

Below is an analysis of the Houston account presented to the UAHuntsville patent attorney as reconstructed largely from Ruling Meng's declaration, deposition, and notebook pages. It has received only the most minor of edits since 14 March 1994 and has not been updated to reflect the additional information received many years later, including several more pages from Meng's notebooks. However, I anticipate that those pages will only confirm my assertions.

*Jim Ashburn
26 October 2011*

Through approximately 9 January 1987:

Exhibit A of Ms. Meng's declaration indicates that the earliest University of Houston compositions tested were identical to those of the original work of J. G. Bednorz and K. A. Muller of IBM Zurich. Bednorz and Muller's original Zeitschrift fur Physik paper noted that the apparent superconducting phase was of the K_2NiF_4 (or "2-1-4") structure. Koichi Kitazawa of the University of Tokyo confirmed this on 5 December 1986 at the Materials Research Society meeting in Boston where Messrs. Chu and Wu were in attendance. It is likely that the Houston group (like the Huntsville group) researched earlier work on the copper oxides by C. Michel, B. Raveau, and coworkers of the Laboratoire de Cristallographie et Sciences des Materiaux (upon which Bednorz and Muller based their work). A substantial portion of the Michel/Raveau team work focused on the "2-1-4" compounds La-Ae-Cu-O (Ae=alkali earth-- Ba, Sr, Ca). Because of the metallic nature of many of these compounds, the Michel/Raveau team performed resistivity tests on many of these materials, with a particular emphasis on the Sr compound, down to 77 K.

Therefore, it was logical for Houston (as it was with Huntsville and others) to examine the 2-1-4 phases as the probable source of superconductivity in the copper oxides. This is indicated in exhibit A of Ms. Meng's declaration and most of the subsequent exhibits. The Michel/Raveau team tested (including resistivity) their 2-1-4 materials over wide ranges of alkali earth contents. Their results demonstrated that the most metallic behavior was achieved with relatively low alkali-earth concentrations (<20% Ae for La substitution). Therefore, it was logical for Houston to begin with a range of compositions (exhibit A, page dated 9 December, samples J-1 to J-6). Initial resistivity tests would quickly reveal that the more metallic low Ba (<15% substitution for La) samples yielded the best results, although the right half of the table typically showing her test results (exhibit A, page dated 9 December) has been curiously omitted. Ms. Meng's statements on paragraph 6 of her declaration are ambiguous concerning which "certain samples" yielded positive results. However, samples J-7 to J-49 of

exhibits A and D indicate that the low Ba (<15%) samples were indeed most promising and subsequent efforts concentrated on such samples. In addition, samples processed at higher temperatures (~1100 °C) were soon found to yield the best results (samples J-17 to J-49, exhibits A and D). The lower alkali earth content and higher processing temperature are still favored today.

Given that samples of composition near $(\text{La}_{0.9}\text{Ba}_{0.1})_2\text{CuO}_4$ processed at ~1100 °C proved optimal for that system, it was “obvious” (Robert Hazen, The Breakthrough: The Race for the Superconductor, Summit Books, New York, 1988, page 43) for the Houston group (as with Huntsville and others) to simply replace Ba with Sr while preserving the basic stoichiometry and temperature. This is indicated by samples SL-1 to SL-13 (exhibit C, early January as indicated by the 7 January date between SL-6 and SL-7). The first sample for which a successful test was performed without a malfunction (SL-2, exhibit C) indicated a 45 K transition onset, higher than that of the analogous Ba samples. The test confirmed that La-Ba-Cu-O was only one superconductor within a class of such materials.

$(\text{La}_{0.9}\text{Ca}_{0.1})_2\text{CuO}_4$ (moving up the alkali earth column) was the obvious next candidate (samples CL-1 and CL-2, exhibit C), presumably tested prior to **the 15 January date of exhibit F** and the 18 January date indicated in exhibit D where the La-Sr-Cu-O series resumes (SL-14 to SL-17). A graph of the results of sample J-31 dated 12 January in a paper co-authored by Ms. Meng (“Discovery and Physics of Superconductivity above 90 K,” Novel Superconductivity, ed. Stuart Wolf and Vladimir Kresin, Plenum, New York/London, 1987, The Proceedings of the International Workshop on Novel Mechanisms of Superconductivity, 22-26 June 1987, Berkeley, CA, bottom of page 583) appears to place the La-Ca-Cu-O samples (also mentioned in Novel Superconductivity, top of page 583) prior to that date. **At the very least, Ms. Meng’s recollection of “on or two [Ca] sample” (deposition, page 40) possibly done concurrently with the Sr substitutions (deposition, page 51) appears to place the Ca materials prior to 28 January, the day the Sr work appears to have been terminated indefinitely.** A transition onset of 30 K is indicated for CL-1 (30 K onset, 16.5 K completion, exhibit C), disappointingly lower than that of $(\text{La}_{0.9}\text{Sr}_{0.1})_2\text{CuO}_4$ and even lower than the better Ba samples.

Approximately 9 January through approximately 11 January 1987:

Without the benefit of further guidance from the Michel/Raveau work, two possible paths were then apparent-- either continue with the alkali earth series (sample ML-1 containing magnesium which undoubtedly failed, exhibit C) or switch to replacing the rare earth element La. In Mr. Hazen's words (The Breakthrough: The Race for the Superconductor, page 49),

So lanthanum was the obvious next element to alter.

In Ms. Meng's words (deposition, page 51),

...so therefore, naturally idea replace the first element.

What is unclear from Ms. Meng's testimony is why barium and not the smaller strontium is "definitely" the "obvious" second element at this point (deposition, page 28),

Obviously only replace the lanthanum so the formulas definitely should be yttrium, barium, copper oxide, or lutetium, barium, copper oxide.

Any individual with minimal superconductivity experience was well aware of the detrimental effect of ferromagnetic impurities in conventional superconductors and so would tend to shy away from the lanthanides. In Mr. Chu's words after the eventual discovery, "to our great surprise, the complete replacement of Y even with the most magnetic Gd does not affect the T_c of these [the "1-2-3"] compounds" (Novel Superconductivity, page 585). However, not all of the lanthanides are ferromagnetic in all of their valence states. In their oxide forms, Ce (as CeO_2) is quadrivalent, thereby emptying its f-shell and possessing no magnetic moment. Lu (as Lu_2O_3), retains a full f-shell and consequently no magnetic moment. All other lanthanides (including Yb, see appendix B) break their f-shell as oxides. Therefore, Ce and Lu, along with the rare earth Y (and the extremely expensive Sc) seemed promising candidates to replace the nonmagnetic La.

Ce, Lu, and Y were all immediately available and samples analogous to $(La_{0.9}Ba_{0.1})_2CuO_4$ and $(La_{0.9}Sr_{0.1})_2CuO_4$ with the appropriate elements substituted for La were prepared (samples CeS-1, CeS-2, CeB-1, CeB-2, YS-1, YB-1, LuS-1, and LuB-

1, exhibit C), again presumably prior to **the 15 January date of exhibit F (describing additional Y-Sr-Cu-O and Y-Ba-Cu-O compositions) and** the 18 January date of exhibit D (**resumption of La-Sr-Cu-O series**). Sample J-31 mentioned above appears to place these new compositions prior to 12 January as well. Possibly stemming from Mr. Chu's extensive work with $\text{Ba}(\text{Pb,Bi})\text{O}_3$, the previous high T_c record holder among perovskites or perovskite-like compounds (see Novel Superconductivity, page 581), a $(\text{La}_{0.9}\text{Pb}_{0.1})_2\text{CuO}_4$ sample (PL-1, exhibit C) was also produced. Note that the favored maximum processing temperature among all of these and subsequent samples continues to be $\sim 1100^\circ\text{C}$. Of the new rare earth samples, none were indicated as superconducting. In fact, the Y and Lu samples were specifically indicated as insulators (exhibit C and deposition, pages 71 and 74), a very discouraging result.

It is likely that several other groups had tested samples similar in composition to YB-1 since the University of Tokyo, for example, reported retesting (after the Huntsville/Houston announcement) their early Y-Ba-Cu-O samples magnetically (having dismissed them as insulating due the distinctive green color consistent with the above stoichiometry) and detecting trace amounts of the superconducting phase (Nova, "The Race for the Superconductor, 1988). **Robert Hazen describes their frustration at the March 1987 APS meeting as follows (The Breakthrough: The Race for the Superconductor, page 237),**

The Tokyo spokesman told of a month of frustration synthesizing "many green stuffs," because the furnace temperature was slightly too high.

Note that only green (Y_2BaCuO_5), blue-green ($\text{Y}_2\text{Cu}_2\text{O}_5$), and transparent (Y_2O_3) phases exist at equilibrium in $(\text{Y}_{1-x}\text{Ba}_x)_2\text{CuO}_4$ when $x \leq 0.25$. Samples YB-1, SB-2, and SB-3 (exhibits C and F) fall into this category. The black superconducting phase exists at equilibrium only in the narrow window $0.33 < x < 0.50$. John Rowell of Bell Communications Research reported that Bellcore prepared several Y-Ba-Cu-O samples on 3 January 1987 which initial tests indicated were not superconducting. Again, after learning of the Huntsville results, the samples were subjected to more thorough testing, which indicated that trace amounts of the 93 K superconducting phase were present (Physics Today, April 1987, page 19). D. R. Clarke of IBM's Thomas J. Watson Research Center noted, "In retrospect, it appears that a number of groups were making a straightforward substitution of Y for La under the assumption that the compound Y_2CuO_4 analogous to La_2CuO_4 exists" (Advanced Ceramic Superconductors,

“Advanced Ceramic Materials,” Volume 2, Number 3B, Special Issue, July 1987, page 275). R. S. Roth, et al. note on page 303 of the same publication, “many physicists attempted to form K_2NiF_4 type phases of the sort ‘ $Y_{2-x}Ba_xCuO_4$ ’.” These commentaries point out the critical factor in the eventual discovery was not the simple use of the element Y (which was attempted by several groups) but instead its combination with Ba (over Sr or Ca) accompanied by a high level of alkali earth substitution for the rare earth element. Note that Mr. Chu’s “high pressure/small ion” arguments are in direct conflict with these two factors.

This premise is outlined in Ms. Meng’s deposition and the Novel Superconductivity paper as follows (**pages 582-583**),

To simulate the pressure effect, we replaced Ba with the smaller Sr and found $(La_{1-x}Sr_x)_2CuO_{4-\delta}$ to superconduct with a $T_{c0} \sim 42.5$ K at ambient pressure... Unfortunately, we observed that $(La_{1-x}Ca_x)_2CuO_{4-\delta}$ only has a $T_c \sim 20$ K, although Ca has a smaller radius than Sr. This immediately showed that the mere reduction in inter-atomic distance cannot continue to raise T_c to above 60 K in oxides with the K_2NiF_4 structure.

In her deposition, she describes it this way (pages 31-33),

A: Right up till we make the first sample, lanthanum, barium, copper oxide, we immediately apply the pressure, the T_c was going up, the transition temperature was going up, so that indicate we should have smaller atomic radius [amended wording] to replace barium. That’s Dr. Chu’s expertise in high pressure/low temperatures, so it’s obvious he can see the result.

Q: Why did higher pressure indicate a smaller atomic radius [amended wording]?

A: Because when you apply the pressure, you are going to squeeze the atom close to each other. The same effect. Just like the same effect. You use more atom in the structure, you can see the uni-cell, small atom, they are close together. If a big atom, you apply the pressure and squeeze them together.

Q: Is my understanding correct that as long as the same family of properties was maintained, the smaller the atomic radius, the more likely it would be to exhibit improved T_c ?

A: Not necessary. For example, calcium is much smaller than strontium, but the transition temperature is lower than strontium.

Q: Okay. Based only on the theory alone of replacement with elements having a smaller atomic radius [amended wording], without regard to actual testing, would you have expected calcium to give a superior T_c ?

A: Yes. Before we tested, we expecting calcium to be higher.

Approximately 11 January through approximately 28 January 1987:

At this point, it is interesting to compare how the initial Ca and Y results were to affect subsequent efforts. Ms. Meng confirms that Mr. Chu's abilities had failed him with the original Ca samples (deposition excerpt above, pages 31-33 and again on pages 49-51), finding a T_c "unfortunately" (Novel Superconductivity, page 583) lower than those of the Ba and Sr samples. Ms. Meng states only a few samples were made (deposition, pages 39) and her declaration indicates that La-Ca-Cu-O was only briefly revisited (CL-4 to CL-7, exhibit D). Whereas the $T_c \sim 25$ K in the early Ca samples was interpreted as a failure, earning the materials only a brief revisit, the early Y samples were indicated as electrically insulating, the worst of all possible results. However, as will be shown below, Y was revisited at an unprecedented pace. Incidentally, the Y^{3+} ion is smaller than the Ca^{2+} ion.

Into mid and late January, tests on La-Ba-Cu-O and La-Sr-Cu-O resumed priority as attempts to find new materials were apparently abandoned. La-Ca-Cu-O compositions bracketing those of the earlier samples were formulated and tested (CL-4 to CL-7, exhibit D). **Analogous** bracketing Y-Sr-Cu-O and Y-Ba-Cu-O compositions were formulated (exhibit F, 15 January), but the weight calculations appear to have been abandoned before completion (see sample YS-3, bottom, exhibit F). Relatively high (33%) alkali earth compositions were considered (samples SY-3 and SB-3, presumably mislabeled from YS-3 and YB-3 as indicated by Ms. Meng's deposition, pages 104-105; similar mislabeling occurred in Huntsville) but crossed out and replaced with very low (0.075) amounts. Presumably, these samples were never made. If they were made and tested, the results were likely equally discouraging. The presence of the $(Y_{0.6}Ba_{0.4})_2CuO_4$ composition in exhibit C (possessing no associated acronym and not reappearing until 29 January) is difficult to reconcile with the trends established in the samples actually fabricated and tested. **Note that no analogous $(Y_{0.6}Ca_{0.4})_2CuO_4$ or $(Y_{0.6}Sr_{0.4})_2CuO_4$ compositions appear in Ms. Meng's notebooks, marking the only example prior to 29 January where the three series diverge.**

Presumably, sample J-31 mentioned above was tested during this period. Ms. Meng's paper describes the detection of superconductivity near 100 K in this "Ba-rich LaBCO" sample processed (strangely enough) in an "oxygen deficient environment." The "Ba-rich" nature of the sample is reiterated in a rather oddly worded sentence at the start of the paragraph leading into the initial Y-Ba-Cu-O results (page 584):

La (in Ba-rich LaBCO) is the largest among all rare-earth elements.

The wording is unusual since La is the largest of the rare-earth ions for a given valence state, independent of the compound in which it occurs. Curiously, Ms. Meng makes no reference to this sample or the corresponding test results in either her declaration or deposition, despite the importance it is given in the paper as a bridge to the first successful yttrium samples (which, of course, were high in barium).

The statement in Novel Superconductivity also calls into question the relative importance of Mr. Chu's high pressure results pointing the way to smaller ions. Note that the ionic radius of barium is among the largest of all cations. In contrast with Mr. Chu's "high pressure/small ion" arguments, his "barium-rich LaBCO" sample would appear to point the way towards larger ions. The high pressure results appear irrelevant, since a Geiger counter would quickly discourage anyone from moving down the periodic table (**to larger ions**) from Barium to Radium or Lanthanum to Actinium (150 times more active than Radium). Robert Hazen states (The Breakthrough: The Race for the Superconductor, page 43),

Even without the striking high-pressure results, the strontium-for-barium substitution was attempted by several other labs,

listing four such groups in addition to Houston. **Incidentally, Bi and Tl are the largest non-rare earth non-radioactive stable trivalent ions. These elements became the basis for the current 100 K+ superconductors.**

In my opinion, the unwarranted emphasis given the high pressure measurements is an attempt to create the impression that Mr. Chu had a unique insight into the materials critical to the discovery that was unavailable to those who did not perform such measurements. A survey of the literature reveals that very few groups perform such high pressure measurements and even fewer specialize in them. **An article in the Houston Chronicle from 16 February 1987 (pages 1 and 5) provides an excellent example of the overemphasis given the high pressure work. The article describes "Chu's**

discovery of the role of pressure in superconductivity, now called the 'Chu effect'" as the "most important issue" in the competition between the various laboratories seeking new materials. The University of Houston dean of natural sciences and mathematics, Roy Weinstein, is quoted as saying,

There is some hope that Chu will get a Nobel Prize out of this. If he does, it will be for discovering the role of pressure.

The article goes on to say,

Weinstein says the Chu effect has revealed a whole new group of substances which are, or may be, superconductors,

presumably a reference to the 12 January University of Houston patent application as suggested by a statement later in the article,

Weinstein said the university has applied for a patent on Chu's discoveries, claiming a huge variety of chemicals and processes to make superconductors.

Weinstein's explanation of the "high pressure/small ion" premise reads,

When you apply pressure you reduce the spacing between the individual parts of the molecules. What's important is to close up the internal spaces. This can be done by filling in those spaces with smaller atoms.

However, I am unaware of any interstitial additions to any existing high-temperature superconductors resulting in an increase in critical temperature. The article even credits Chu with discovering that high pressures influence superconducting properties,

Before Chu's discovery, pressure was not thought to have any effect on superconducting materials.

In addition to wrongfully attributing the discovery to Chu's "high pressure/small ion" premise, the article misrepresents the nature of the original IBM-Zurich discovery, stating,

Weinstein says... the actual production of a superconductor from [the original IBM-Zurich] material... was first achieved at the University of Houston.

Weinstein is further quoted as saying,

IBM-Zurich found some promising material. They didn't know how to make it a superconductor.

Ms. Meng's confidence in Mr. Chu's abilities to predict the success of new materials is difficult to quantify. With regard to the promise of the rare earth compositions, she uses phrase "just hopefully" on page 21 of her deposition. In marked contrast, with regard to the promise of the first La-Sr-Cu-O compositions, she states on page 32, "it's obvious he [Chu] can see the result." On the other hand, the Novel Superconductivity paper (presumably with Mr. Chu as its principal author) states on page 581, "There exist, to date, no definitive guidelines to predict material systems that will exhibit high T_c and/or novel superconducting mechanisms." In Ms. Meng's words (deposition, pages 108-109),

Well, so far nobody can predict what kind of material or what kind of formula would be at high transition temperature, unfortunately... We do have some kind of rule to follow, but not exactly know which one this one definitely can tell that that one definitely have high temperature. I don't think we can predict it at that time.

After 28 January 1987:

With the La-Sr-Cu-O work still unfinished, the search for new materials is suddenly revived at an unprecedented pace on 29 January (exhibit G); 26 new compositions are formulated before any raw material weights are calculated and presumably before any initial test results are obtained. Unexplainably, the emphasis shifts to compositions with high fractions ($\geq 20\%$) of large divalent ions (Ba, Pb) and lesser amounts of small trivalent ions (Y, Lu, and the rare and expensive Sc), consistent with the logic outlined in my dissertation (page 10 ff.) and again inconsistent with Mr. Chu's "high pressure/small ion" arguments. Apparently in an attempt to reconcile Mr. Chu's explanation with the actual sample compositions, J. C. Phillips of AT&T Bell Laboratories interprets the original Y-Ba-Cu-O composition as an attempt at "increasing T_c through an internal pressure generated by a large A-B size difference in an ABCuO

compound” (Physics of High-T_c Superconductors, Academic Press, Boston, 1989, page 86). While Mr. Chu has made no reference to attempting to increase the size difference, a motivation for doing so does appear in my dissertation (page 9). **Ironically, only a few pages earlier, Mr. Phillips states (Physics of High-T_c Superconductors, page 81),**

Even more important for full oxidation may be the internal stress associated with differences in the A and B ionic sizes in La_{2-x}M_xCuO₄. The Pauling ionic radii for La³⁺, Ca²⁺, Sr²⁺ and Ba²⁺ are respectively (Å), 1.15, 0.99, 1.13 and 1.35. Thus La³⁺ and Sr²⁺ are very well matched, which correlates very well with the highest T_c and smallest ΔT_c for M=Sr.

That is, a smaller A-B size difference results in lower stresses and consequently a higher and narrower transition. Bednorz and Muller agree with this premise (Science, volume 237, 1987, page 1133), attributing the degradation in T_c with the larger Ba and smaller Ca ions to increased local stresses as a result of their poor size match with La, consistent with the arguments outlined in my dissertation.

It is curious that no similar program of study was planned for (Y/Sc/Lu)-Sr-Cu-O (since La-Sr-Cu-O yielded consistently higher T_c's than La-Ba-Cu-O and the earlier Y-Sr-Cu-O test results were no more dismal than the earlier Y-Ba-Cu-O results). Instead, one was implemented for (Y/Sc/Lu)-Pb-Cu-O. **Paragraph 19 of Ms. Meng's declaration states that the compositions she formulated on 29 January involved “substitution variously for the La and Ba of a La-Ba-Cu-O composition by other smaller radii atomic elements.”** Since La and Ba represent the largest non-radioactive ions with stable trivalent and divalent states, respectively, the "high pressure/small ionic size" premise was irrelevant. However, what is unique about the prevalence of Ba and Pb as the preferred second elements in the 29 January compositions is that they represent the only two non-radioactive ions with stable divalent states in oxides that are larger than Sr. Recall that to this point the La-Sr-Cu-O material yielded the highest reproducible transitions and would therefore represent the most logical reference point against which new materials would be formulated.

These arguments suggest that the **Pb** compositions were formulated under the premise that divalent ions larger than Sr were essential to balance the smaller size of the trivalent ions. While this is inconsistent with Mr. Chu's “high pressure/small ion”

premise, it is consistent with the arguments outlined in my dissertation. **Note also that the Pb samples indicate the first occurrences of two “unproven” (at least as indicated by Ms. Meng’s declaration) elements incorporated simultaneously (compare exhibit C, noting no Ce-Mg, Ce-Pb, Y-Mg, Y-Pb, Lu-Mg, or Lu-Pb compositions; in each case only one "new" element is introduced at a time).**

Priority among the new compositions appears to be given to Y-Ba-Cu-O (samples 1-4, 26). The “**same** program” (declaration, paragraphs 10 and **18**) of samples to which Ms. Meng compares the Y-Ba-Cu-O compositions with early La-Ba-Cu-O samples are curiously different. The Y-Ba-Cu-O program has no low-Ba compositions (which had proven to yield the highest reproducible T_c 's) and new very high-Ba compositions (which had been virtually abandoned since early December), indicating that the earlier low-Ba Y-Ba-Cu-O samples (beginning with YB-1, which she fails to mention in either her declaration or deposition) had indeed already been made and tested. The new numbering system (beginning with YB-101) further indicates that the “YB-1” acronym had already been used.

The “YB-1” weights of exhibit H in the margin of page H56 corresponding precisely to a $Y_{1.8}Ba_{0.2}CuO_4$ composition appears to have been copied from another (presumably earlier) source (since none of the intermediate raw material weight calculations are present as with the other samples on the page). The “YB-1” acronym and corresponding composition of page H56 further confirms the existence of the earlier Y-Ba-Cu-O samples.

The Y-Ba-Cu-O compositions bracket $(Y_{0.6}Ba_{0.4})_2CuO_4$ (consistent with earlier patterns of bracketing compositions following a successful composition-- in this case, presumably the original Huntsville Y-Ba-Cu-O composition) and the pattern is mimicked among the other compositions of exhibit G. Curiously, $(Y_{0.6}Ba_{0.4})_2CuO_4$, which is listed second, is tested first (deposition, page 90). This appears to represent a rare occurrence of samples tested out of numerical order. **Samples YB-105 and YB-106 (exhibit H, page H58) appear to bracket the $(Y_{0.6}Ba_{0.4})_2CuO_4$ composition more closely. Samples YB-107 and YB-108 (exhibit H, page H61) bracket $(Y_{0.6}Ba_{0.4})_2CuO_4$ more closely still. Note that Ms. Meng’s testimony and exhibits suggest no testing was performed during the last three days of January. Presumably much of this period was devoted to producing the many new compositions indicated in exhibits G and H. Ms. Meng’s deposition also suggests that much of this period was devoted to testing the samples brought by the Huntsville representatives (pages 79-80, 82-83). If**

indeed at least some of the four additional Y-Ba-Cu-O composition were formulated prior to the first successful (at least as suggested by Ms. Meng's declaration) $(Y_{0.6}Ba_{0.4})_2CuO_4$ test on 1 February, then it is difficult to explain how the new compositions symmetrically bracketed $(Y_{0.6}Ba_{0.4})_2CuO_4$ in anticipation of positive results with this particular composition, unless, of course, one allows for communication of the 29 January Huntsville results. The 1 February date on page H61 of exhibit H appears to suggest that at least YB-105 and YB-106 were formulated prior to 1 February.

It is difficult to reconcile the 7-18 (probably 7-12) January Y and Lu samples with Ms. Meng's testimony concerning the unavailability of both Y and Lu prior to 28/29 January (deposition, pages 15-16 and 78-79). Simultaneous exhaustion of supplies of both elements would seem unlikely since the oxides are typically purchased in units of at least hundreds of grams (the original Huntsville container was Kg-sized) while the typical sample utilized hundreds of milligrams. Ms. Meng's declaration fails to mention the unavailability of Y but instead states that her "instruction...to prepare higher quality samples of La-Sr-Cu-O consequently delayed the time at which [she] could begin preparation of samples of Y-Ba-Cu-O" (paragraph 13 **and deposition, page 37**). **Strangely, Ms. Meng's begins her attempts at "higher quality" La-Sr-Cu-O on 23 December (declaration, paragraph 14), at least two days before the "poor tests results" in Houston (declaration, paragraph 6) "after Christmas" (declaration, paragraph 11) moved Mr. Chu to request her to do so. Her declaration states that "by January 28, 1987, [she] had substantially completed [her] assignment to prepare and investigated higher quality samples of La-Sr-Cu-O" (paragraph 18). Her deposition (page 61-62) defines this as having "optimized the sintering condition, such as temperature, oxygen content, and sintering time." However, her samples SL18-SL31 of January 18-28 (declaration, paragraph 14) are shown in exhibit E to have been processed at temperatures between 900 and 1200 °C, atmospheres of both air and pure oxygen, and sintering times ranging from 16 hours to 44 hours with no apparent trend toward the stability one would tend to associate with "optimization" of these conditions. In addition, the number of sinterings varies between one and two, the stoichiometries vary significantly, and the transition onsets and widths indicated also show no apparent trend toward "optimization."** Based on the above arguments, the supposed unavailability of yttrium, Ms. Meng's "number 1 reason" (deposition, pages 15 **and** 79) for postponing the Y-Ba-Cu-O work, must yield to her "number 2 reason," the 29 January Huntsville results (deposition, page 79).

With the new compositions, the favored maximum processing temperature unexplainably drops to 1000 °C (declaration, paragraph 20). The earlier Y and Lu samples as well as the bulk of the La samples had focused on 1100 °C processing (exhibits C, D, and E). It is curious that between the 28th and 29th of January the elements (La to Y, Sr to Ba), stoichiometry (10% to ≥20% alkali earth), temperature (1100 °C to 1000 °C), and processing time (≥4 hours to as little as 20 minutes) were changed simultaneously when previous tests had indicated a pattern of changing one variable at a time.

Exhibit H (page H54) indicates that the preference for 1100 °C had not been entirely abandoned. It is interesting to note here that the Huntsville work focused almost exclusively on 1000 °C processing since it was the maximum temperature attainable with the only furnace to which exclusive access was available. Only a few Huntsville samples were processed above 1000 °C in a furnace otherwise dedicated to ZnSe crystal growth. Incidentally, temperatures above 1000 °C are detrimental to the superconducting properties of the Y-Ba-Cu-O material since the superconducting phase melts incongruently between about 1000 and 1020 °C, depending upon the oxygen pressure. My dissertation offers a detailed explanation of why the elements and stoichiometry were changed simultaneously in Huntsville.

The first successful test of an $(Y_{0.6}Ba_{0.4})_2CuO_4$ composition to which Ms. Meng makes reference is described in paragraph 21 of her declaration. Curiously, the sample was sintered for only 20 minutes. This is unusual since all of Ms. Meng's earlier samples had been sintered for at least 4 hours and often for more than 24 hours. This is difficult to reconcile with longer sintering times of the earlier rare earth attempts. Perhaps the short sintering time suggests a degree of impatience in anticipation of successful results. Note that the second batch of UAH Y-Ba-Cu-O samples on 29 January was removed impatiently after only a short sintering and found to be slightly superior to the first batch (probably compensating somewhat for the slightly high 1000 °C temperature).

By 30 January (exhibit H, the “29-” apparently added later since it seems unlikely that space was left to insert “-30” later), with Mr. Wu and myself in Houston, the samples compositions suddenly take on a new level of complexity (5 elements) and remarkable precision, with numbers like 0.155, 0.845, 0.26, 0.74, 0.378, and 0.622 as if dictated by an equation. **It curious that these 5 element compositions were also formulated prior to the first successful (as suggested by Ms. Meng's declaration) Y-Ba-Cu-O tests of 1**

February. In a separate document, I will demonstrate precisely that these compositions are traceable to equations derived from the logic outlined in my dissertation (page 10 ff.). By early February (exhibit H, page H61), Mr. Wu and I had left and the **composition coefficients** resumed their less “precise” nature (generally multiples of 0.025).

Chronology Comparison and the Houston/Huntsville Relationship:

The chronology of the work in Houston can be broken up into several distinct phases. Several of the dates below are estimates extrapolated from documented dates assuming a fixed rate of sample production and testing between the reference dates.

- 11/15 - 12/4: Original Bednorz/Muller formula (appr. 9 samples)
- 11/25 - 1/9: 2-1-4 formulas (appr. 40 samples)
 - 11/25 - 1/2: Ba 2-1-4 formulas (appr. 25 samples)
 - 1/3 - 1/8: Sr 2-1-4 formulas (appr. 13 samples)
 - 1/8 - 1/9: Ca 2-1-4 formulas (appr. 2 samples)
- 1/9 - 1/11: “New” formulas (Mg, Pb, and rare earths, appr. 10 samples)
- 1/11 - 1/28: 2-1-4 formulas (appr. 52 samples)
 - 11/11 - 1/19: Ba 2-1-4 formulas (appr. 24 samples)
 - 1/20 - 1/21: Sr 2-1-4 formulas (appr. 4 samples)
 - 1/21 - 1/22: Ca 2-1-4 formulas (appr. 5 samples)
 - 1/23 - 1/28: Sr 2-1-4 formulas (appr. 19 samples)

A comparison with a chronology of the work in Huntsville is interesting. The Huntsville work shows three different areas of emphasis that tend to overlap. The Huntsville records permit more precise determination of the test dates. The main thrust of the work consisted of studies on the Michel/Raveau Sr-based 2-1-4 formulas.

- 12/15 - 12/27: Sr 2-1-4 formulas, resistivity at ambient pressure (~28 tests)
- 12/29 - 1/15: Sr 2-1-4 formulas, resistivity and susceptibility under pressure (~49 tests)
- ~1/7 - ~1/22: Sr 2-1-4 formulas, Hall effect measurements (7+ tests)

The Hall effect measurements were performed by Mr. Wu at the lab of Frank Szofran at NASA’s Space Sciences Lab. During this time, Mr. Wu also had an increased interest in microstructure analysis of the La-Sr-Cu-O compounds, working with Alice Jones (?) and Gretchen Perry (?) on the scanning electron microscope at NASA’s Space Sciences Lab. Mr. Wu also attempted to characterize the samples by X-ray powder diffraction

(Huntsville records indicate at least one attempt on 17 January) but was unsuccessful due to problems with the equipment.

Beginning about the same time as Mr. Wu's Hall effect measurements, I initiated a parallel effort to study the effects of La-Sr disorder in the Sr 2-1-4 formulas.

1/7 - 1/13: Sr 2-1-4 formulas, ball-mill processing (~30 tests)

1/14 - 1/15: Sr 2-1-4 formulas, coprecipitation processing (~1 test)

1/20 - 1/23: Sr 2-1-4 formulas, diffusion study (~3 tests)

Twenty-four of the ball-mill sample tests (1/7 - 1/13) and tests under pressure (12/29 - 1/15) are common. I initiated a third parallel effort involving a search for new materials around 11 January (coincidentally about the same time Houston was abandoning similar efforts) following the observation of the 20 K transition in La-Ca-Cu-O and the insulating behavior of La-Mg-Cu-O.

1/11 - 1/17: Substitutions for Cu in Sr 2-1-4 formulas (~6 tests)

1/18 - 1/20: Two-element substitutions for Sr in Sr 2-1-4 formulas, size balance and valence considerations (~7 tests)

1/26 - 1/28: One-element substitutions for Sr in Sr 2-1-4 formulas, size match and valence considerations (~8 tests)

After the series of Cu substitutions, Mr. Wu's enthusiasm for finding new materials waned considerably, not to be revived until the mercury (Hg) results of 26 January (see Ashburn dissertation).

Page 59 of Ms. Meng's deposition provides an excellent example of what was the true nature of the working relationship between Huntsville and Houston. She states, "in our university, the facility at that time is very limited. Some of the property, we may not be able to test it, so we really happy to send sample out to other people to do other testing." In such cases, the "assisting" organization traditionally receives "second billing" on any publication. Ms. Meng's testimony fails to explain why the Huntsville team was given first billing on the eventual YBCO publication. **The popular explanation has been Mr. Chu's humility (Robert Hazen, The Breakthrough: The Race for the Superconductor, pages 59 and 260),**

Paul Chu insisted that his name appear last, in spite of his central role.

... he [Chu] has consistently taken more pleasure in praising his colleagues than talking about himself.

Based upon the test records of both Houston and Huntsville, there is little evidence for the level of coordination between the two universities implied by Ms. Meng. There is no evidence of coordinated attempts to prevent overlapping efforts as suggested by Ms. Meng. In fact, the degree of overlap is perfectly consistent with that of two groups working independently but drawing from some common sources of information (including the early work by Michel, Raveau, and coworkers on La-Ae-Cu-O materials, Ae=alkali earth, and reports of studies at IBM, AT&T Bell Labs, and Tokyo). If there is any pattern, it is that, with the exception of the original La-Ba-Cu-O material, evidence for superconductivity was detected in La-Sr-Cu-O, La-Ca-Cu-O, La-Hg-Cu-O, and Y-Ba-Cu-O in Huntsville between one day and two weeks before similar tests were conducted in Houston. I suspect evidence for a similar case with Bi-Sr-Cu-O could likely be found as well. The parallels between the Huntsville and Houston efforts are no more or less striking than the parallels between the fiercely competitive efforts of IBM, AT&T, and Tokyo during this time period.

Final comments:

For the sake of argument, let us assume that the information that Ms. Meng claims was communicated from representatives of Houston to Mr. Wu and myself during our stay in Houston on or about 1 January 1987 consisted of the totality of knowledge possessed by Ms. Meng, Mr. Chu, and their coworkers concerning the process of creating yttrium-containing materials which superconduct above the boiling point of liquid nitrogen. If exhibit C is any indication of the quality and extent of that knowledge prior to 7 January 1987, then it was grossly inadequate-- wrong composition (alkali earth poor), wrong temperature (≥ 100 °C too hot), uncertainty about alkali earth metal (Ba, Sr, Ca, or Mg), uncertainty about rare earth metal (La, Y, Ce, or Lu), etc. To my knowledge, the failures of early January were never communicated to Huntsville. Prior to the Science article of August 1988, I was unaware that Houston had made any yttrium samples prior to their learning of the Huntsville results on 29 January.

Interestingly, Mr. Chu's comments in the Science article are consistent with Ms. Meng's statements concerning the failure of these early samples due to the mistakes of inexperienced undergraduate students (Meng deposition, pages 41-42 and 59). Robert Hazen also mentions these undergraduate students (The Breakthrough: The Race for the

Superconductor, page 50) and the possibility that the early Y failures were the result of their mixing the materials incorrectly. However, exhibit C indicates that the failures were due to the fact that the students mixed and processed the samples exactly as they had been instructed.

Ms. Meng's repeated statements concerning the supposed poor quality of the Huntsville samples are difficult to reconcile with some of her written work. For example, page 81 of her deposition states that the original Huntsville Y-Ba-Cu-O sample did not achieve zero resistance. However, Ms. Meng's paper in Novel Superconductivity states that the tests of 29 January 1987 by "us at Houston and Alabama" (presumably the latter location since Ms. Meng states that no Y-Ba-Cu-O tests were performed in Houston in January) not only achieved zero resistance, but did so at 80 K, above the boiling point of liquid nitrogen (page 584). The next sentences state,

Meissner effect was clearly evident in <24% of the samples below ~90 K in these compounds. Consequently, superconductivity above 77 K was finally unambiguously and reproducibly achieved.

One can only presume that this last statement meant that the "necessary and sufficient criteria for the establishment of superconductivity" outlined a few pages later (page 591) were met with these original samples:

We all know that the two necessary and sufficient criteria for the establishment of superconductivity are: 1) zero resistivity and 2) Meissner effect in a large fraction of the samples... For the convenience of discussion and for practicality, we would like to add two more constraints: 3) stability and 4) reproducibility.

The very next sentence in her account of the discovery reads,

Subsequent magnetic field effect measurements up to 7T, made by us in Houston, indicated a record-high upper critical field $H_{c2} \sim 180T$ at 0 K for these compounds.

Note that these measurements were "subsequent" to confirmation of superconductivity. Unlike the previous measurements that confirmed superconductivity, these are specifically attributed to the Houston group, as are "subsequent dc-magnetization measurements" attributed specifically to "Lockheed and Los Alamos" (page 584).

Strangely, the criteria for establishing superconductivity outlined by Ms. Meng in her declaration (page 2) and deposition (page 92) include these field effect measurements.

In contrast to Ms. Meng's comments about the Huntsville work, Houston successes appear to be habitually exaggerated. The paper in Novel Superconductivity alone provides several examples. Page 584 reports that soon after the discovery the Houston group enhanced the Y-Ba-Cu-O transition to between 98 and 94 K. These figures are still several degrees higher than accepted values today. On page 591, Mr. Chu refers to claims of unstable superconductivity detected by his group at 225 K (reference 72, a preprint possibly never published) and 240 K (reference 74, an NSF news release). In the seven years since the Y-Ba-Cu-O discovery, these claims have yet to be substantiated. On page 593, he reports, "reproducibility of achieving an onset superconductivity between 110 K and 130 K has tremendously improved." The example given is of a Gd-Ba-Cu-O sample (Figure 5, page 592). However, based upon the properties of this material established over the last seven years, my assumption would be that an error in thermometry occurred during the test, since such behavior in this material is yet to be verified.

It is interesting to compare the samples and tests of which Ms. Meng has a good recollection with those about which her memory is unclear. **Page 22 of her deposition indicates that test results were discussed daily with her colleagues and Mr. Chu.** In her declaration (page 6) she recalls testing the La-Sr-Cu-O samples brought to Houston by the Huntsville team. She recalls the results of those tests as well. On pages 21 and 22 of her deposition, she recalls being informed of the results of tests on some of her earliest La-Ba-Cu-O samples. On page 23 she recalls the results of those tests. On page 39 of her deposition she recalls the results of the disappointing tests on La-Ca-Cu-O samples. She refers to these results in her paper in Novel Superconductivity (page 583). However, when her thirteen year old "dream" (deposition, page 58 **and 60**) of high-temperature superconductivity is finally realized with the Huntsville samples, her memory is unclear (deposition, pages 82-83). **With regard to conversations between herself and Mr. Chu, she generally cannot recall the day, time, and sometimes month (deposition, pages 46, 47, 48, 50, et al.). Curiously however, she is quick to point out that 29 January Y-Ba-Cu-O compositions were formulated "in the daytime" (deposition, page 79), placing them conveniently prior to the phone call from Huntsville to Houston that evening announcing the discovery. The coincidental timing of events on 28-30 January as described by Ms. Meng are truly remarkable. First, the La-Sr-**

Cu-O work was “substantially completed” on 28 January (declaration, paragraph 18). Next, the rare earth oxides arrive and the Y-Ba-Cu-O compositions were formulated 29 January (deposition, pages 79). Ms. Meng’s deposition is unclear about which of these two events occurred first,

It took two week for us to receive the material. Okay, that’s one reason we started high concentration to do it, that is the number 1 reason.

And number 2 reason is due to -- well, in fact we had do it in the daytime already in the 29th before we got the material.

The next page of her deposition (page 80) suggests that the compositions were formulated first. Lastly, Mr. Chu receives the phone call from Huntsville on the same day (deposition, page 79). Based upon Ms. Meng’s awareness of the Huntsville results, it is difficult to explain why several days passed between the preparation of the Y-Ba-Cu-O samples prior to the 29 January phone call (deposition, page 79) and the first Y-Ba-Cu-O sample test to which Ms. Meng makes reference on 1 February (declaration, paragraph 21). Note also that nothing in Ms. Meng’s answers on page 79 of her deposition or any other comments elsewhere in her testimony indicate that the results of the tests on the Huntsville samples in Houston disproved (at least in her mind) the claims of “higher transition above [amended wording] 77 something... above [amended wording] a liquid nitrogen temperature” (deposition, page 79) made by the Huntsville team in the 29 January phone call.

The timeframe of the Novel Superconductivity paper is especially interesting. Novel Superconductivity represents the proceedings of a meeting conducted in June of 1987. Presumably, the papers were submitted sometime in the spring, within a few months of the discovery. Therefore, it may represent the earliest (and least corrupted) recollection by the Houston team of the events preceding the discovery.

Summary of Key Points:

- Ms. Meng’s explanation of Mr. Chu’s “high pressure/small ion” arguments are inadequate to explain the compositions formulated in Houston during the last few days of January. In most cases, they are, in fact, in direct conflict with those compositions.

- **Yttrium as a potential substitute for lanthanum was obvious to several groups. However, its use was not the critical step in the discovery. Its use with barium instead of strontium or calcium accompanied by a stoichiometry dramatically different from the “2-1-4” materials was the key.**
- **Rare earth elements were available at Houston in early January.**
- **Failures with the rare earth substitutions by Houston in early January were very similar to those reported by other groups.**
- **Superconductivity above 77 K in Y-Ba-Cu-O could not have been predicted.**
- **Houston resumed their efforts with materials containing rare earths other than lanthanum as a direct result of the Huntsville successes. Resumption of the work was neither the result of the receipt of rare earth oxides nor completion of work on La-Sr-Cu-O.**
- **The arguments outlined in my dissertation are adequate and, in fact, necessary to explain the compositions formulated in Houston during the last few days of January.**
- **The sudden change in the pattern of sample formulation and fabrication at Houston on 29 January are consistent with the arguments outlined in my dissertation and with experience gained from samples formulated and tested in Huntsville during the period 26-29 January.**
- **Tests in Houston on Huntsville samples during 30-31 January confirmed superconductivity above 77 K in Y-Ba-Cu-O. Tests in Houston on Y-Ba-Cu-O samples fabricated in Houston were subsequent to this confirmation.**
- **Samples formulated and tested in Huntsville prior to 29 January are consistent with the arguments described in my dissertation.**
- **No evidence exists for the level of coordination between Huntsville and Houston either claimed or implied by Ms. Meng.**
- **The knowledge possessed by the Houston team at the time Ms. Meng claims the concept for substituting yttrium in the materials was communicated to**

the Huntsville team was not sufficiently specific to have been critical to the eventual discovery.