Cryogenic Engineering Conference & International Cryogenic Material Conference 2023 Honolulu, July 11, 2023

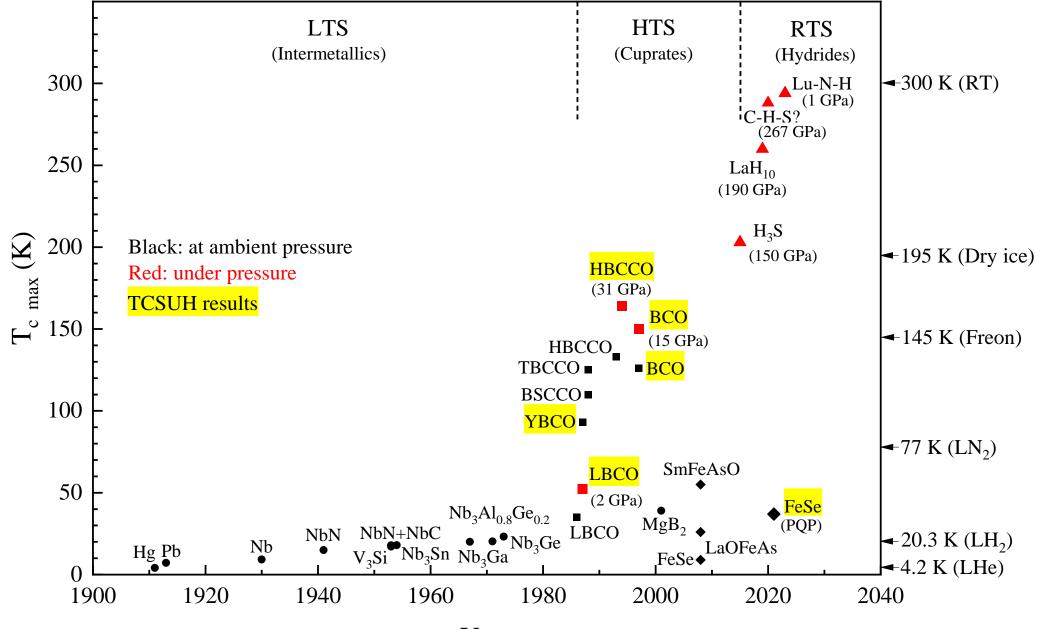
From High Temperature Superconductivity to Room Temperature Superconductivity*:

from high pressure to ambient; from very high pressure to ambient again !?

L. Z. Deng, T. Bontke, D. Schulze, Z. Wu, M. Gooch, T. Habamohoro, T. W. Kuo and C. W. Chu

Department of Physics and the Texas Center for Superconductivity University of Houston, Houston, TX

*Work supported in part by AFOSR, State of Texas, Temple Foundation and Mores Foundation



Milestones in the search for LTS, HTS & RTS

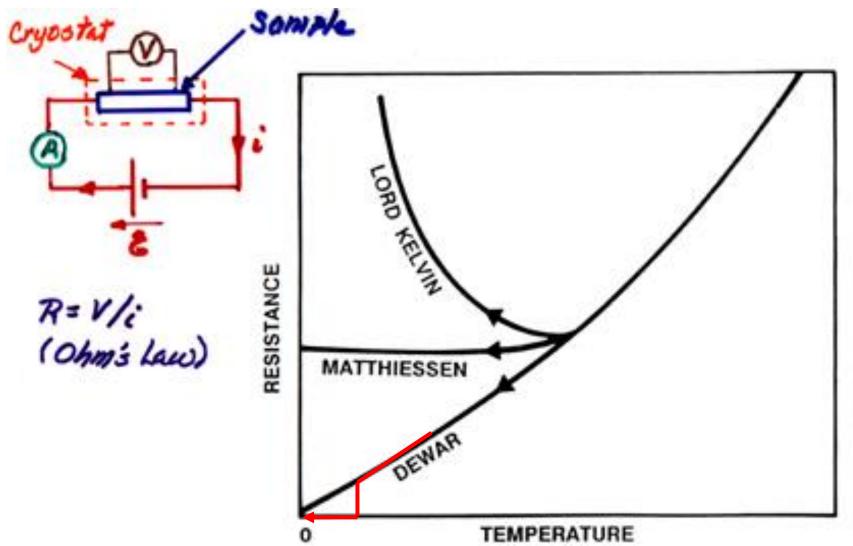
- Liquid H₂ 20.3 K [*Nb₃(Ge,Al) 21 K*] (Matthias et al. 1967) [LTS]
- Liquid N₂ 77 K [*RBCO 90's K*] (Chu et al. 1987) <u>the holy grail then [HTS]</u>
- Space Shuttle 100 K [BSCCO 110 K] (Maeda et al. 1988)
- Liquid Natural Gas 120 K [TBCCO 120 K] (Hermann et al. 1988)
- CF₄ 148 K [HBCCO -164 K, 31 GPa] (Chu et al. 1993) high pressure required and ozone layer effect
- RTS ≥ 203 K [Hydrides under very high pressures]

H₃S – ~ 203 K at ~ 155 GPa (Eremets et al. 2015 [RTS]

LaH₁₀ - ~ 260 K at ~ 180-200 GPa (Hemley et al. 2019)

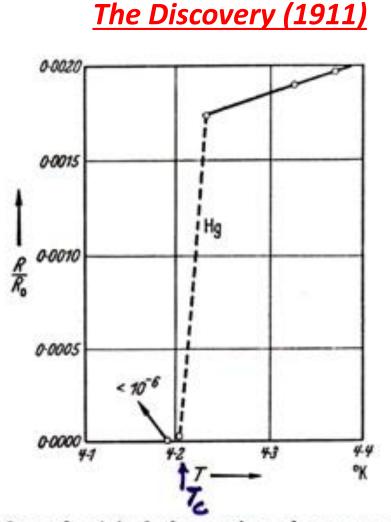
C-S-H - ~ 287 K at – 267 GPa (Dias et al. 2000)

Lu-N-H - ~ 294 K at 1GPa (Dias et al. 2023) – the holy grail today



Three predictions of metallic resistance behavior near absolute zero.

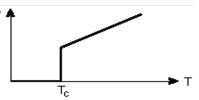
Komerlingh Dnnes



KAMERLINGH ONNES' original observation of superconductivity in mercury (1911). R = resistance of specimen; $R_0 =$ resistance at 0° C. The temperature scale used at the time was incorrect, the transition occurs actually at $4 \cdot 1^\circ$ K.

BASIC PROPERTIES OF A SUPERCONDUCTOR

• COMPLETE DISAPPEARANCE OF ELECTRICAL RESISTANCE (1911)



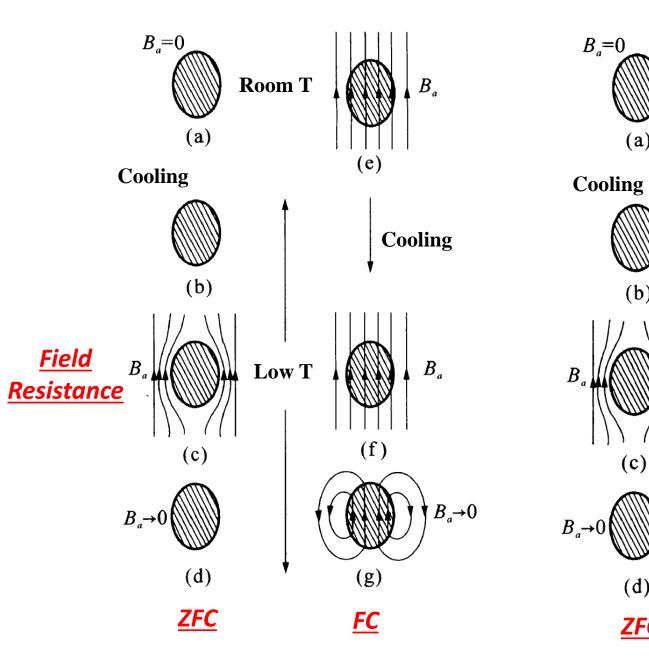
• COMPLETE EXPULSION OF EXTERNALLY APPLIED MAGNETIC FIELD (1933)

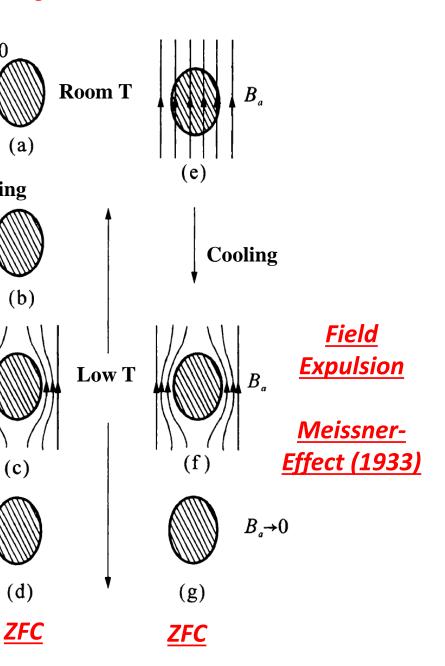


- MACROSCOPIC QUANTUM PHENOMENON or A COHERENT QUANTUM STATE (1930's, 1962)
 - T_c SC Transition Temperature J_c Critical Current Density
 - H_c Critical Magnetic Field

Perfect Conductor







- Superconductivity Science and Technology
- Science T_c, Mechanism,....; Technology......
- Theoretical (Einsteinian) vs, Empirical (Edisonian):

-BCS: $T_c = 1.14\theta_D \exp(-1/NV)$ – electron pairing, attractive interaction - McMillan: $T_c = [\theta/1.45] \{-[1.04(1+\lambda)]/[\lambda-\mu^*(1+0.62\lambda)]\}$

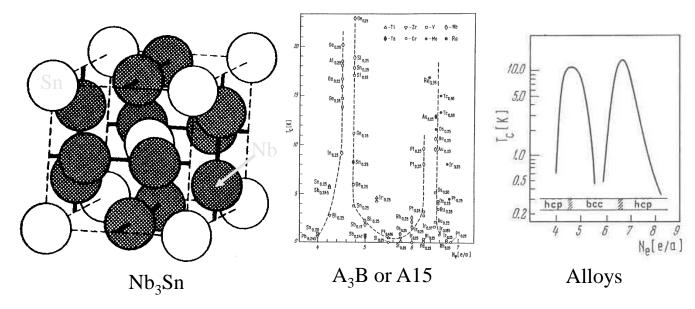
- Matthias: $T_c \sim e/a 4.75, 6.4$ (LTS);
- Presland: $T_c/T_{c,max+} \sim 1 \sim 82.6 \ (n-n_o)^2 \ (HTS)$
- <mark>- BCS</mark> characteristic temperature Θ ~ 1/M^{- α} (Isotope Effect)
- e-ph interaction, mass and instabilities, LTS
- e-e interaction, magnetic fluctuations, e-e correlations, HTS
- e-ph interaction, RTS !?

LTS (before 1986)

- The Enlightened Empirical Approach
- Matthias empirical rule (1953): T_c peaks at e/a ~ 4.75 and 6.4



- Most effective approach even after 1986



• Works well for crystalline inter-metallic materials only

• Recognizes the importance of instabilities



The BCS Approach:

 $T_c = 1.14\Theta_D \exp[-1/N(0)V]$ or $\theta_{CH} \exp[-1/g]$

- To raise the T_c enhance θ_D , N(0) & V; or θ_{CH} & g
- Excellent descriptive power but no or poor predictive ability
 - Almost all parameters are closely coupled instabilities (structural, CDW, SDW, magnetic, Peierls, I-M...)
 - The small energy scale of superconductivity
- New mechanisms: phonon, electron, magnetic, charge...
 *1D Little (64): organic materials
 *2D Ginzburg (64): TaS2 (71), Al/organic.....

*oxides – Matthias (64): AxWO3, LiTi2O4 (73), BaPbBiO3 (75) *interfacial – ABB (73): Pb/Te, Au/Ge,...

1986: the critical year

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



1/1-

Possible High T_e Superconductivity in the Ba - La - Cu - O System

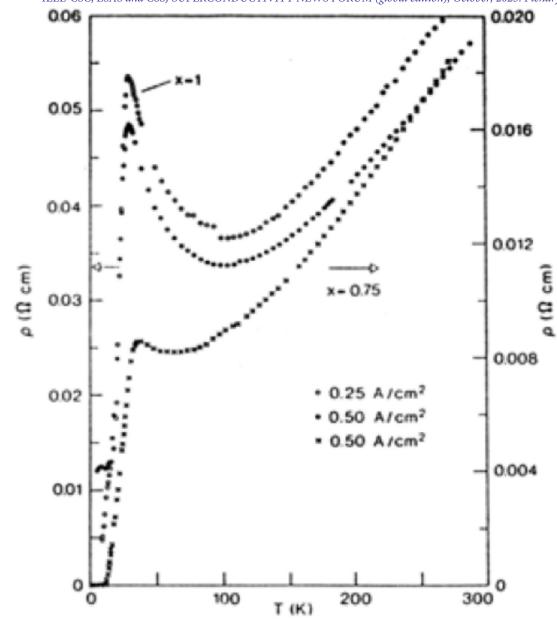


J.G. Bednorz and K.A. Müller IBM Zürich Research Laboratory, Rüschlikon, Switzerland

Received April 17, 1986

Metallic, oxygen-deficient compounds in the Ba – La – Cu – O system, with the composition Ba, La₁ – Cu₂O₃₍₃ – ...) 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.

 $La_{2-x}Ba_{x}CuO_{4}$ (214) – new T_{c} record to 35 K in a new oxide



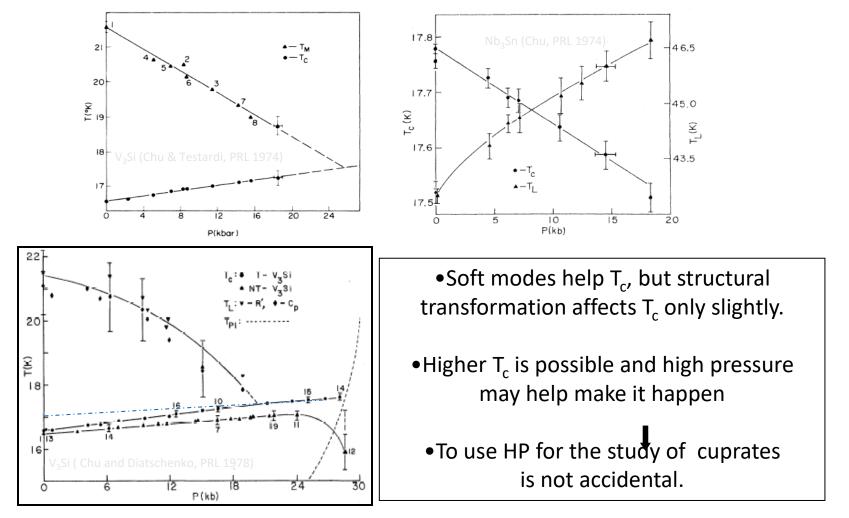
IEEE-CSC, ESAS and CSSJ SUPERCONDUCTIVITY NEWS FORUM (global edition), October, 2023. Plenary presentation given at CEC-ICMC, July, 2023, Honolulu, Hawaii, USA

G. Bednorz and A. Mueller Z. Phys. B 64, 189 (1986).

- The paper was initially greeted with skepticism by most except a few groups (Tokyo, Houston, Beijing, IBM-Yorktown)
 - The Houston group and the Tokyo group confirmed their results and
 - The Tokyo group further identified the 214 superconducting phase
 - The MRS Meeting, December 4, 1986

• The BCS Approach: $T_c = 1.14\Theta_D exp[-1/N(E_F)V]$

- instabilities: (structural, CDW, SDW, magnetic, Peierls, I-M.....)



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 La₂O₃, CuO, and BaCO₃ 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.

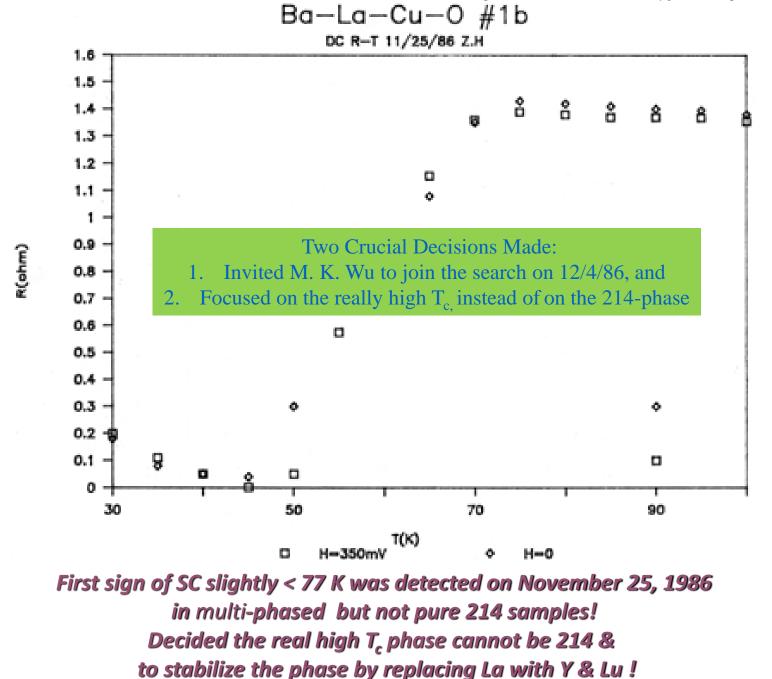
PACS numbers: 74.70.Ya

Superconductivity at 52.5 K in the Lanthanum-Barium-Copper-Oxide System Science235,567(198)

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.

> The unusually large pressure effect on T_c Enhanced T_c to 40.2 and then to 52.4 K => The compound is unusual!!! A T_c>40 K defies the then theoretical prediction!!!



NATIONAL SCIENCE FOUNDATION WASHINGTON, D.C. 20550 12/3/86 Den Drs. Bednoz + Miller, This to past to inform you that say group at the U. of How ton has reproduced your NESULTO (2. Theys. B 64, 189 (8)) There weeks ago. A small ac diamagnetic signal was also detected. Magnetic field was found to suppress The transition. I believe that it to superconducty. Now the question is "taket phase" or "moved pleases". Soon, you will here from us more. Please send me more impravation ! Smeenly yours My Phone: (202) 357-9737 C.W. Chu (also Physics. Univ of Houston) Houston, TX 77004 1713) 749-2842 YOUN phone No. 7 P.S. Currently, I am the Director of Solid Physic Program at the National Science Foundation.

(From G. Bednorz) & a phone call from Mueller

九

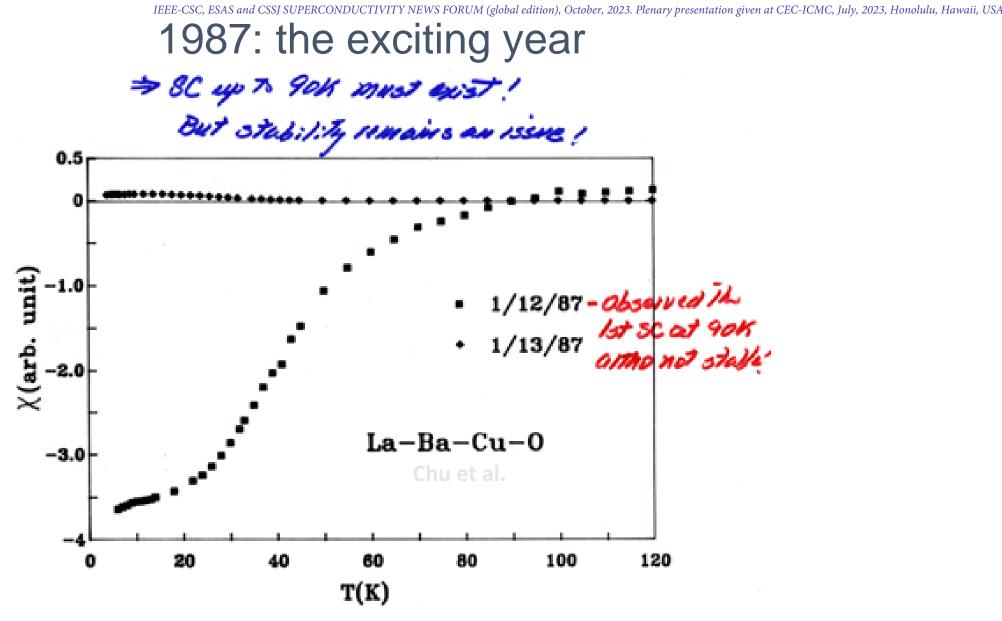
Christmas the warmth and joy of remembering friends

Dear Wei-kan & Agnus, Wish everything happens to you in this coming year as you wish! Ching-Wu & May

P.S. Just got the highest T_c of 40.2 K. Next week very likely 50 K. Now, I am full of confidence of 77 K.

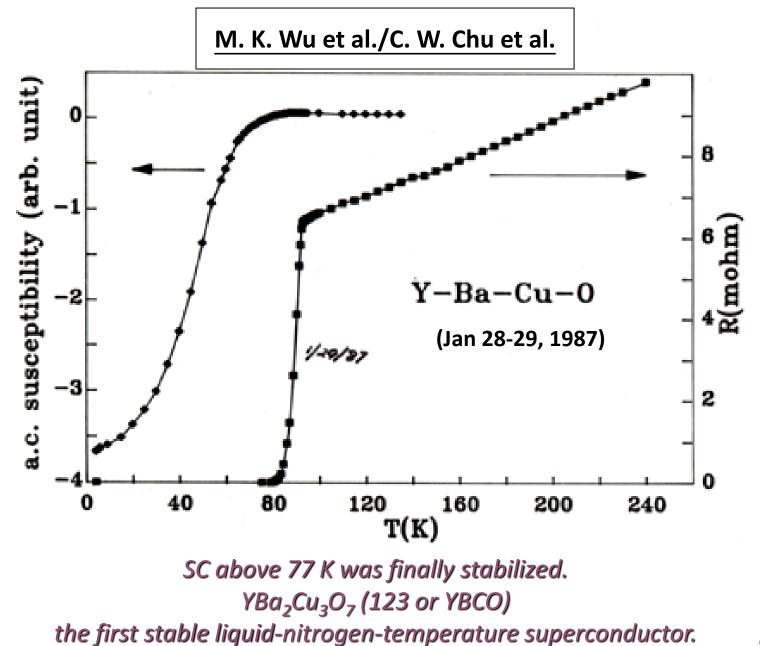
123.: Just got highest Te of 40.2K Next week very likely to 50K I'm full of confidence about 77K

(From W. K. CHU)



First 90 K - SC was unambiguously observed, although not yet stable. Later analysis of the X-ray data showed it was LaBa₂Cu₃O₇(123 or LBCO)

1987: The Exciting Year



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.

YBa₂Cu₃O₇ (YBCO or 123) [was intended to be a one sentence paper]

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

andwiched

Superconductivity above 90 K in the Square-Planar Compound System $ABa_2Cu_3O_{6+x}$ 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 $ABa_2Cu_3O_{6+x}$ 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 partic-

- Found R electronically decoupled from the sc system
 - Synthesized and discovered all RBCOs in about 48 hours in a reduced atmosphere

Superconductivity above 50 it was mor report the mixed-phase La-Ba-Cu-O compound system. Subsequent studies attributed 1.2 the superconductivity observed in this and other related compounds to the single layeredlike K2NiF4 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 reduced3 to 1.4 K. Recently, superconductivity starting at 98 K with a zero-resistance state at 94 K was discovered^{6,7} in the mixed-phase Y-Ba-Cu-O system with nominal compositions represented by Y1,2Ba0.8- $CuO_{4-\delta}$. Later, superconductivity near 90 K with a zero-resistance state at ~70 K was also reported* in the mixed-phase Lu_{1.8}Ba_{0.2}CuO₄ compounds. Preliminary examinations showed9 that the Y-Ba-Cu-O compounds

between the A layers. The significance of the interplane coupling or screening within the layer assembly is especially evident from the enhancement of the superconducting transition from ~ 30 K in the K₂NiF₄ structure^{1,2} to ~ 90 K in the ABa₂Cu₃O_{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 $ABa_2Cu_3O_{6+x}$ structure and A=Y, La, Nd, Sm, Eu, Gd, Ho, Er, and Lu were synthesized by the solid-state reaction of appropriate amounts of sesqui-oxides of La, Nd, Sm, Eu, Gd, Ho, Er, and Lu, BaCO₃, and CuO in a fashion similar to that previously described.⁵ Structural analyses were carried out with a Rigaku D-MAX x-ray powder diffractometer. Samples of dimensions $\sim 1 \text{ mm} \times 0.5 \text{ mm} \times 4 \text{ mm}$ were out from the sintered cylinders. A standard four-lead 070714CWC

HTS Cuprates

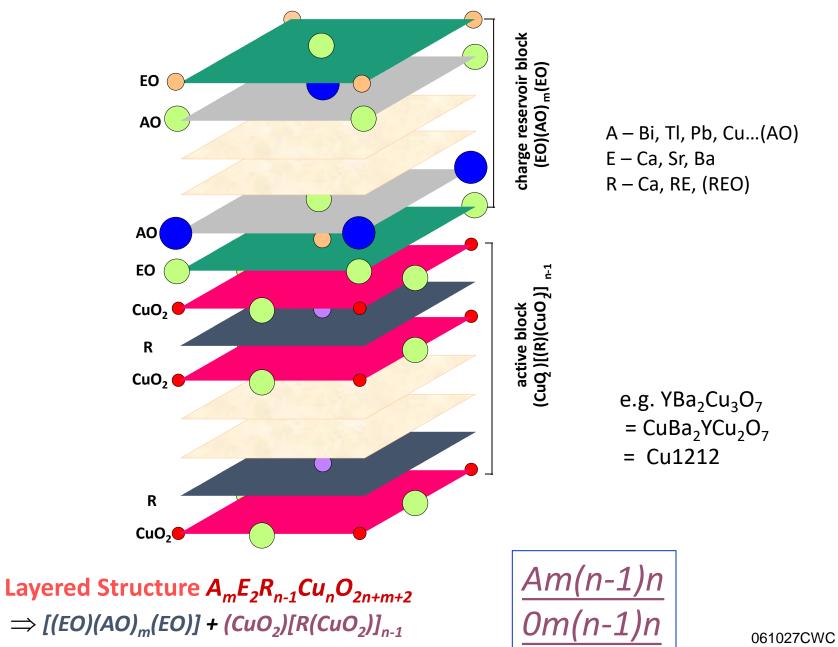
• All Cuprate HTSrs – Represented by a Generic Formula & a Perovskite-Like

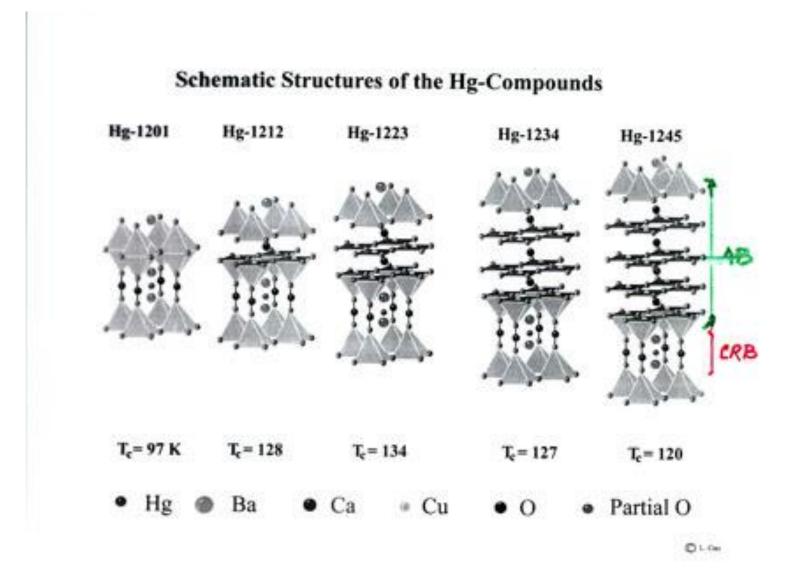
Layered Structure $A_m E_2 R_{n-1} C u_n O_{2n+m+2}$

 $[(EO)(AO)_{m}(EO)] + \{(CuO_{2})[R(CuO_{2})]_{n-1}\}$

[A-m2(n-1)n or O2(n-1)n when A is absent][A, E, R – cations, often with E = Ba or Sr and R = Ca or a rare-earth element; (AO) may be replaced by more complex slabs; R may be replaced by (RO)-slab]

Current Status - Known





Room Temperature Superconductors?



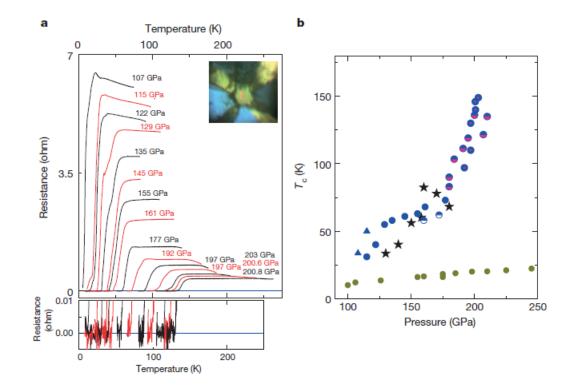
IEEE-CSC, ESAS and CSSJ SUPERCONDUCTIVITY NEWS FORUM (global edition), October, 2023. Plenary presentation given at CEC-ICMC, July, 2023, Honolulu, Hawaii, USA A Room Temperature Superconductor was found in 2009 by James Cameron



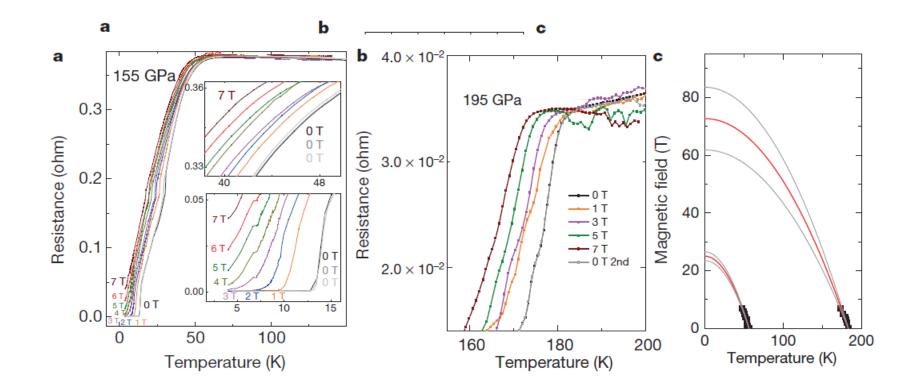
RTS (2005- the dawn of RTS, VHP)

Conventional superconductivity at 203 kelvin at high pressures in the sulfur hydride system <u>Nature 525, 73-76 (2015).</u>

A. P. Drozdov1*, M. I. Eremets1*, I. A. Troyan1, V. Ksenofontov2 & S. I. Shylin2



Parallel Down-shift by field?



RESEARCH ARTICLE



60 years of pss

Magnetic Penetration Depth and Coherence Length in a Single-Crystal $YBa_2Cu_3O_{7-\delta}$

Ahmed Abou El Hassan, Abdelaziz Labrag,* Ahmed Taoufik, Mustapha Bghour, Hassan El Ouaddi, Ahmed Tirbiyine, Brahim Lmouden, Abdelhalim Hafid, and Habiba El Hamidi

Phys. Status Solidi B 2021, 258, 2100292

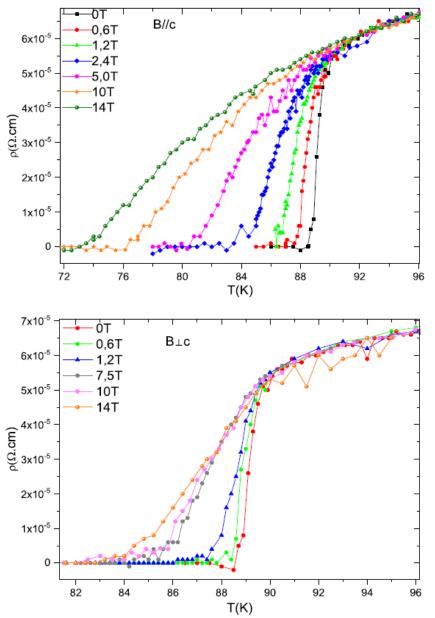
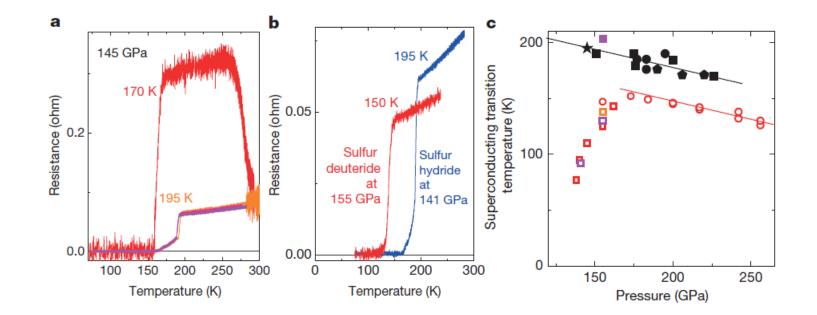


Figure 4. Resistivity plots of $YBa_2Cu_3O_{7-\delta}$ for several magnetic fields i the *c*-axis direction and the *ab*-plane direction with a DC transport currer of 100 nA.

Isotope Effect



<u>R vs T of H_nS to show the transition is P-T path dependent</u>

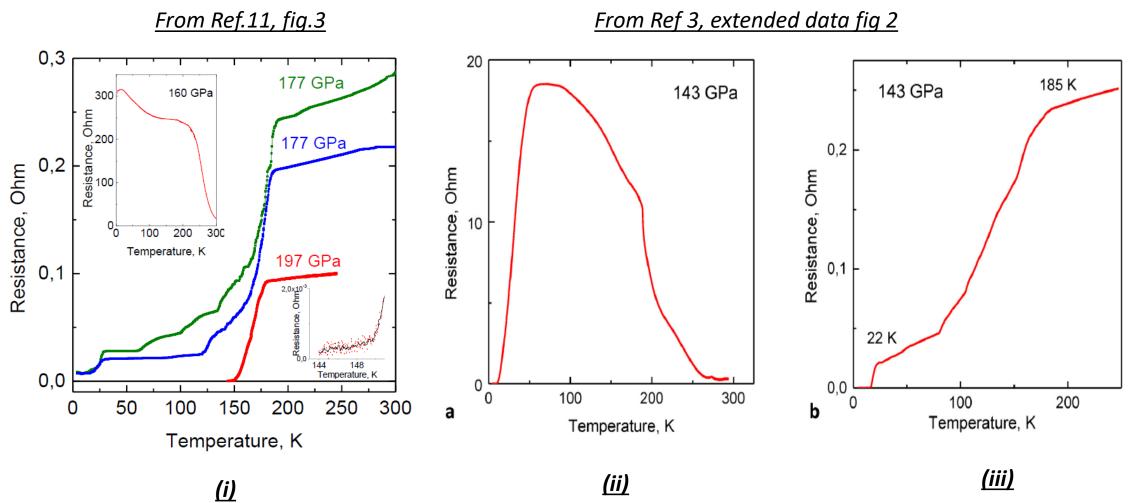
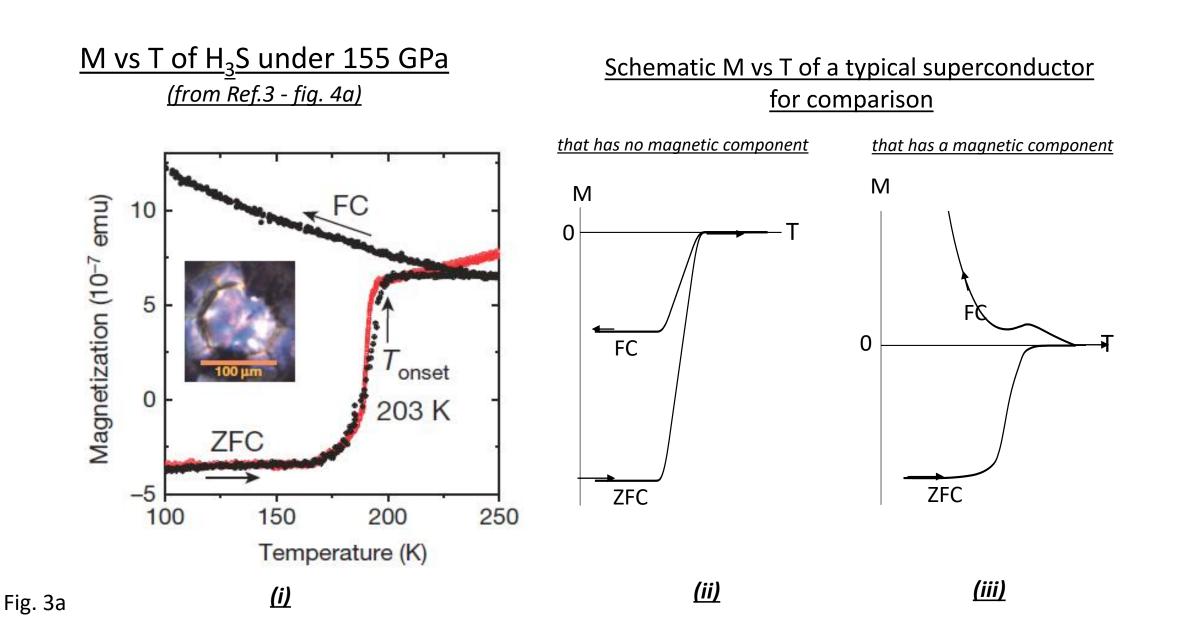
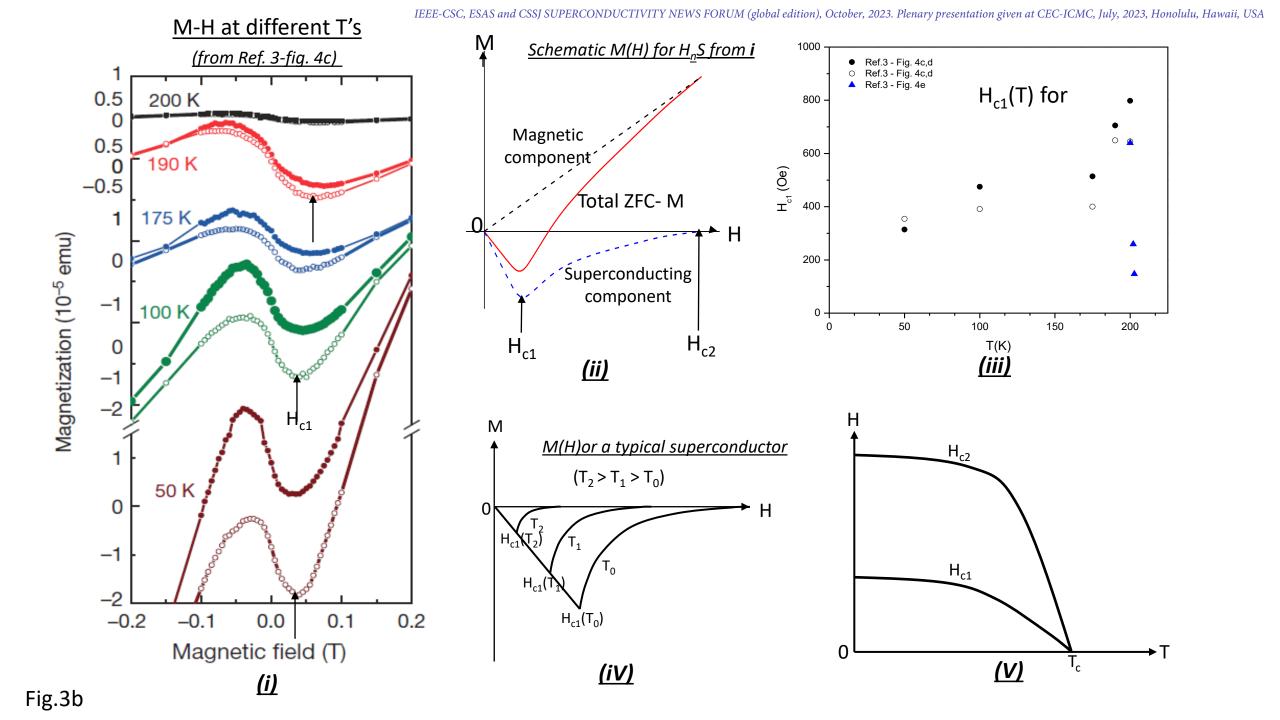


Fig. 2





PHYSICAL REVIEW LETTERS 122, 027001 (2019)

Suggestion Featured in Physics

Hemley et al. - 269 K at 189-100 GPA

Evidence for Superconductivity above 260 K in Lanthanum Superhydride

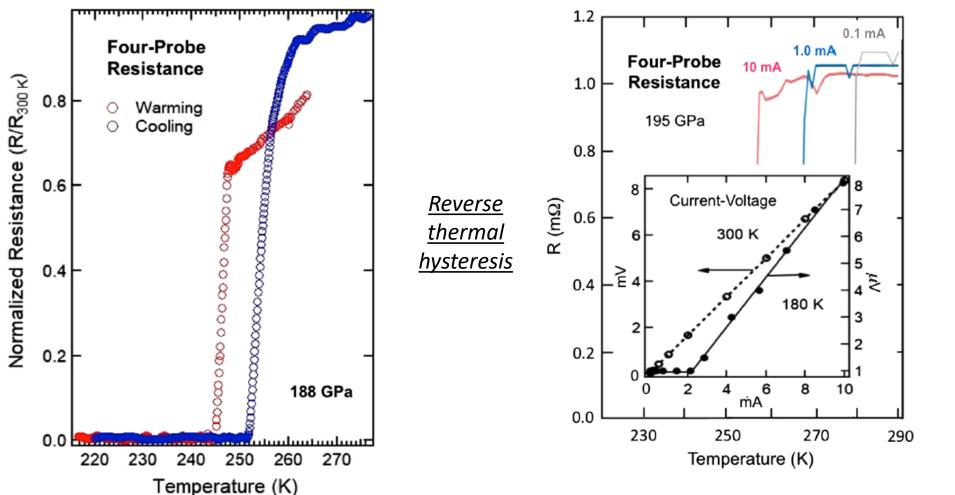


FIG 4 Electrical resistance measurements using the four-prob

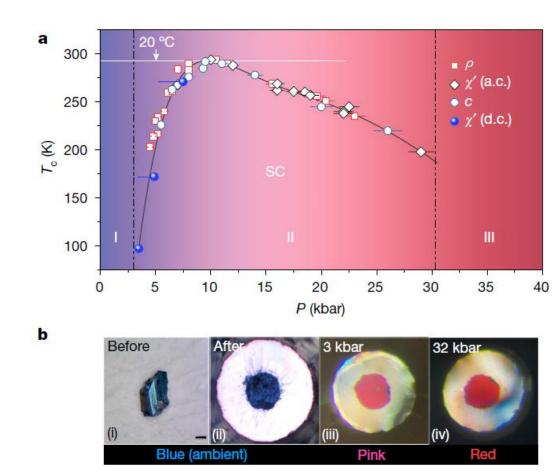
Evidence of near-ambient superconductivity in a N-doped lutetium hydride

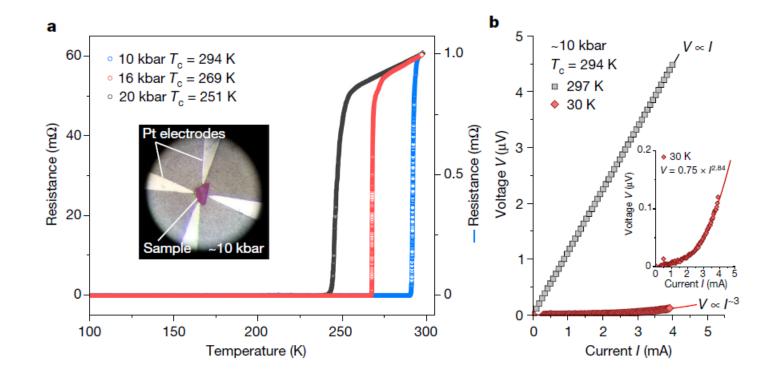
Dias et al, - Lu-NH - 294 K at 1GPa

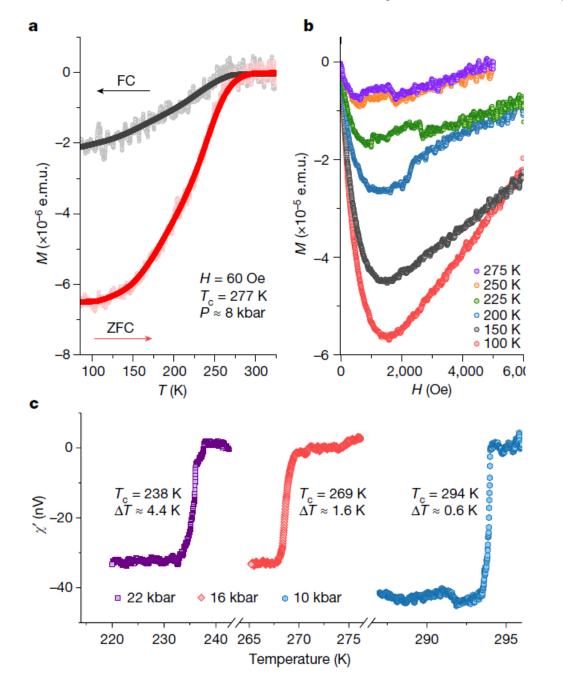
https://doi.org/10.1038/s41586-023-05742-0

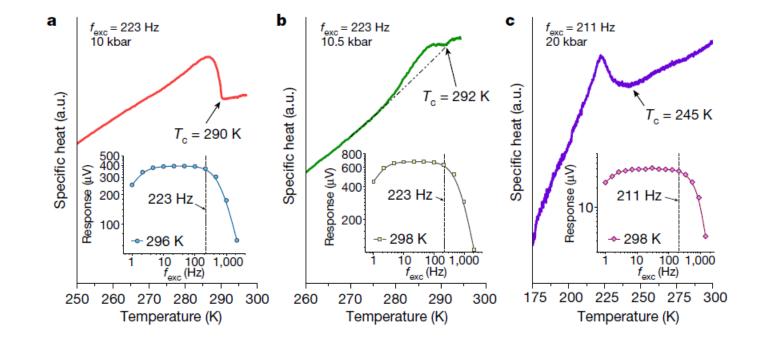
Received: 26 April 2022

Nathan Dasenbrock-Gammon^{1,4}, Elliot Snider^{2,4}, Raymond McBride^{2,4}, Hiranya Pasan^{1,4}, Dylan Durkee^{1,4}, Nugzari Khalvashi-Sutter², Sasanka Munasinghe², Sachith E. Dissanayake², Keith V. Lawler³, Ashkan Salamat³ & Ranga P. Dias^{1,2}







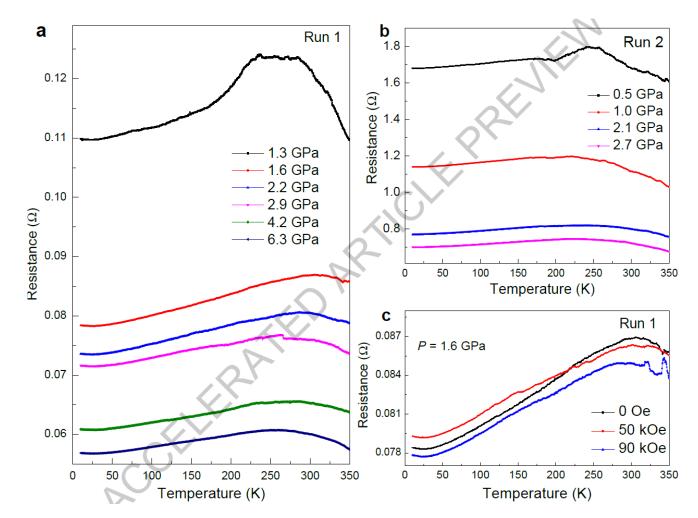




https://doi.org/10.1038/s41586-023-06162-w

Accelerated Article Preview

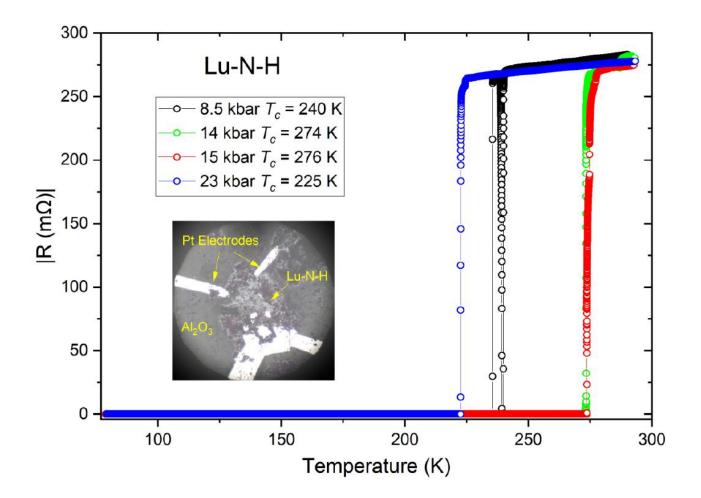




IEEE-CSC, ESAS and CSSJ SUPERCONDUCTIVITY NEWS FORUM (global edition), October, 2023. Plenary presentation given at CEC-ICMC, July, 2023, Honolulu, Hawaii, USA

Evidence for Near Ambient Superconductivity in the Lu-N-H System

Nilesh P. Salke₁, Alexander C. Mark₁, Muhtar Ahart₁, Russell J. Hemley_{1,2,3} 1Department of Physics, 2Department of Chemistry, 3Department of Earth and Environmental Sciences, University of Illinois Chicago, Chicago, IL 60607 USA



The near room-temperature upsurge of electrical resistivity in Lu-H-N is not superconductivity, but a metal-to-poor-conductor transition <u>arXiv. 7/1/23</u>

Di Peng1,2,3, Qiaoshi Zeng1,4,*, Fujun Lan1, Zhenfang Xing1,5, Yang Ding1, Ho-kwang Mao1,4,*

L Center for High Pressure Science and Technology Advanced Research, Shanghai 201203, China

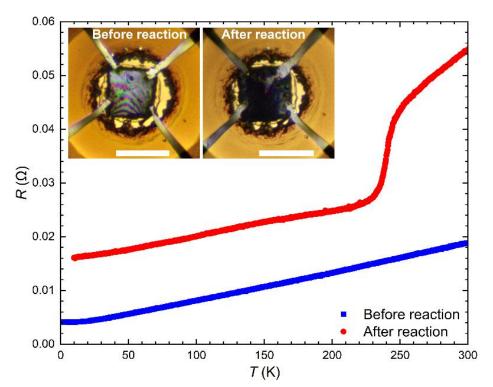
² Key Laboratory of Materials Physics, Institute of Solid State Physics, HFIPS, Chinese Academy of Sciences, Hefei 230031, China

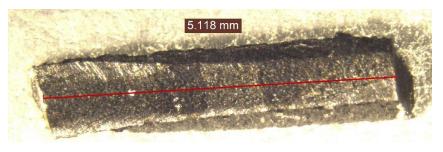
3. University of Science and Technology of China, Hefei 230026, China

A Shanghai Key Laboratory of Material Frontiers Research in Extreme Environments (MFree), Shanghai Advanced Research in Physical Sciences (SHARPS), Shanghai 201203, China

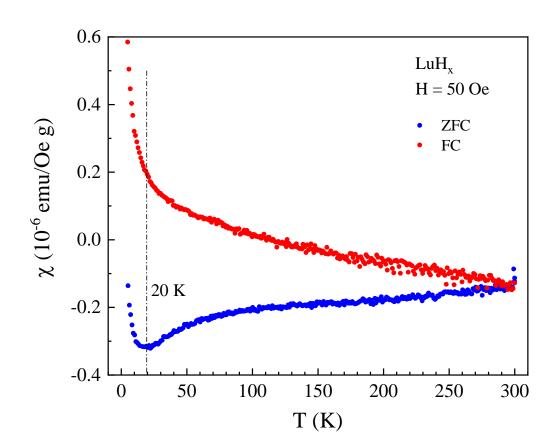
s. State Key Laboratory of Superhard Materials, Institute of Physics, Jilin University, Changchun 130012, China

* E-mail: zengqs@hpstar.ac.cn, or maohk@hpstar.ac.cn

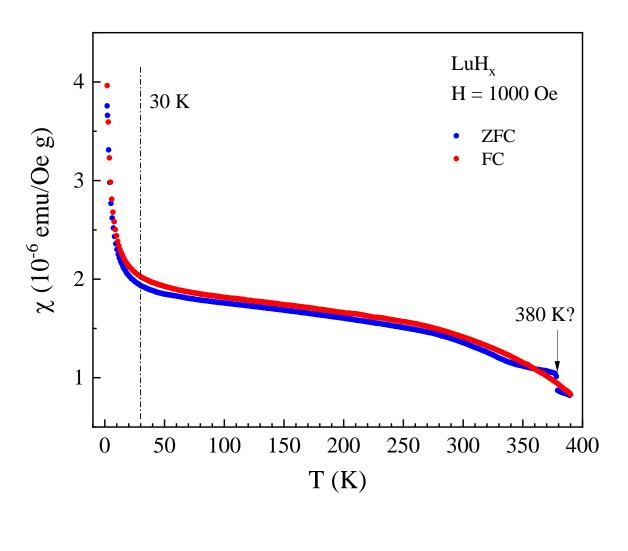




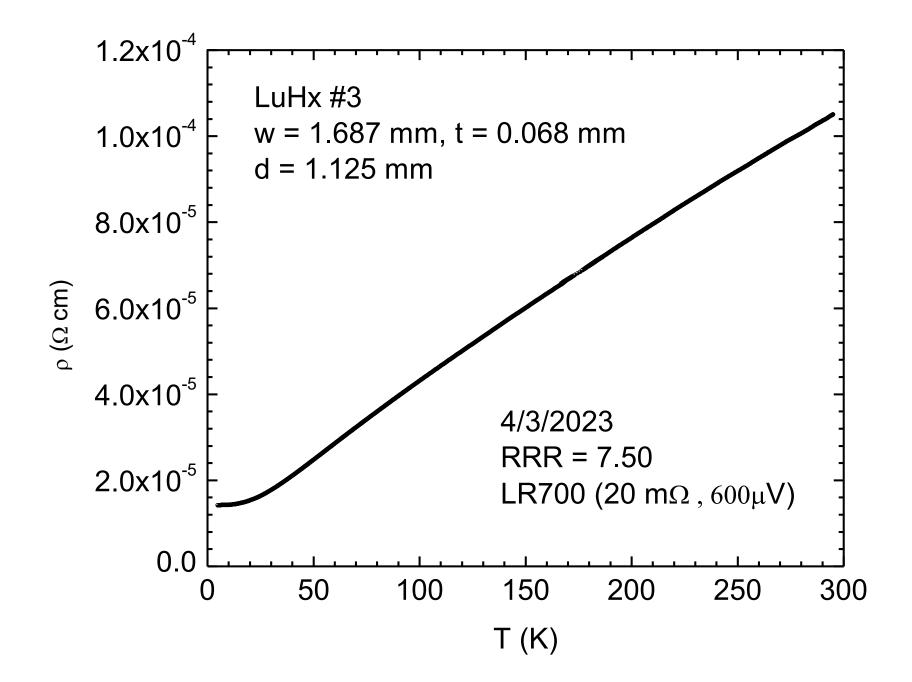
- #1 LuH_x: 5.118 mm \times 1.152 mm \times 0.495 mm
- mass: 23 mg
- Under continuous H_2 , 65 C, for 28.5 hours

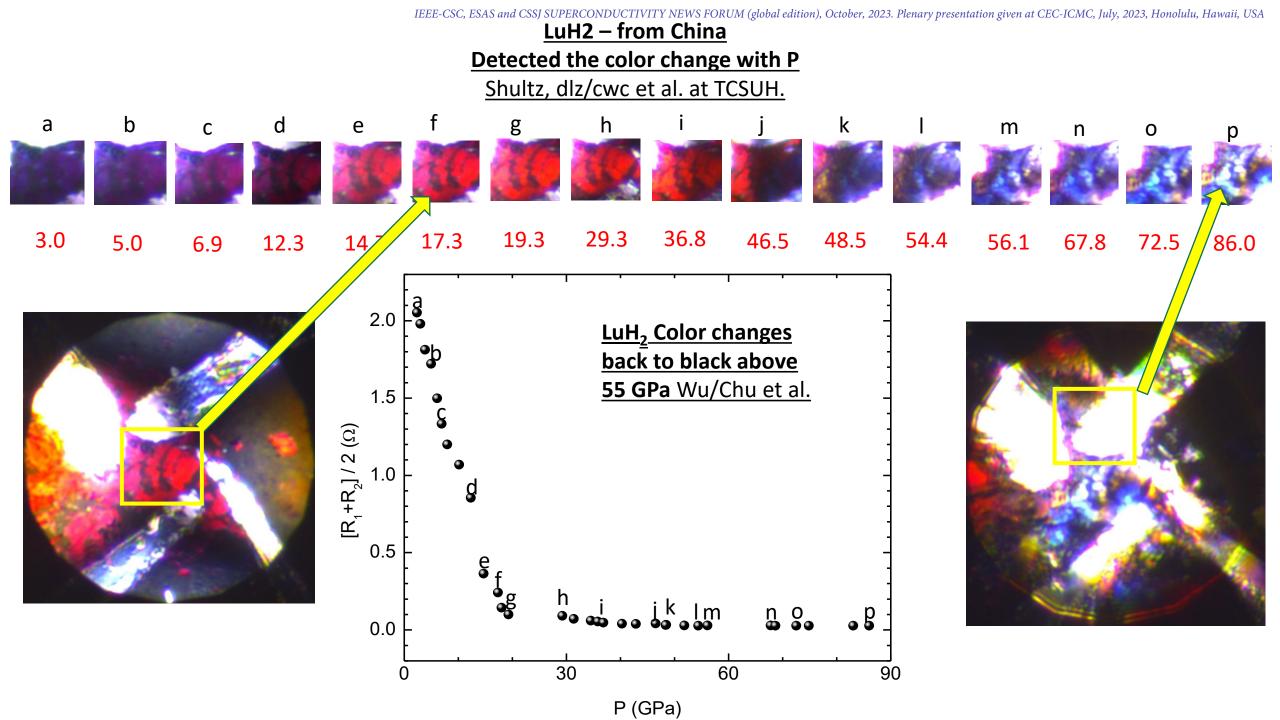


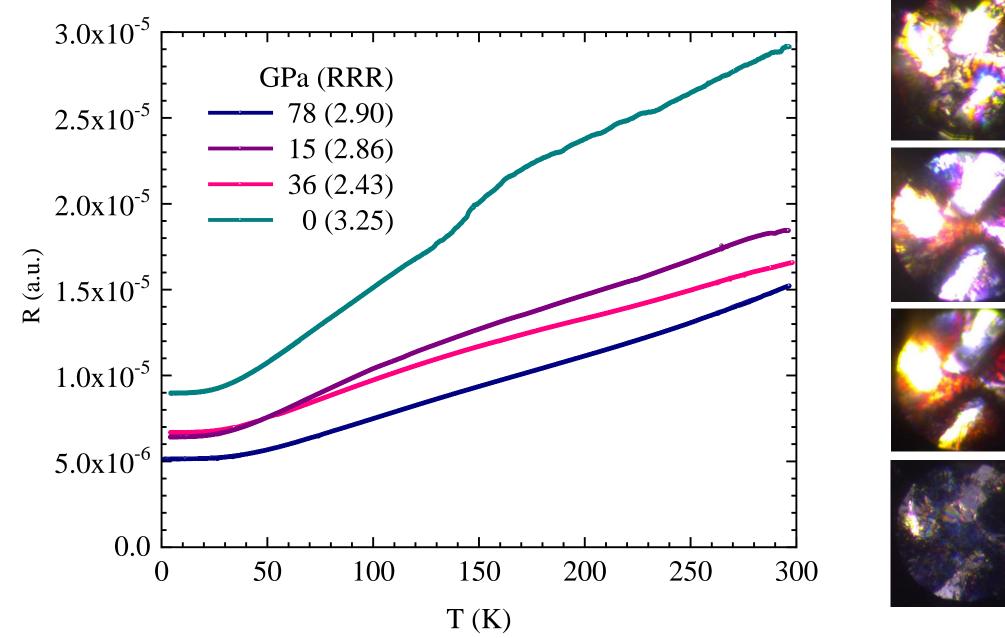
Some Lu-H work at Houston



03/26-27/23







D. Schulze, Z. Wu

78 GPa

15 GPa

36 GPa

Ambient

- If all proven to be true, we now enter the RTS era of hydrides/HTS by replacing the formidable temperature barrier unfortunately by an even more challenging pressure barrier
 - A possible solution- controlled PQP

Pressure-Quench-Process (PQP)

the concept is not new but it is first time used for superconductivity

- "Most of the alloys used in industrial applications are actually metastable at atmospheric pressure and room temperature, and these metastable phases possess desired and/or enhanced properties that their stable counterpart lack."
- Pol Duwez- metastable, supercooled, splat-cooling, Nb₃Ge thin film, diamond
- The high-pressure-induced phases in HTS and RTS may be considered metastable, i.e. kinetically stable but thermodynamically not, protected only by energy barriers. We have taken advantage of these energy barriers to stabilize the metastable or "supercooled" states via pressure-quench at a specific quench-pressure (P_q) and a chosen quench-temperature (T_q)
- Simple element -> binary FeSe -> HBCCO -> hydrides

The PQP for HTS and RTS

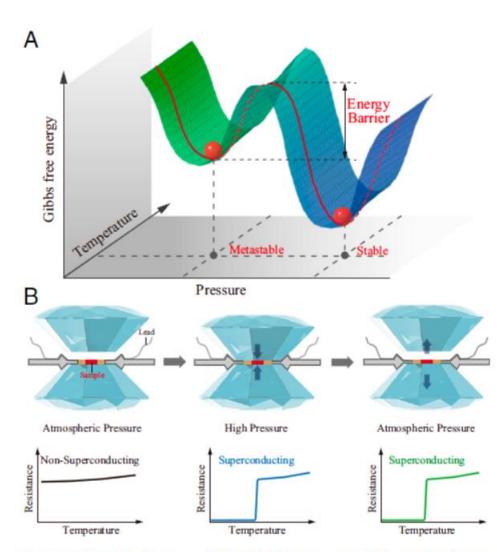
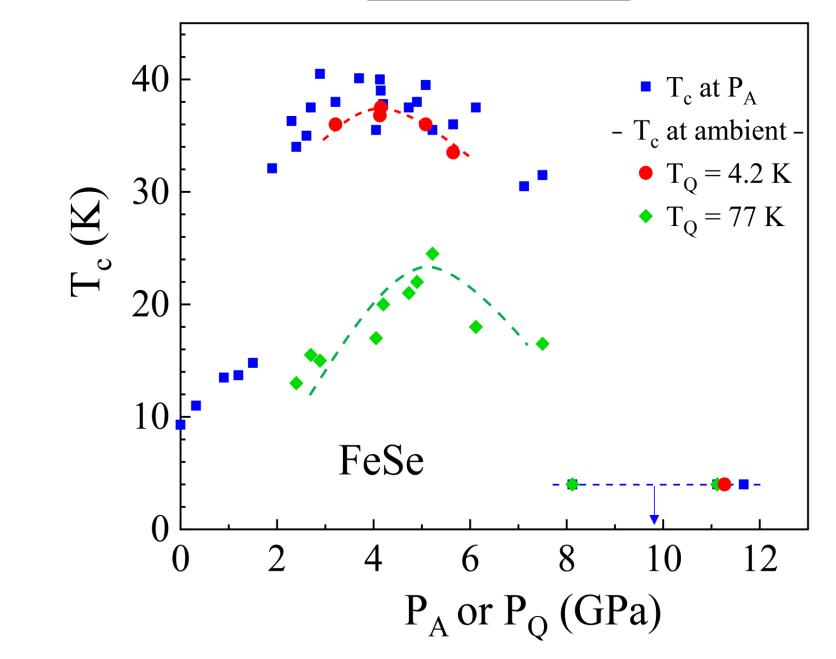
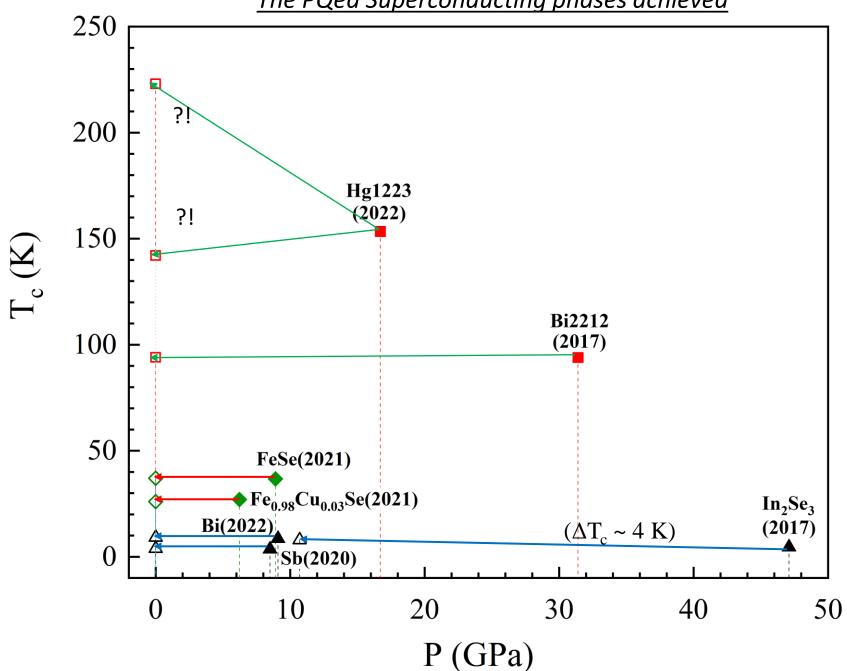


Fig. 1. Schematic diagrams of (A) Gibbs free energy and the energy barrier between the metastable and stable states and (B) the sequence of main experimental steps.

Deng et al. PNAS (2021)





The PQed Superconducting phases achieved

IEEE CSC & ESAS SUPERCONDUCTIVITY NEWS FORUM (global edition), January 2021.

Room-temperature Superconductivity – What More Needs to be Further Studied!

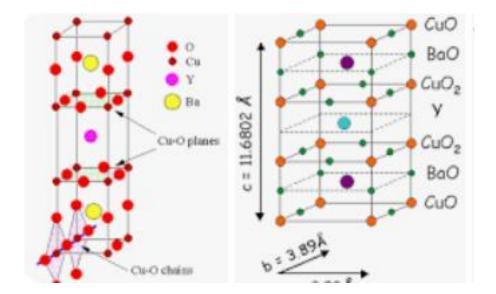
C. W. Chu

TCSUH, University of Houston, Texas

- 1. The existence of a pressure-induced insulator-metal (I-M) transition at a temperature T_m above T_c this is important for exacting information about the normal-state behavior of the superconductor [21].
- 2. The achievement of a real "zero-resistance" state it is extremely challenging to determine the "zero-resistance" or more so the "zero-resistivity" state due to the small size of the sample and the large change of resistance at the transition.
- 3. The field effect on the transition a similar effect has been observed for the not-superconducting I-M transition [22].
- 4. The isotope effect on the transition a similar effect has been observed for the not- superconducting I-M transition [23].
- 5. The diamagnetic shift in ac magnetic susceptibility a similar effect has been detected in a temperature region where resistance changes greatly due to the eddy current.
- 6. Only the detection of the true Meissner effect (in the field-cooled mode) can clarify the above confusion, although the possible inherent defects in the sample under pressure may make such a test difficult. However, the sharpness of the transition may imply that the defects in the sample are small.
- 7. The very sharp transition and the almost downward shift of the transition in the presence of field suggest that the absence of flux flow is very puzzling for a type-II superconductor with such high a T_c [24].
- 8. The absence of a systematic experiment on the same individual sample for different types of measurements makes difficult the judgement of the reproducibility of the experiment this is especially critical in determining the isotope effect [25].
- 9. The exact role of hydrogen in the samples investigated appears not to be clear for instance, the role of B in the B-rich superconducting ZrB_{12} is rather limited [26].
- 10. The retention at ambient without pressure of the ultrahigh-pressure-induced room-temperature superconducting phase in these hydrogen-rich molecular solids should be the most exciting and rewarding endeavor in superconductivity science and technology research and development. Recent preliminary work on several superconducting elements and compounds has demonstrated such a possibility [2].

A Complex Superconductor needs a Skeleton to host substructures Active Component + Charge Reservoir

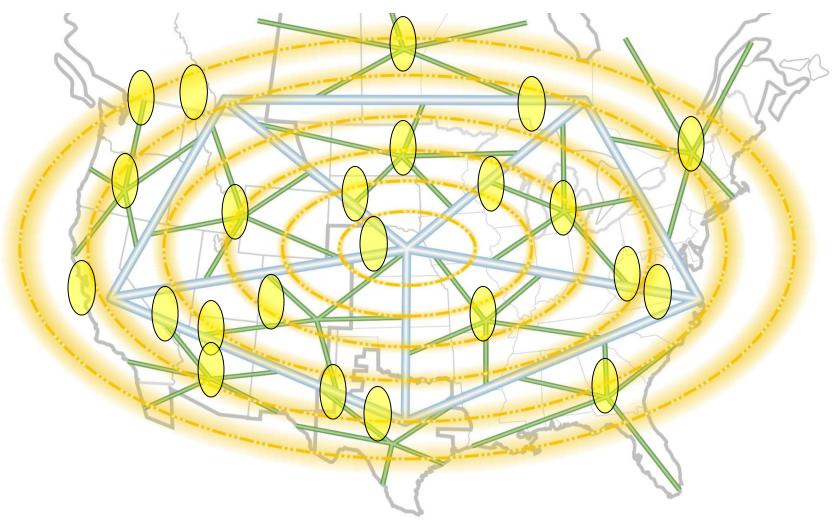
- Laves Phase RERu₂
 A15 NbSn₃
 Chevrel Phase REMo₆S₈
 Rhodium Borides RERh₄B₄
- 5. Cuprates 123 REBa₂Cu₃O₇
- 6. Rare-Earth Hydrides REH_X <u>RE – skeleton, H – active part & charge</u> <u>reservoir? – need more data!</u>



RE affects (1-4) or does not (5, 6?) affect SC. [cwc]

NationalGrid (Jimmy Glotfelty)

Plus Integrated Communications and Controls Architecture



Thank You!