

The 20th Anniversary of the discovery of RBCO
Denver, CO, March 5, 2007

“The Brief History of RBCO”

C. W. Chu

TCSUH, University of Houston
Hong Kong University of Science and Technology
Lawrence Berkeley National Laboratory





Figure
held
New

New York Hilton Hotel, evening of March 18, 1987

Woodstock of Physics

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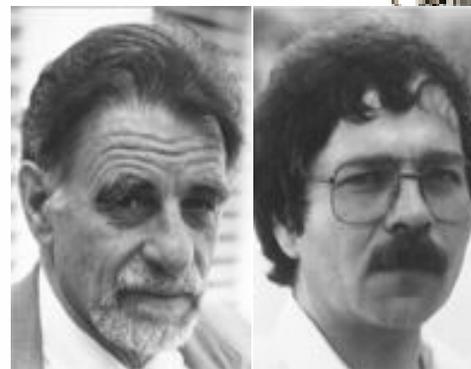
Before Bednorz and Mueller

- Experimentally:
 - $T_c \leq 23.2$ K (1974 - 1986)
 - search for novel materials
- Theoretically:
 - $T_c < 30$'s K (instabilities)
 - propose novel mechanisms
- Confidence crisis in achieving higher T_c

1986: the critical year

Z. Phys. B - Condensed Matter 64, 189-191 (1986)

Condensed
Matter
Zeitschrift
für Physik B
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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 $Ba_xLa_{2-x}Cu_3O_{7-y}$ 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, but 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

- The paper was initially greeted with skepticism by most except a few groups (Tokyo, Houston, Beijing, IBM-Yorktown)
- We confirmed their results in late November
 - The 1986 Fall MRS Meeting (Dec. 4):
 - invited M. K. Wu to join our search
 - showed our preliminary resistive data
 - learned Tokyo's magnetic and structure data

My group was lucky in the right time with the right experience to tackle the High T_c problem

- searched for FE TiO_{2-x} and SrTiO_{3-x} (1968-71) – learned something about perovskites, FE, and handling oxides
- studied $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ (1975-81) – recognized the importance of oxygen in electronic properties and oxide single crystal growth
- controlled the structural instabilities by pressure (1974-78) – gained faith in high T_c since structural instabilities do not suppress T_c much
- examined novel mechanisms proposed – recognized the importance of low dimensionality

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.

PACS numbers: 74.70.Ya

Superconductivity at 52.5 K in the Lanthanum-Barium-Copper-Oxide System *Science*235,567(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 $(\text{La}_{0.9}\text{Ba}_{0.1})_2\text{CuO}_{4-y}$. 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!!!

The New York Times

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NEW YORK, WEDNESDAY, DECEMBER 31, 1986

Front Page

2 Groups Report a Breakthrough In Field of Electrical Conductivity

By WALTER SULLIVAN

After a dozen years of futile efforts to raise the temperature at which materials become superconducting, researchers at the University of Houston and at

....at the University of Houston and at
AT&T Bell Laboratories....

transmission and generation, energy storage and the generation of fusion energy.

Possible Applications

The achievements also mean that superconductivity, in which materials lose all resistance to electricity, can be more widely applied for scientific research and could substantially reduce the cost of the proposed superconducting atom smasher with a 60-mile acceleration ring.

In the early 1970's researchers at Bell Laboratories and Westinghouse found substances that became superconducting when cooled to 23 degrees Kelvin, 23 degrees above absolute zero.

Absolute zero, the total absence of heat, occurs at minus 273 degrees Celsius, or 460 degrees below zero Fahrenheit: 23 Kelvin is equal to minus 250 Celsius,

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Paul C. W. Chu at the University of Houston reported that under high pressure, hundreds of thousands of pounds per square inch, a compound of lanthanum, barium, copper and oxygen becomes superconducting at 40.2 degrees Kelvin.

However, A.T.&T. Bell Laboratories, following a similar line of research, yesterday reported production of an alloy that at normal pressure begins its transition to superconductivity at 40 degrees Kelvin and becomes fully superconducting when cooled to 36 degrees. Participants in that project, while reluctant to provide details until

Continued on Page A13, Column 1

Reproduced B&M results:
Notes to Alex Mueller & CW Chu expressing my confidence on $T_c = 77$ K

Submitted in November
before the deadline 12/5/86
for the APS Meeting in
New York in March 1987

Abstract Submitted
for the March 1987 Meeting of the
American Physical Society
March 16-20, 1987

Sorting C
22a

Study of Oxygen-Deficient Perovskite-Like
 $Ba_xLa_{5-x}Cu_5O_{5(3-y)}$ Compounds. C.W. CHU, K. FOST

GAO, P.H. HOR, Z.J. HUANG, R.L. MENG, S.C. MOSS,
ROBERTSON and Z.X. Zhao, U. of HOUSTON -
Recently, possible percolative superconductivity
~35K was proposed by Bednorg and Müller in oxygen
deficient Ba-La-Cu-O compounds following the dete
of a large resistance R-drop on cooling with an o
suppressable by current. Coprecipitation from aq
solution and low temperature treatments were sugg
to be crucial for the observation of the R-drop.
However, by employing a non-coprecipitation techn
we have obtained $Ba_xLa_{5-x}Cu_5O_{5(3-y)}$ compounds pre
nantly with a tetragonal perovskite structure. S
samples with $x=1$ exhibit a R behavior similar to
previously reported with a ~36 fold R-drop below
An ac diamagnetic signal of <1% occurs at 4K. No
temperature powder x-ray data for samples with an
without the R-drop are very similar except for tw
extremely weak lines. The R-drop disappears afte
samples were exposed to air for six days, resulti
a 10 fold increase in R. At present, the exact n
of the R-drop in $Ba_xLa_{5-x}Cu_5O_{5(3-y)}$ remains unkno
More detailed and systematic studies in sample pr
tion and characterization are in progress.

很可惜到
到SPK
我目前
对77K
充满信心！
下周

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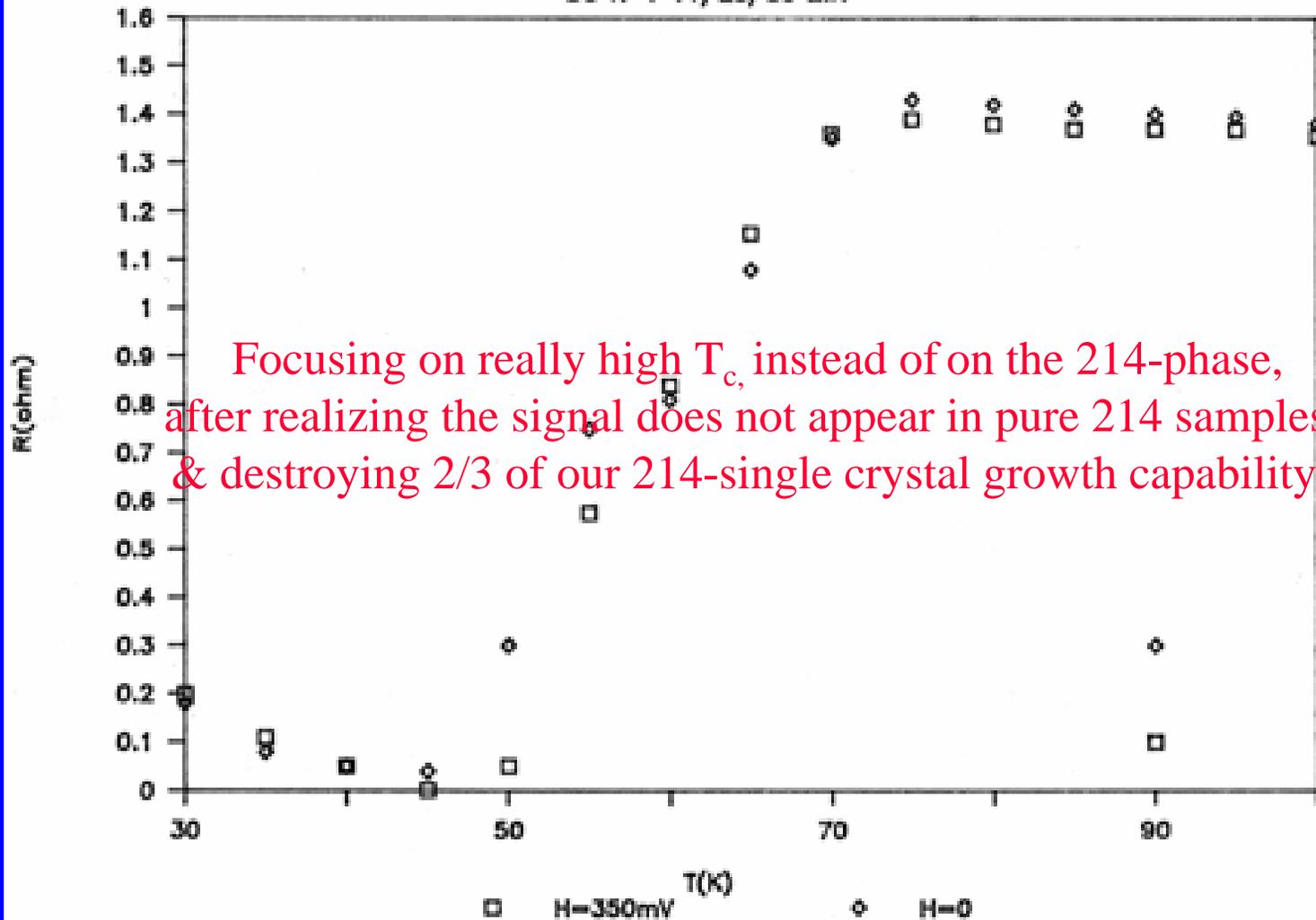
Christmas
the warmth and joy
of remembering friends

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.

Ba-La-Cu-O #1b

DC R-T 11/25/86 Z.H



*First sign of SC above 77 K was detected on November 25, 1986
in multi-phased but not pure 214 samples!
Decided the real high T_c phase cannot be 214 &
to stabilize the phase by replacing La with Y & Lu !*

1987: The Exciting Year



UNITED STATES DEPARTMENT OF COMMERCE
Patent and Trademark Office
Address: COMMISSIONER OF PATENTS AND TRADEMARKS
Washington, D.C. 20231

ARNOLD, WHITE & DURKEE
P.O. BOX 4433
HOUSTON, TX 77210

MAILED

MAR 2 1987

Applicant(s): CHING W. CHU
Serial Number: _____
Filing Date: 1/12/87
Title: SUPERCONDUCTING COMPOSITION
AND METHOD

APPLICATION BRANCH
NOTICE TO FILE MISSING PARTS OF APPLICATION—
FILING DATE GRANTED *Docdel # UNIA: 011*

SEE
UNIA:
011

A filing date has been granted to this application. However, the following parts have been found missing.

If all missing parts are filed within the period set below, the total amount owed by applicant as a large entity, small entity (verified statement filed), is \$ 480.00

- The statutory basic filing fee is: missing, insufficient. Applicant as a large entity, small entity, must submit \$ 480.00 to complete the basic filing fee and MUST ALSO SUBMIT THE SURCHARGE AS INDICATED BELOW.
- Additional claim fees of \$ 34.00 as a large entity, small entity, including any required multiple dependent claim fee, are required. Applicant must submit the additional claim fees or cancel the additional claims for which fees are due. NO SURCHARGE IS REQUIRED FOR THIS ITEM.

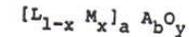
*Under the Urge of the University,
I prepared a patent application in late
December and filed it on January 12,
1987.*

- The signature to the oath or declaration is: missing; a reproduction; by a person other than the inventor or a person qualified under 37 CFR 1.42, 1.43, or 1.47. A properly signed oath or declaration in compliance with 37 CFR 1.63, identifying the application by the above Serial Number and Filing Date is required. A SURCHARGE MUST ALSO BE SUBMITTED AS INDICATED BELOW.
- The signature of the following joint inventor(s) is missing from the oath or declaration: _____ Applicant(s) should provide, if possible an oath or declaration signed by the omitted inventor(s), identifying this application by the above Serial Number and Filing Date. A SURCHARGE MUST ALSO BE SUBMITTED AS INDICATED BELOW.
- The application was filed in a language other than English. Applicant must file a verified English translation of the application and a fee of \$26.00 under 37 CFR 1.17(k), unless this fee has already been paid NO SURCHARGE UNDER 37 CFR 1.16(e) IS REQUIRED FOR THIS ITEM.
- Other:

-17-

WHAT IS CLAIMED IS:

- A superconducting composition having a superconducting transition temperature above about 40° Kelvin. *This was the basis for our work to discover the Y-Ba-Cu 93K superconductor (including the x, a, b)*
- compositio interatomi at atmosph *re in said metal that has those of such at are maintained erature.*
- compositio following *[PR 52, 908 (1987)] re in said defined by the*



wherein L is an element selected from the group consisting of lanthanum, lutetium and yttrium or a mixture of one or more of these elements.

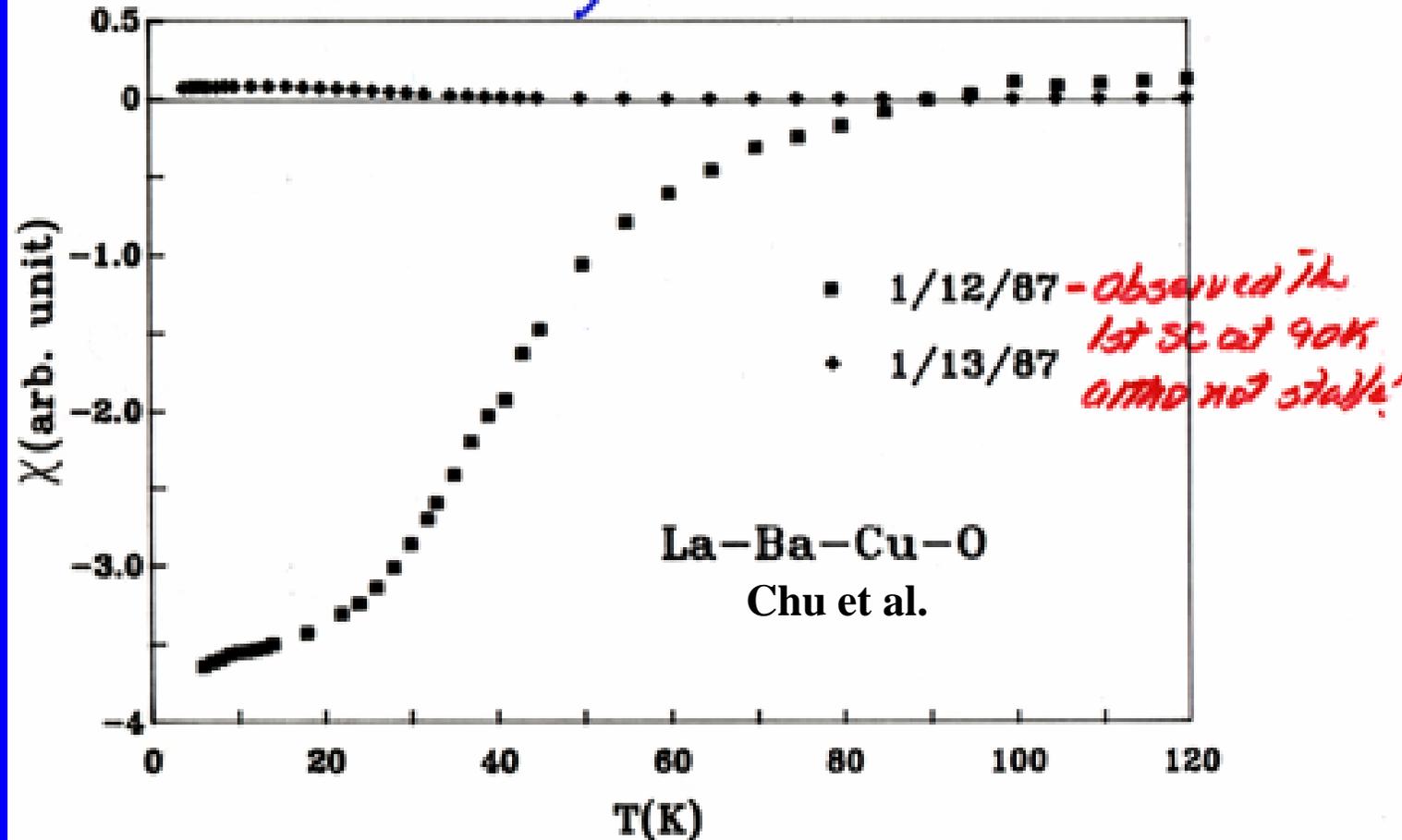
*“..L is an element selected from the group consisting of La, Lu and Y.”
- the basis of later discovery of LBCO & YBCO!*

wherein M is an element selected from the group consisting of barium, strontium, calcium and magnesium or a mixture of one or more of these elements; and

1987: the exciting year

⇒ SC up to 90K must exist!

But stability remains an issue!

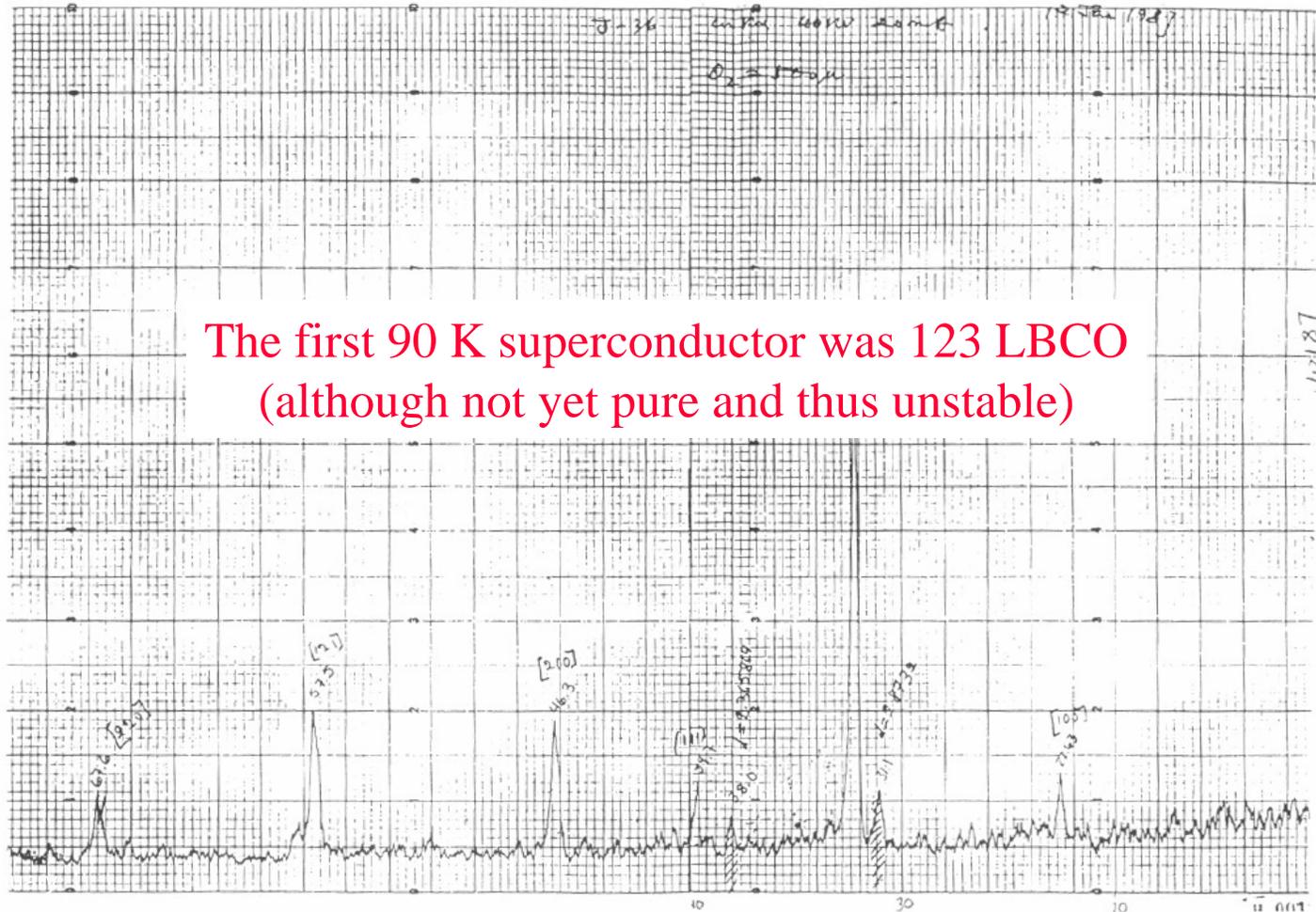


First 90 K - SC was unambiguously observed, although not yet stable.

Later analysis of the X-ray data showed it was

$\text{LaBa}_2\text{Cu}_3\text{O}_7$ (123 or LBCO)

1987: the exciting year

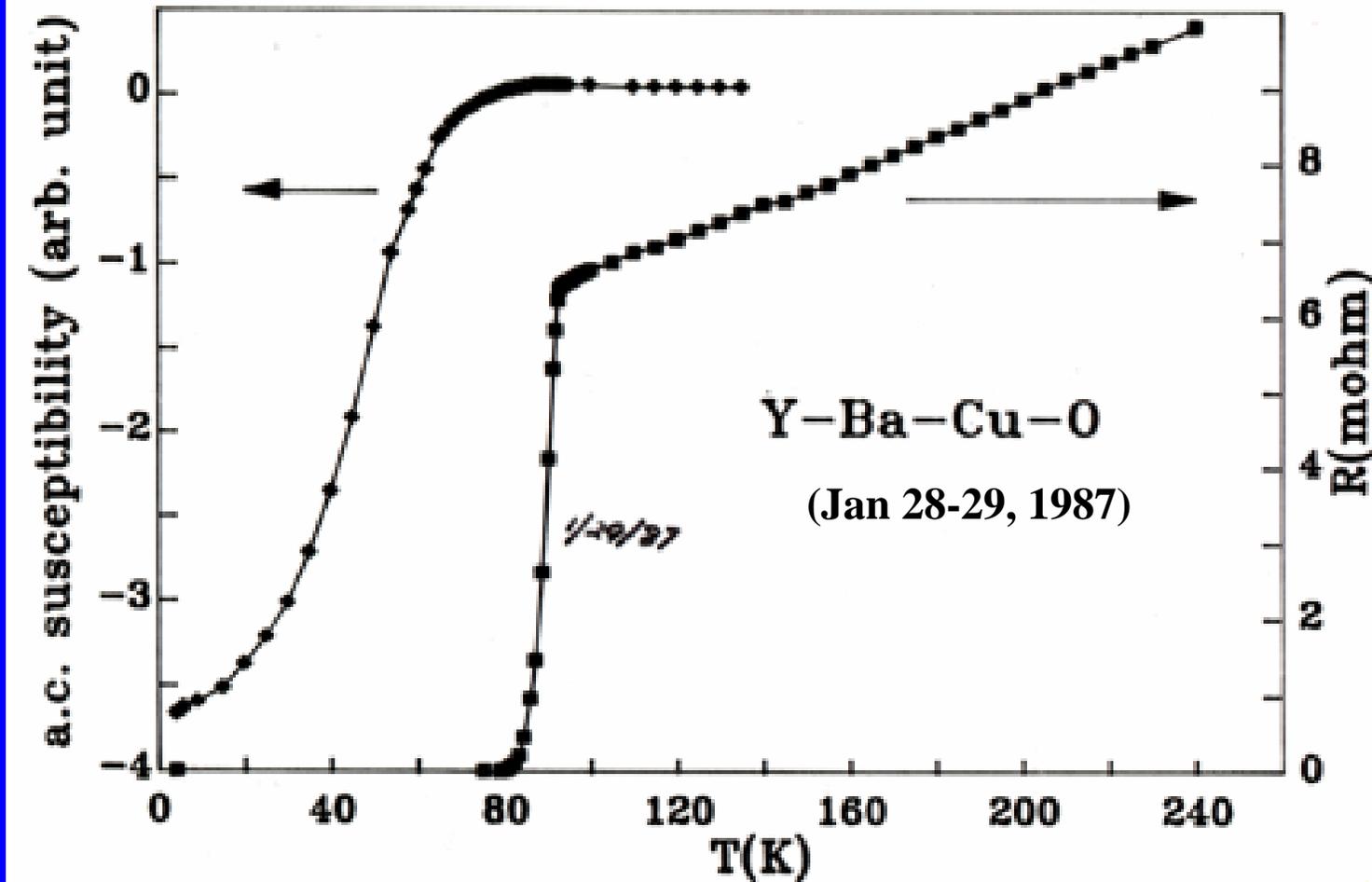


The first 90 K superconductor was 123 LBCO
(although not yet pure and thus unstable)

Figure 7. The November 12, 1987 X-ray powder diffraction of the LBCO sample which displayed the large diamagnetic χ_{ac} -shift indicative of a superconducting transition [Fig. 6), showed the R-123 structure but was only recognized later in March when the R-123 structure was solved [C. W. Chu, Proc. Nat. Acad. Sci. USA 84, 4681 (1987)].

1987: The Exciting Year

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



*SC above 77 K was finally stabilized.
YBa₂Cu₃O₇ (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 at Ambient Pressure

M. K. Wu, J. R. Ashburn, and C. J. Torng

Department of Physics, University of Alabama, Huntsville, Alabama 35894

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 $ABa_2Cu_3O_{6+x}$ 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 $A = La, Nd, Sm, Eu, Gd,$

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

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 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 $Y_{1.2}Ba_{0.8}CuO_{4-\delta}$. Later, superconductivity near 90 K with a zero-resistance state at ~ 70 K was also reported⁸ in the mixed-phase $Lu_{1.8}Ba_{0.2}CuO_4$ compounds. Preliminary examinations showed⁹ that the Y-Ba-Cu-O compounds

are different from those with the K_2NiF_4 structure. Especially evident from the enhancement of the superconducting transition from ~ 30 K in the K_2NiF_4 structure^{1,2} to ~ 90 K in the $ABa_2Cu_3O_{6+x}$ 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 $ABa_2Cu_3O_{6+x}$ 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, $BaCO_3$, 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 ~ 1 mm \times 0.5 mm \times 4 mm were cut from the sintered cylinders. A standard four-lead

YBCO:

- *quality epi-films*
- *robust*
- *high J_c & high H_{ir} above 77 K*



The best material for HTS technology



YBCO was included in the White House Millennium Time Capsule
Closing Ceremony - December 6, 2000 in the National Archives, Washington DC

070221CWC

After 20 years, we have learned:

- *There is no evidence, experimental or theoretical, telling us that room temperature superconductivity is an impossibility.*
- *Be prepared to expect the unexpected.*
 - *More excitements are yet to come.*
- *In Houston, we continue to look for novel HTS, improve existing HTS, understand HTS and develop new uses of HTS & related materials*

THANKS TO

Alex Müller + George Bednorz -

Bernd Matthias + Art Sleight -

John Bardeen, Marvin Cohen, Ted Geballe +

C. Y. Huang -

Art Freeman -

NSF, NASA + UH -

My Colleagues + Students -

7:30 pm
3/18/87
Woodstock
of Physics

The 1987 Team

TCSUH

C. W. Chu: K. Foster, L. Gao, P. H. Hor
Z. J. Huang, R. L. Meng and Y. Q. Wang

Alabama

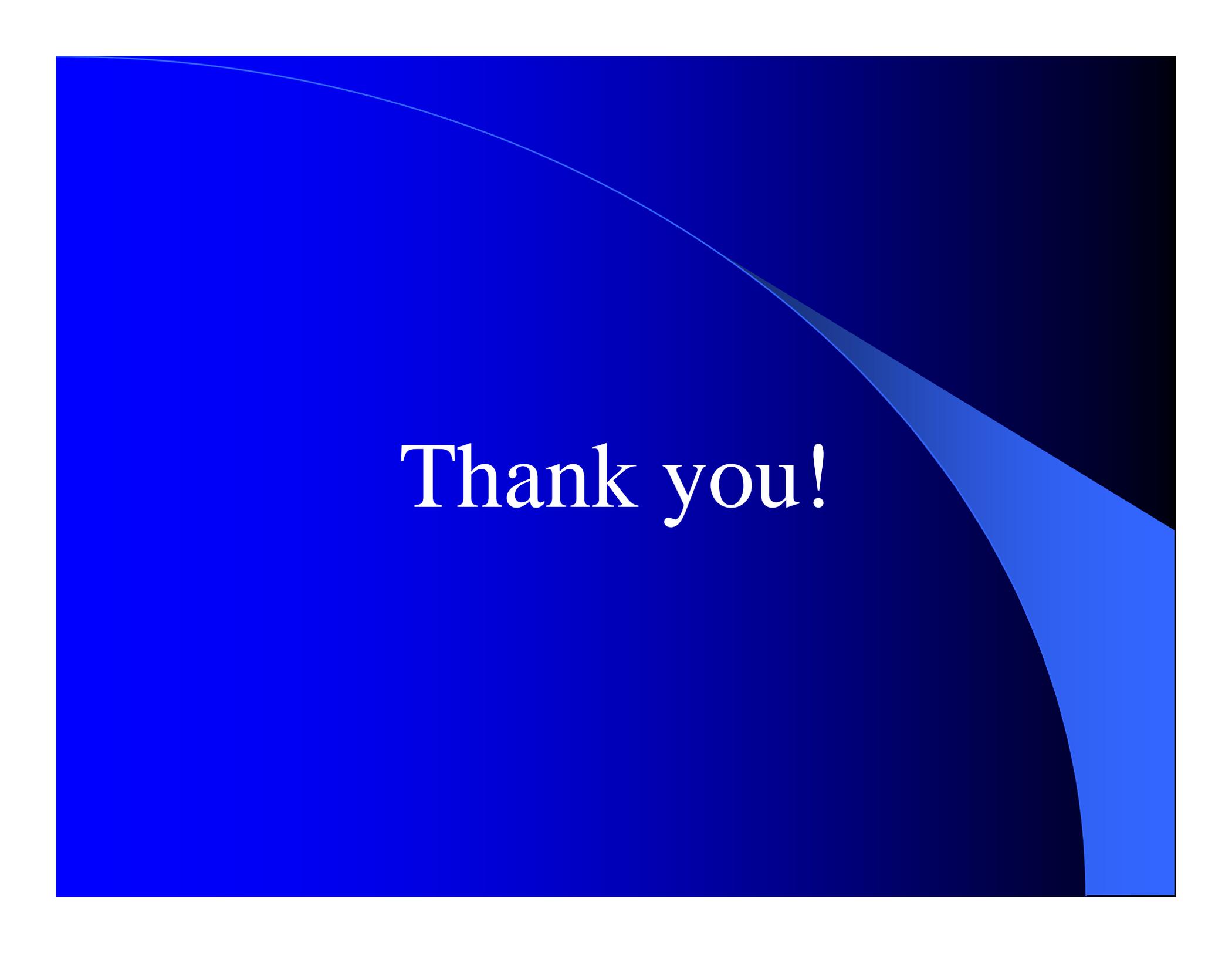
M. K. Wu: J. Ashburn and J. C. Torng

Geophysical Lab

R. Hazan: D. Mao

LANL

C. Y. Huang

The image features a solid blue background with a subtle gradient. A white serif font is centered on the page, reading "Thank you!". The text is the primary focus, set against the uniform blue backdrop.

Thank you!

The Origin of Woodstock of Physics In NY City March 18, 1987

Abstract Submitted
for the March 1987 Meeting of the
American Physical Society
March 16-20, 1987

Sorting Category
22a

Study of Oxygen-Deficient Perovskite-Like
 $Ba_xLa_{5-x}Cu_5O_{5(3-y)}$ Compounds. C.W. CHU, K. FOSTER, L.

GAO, P.H. HOR, Z.J. HUANG, R.L. MENG, S.C. MOSS, L. ROBERTSON and Z.X. Zhao. U. of HOUSTON - Recently, possible percolative superconductivity up to ~35K was proposed by Bednorg and Müller in oxygen-deficient Ba-La-Cu-O compounds following the detection of a large resistance R-drop on cooling with an onset suppressible by current. Coprecipitation from aqueous solution and low temperature treatments were suggested to be crucial for the observation of the R-drop. However, by employing a non-coprecipitation technique, we have obtained $Ba_xLa_{5-x}Cu_5O_{5(3-y)}$ compounds predominantly with a tetragonal perovskite structure. Some samples with $x=1$ exhibit a R behavior similar to that previously reported with a ~36 fold R-drop below ~30K. An ac diamagnetic signal of <1% occurs at 4K. Room temperature powder x-ray data for samples with and without the R-drop are very similar except for two extremely weak lines. The R-drop disappears after some samples were exposed to air for six days, resulting in a 10 fold increase in R. At present, the exact nature of the R-drop in $Ba_xLa_{5-x}Cu_5O_{5(3-y)}$ remains unknown. More detailed and systematic studies in sample preparation and characterization are in progress.

The American Physical Society

W. W. HAVENS, JR., EXECUTIVE SECRETARY
M. A. FORMAN, DEPUTY EXECUTIVE SECRETARY

335 EAST 48TH STREET
NEW YORK, N.Y. 10017
(212) 682-7341

8 December 1986

Dear Colleague:

Your abstract has been rejected for the meeting of the American Physical Society for which you submitted it because it did not conform to the rules and regulations for submission of abstracts specified by the Executive Secretary and approved by the Council.

The rule to which your abstract did not conform is checked below:

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() Your abstract was not signed in the lower right hand corner.

() Your abstract did not include the name of the author or his affiliation in the abstract.

*Origin of the
"Woodstock of
Physics" held*

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Figure
held
New

New York Hilton Hotel, evening of March 18, 1987

Woodstock of Physics

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The Panel Discussion, March 18, 1987



Figure 1.3 Some of the protagonists of the special session on superconductivity (March 1987, APS Meeting, Hilton Hotel, New York City). From left to right: Alex Müller, Paul Chu, and Shoji Tanaka. (Courtesy of the American Institute of Physics Niels Bohr Library.)

