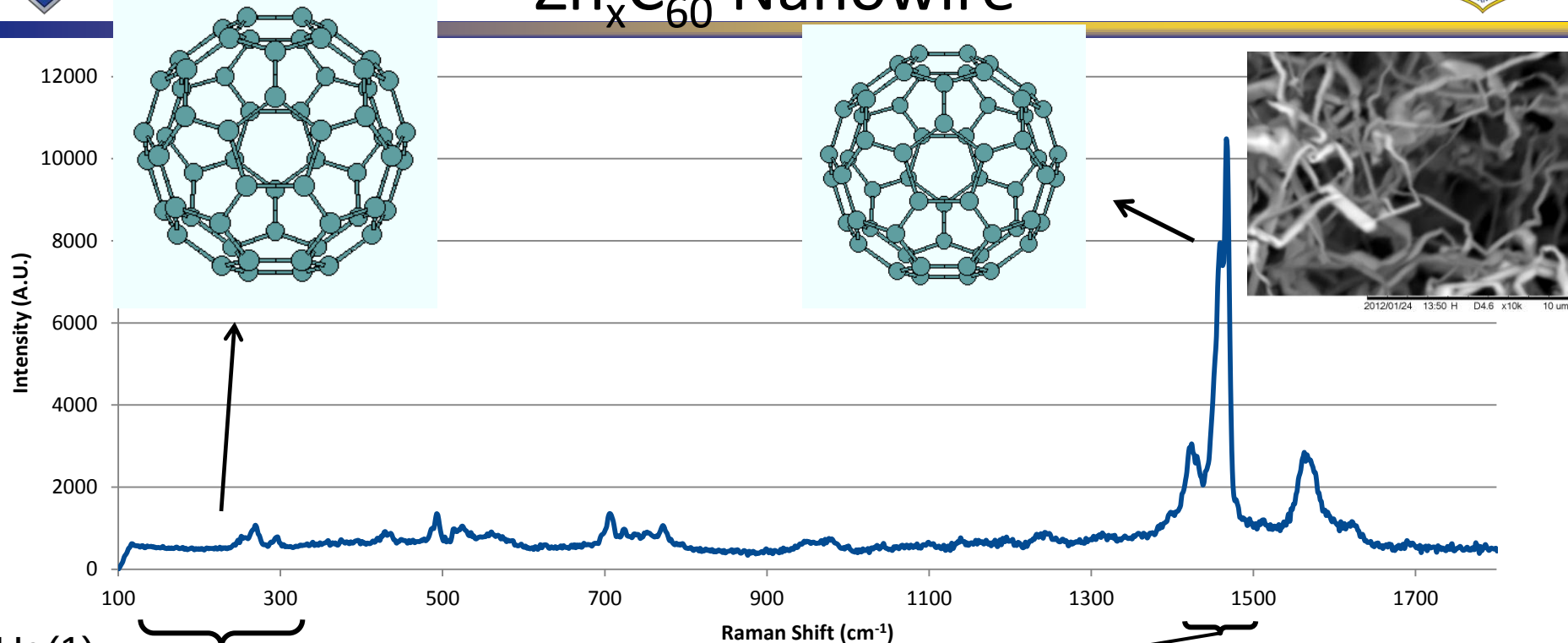


# Raman Spectroscopy of $\text{Zn}_x\text{C}_{60}$ produced by bulk synthesis route

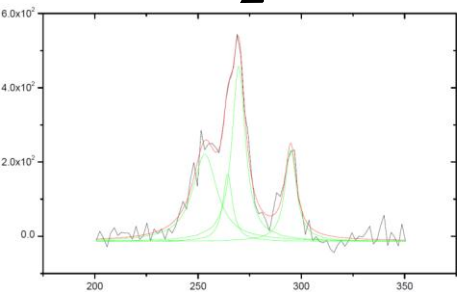




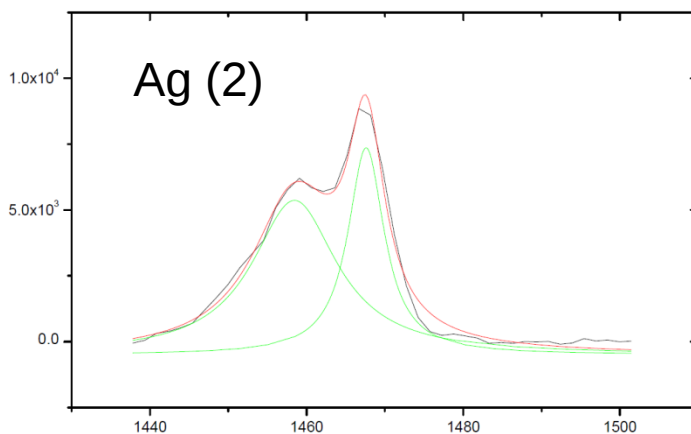
# Raman Spectroscopy of $\text{Zn}_x\text{C}_{60}$ Nanowire



Hg(1)



Ag (2)

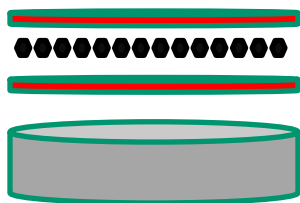


Ag(2) peak occurs at  $1468 \text{ cm}^{-1}$  and  $1458 \text{ cm}^{-1}$  which is suggestive of two  $\text{C}_{60}$  phases. Approximately 60% of the  $\text{C}_{60}$  is incorporated to the nanowire and charged. However, the remainder is most likely in a second phase and not closely associated with the majority zinc wire structure.



# Thermal Properties of Fulleride Compound

- Thin Film



$$\kappa = 0.13 \text{ W}/(\text{m}^*\text{K})$$

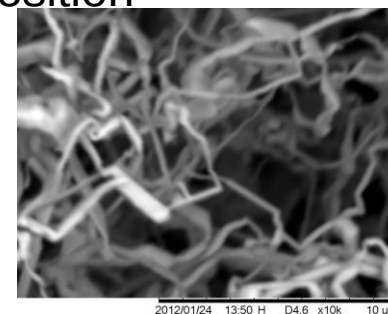
TDTR

- Wet Synthesis

$$\kappa = 0.24 \text{ W}/(\text{m}^*\text{K})$$

HotDisk

- Chemical Vapor Deposition



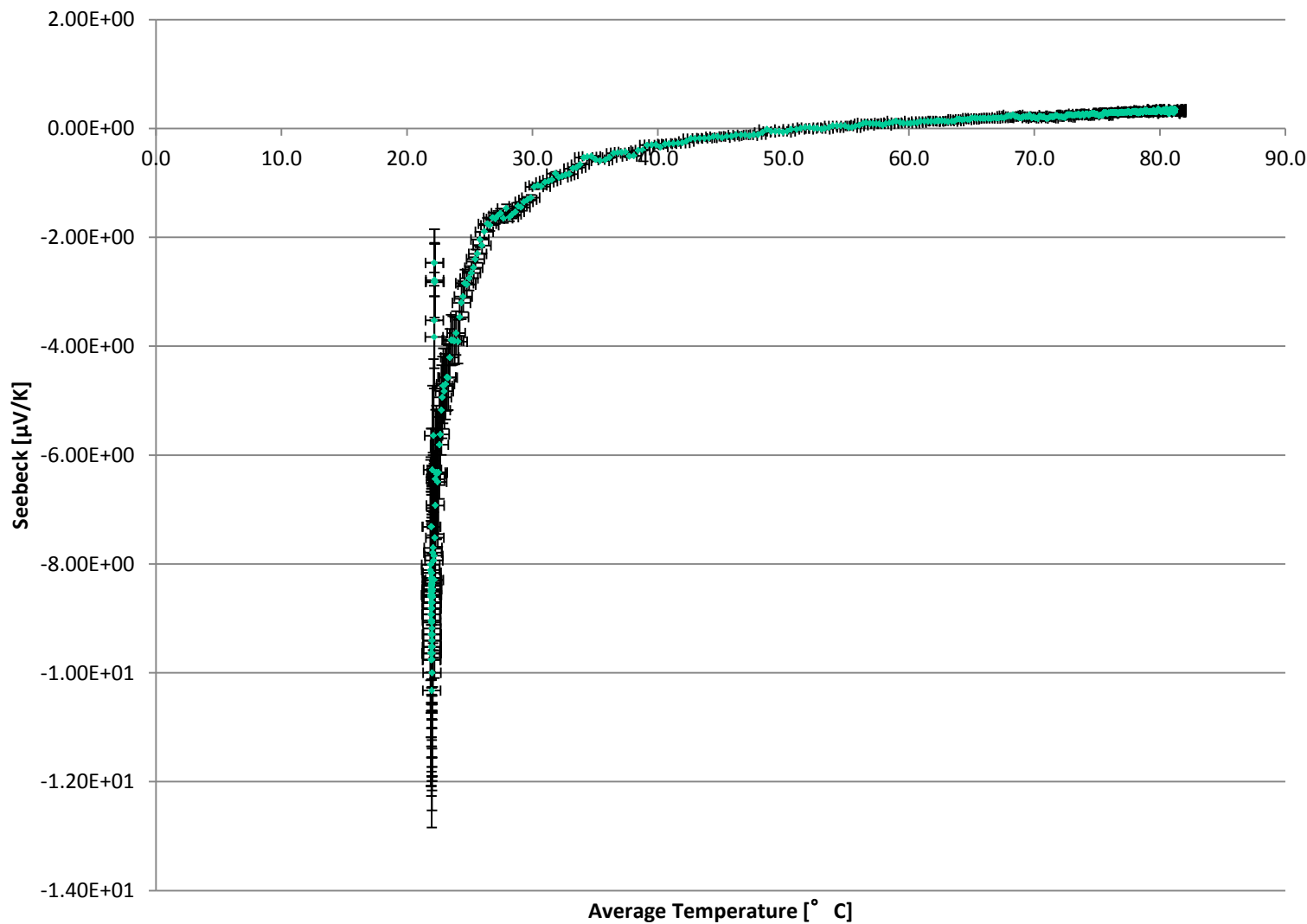
$$\kappa = 3 - 5 \text{ W}/(\text{m}^*\text{K})$$

HotDisk

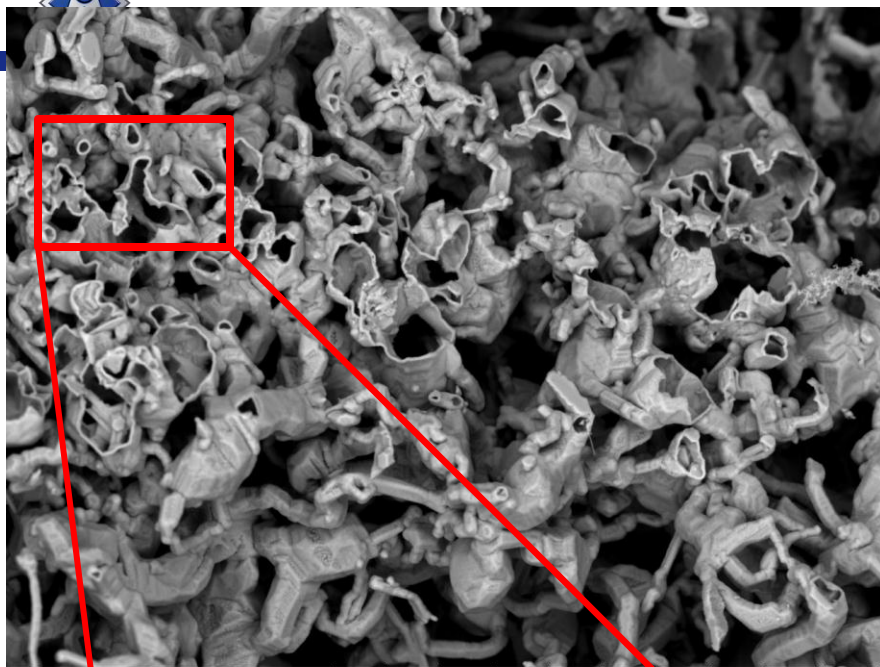
Thermal Conductivity of Glass =  $1 \text{ W}/(\text{m}^*\text{K})$



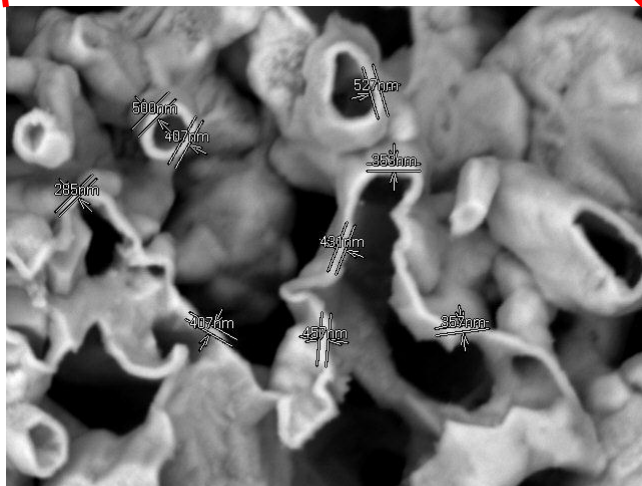
# Zn-Fulleride + Zn Nanowire Composites



# Zinc Phosphide Nanotube Growth



Zn<sub>3</sub>P<sub>2</sub> tube 2012/01/11 10:03 H D4.6 x1.0k 100 um



Zn<sub>3</sub>P<sub>2</sub> tube 2012/01/11 10:07 H D4.5 x5.0k 20 um

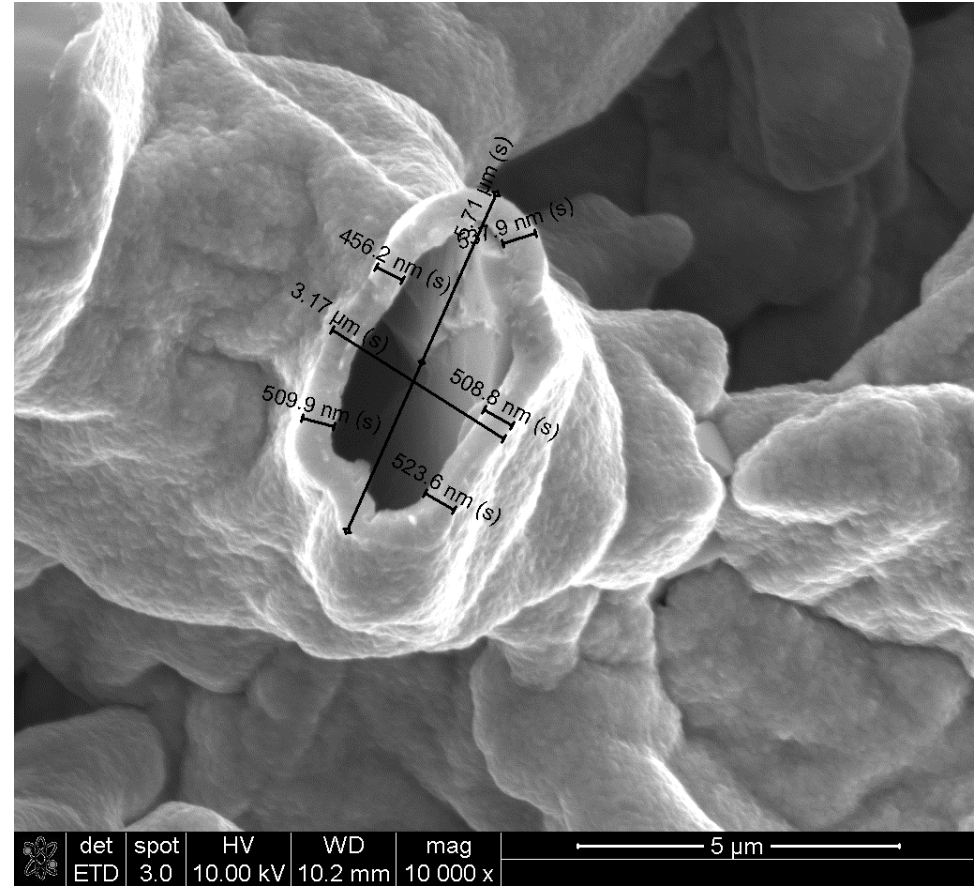
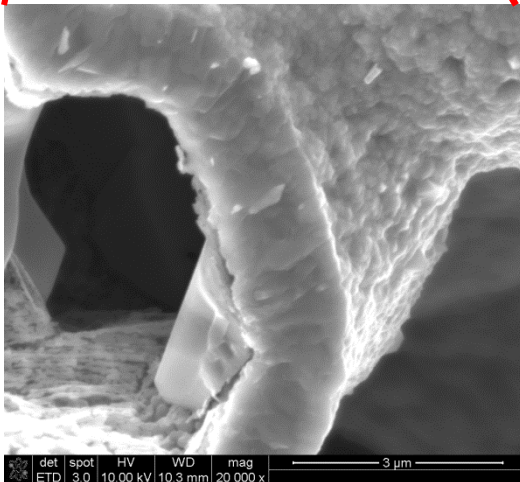
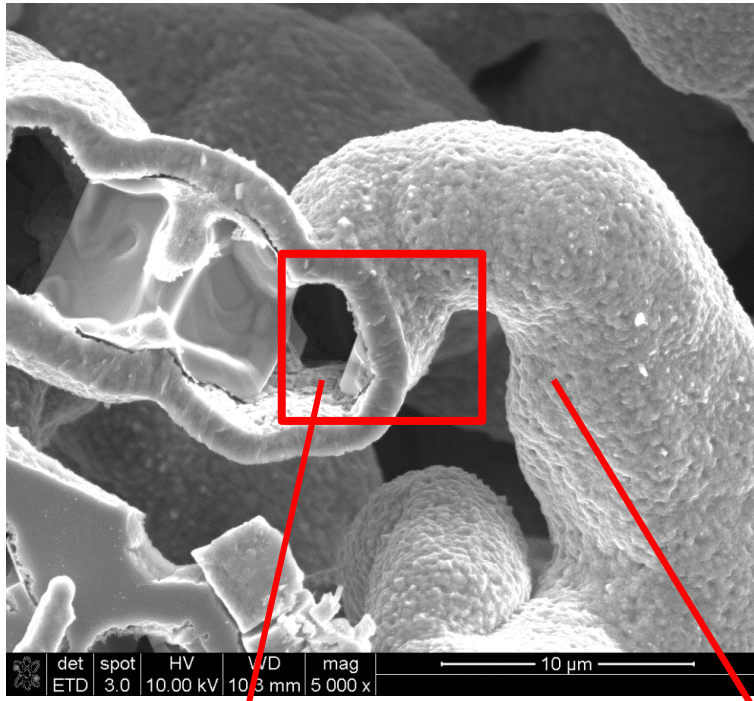
- Zinc nanowire were first grown under std conditions and then Red Phosphorus was evaporated and reacted on the tubes
- Zn<sub>3</sub>P<sub>2</sub> Micro/Nanotubes were grown
- Two distinct types of tubes were identified
- Possible reaction mechanism is presented



Zn<sub>3</sub>P<sub>2</sub> tube 2012/01/11 09:51 H D4.9 x800 100 um



# Zinc Phosphide Tubes High Res SEM

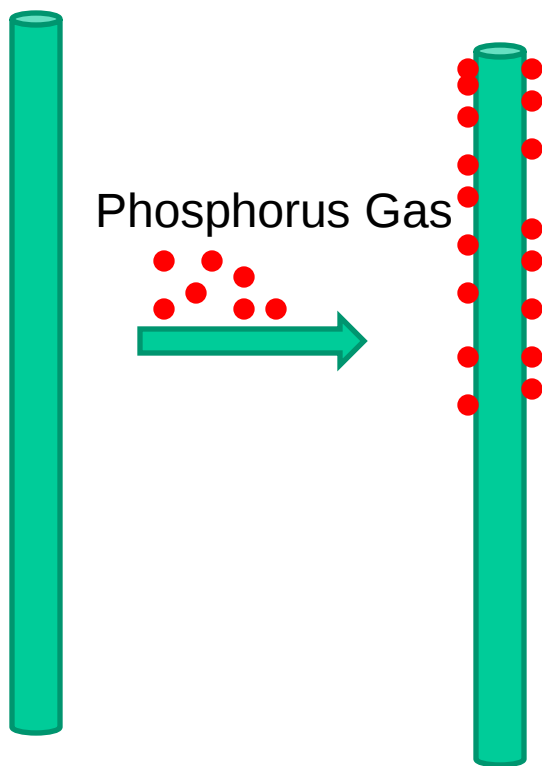




# Self Templated growth of Zinc Phosphide Nanotube Growth

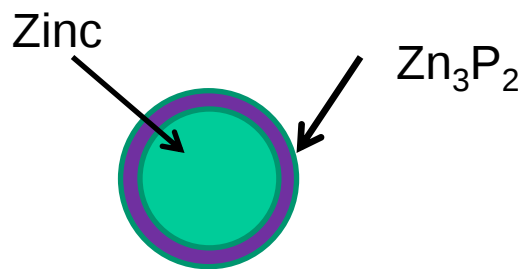
Phosphorus reaction with ZNW

Zinc Nanowire



Wire Cross Section

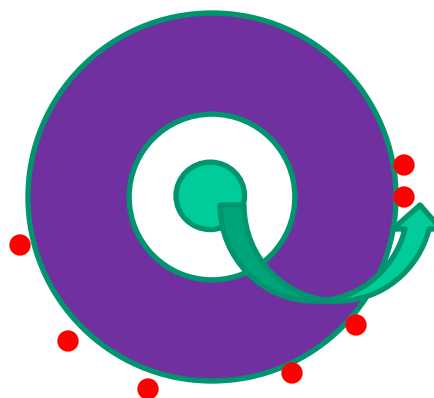
Initial creation of  $\text{Zn}_3\text{P}_2$  monolayer



Initiation and reaction held at  $400^\circ \text{C}$

Zinc Phosphide growth is mediated by template of the Zinc wires that initiate the reaction.

$\text{Zn}_3\text{P}_2$  Nanotube Growth



Zinc diffusing out of core



# Confirmation Tests to Identify Fulleride Product



1. UV/Vis-NIR: Examine Near Infrared region of spectrum to determine oxidation state of fulleride ion. Each oxidation state has very specific  $\lambda_{\text{max(es)}}$  in this region.
2. RF-ICP: Determine counter-ion/cation to fulleride
  - The ICP analysis of the THF solution containing  $\text{Zn}_x(\text{C}_{60})_y$  had emission peaks at 213.86 nm from the contents of zinc and 193.09 nm from the carbon contents.
  - Leads us to believe that  $\text{C}_{60}$  is present with  $\text{Zn}^{2+}$  as its counter-ion.
3. XPS: Determine surface molecular contents of crystallized complexes of products collected
4. Raman: Determine vibrational modes present in crystallized samples.
5. EPR: Determine if fullerene is holding a charge.
6.  $^{13}\text{C}$ -NMR: Amount of downfield shift can also determine oxidation state of fulleride, as well as determine if fulleride is present and intact
7. SEM of powder appeared to be homogenous



# Conclusions



- 3 different preparation routes for fulleride synthesis
- Demonstration of ultra-low thermal conductivities
- Gradient sample were able to produce thousands of different stoichiometries on one sample

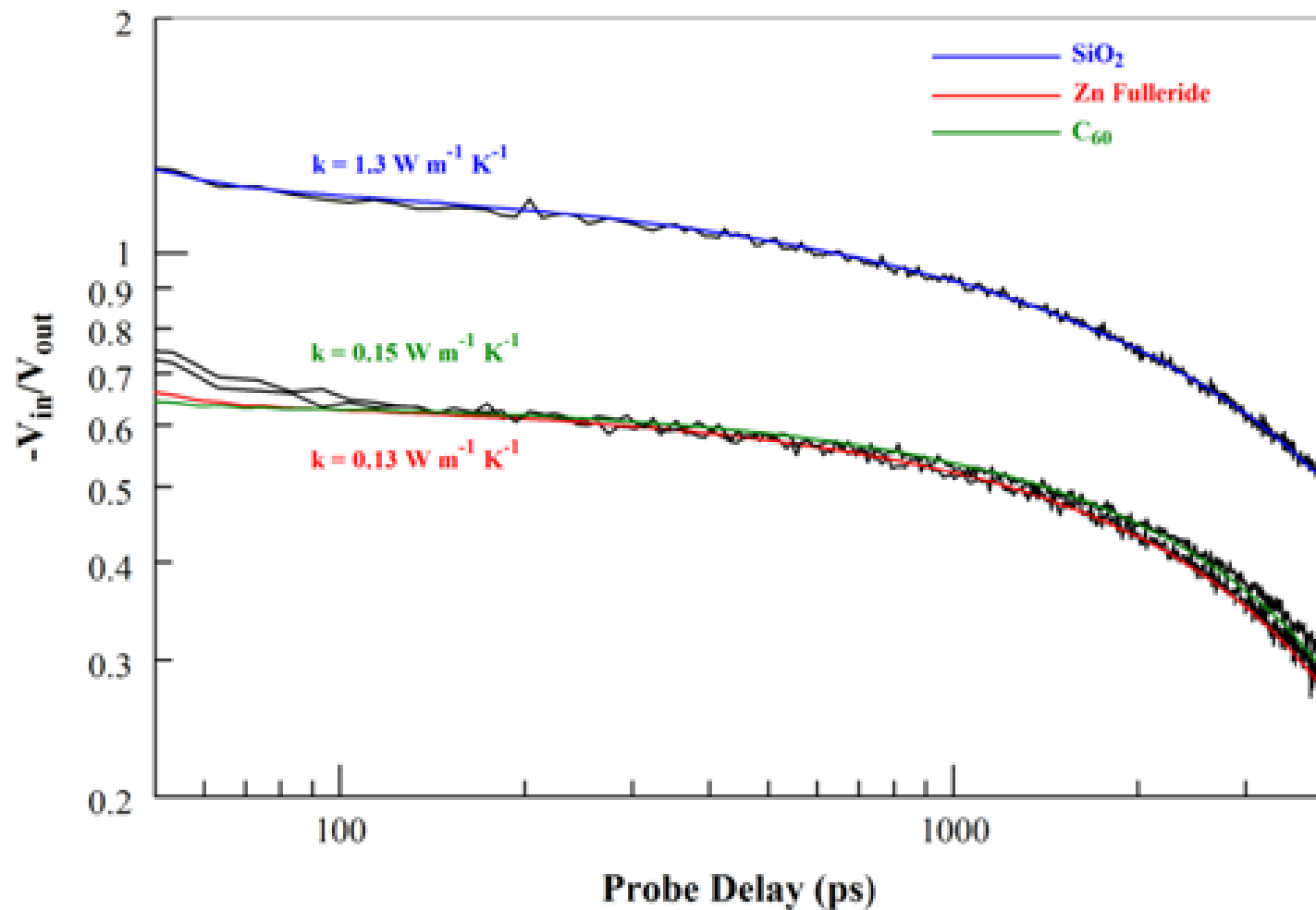


# Questions?





## TDTR





# Third Remarkable Fullene Characteristic: Fulleride Formation



## “High” $T_c$ Molecular Superconductors

**Table 6.3.** Lattice constants ( $a_0$ ) and position of the alkali elements for  $A_3C_{60}$  fullerides at ambient temperature

| $A_3C_{60}$            | $a_0$ (Å)    | $A_1(T)A_2(T)A_3(O)$      | Type                 | $T_c$ (K)       |
|------------------------|--------------|---------------------------|----------------------|-----------------|
| $Cs_3C_{60}$           | —            |                           | A15                  | 40 <sup>a</sup> |
| $RbCs_2C_{60}$         | 14.555       | $Rb(T)Cs(T)Cs(O)$         | fcc                  | 33              |
| $KCs_2C_{60}$          | unstable     |                           | fcc                  | —               |
| $Rb_2CsC_{60}$         | 14.431       | $Rb(T)Rb(T)Cs(O)$         | fcc                  | 31              |
| $Rb_3C_{60}$           | 14.384       | $Rb(T)Rb(T)Rb(O)$         | fcc                  | 29              |
| $KRb_2C_{60}$          | 14.337       | $K(T)Rb(T)Rb(O)$          | fcc                  | 27              |
| $K_2CsC_{60}$          | 14.292       | $K(T)K(T)Cs(O)$           | fcc                  | 24              |
| $K_2RbC_{60}$          | 14.267       | $K(T)K(T)Rb(O)$           | fcc                  | 23              |
| $K_3C_{60}$            | 14.240       | $K(T)K(T)K(O)$            | fcc                  | 19              |
| $Na_2CsC_{60}$         | 14.126       | $Na(T)Na(T)Cs(O)$         | fcc $\rightarrow$ sc | 12              |
| $Na_2RbC_{60}$         | 14.092       | $Na(T)Na(T)Rb(O)$         | fcc $\rightarrow$ sc | 3.5             |
| $Na_2KC_{60}$          | 14.122       | $Na(T)Na(T)K(O)$          | fcc $\rightarrow$ sc | 2.5             |
| $Na_3C_{60}$           | 14.191       | $Na(T)Na(T)Na(O)$         | fcc <sup>b</sup>     | < 2 K           |
| $Li_2CsC_{60}$         | 14.075       | $Li(T)Li(T)Cs(O)$         | fcc                  | < 50 mK         |
| $Li_2CsC_{60}^{\#}$    | 14.008       | $Li(T)Li(T)Cs(O)$         | fcc                  | < 50 mK         |
| $Li_2KC_{60}$          | 13.896       | $Li(T)Li(T)Rb(O)$         | —                    | < 50 mK         |
| $Li_2KC_{60}$          | multiphase   | —                         | —                    | —               |
| $Na_2Cs(NH_3)_4C_{60}$ | 14.473       | $Na(T)Cs(T)Na(NH_3)_4(O)$ | fcc                  | 30              |
| $Ba_6C_{60}$           | 11.182       |                           | bcc                  | 6               |
| $Sr_6C_{60}$           | 10.975       |                           | bcc                  | 4               |
| $Ca_5C_{60}$           | 14.01        |                           | sc                   | 8.5             |
| $Yb_{2.75}C_{60}$      | superlattice |                           | orthorhombic         | 6               |
| $Sm_{2.75}C_{60}$      | superlattice |                           | orthorhombic         | 8               |

<sup>a</sup> Under hydrostatic pressure.

<sup>b</sup> Stable at  $T > 180$  K.

<sup>#</sup> Different batch of samples.



X =

Alkali

Alkaline Earth

Transition Metal

Rare Earth Metal

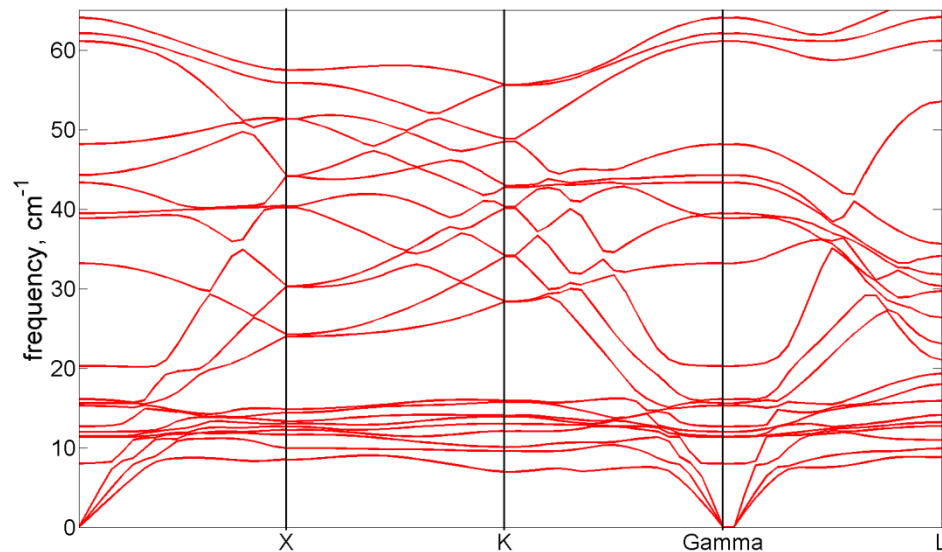
Main Group

**Many fullerides known;  
semiconductive  
fullerides relatively  
unexplored!**

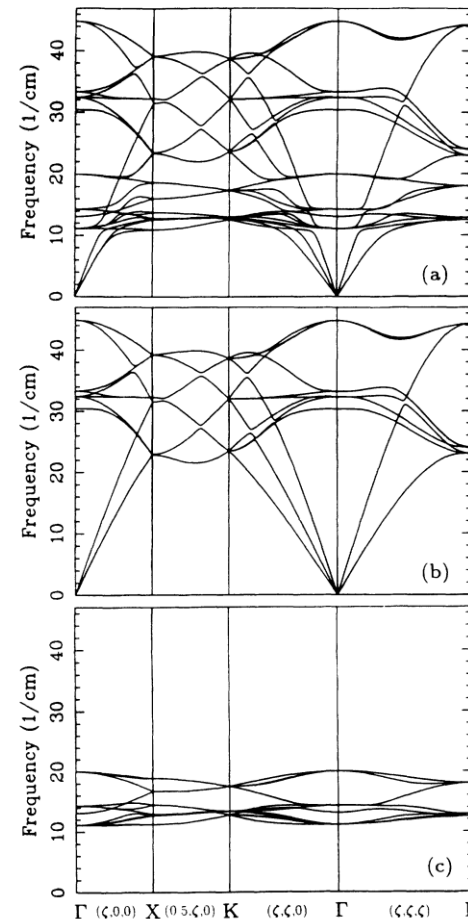
“Handbook of Conductive Molecules and Polymers,”  
H. S. Nalwa, ed., Wiley & Sons, 1997, Vol. 1, p. 317



# $C_{60}$ FCC Dispersion – Validation



REBO Force Field



PHYSICAL REVIEW B

VOLUME 46, NUMBER 7

15 AUGUST 1992-I

## Ground-state structural and dynamical properties of solid $C_{60}$ from an empirical intermolecular potential

X.-P. Li

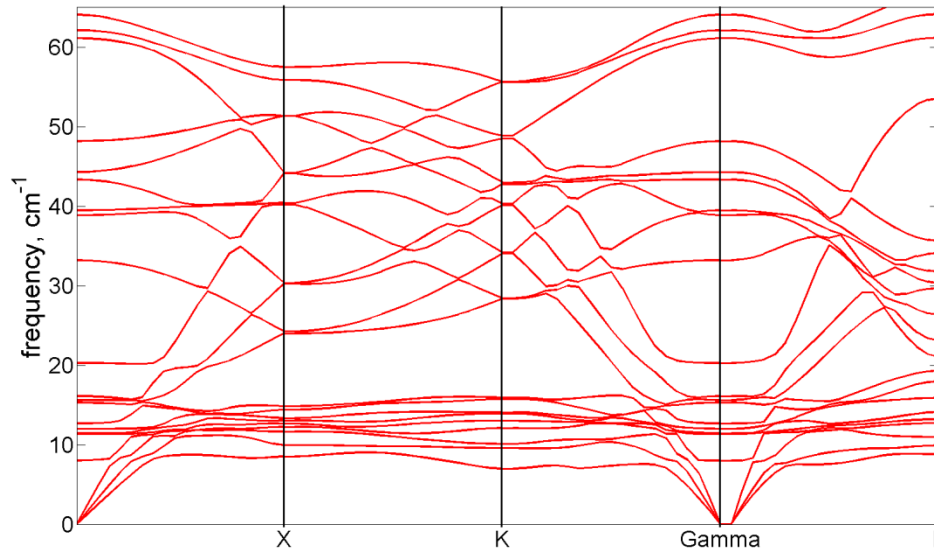
*Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08855*

Jian Ping Lu and Richard M. Martin

*Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801  
and Materials Research Laboratory, University of Illinois at Urbana-Champaign, 1110 West Green Street,  
Urbana, Illinois 61801*



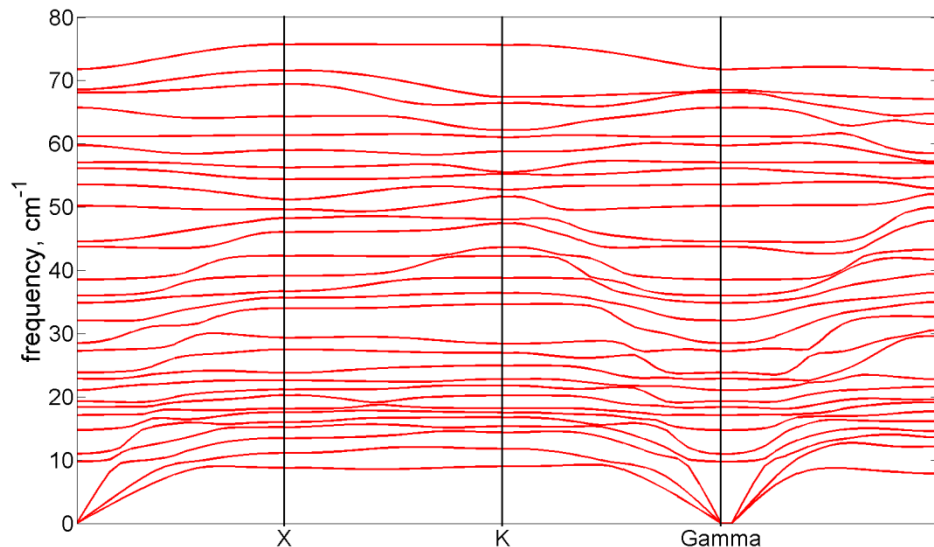
# Ba<sub>3</sub>C<sub>60</sub> BCC Dispersion and C<sub>v</sub>



C<sub>60</sub>

$$C_v = 0.026824 \text{ eV/K}$$

Molecule breaks symmetry –  
lattice constants 9.98, 12.80, 12.83



Ba<sub>3</sub>C<sub>60</sub>

$$C_v = 0.015051 \text{ eV/K}$$

Still plotting the high symmetry  
points of FCC. Group velocities  
appear lower

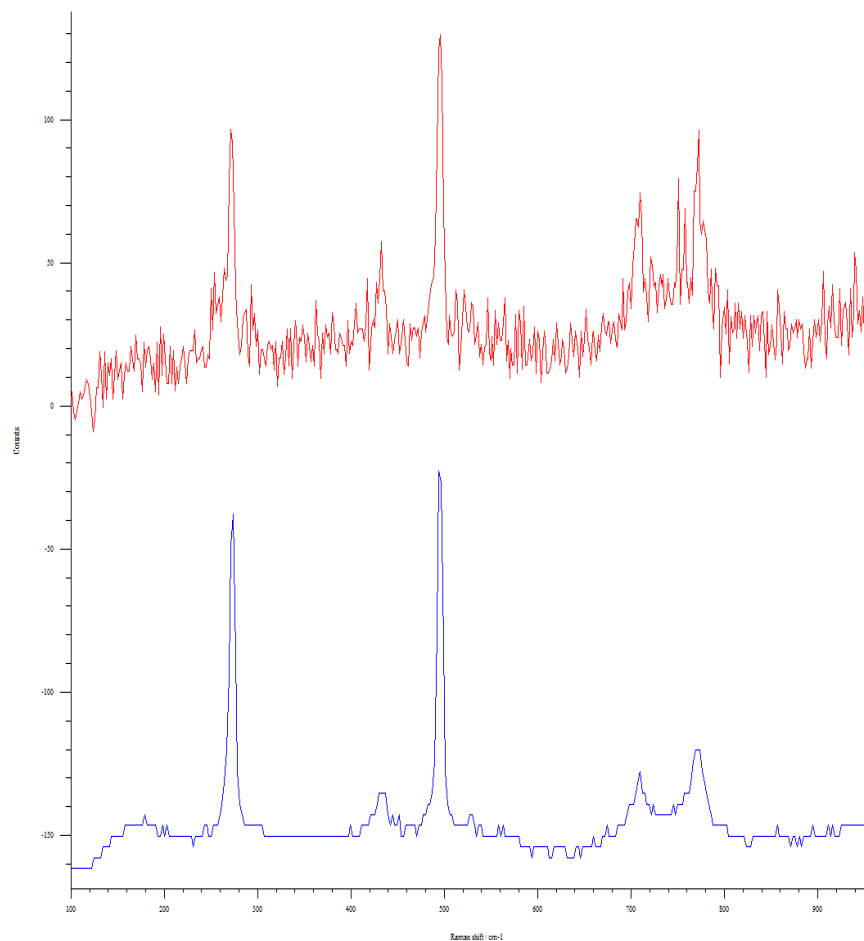
$$k = \frac{1}{3} C_v v_g l$$



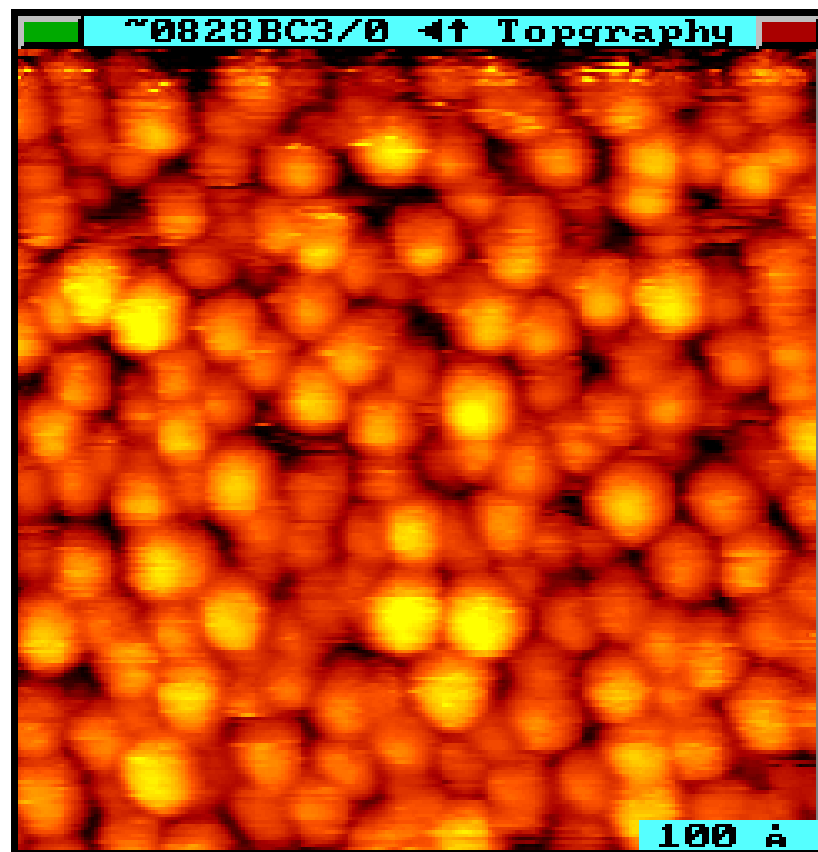
# Thermal Evaporation of C<sub>60</sub>



## Raman Spectra of Thermal Evap C<sub>60</sub>



| Visible | Ht | Quality  | Library     | Spectrum Info                   | Library Index |
|---------|----|----------|-------------|---------------------------------|---------------|
|         | 1  | 0.342296 | Inorgan.lib | Buckminster Fullerene (Organic) | 561           |
|         | 2  | 0.169309 | Inorgan.lib | Buckminster Fullerene (Organic) | 789           |



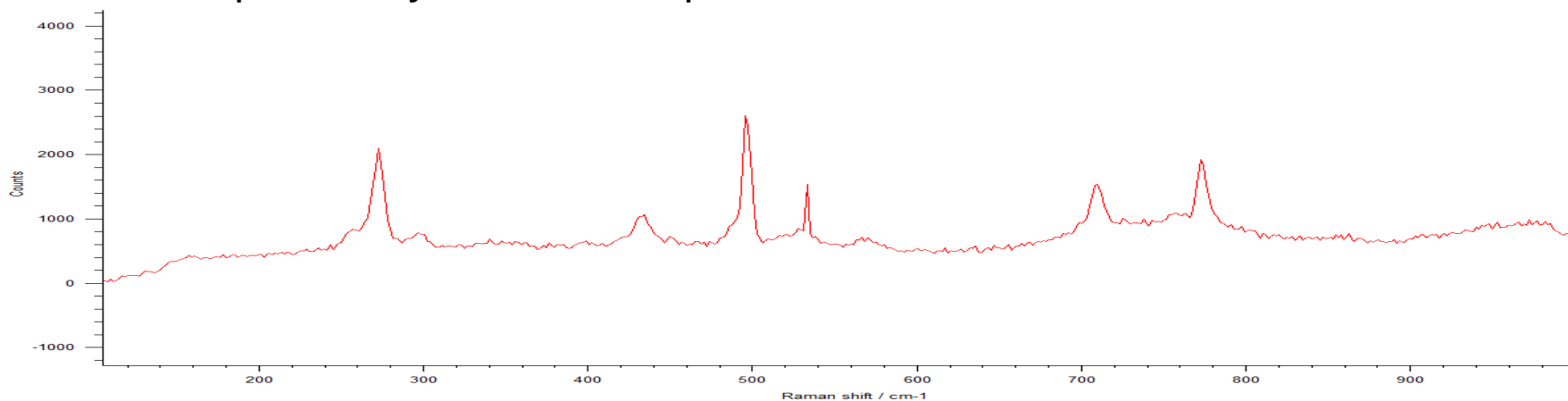
STM Image Courtesy of Dr. Altfeder



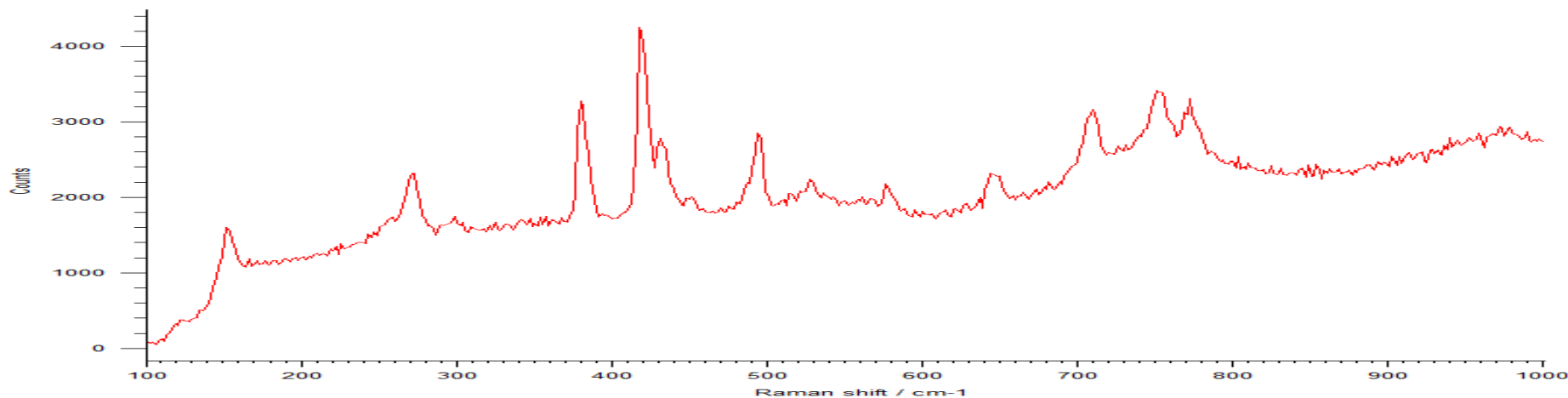
# Raman Spectroscopy of $C_{60}$

Sample is 75 Layers of  $C_{60}$  and Zn ( $C_{60}$  and Zn Layers are 10nm thick) After Annealing in furnace at  $400^{\circ}\text{C}$

Pure  $C_{60}$  – Deposited by Thermal Evap



Zn- $C_{60}$  after the anneal

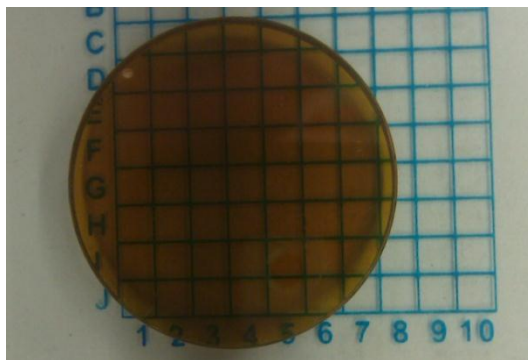
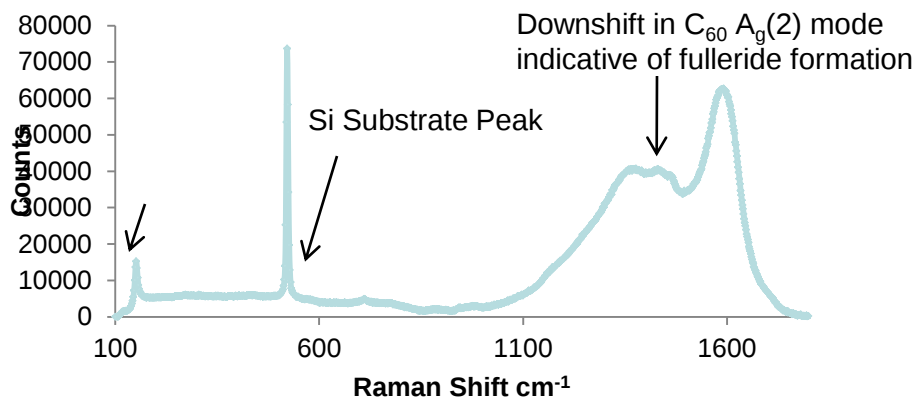




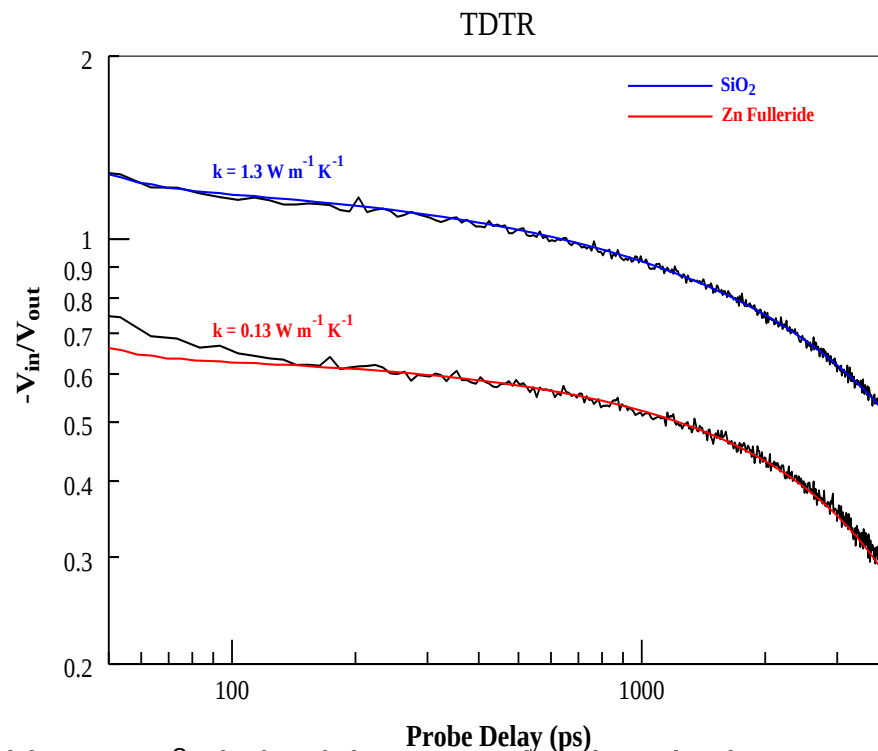
# Project Results: Increased $\sigma$ , Decreased $\kappa$ And ...



## $\text{Zn}_x\text{C}_{60}$ after Anneal Step



Time domain thermal reflectance data of Fulleride materials shows a 10x reduction in Thermal conductivity compared to glass



## SUCCESSSES:

- Exceptionally good phonon blocking achieved with a  $\sim 10^8$  (S/cm) increase in electrical conductivity
- Construction of automated thermal evaporator for layered materials synthesis
- Unanticipated optically transparent electrically conductive films created