BCS@50

Champaign Urbana, IL October 12, 2007

From BCS through HTS to RTS

Paul C. W. Chu
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&
Hong Kong University of Science and Technology

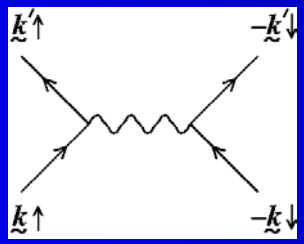
071016CWC

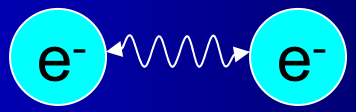
"What is it that confers the noblest delight? What is that swells a man's breast with pride above that which any other experience can bring to him? ***Discovery!*** *To know that you are walking where none others have walked; that you are beholding what human eye has not seen before; that you are breathing a virgin atmosphere. To give birth to an idea – to discover a great thought." ---Mark Twain*

(to discover a new compound;
a novel superconductor)

Searching for a new superconductor with a higher T_c has long been the driving force in superconductivity research

- Superconductivity needs electrons pairing & phase coherence (BCS)
- Electrons pairing requires an effective attraction (BCS)





- At a higher temperature, thermal excitation energy is greater
- If the thermal excitation energy exceeds the pairing energy, the pairs breakup and superconductivity disappears

The BCS theory is simple, elegant and descriptive but lacks the predictive power for high T_c.

Before 1986

- **The BCS Approach:** $T_c = 1.14\,\Theta_D \exp[-1/N(0)V]$ or $\theta_{Ch} \exp[-1/g]$, to raise T_c

  - enhance θ_D and/or N(0)V; θ_{Ch} and/or g

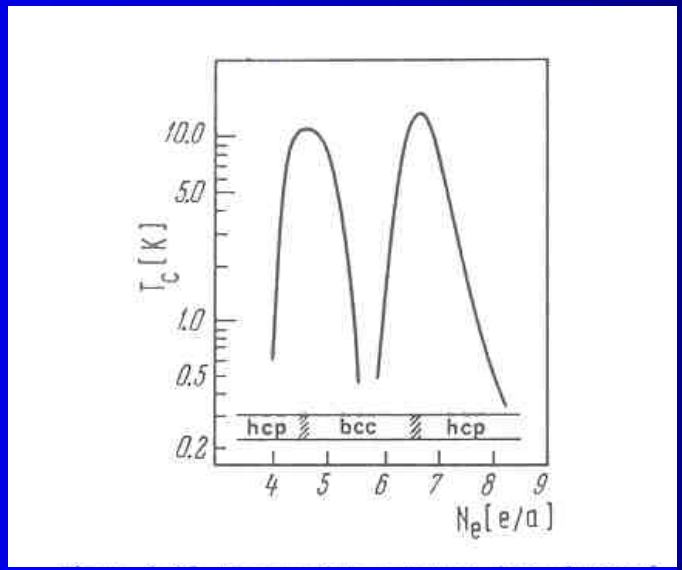
  - phononic, electronic and/or chemical instabilities: (structural, CDW, SDW, magnetic, Peierls, I-M, oxygen loss.....)

  - new mechanisms: excitons, plasmons, magnons,….

The challenge is how to enhance the pairing potential without triggering catastrophic instabilities

Before 1986

- Enlighten Empirical Approach: the most effective way (even after 1986)
  - Matthias empirical rule (1953): T_c peaks at e/a ~ 4.75 and 6.4



Works well for crystalline inter-metallic materials but not for amorphous inter-metallic materials nor for HTSs.

Before 1986

- Experimentally:
  - $T_c \leq 23.2$ K (1973 - 1986)
  - search for novel materials
- Theoretically:
  - $T_c < 30$'s K (instabilities)
  - propose novel mechanisms

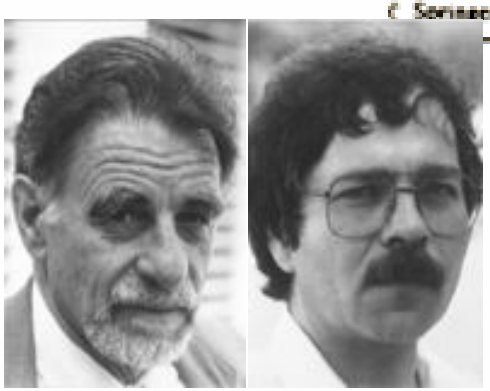
Confidence crisis in the search for higher T_c

1986: the critical year

Z. Phys. B - Condensed Matter 64, 189–193 (1986)

Condensed Matter
Zeitschrift für Physik B

© Springer-Verlag 1986



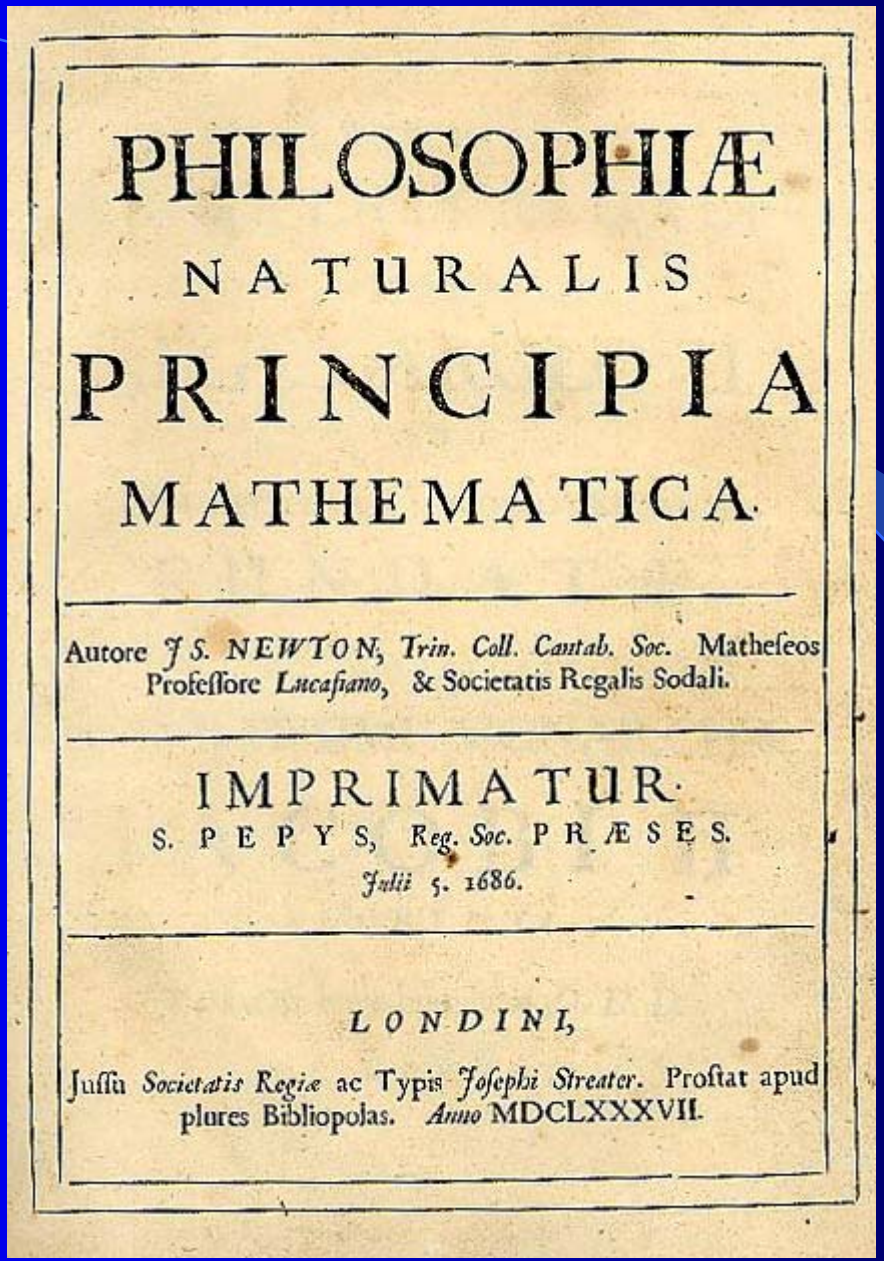
Possible High T_c Superconductivity in the Ba – La – Cu – O System

J.G. Bednorz and K.A. Müller
IBM Zürich Research Laboratory, Rüschlikon, Switzerland

Received April 17, 1986

Metallic, oxygen-deficient compounds in the Ba – La – Cu – O system, with the composition $Ba_xLa_{1-x}Cu_yO_{3(y-\delta)}$, have been prepared in polycrystalline form. Samples with $x = 1$ and 0.75, $y > 0$, annealed below 900 °C under reducing conditions, consist of three phases, one of them a perovskite-like mixed-valent copper compound. Upon cooling, the samples show a linear decrease in resistivity, then an approximately logarithmic increase, interpreted as a beginning of localization. Finally an abrupt decrease by up to three orders of magnitude occurs, reminiscent of the onset of percolative superconductivity. The highest onset temperature is observed in the 30 K range. It is markedly reduced by high current densities. Thus, it results partially from the percolative nature, bute possibly also from 2D superconducting fluctuations of double perovskite layers of one of the phases present.

$La_{2-x}Ba_xCuO_4$ (214) – new T_c record to 35 K in a new oxides



PHILOSOPHIÆ
NATURALIS
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MATHEMATICA

Autore *J S. NEWTON, Trin. Coll. Cantab. Soc.* Matheſeos Profeſſore *Lucaſiano,* & Societatis Regalis Sodali.

IMPRIMATUR.
S. PEPYS, *Reg. Soc.* PRÆSES.
Julii 5. 1686.

LONDINI,
Juſſu *Societatis Regiæ* ac Typis *Joſephi Streater.* Proſtat apud plures Bibliopolas. *Anno* MDCLXXXVII.

1986 - 300th Anniversary
(250 years before Cooper pairs)

- The paper was initially greeted with skepticism by most except a few groups (Tokyo, Houston*, IBM-Yorktown & Almaden, Beijing)

- We confirmed their results in late November

- The 1986 Fall MRS Meeting (Dec. 4):
  - showed our preliminary resistive data
  - learned Tokyo's magnetic and structure data

VOLUME 58, NUMBER 4 PHYSICAL REVIEW LETTERS 26 JANUARY 1987

Evidence for Superconductivity above 40 K in the La-Ba-Cu-O Compound System

C. W. Chu,[a] P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, and Y. Q. Wang
Department of Physics and Magnetic Information Research Laboratory
University of Houston, Houston, Texas 77004
(Received 15 December 1986)

An apparent superconducting transition with an onset temperature above 40 K has been detected under pressure in the La-Ba-Cu-O compound system synthesized directly from a solid-state reaction of La_2O_3, CuO, and $BaCO_3$ followed by a decomposition of the mixture in a reduced atmosphere. The experiment is described and the results of effects of magnetic field and pressure are discussed.

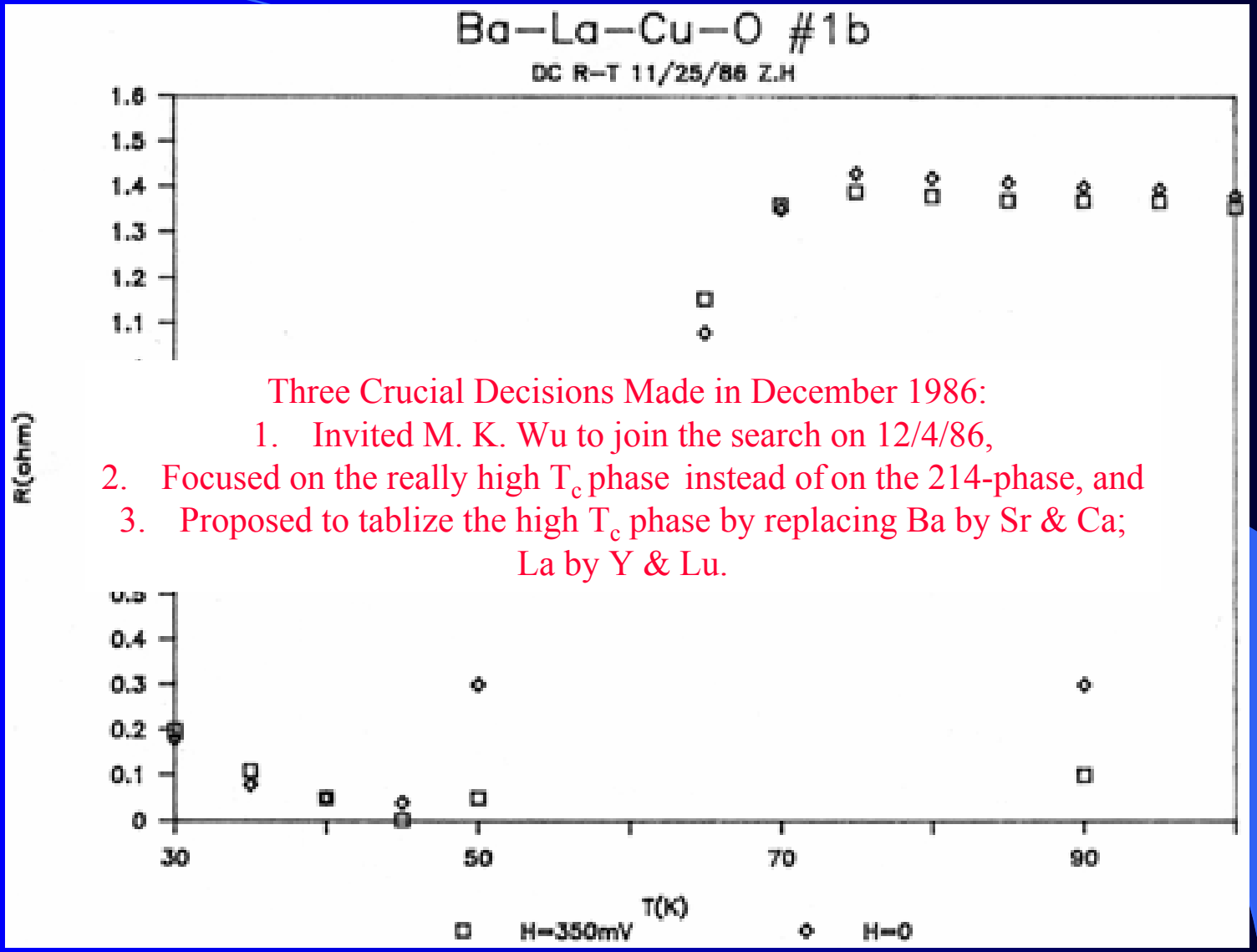
Superconductivity at 52.5 K in the Lanthanum-Barium-Copper-Oxide System

Science235,567(1987)

C. W. CHU,* P. H. HOR, R. L. MENG, L. GAO, Z. J. HUANG

A superconducting transition with an onset temperature of 52.5 K has been observed under hydrostatic pressure in compounds with nominal compositions given by $(La_{0.9}Ba_{0.1})_2 CuO_{4-y}$. Possible causes for the high-temperature superconductivity are discussed.

- *Enhanced T_c to 40.2 and then to 52.4 K*
- *A T_c> 40 K defies the then theoretical prediction***
- *The unusually large pressure effect on T_c => cuprates are unusual and warrant further study*
- *Proposed to replace Ba by Sr & Ca*

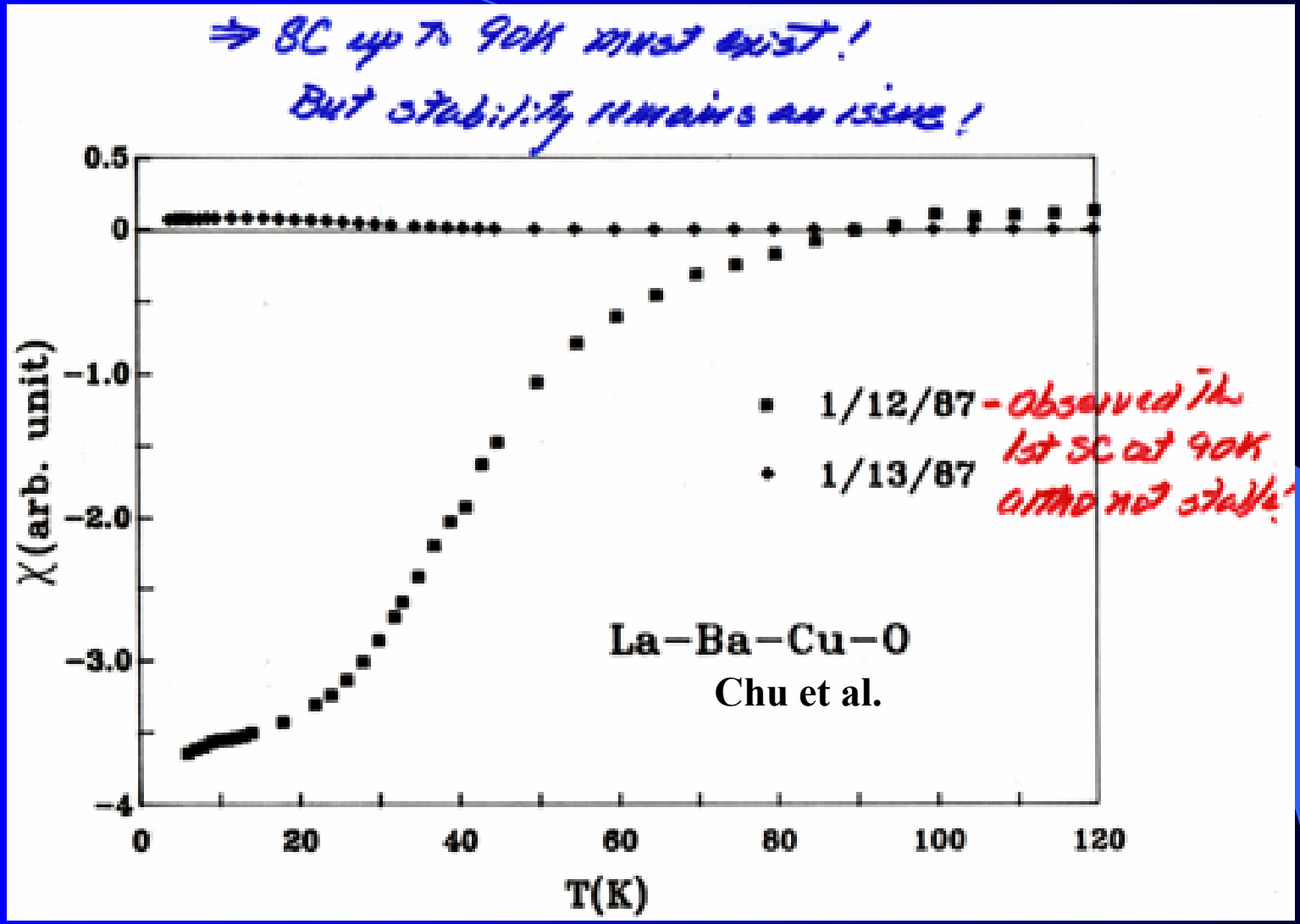


Three Crucial Decisions Made in December 1986:

1. Invited M. K. Wu to join the search on 12/4/86,
2. Focused on the really high T_c phase instead of on the 214-phase, and
3. Proposed to tablize the high T_c phase by replacing Ba by Sr & Ca; La by Y & Lu.

- ***First sign of SC slightly ~ 77 K was detected on November 25, 1986 in multi-phased but not pure 214 samples!***
- ***Concluded that the real high T_c phase cannot be 214***

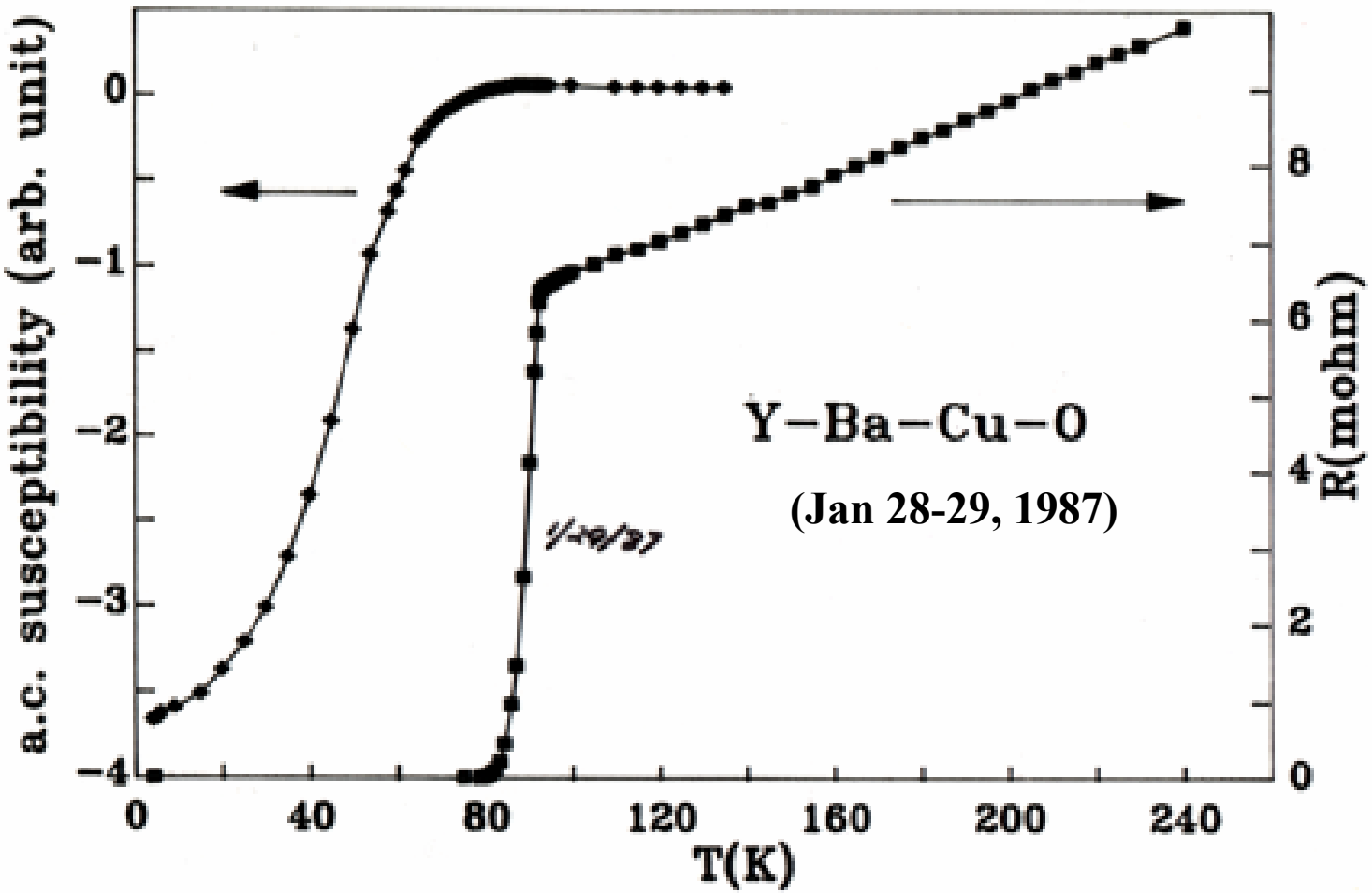
1987: the exciting year



- *First 90 K - SC was unambiguously observed, although not yet stable.*
- *Later analysis of the X-ray data showed it was* $LaBa_2Cu_3O_7$ *(123 or LBCO)*

1987: The Exciting Year

M. K. Wu et al./C. W. Chu et al*.



- *SC above 77 K was finally stabilized.*
- *$YBa_2Cu_3O_7$ (123 or YBCO) -*

the first stable liquid-nitrogen-temperature superconductor.

1987: The Exciting Year

VOLUME 58, NUMBER 9 PHYSICAL REVIEW LETTERS 2 MARCH 1987

Superconductivity at 93 K in a New Mixed-Phase Y-Ba-Cu-O Compound System at Ambient Pressure

M. K. Wu, J. R. Ashburn, and C. J. Torng
Department of Physics, University of Alabama, Huntsville, Alabama 35899

and

P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu [a]
Department of Physics and Space Vacuum Epitaxy Center, University of Houston, Houston, Texas 77004
(Received 6 February 1987; Revised manuscript received 18 February 1987)

A stable and reproducible superconductivity transition between 80 and 93 K has been unambiguously observed both resistively and magnetically in a new Y-Ba-Cu-O compound system at ambient pressure. An estimated upper critical field $H_{c2}(0)$ between 80 and 180 T was obtained.

$YBa_2Cu_3O_7$ (YBCO or 123)*

March 2, 1987 was a super-day for physics – >90K SC, supernova, SSC!!!

1987: The Exciting Year

VOLUME 58, NUMBER 18 PHYSICAL REVIEW LETTERS 4 MAY 1987

Superconductivity above 90 K in the Square-Planar Compound System $A Ba_2Cu_3O_{6+x}$ with A = Y, La, Nd, Sm, Eu, Gd, Ho, Er, and Lu

P. H. Hor, R. L. Meng, Y. Q. Wang, L. Gao, Z. J. Huang, J. Bechtold, K. Forster, and C. W. Chu [a]

Department of Physics and Space Vacuum Epitaxy Center, University of Houston, Houston, Texas 77004

(Received 16 March 1987; revised manuscript received 13 April 1987)

We have found superconductivity in the 90-K range in $A Ba_2Cu_3O_{6+x}$ with A = La, Nd, Sm, Eu, Gd, Ho, Er, and Lu in addition to Y. The results suggest that the unique square-planar Cu atoms, each surrounded by four or six oxygen atoms, are crucial to the superconductivity of oxides in general. In particular, the high T_c of $A Ba_2Cu_3O_{6+x}$ is attributed mainly to the quasi two-dimensional assembly of the

- Determined the YBCO structure with Hazan et al.
- Found R electronically decoupled from the sc system
- Synthesized and discovered all the RBCOs in about 48 hours in a reduced atmosphere

Super… dwiched
the mixe… terplane
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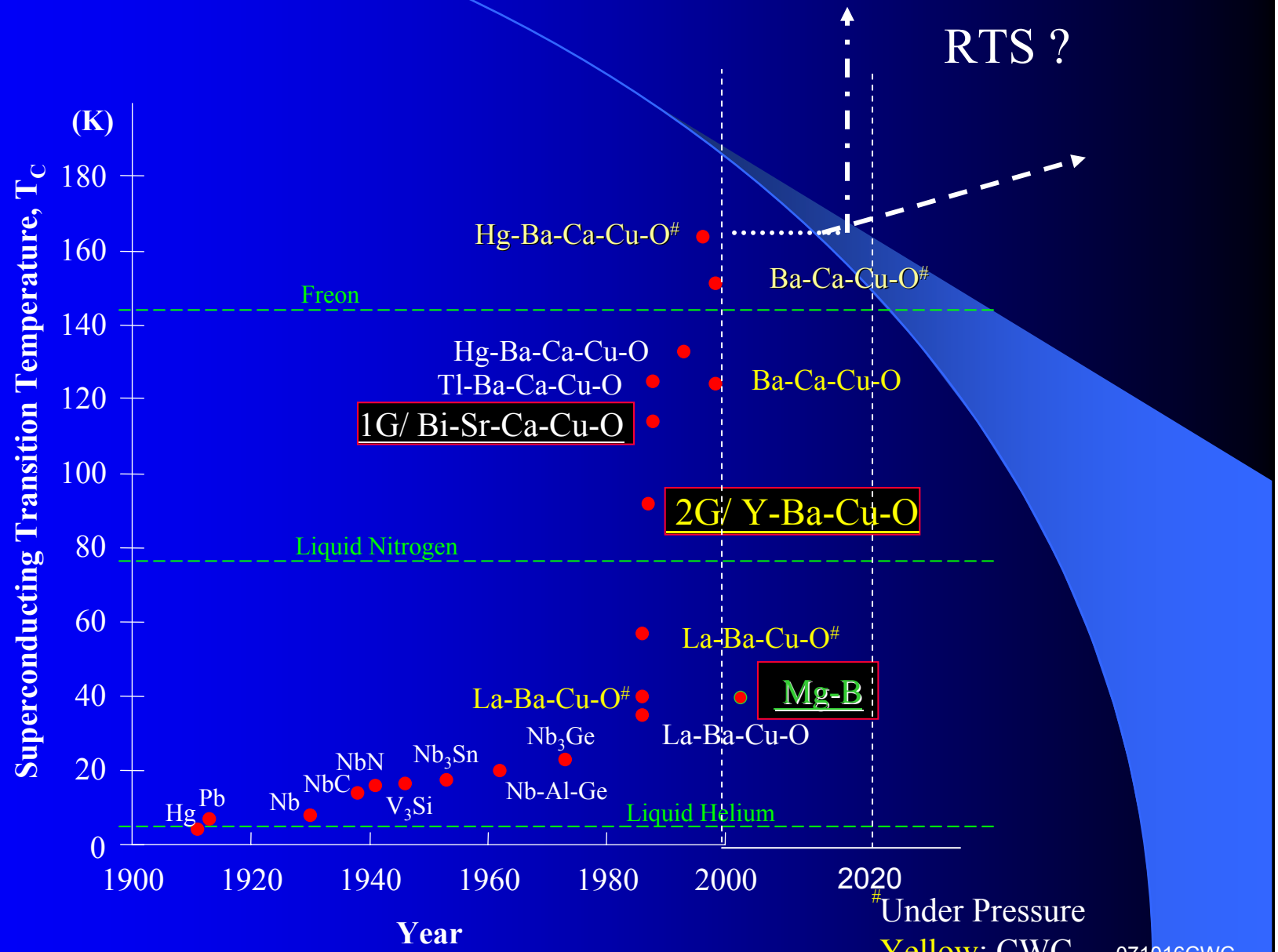
served in this and other related compounds to the single layeredlike K_2NiF_4 structural phase. With the steady improvements in sample conditions and the application of pressure, the superconducting transition temperature has been raised to above 40 K at ambient pressure[3,4] and 57 K under pressure,[5] and the transition width has been reduced[3] to 1.4 K. Recently, superconductivity starting

cially evident from the enhancement of the superconducting transition from ~30 K in the K_2NiF_4 structure[1,2] to ~90 K in the $A Ba_2Cu_3O_{6+x}$ structure in the La-Ba-Cu-O system observed in this study. Bigger layer assembly is predicted for higher-T_c superconducting oxides.

All samples with the $A Ba_2Cu_3O_{6+x}$ structure and

From LTS to HTS



#Under Pressure

Yellow: CWC

071016CWC

ROOM TEMPERATURE SUPERCONDUCTIVITY

It is all relative with respect to the environment

Edge of the Universe	**3 K (1911)**
Liquid Helium	**4 K (1911)**
Liquid Hydrogen	**20 K (1967)**
Liquid Nitrogen	**77 K (1987)**
Space Shuttle	**~100 K (1988)**
Liquid Natural Gas	**120 K (1988)**
CF_4	**148 K (1993)**
Dry Ice	**198 K (?)**
Room Temperature	**300 K (?)**

RTS: $T_c \sim 300 - 400K$

After 1987

- Over-confidence crisis:

  - sky was the limit to T_c

  - extravagant claims from everywhere: the US, China, the former Soviet Union, Russia, Japan, France, Croatia --- USO's

- But 2006 Barth and Marx:

  - scientometric prediction of the end of HTS 2010-15

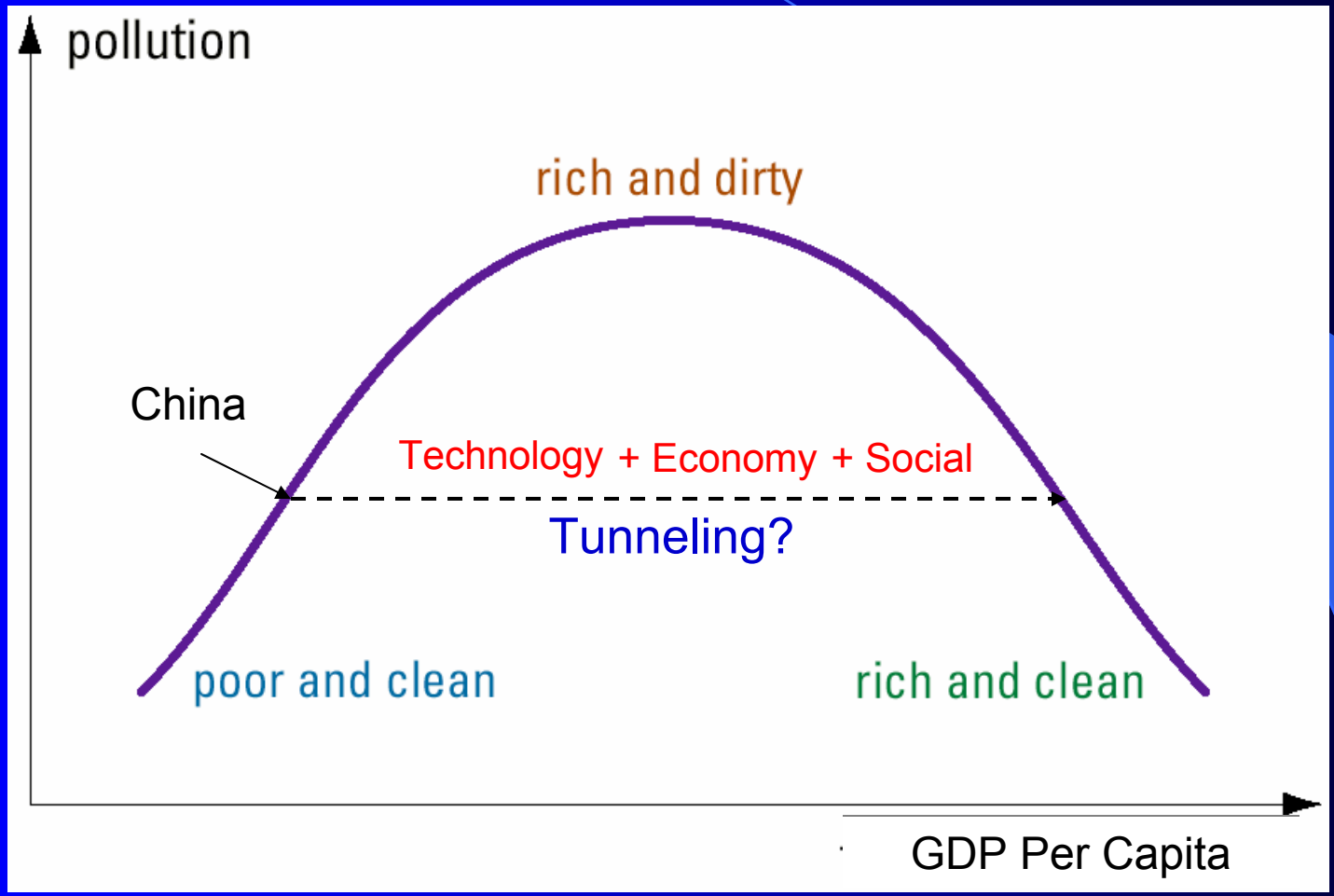
  - but the discovery of a RTS will change it all

WHY RTS?

Constraints for Future Global Economic Growth:
Energy, Environment and Resources
(Reduce, Reuse, Recycle and Remanufacture)

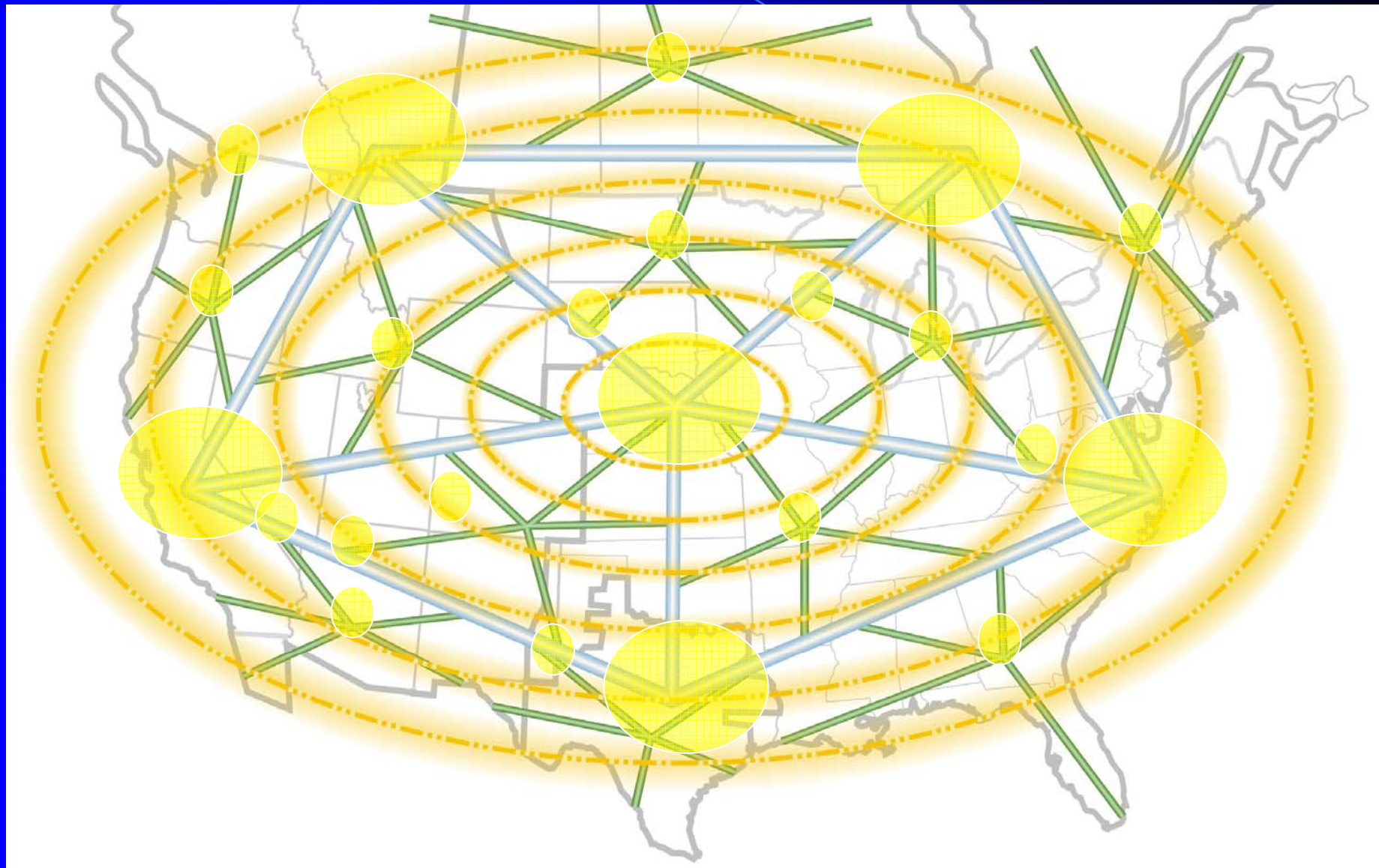
Not to mention other areas, including medical diagnostic, transportation, computation, communication, etc.

Traditional Path for Industrialization

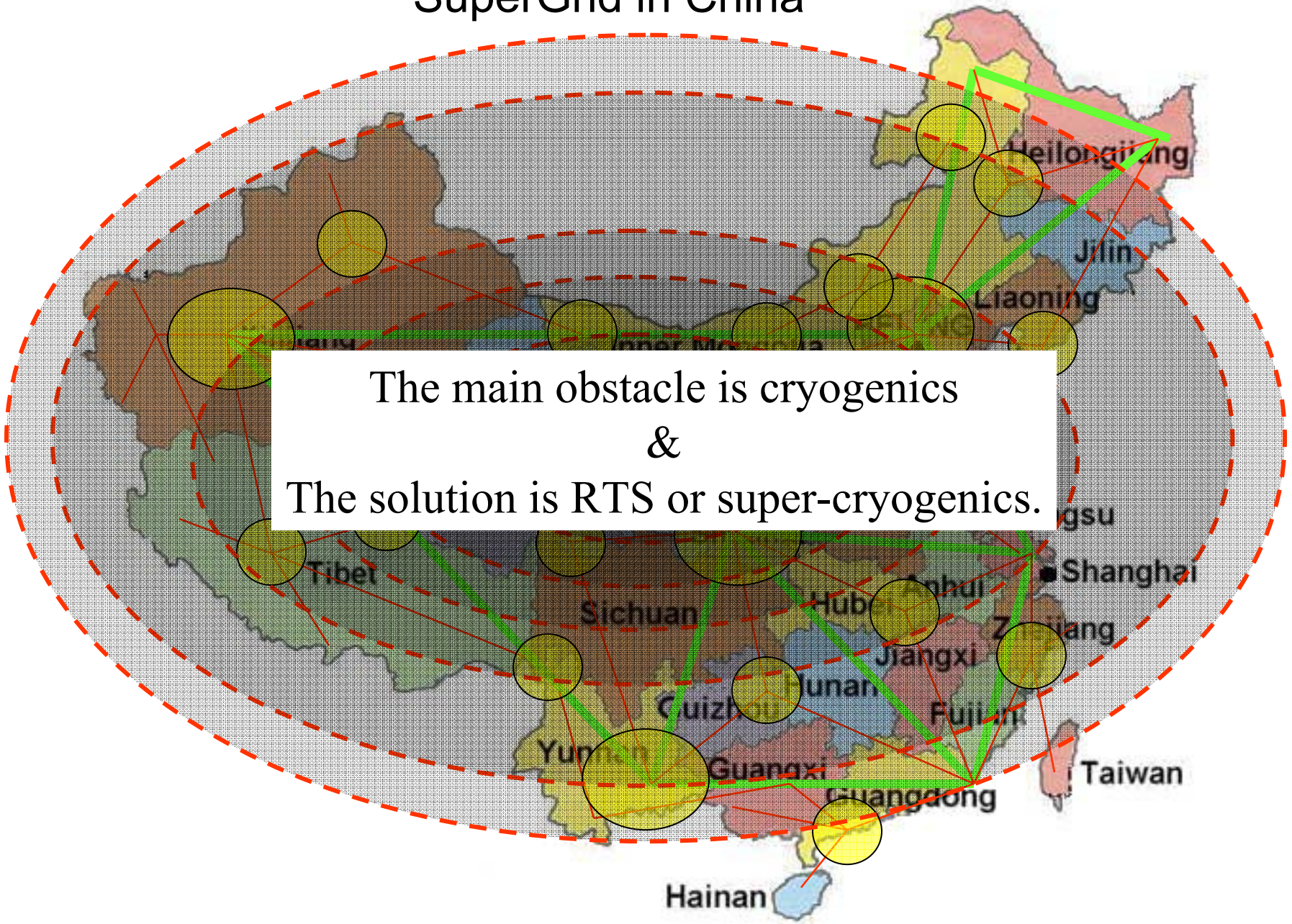


(Xu K. D., President, CAE)

SuperGrid in North America (Jimmy Glotfelty)
backbone, regional, micro and IT



SuperGrid in China*



The main obstacle is cryogenics
&
The solution is RTS or super-cryogenics.

Past

- **<u>Some Interesting Encounters:</u>**
  - a California company: a modified polymer material
  - a sample from a former in Arizona
  - a material from Croatia

- **Some Interesting Reports**
  - 1946 Ogg – Na/Amonia (160 K)
  - 1977 Rusakov et al. - CuCl (180 K);
    1978 Chu & Geballe (160 K?)
  - 1987 Chen et al. – YBCO (240 K)
  - 1993 Lagues e
  - 1994 Tholenc
  - 1999 Reich et al. – Na/WO_3 (91 K)

Unidentified Superconducting Objects (USO's)

too tantalizing to ignore; too fleeing to confirm

Past (cont.)

Some Interesting Predictions

- 1964 Little
- 1964 Ginzburg
- 1968 Ashcroft
- 1973 Allender, Bray and Bardeen
- 1987 Lee – Why is T_c so low?
- 1987 Chu – no T_c ceiling
- 1997 Rice - $T_c > 300$ K
- 2004 Schrieffer - $T_c > 1000$ K*
- 2006 Edwards et al. - $T_c > 230$ K

PAST (cont.)

Some common features of HTS

- electron pairing, phase coherence
- highly correlated electrons
- multi-interactions, e.g. sc, afm & fm
- multi-subsystems, e.g. charge reservoir & active block
- instabilities, e.g. physical and chemical
- M-I border,
- low carrier concentration,
- strong covalent bonding,
- mixed valence, e.g. Cu^{2+} & Cu^{3+}
- quasi-2D,
- spin ½,
- high polarizability

Experiments being made by my group (pressure, fields, chemical, physical):

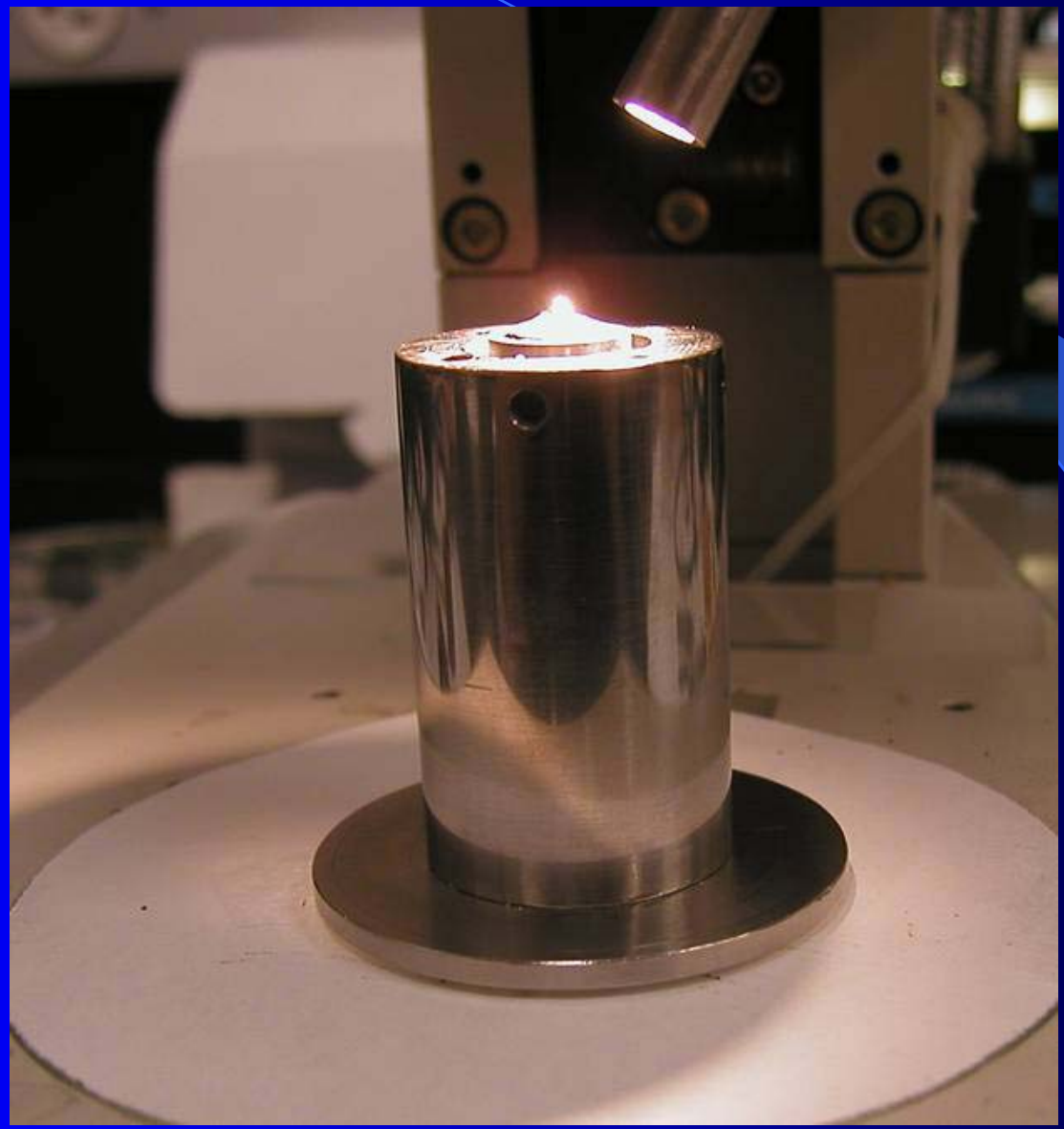
- meta-stable phase
- a negative dielectric constant
- optimization of multi-interactions in highly correlated electron systems (e.g. FE→SC)
- light ionic system (Li-B, Li-Be)
- organic-inorganic hybrid system
- non-cuprate square planar systems
- improvement of cuprates

Experiments being planned by my group (pressure, fields, chemical, physical):

- Na-ammonia
- Na/WO3
- nano- clusters and cluster compounds
- delocalization of the covalent bond electrons
- multi-energy scale systems (H2,IVa-H)
- ABB (interfaces)
- USOs

Search Metastable Phases

(Diatchenko/Chu, 2005)



Search for Metastable Phases via Extreme conditions

(Diatchenko/Chu, 2005)

HPDC for in-situ synthesis, fast quenching and characterization

Search Metastable Phases

(Diatchenko/Chu, 2005)

070515CWC

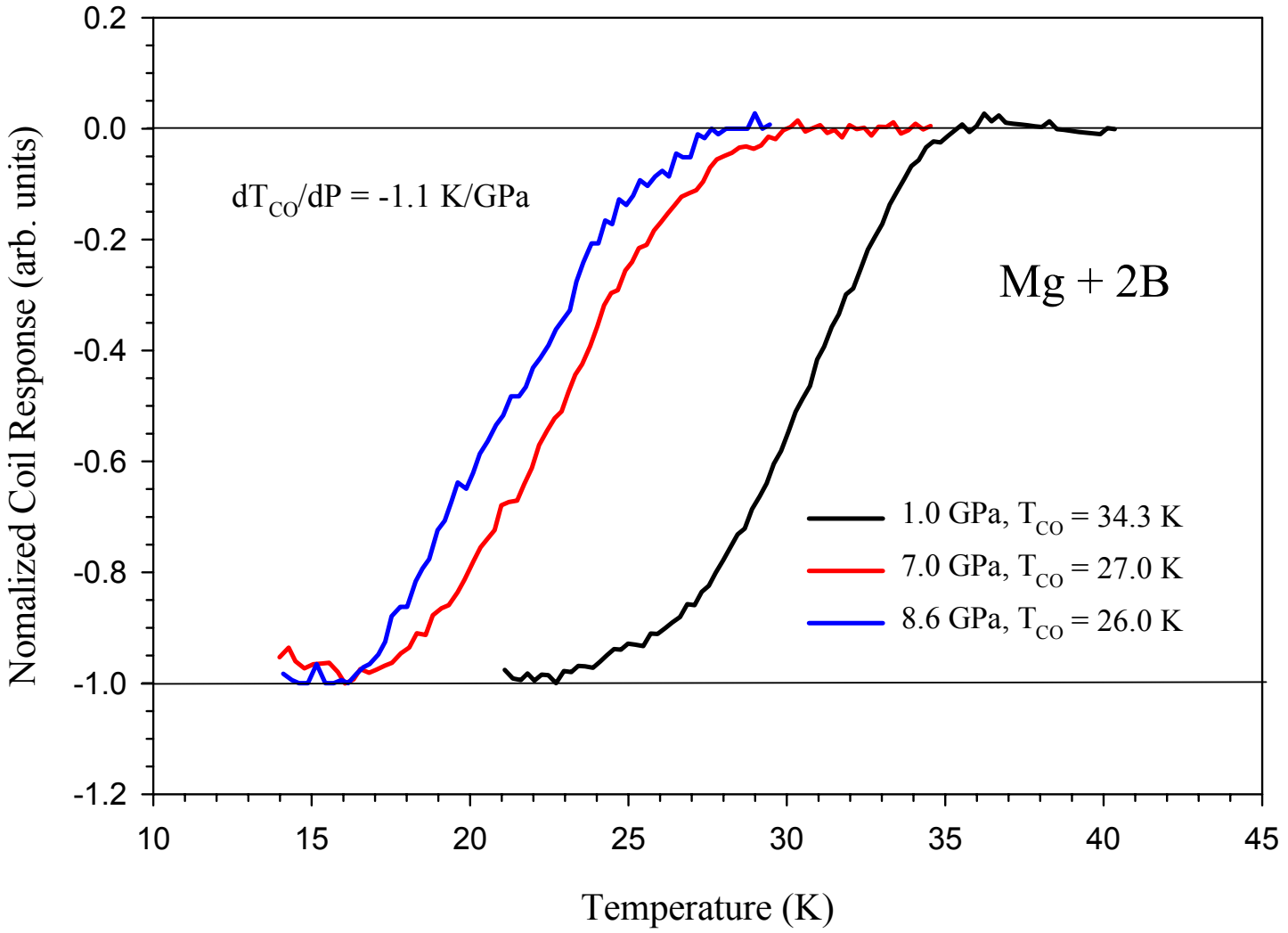

0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
Nomalized Coil Response (arb. units)
dT$_{CO}$/dP = -1.1 K/GPa
Mg + 2B
1.0 GPa, T$_{CO}$ = 34.3 K
7.0 GPa, T$_{CO}$ = 27.0 K
8.6 GPa, T$_{CO}$ = 26.0 K
10
15
20
25
30
35
40
45
Temperature (K)

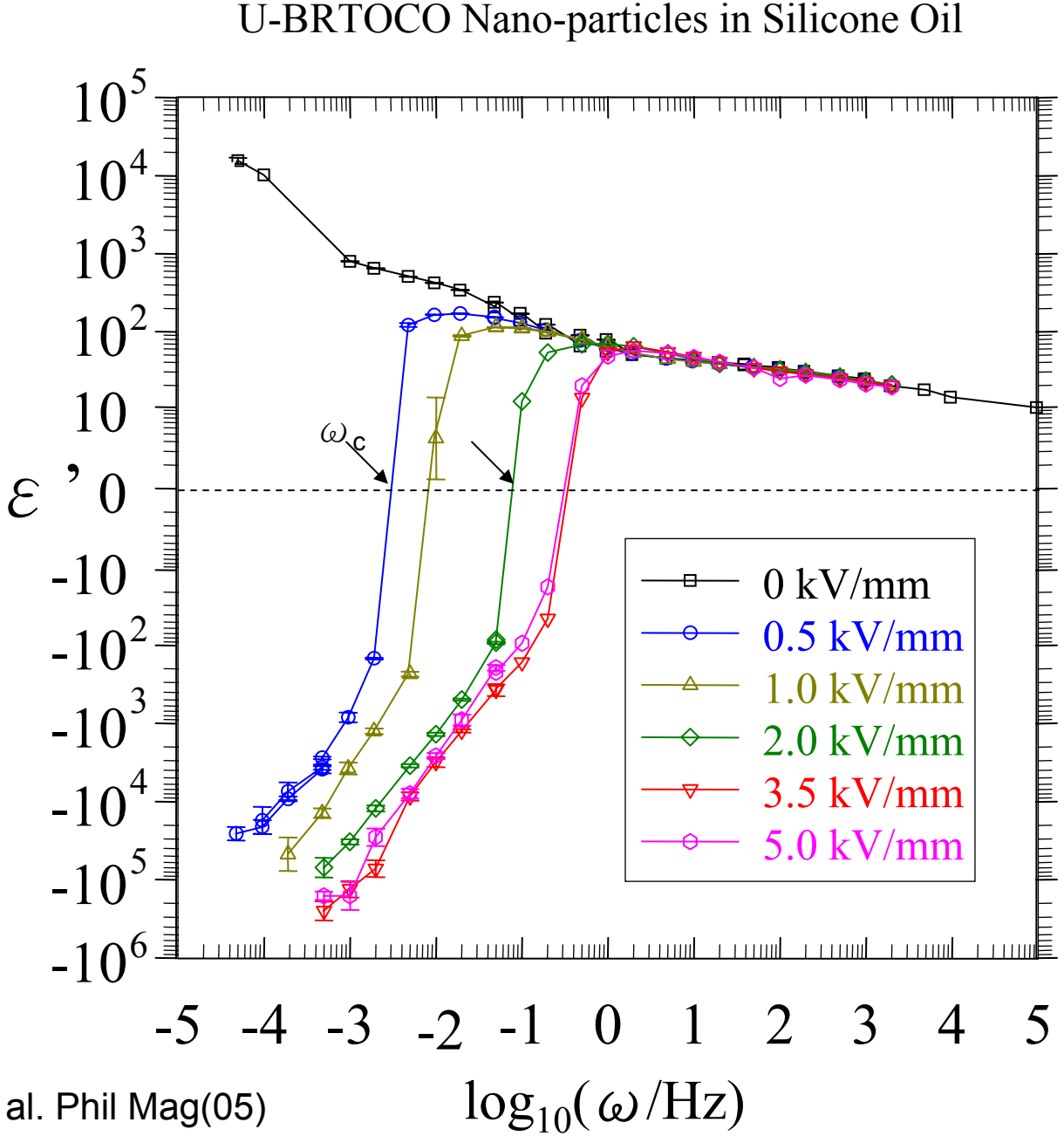
Figure 7

- Field-induced changes in the
  - sign
  - magnitude, and
  - ω_c

of ε at low ω and 300 K

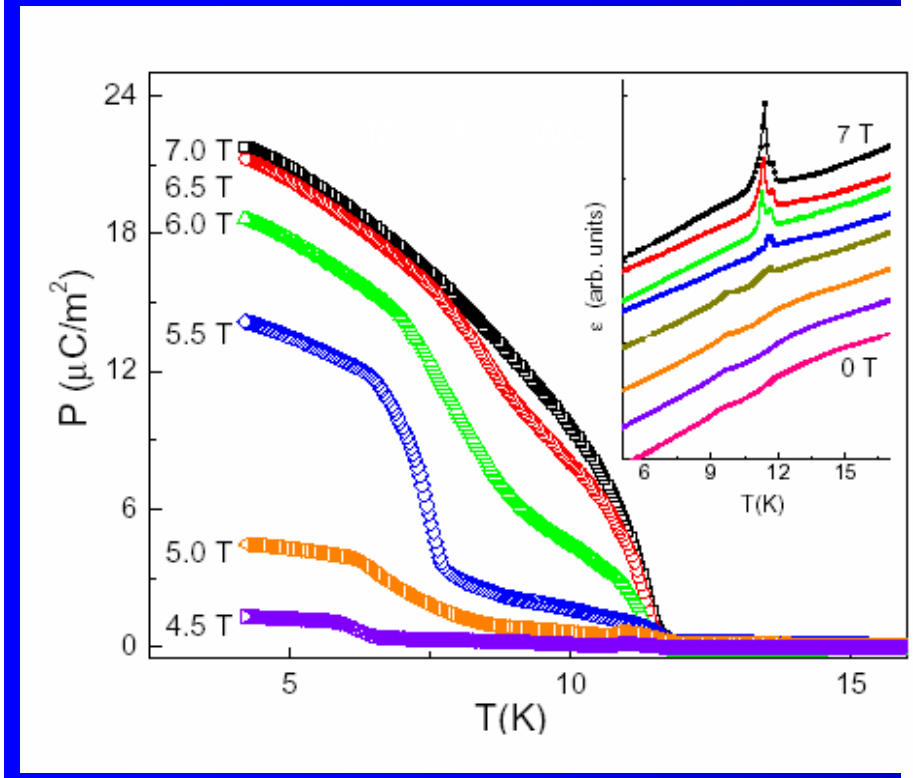
- Like a quantum phenomenon

- Superconductivity?

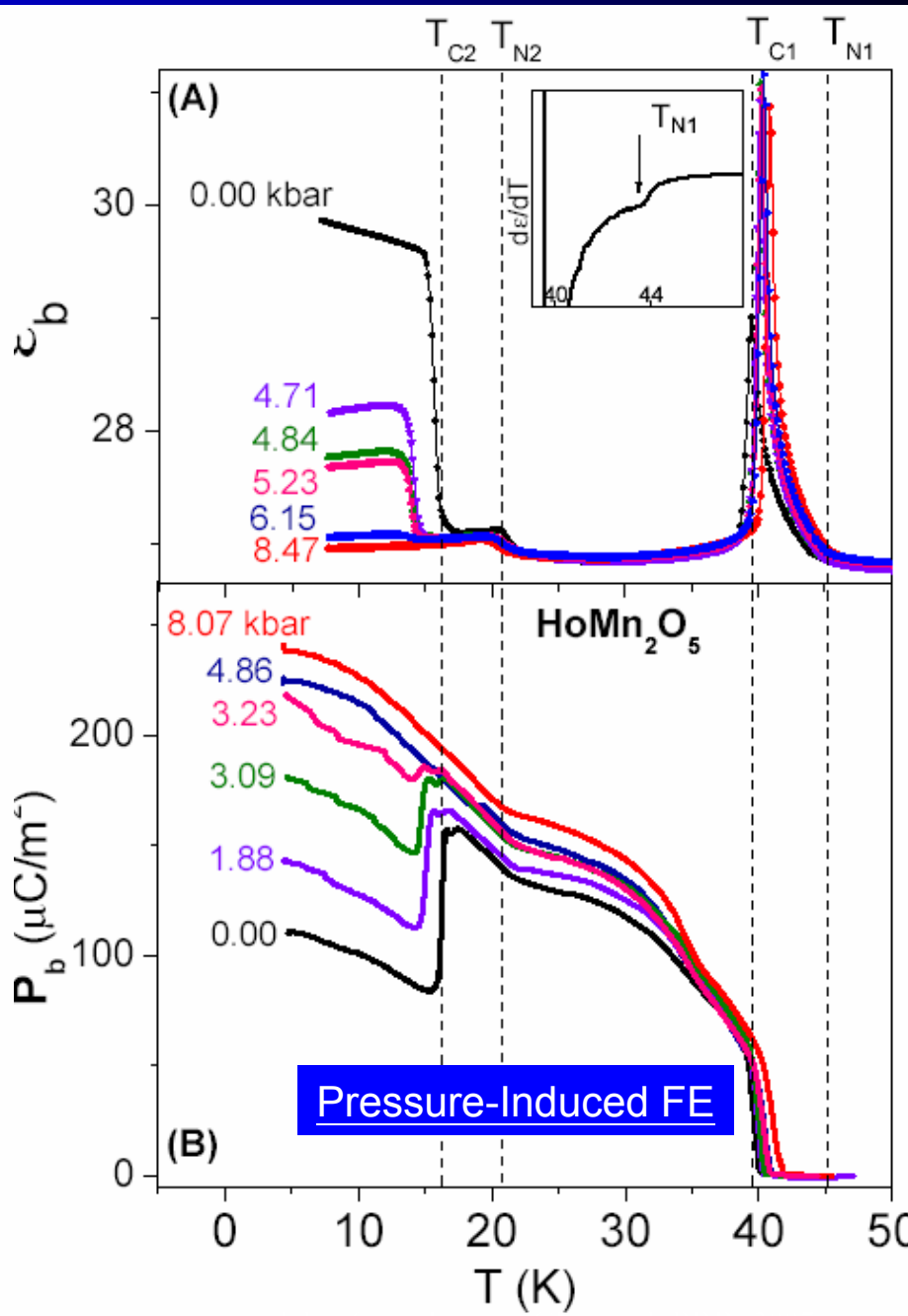


Wen/Chen&CWC et al. Phil Mag(05)

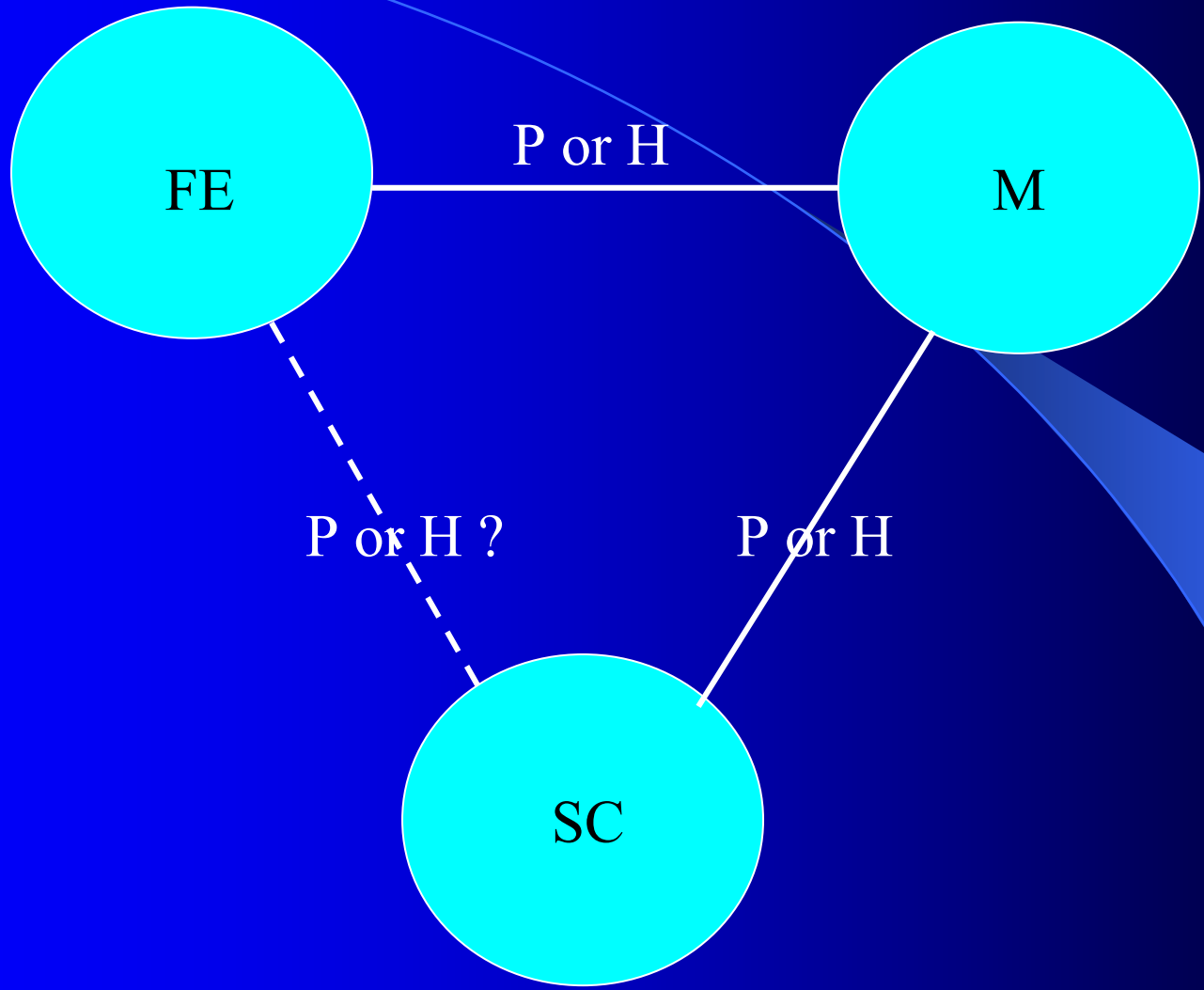
Field-Induced FE



Chaudhury/Lorenz/Chu et al. (2007)

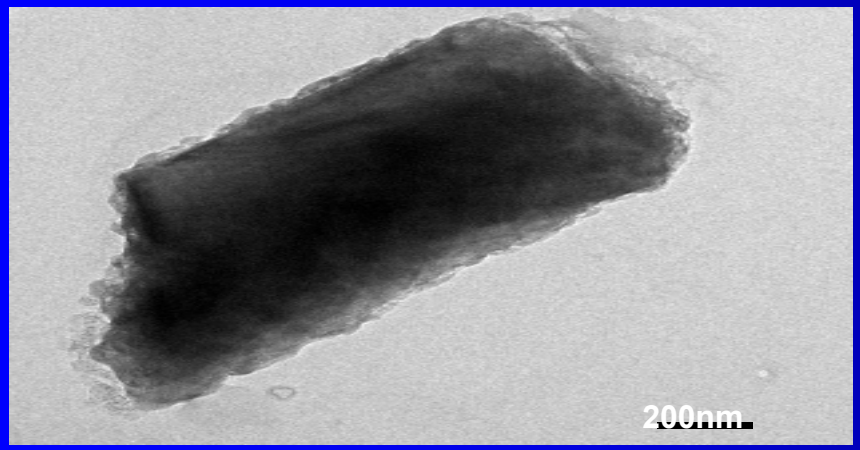


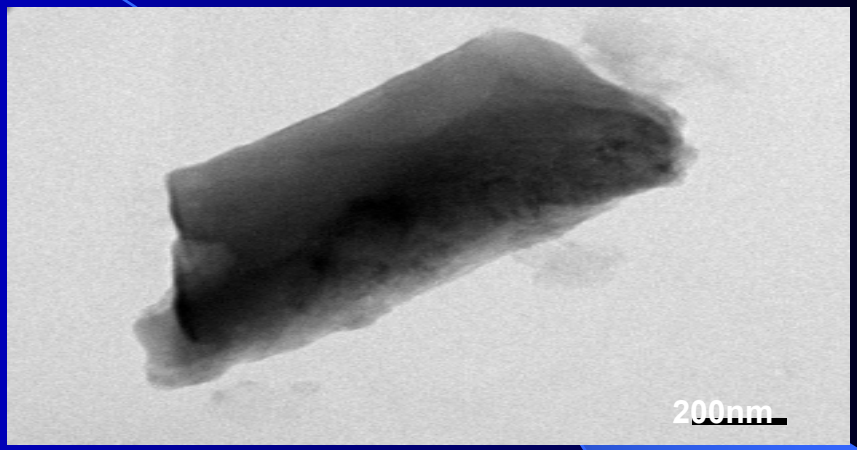
Pressure-Induced FE



Highly correlated electron systems:
Many orders with different ordering temperatures

SEM images showing the morphology of our Li-B samples



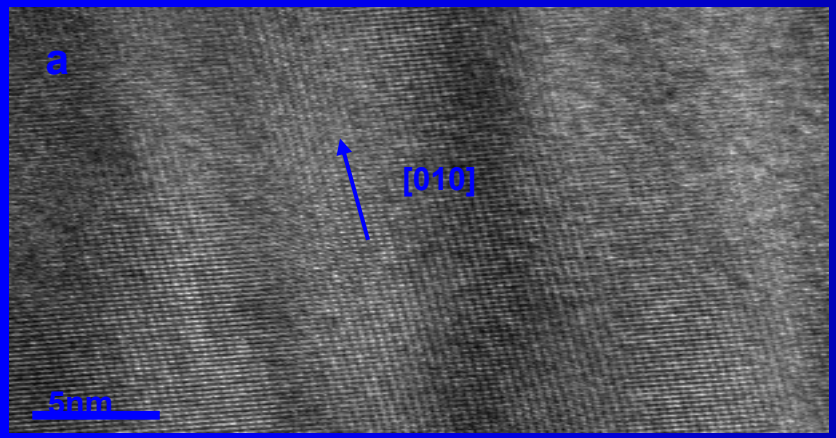


1. Metallic
2. Li-content is small not yet definitively determined
3. Hexagonal: a = b = 8.26 A, c = 4.22 A
4. Possible cage-like structure: main diffraction lines $3 \leq d \leq 7.2$ A

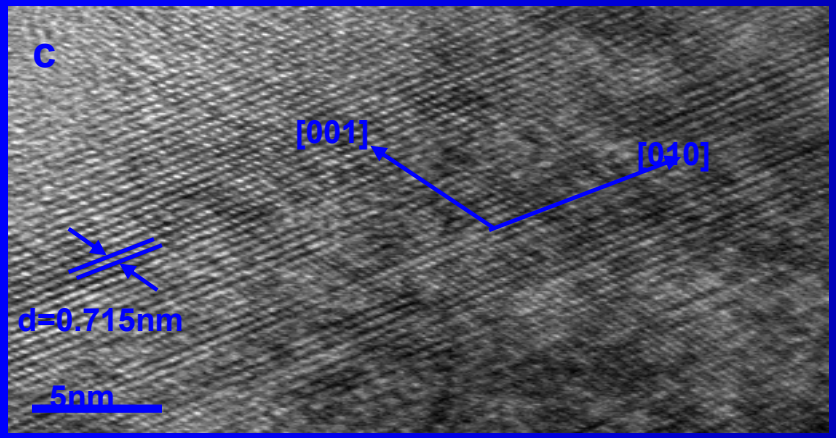
E. Galspyan /N. Wang/C. W. Chu et al. 2007

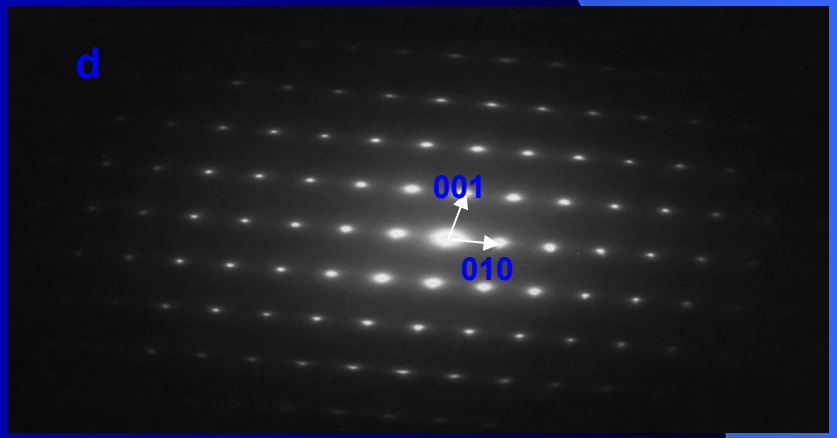
HRTEM images and the corresponding diffraction patterns.

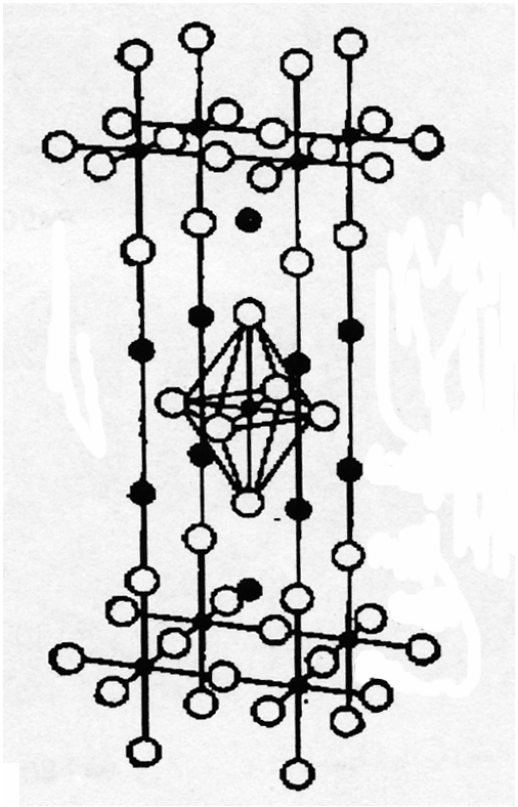
a) Viewed from [210] direction and b) the corresponding diffraction pattern



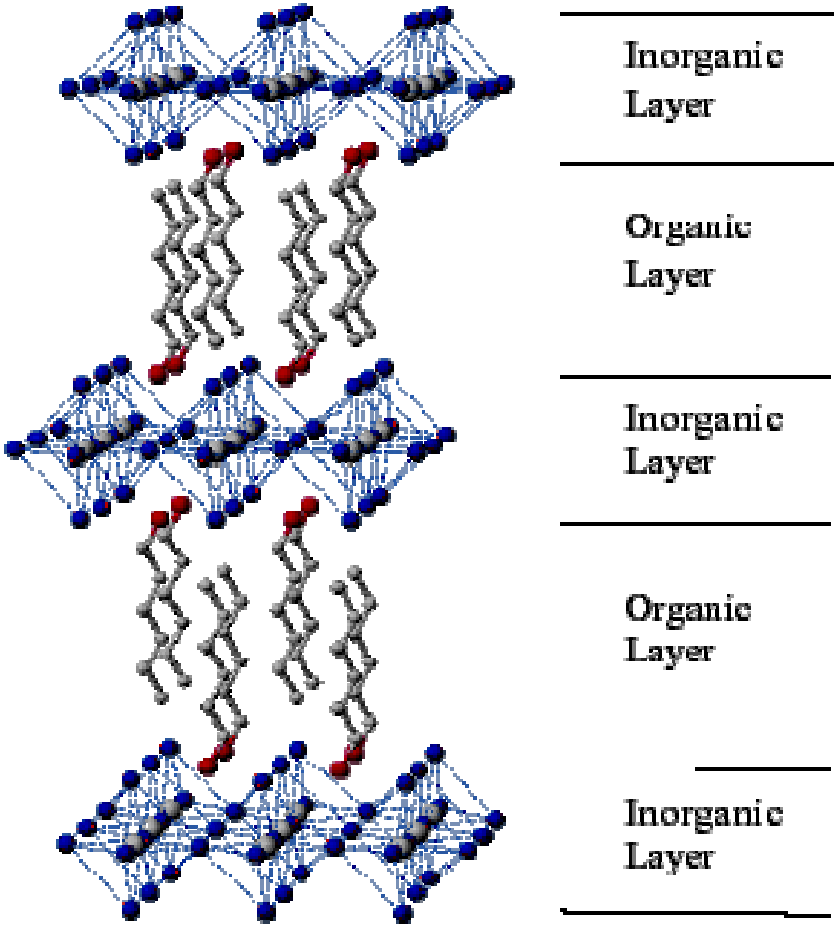
c) Viewed from [100] direction and d) the corresponding diffraction pattern







K_2NiF_4



WG/CWC2007

50 years after BCS & 20 years after YBCO we have learned:

- *There is no evidence, experimental or theoretical, telling us that room temperature superconductivity is an impossibility.*
- *Whatever physics law doesn't say won't happen will happen.*
- *Be prepared to expect the unexpected.*
- *More excitements are yet to come.*
- *Next grand challenge in SC is to find RTS – DoE, AFOSR*

I am optimistic but cautious because I also remember the interesting comments made in the 70's about RTS by BTM.

- RTS *belongs to the domain of science fiction and to occur only at an astronomical distance under an astronomical pressure*

- *present theoretical attempts to raise the T_c are the opium in the real world of superconductivity. Unless we accept the fact and submit to a dose of reality, honest and not so honest speculations will persist until all that is left in this field will be these scientific opium addicts, dreaming and reading each other's absurdities in a blue haze.*

- *the deluge of idle speculations coming to us these days from all sides just won't do it – all it will manage to do is to widen the credibility gap instead of the energy gap.*

Thank You!