The discovery of high T_C Superconductivity

Case study for the high level conversation PRO-RES project

(PROmoting integrity in the use of RESearch results)

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Introduction

Superconductors[1] were discovered by the Dutch physicist Heike Kamerlingh Onnes at 1911, in Leiden, The Netherlands. Despite the fact that physical properties like "*zero electrical resistance*" and "*complete expulsion of magnetic flux fields*" are definitely extremely useful for a myriad of applications, they occur in extremely low temperatures, near absolute zero. This posed an insurmountable barrier for the application of superconductors at the time of their discovery. For more than three quarters of a century the critical temperature for the appearance of superconductivity raised from 4.2 K up to 23 K, a rather hectic progress. As a result, the large scale application of superconductors demanded the use of expensive liquid helium, rendering large scale application of superconductors unfeasible. The only way out of this deadlock was the invention of high temperature or high T_C superconductors, meaning the production of superconducting materials with T_C higher than liquid nitrogen temperature (i.e. $T_C \geq 77$ K), since liquid nitrogen is cheaper than liquid helium, by a factor of 100. High T_C superconductors had been turned into a chimera, while the related scientific research was sometimes described (not always with the best of intentions) as the quest for the "Holy Grail" of materials science or modern Alchemy.

This situation changed in 1986, when two IBM scientists working in Zurich, Switzerland, Johann Georg Bednorz and Karl Alex Müller demonstrated superconductivity in a metal oxide well above the previous temperature threshold, namely at 30 K. Their publication did not cause great excitement. The scientific literature abounded with publications announcing alleged high T_C superconductors, only to be withdrawn after the first failed replication tests. The scientific community on superconductors was tired and disappointed, showing signs of indifference. However, physicist Paul Chu from the University of Houston, based on the above publication of the IBM scientists, developed a completely new material that became a superconductor below 93 K, i.e. well above the temperature of cheap liquid nitrogen. This invention could trigger a major technological revolution, a breakthrough of monumental magnitude, since it rendered commercial applications of superconductors possible.

The story of the revolutionary invention from Paul Chu and his research group reveals numerous examples of breaches of research integrity. The stakes were extremely high; at the beginning of 1987 Chu was a potential Nobel Prize in Physics laureate and his Institute (the University of Houston) could benefit (as long as the right patenting strategy was followed) from an invention that was bound to create a multibillion dollar market.

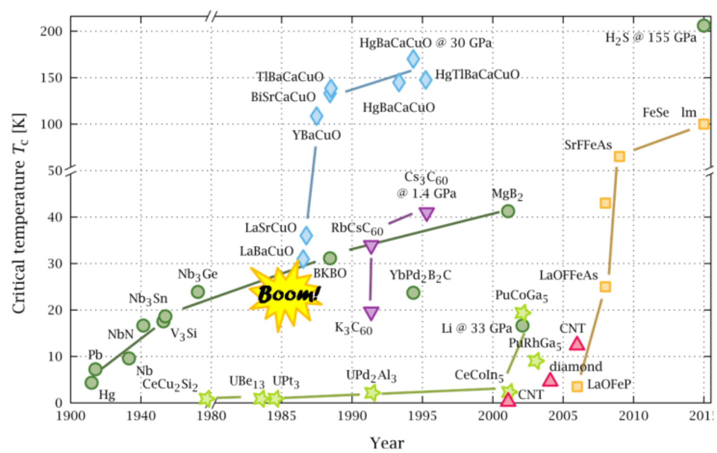

Figure 1: T_C rising – an overview. The "Boom" sign indicates the revolutionary invention of Paul Chu and his research group.

In the section below, we present cases of (a) plagiarism, (b) data manipulation, (c) scientific fraud, (d) application of questionable research practices and sloppy science, (e) efforts of manipulation of researchers by policy makers (based on

[1]Superconductivity is the phenomenon of exactly zero electrical resistance and complete expulsion of magnetic flux fields occurring in certain materials, called superconductors. This phenomenon appears when a material is cooled below a characteristic temperature, called "*critical temperature*" (T_C).

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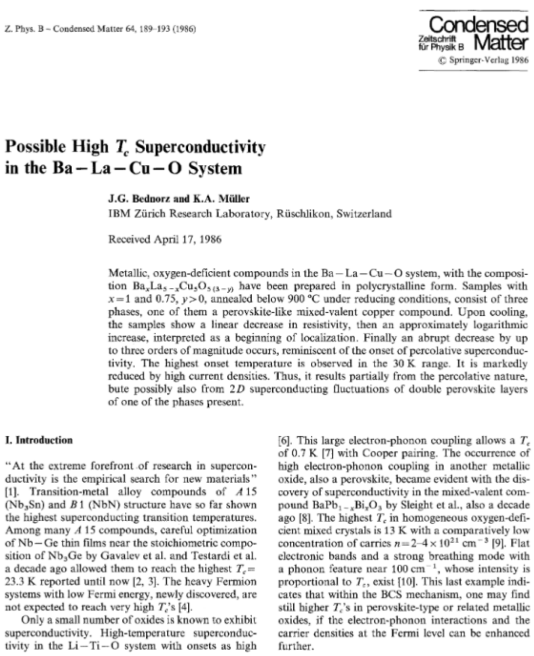
arguments of national security) and (f) efforts of manipulation of researchers by research administrators (based on arguments of economic benefits), which were directly related to the so-called “*race for the superconductor*”.

The prelude

Bednorz and Müller, based on the findings of Claude Michel from the University of Caen who had produced copper oxide-based compounds with surprisingly high conductivity, succeeded in revealing superconductivity at the very same compounds at the record T_C of 30 K. Despite the fact that this result was confirmed beyond any doubt on January 1986, the two researchers submitted the related manuscript three months later at the not so famous journal *Zeitschrift Für Physik*. This selection was based on the fact that the two researchers had some relations with the editorial team that ensured a degree of confidentiality. Even after the manuscript was accepted for publication the two researchers kept a low profile and they did not reveal their discovery, not even to their colleagues in IBM. Their article was published in September 1986, without causing any kind of scientific elation whatsoever.



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

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Metallic, oxygen-deficient compounds in the Ba – La – Cu – O system, with the composition $Ba_xLa_{5-x}Cu_5O_{5(3-y)}$ 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, bute possibly also from 2*D* superconducting fluctuations of double perovskite layers of one of the phases present.

I. Introduction

“At the extreme forefront of research in superconductivity is the empirical search for new materials” [1]. Transition-metal alloy compounds of *A* 15 (Nb_3Sn) and *B* 1 (NbN) structure have so far shown the highest superconducting transition temperatures. Among many *A* 15 compounds, careful optimization of Nb – Ge thin films near the stoichiometric composition of Nb_3Ge by Gavalev et al. and Testardi et al. a decade ago allowed them to reach the highest $T_c=$ 23.3 K reported until now [2, 3]. The heavy Fermion systems with low Fermi energy, newly discovered, are not expected to reach very high T_c's [4].

Only a small number of oxides is known to exhibit superconductivity. High-temperature superconductivity in the Li – Ti – O system with onsets as high [6]. This large electron-phonon coupling allows a T_c of 0.7 K [7] with Cooper pairing. The occurrence of high electron-phonon coupling in another metallic oxide, also a perovskite, became evident with the discovery of superconductivity in the mixed-valent compound $BaPb_{1-x}Bi_xO_3$ by Sleight et al., also a decade ago [8]. The highest T_c in homogeneous oxygen-deficient mixed crystals is 13 K with a comparatively low concentration of carries $n=2$–4×10^{21} cm^{-3} [9]. Flat electronic bands and a strong breathing mode with a phonon feature near 100 cm^{-1}, whose intensity is proportional to T_c, exist [10]. This last example indicates that within the BCS mechanism, one may find still higher T_c's in perovskite-type or related metallic oxides, if the electron-phonon interactions and the carrier densities at the Fermi level can be enhanced further.

Figure 2: The original paper of Bednorz and Müller, moderately entitled: “Possible High T_C Superconductivity in the Ba-La-Cu-O System”.

This paper was taken seriously by physicist Chu from the University of Houston. Chu was struggling to get funding for his research on superconductivity, an endeavor that was becoming more and more difficult since high T_C superconductivity was stubbornly resisting making its appearance, despite the efforts of two generations of scientists. Chu and his team saw the publication of Bednorz and Müller as a *Deus Ex Machina* revealing its presence from the other side of the Atlantic. They seized the opportunity; and they seized it “big time”.

The experimental protocol for duplicating the research in superconductivity is (a) to synthesize the alleged superconducting compound, (b) to pinpoint T_C, (c) to reveal the existence of the “Meissner effect” and (d) to isolate and characterize the crystallographic structure of the superconducting phase, since the superconducting compound of Bednorz and Müller would, most probably, be composed of more than one phases. Chu and his team succeeded in reproducing superconductivity at 30 K, but they were skeptical to announce such a result to a scientific community that was indifferent to such “Messianic” findings; to a scientific community that did not take Bednorz and Müller’s article so seriously, if their paper was even given the chance for a quick look. After all, they had followed only the two out of four steps of the experimental verification protocol. Chu and his team continued to work day and night, following a laborious process of trial and error, until something happened: on the 25th of November 1986 their experimental devices showed superconductive transition at 73 K!

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The unfolding drama

Chu knew that in order to make quicker progress, they had to consult an expert on X-Ray Diffraction analysis; they had to structurally characterize their "super" samples. Needless to say, they would not go to a state of the art laboratory, since their secret finding would most probably stop being so secret. Chu knew that once such a breakthrough discovery was revealed, industrial laboratories like those of AT&T Bell Labs, Westinghouse, IBM Research would start devoting vast manpower and resources, not to mention prestigious academic opponents like Stanford, Berkeley or Northwestern Universities or Argonne National Laboratory; Chu's path to glory would have been lost forever. After all, Chu was a scientist who was struggling to keep his small research group alive. That is why he chose the XRD laboratory of Simon Moss (a renowned expert in XRD analysis) that was almost next door to him. Moss, almost reluctantly, provided one of the PhD candidates he supervised (Ken Forster) to help Chu with the crystallographic analysis of the alleged high T_C superconductor.

Chu realized that he was perhaps sailing close to the wind, when he decided to announce the replication of Bednorz and Müller's discovery to the Annual Congress of Materials Research at the beginning of 1987. His presentation was interrupted by a Japanese professor of industrial chemistry from the University of Tokyo, named Koichi Kitazawa, who was possibly forced to announce that the superconducting phase of Bednorz and Müller was isolated and almost fully characterized by his team. That meant that the key to the discovery of higher T_C superconductors lay in the hands of the Japanese. It would only be a matter of time before discovery of the "super" samples his group had produced a few weeks ago. To complicate things, the replication of Bednorz and Müller's results from Houston and Tokyo Universities produced a cascade effect: almost immediately, dozens of laboratories all over the world started studying the superconductivity at the La-Ba-Cu-O system. For Chu it was time to publish; he hastily prepared a manuscript entitled: "Evidence for superconductivity above 40 Kin the La-Ba-Cu-O compound system" in *Physical Review Letters*, eventually published on 26 January 1987 (*since then it has received 1785 citations*).

Figure 3: Paul Chu at the age of his great discovery.

During December 1986 a "gold rush" for high T_C superconductors was in full scale. Chu's group was making serious progress breaking one T_C record after another, without announcing anything. On 27 December 1986 a Beijing newspaper announced that Chinese scientists had discovered a compound that became a superconductor at 70 K; this article was shown to be inaccurate after a few months. Chu's research group started working under a cloud of mutual suspicion, since Chu believed that he had an informer in his team; most of his group's researchers had Chinese origins. Chu prepared another article entitled "Superconductivity at 52.5 K in the lanthanum-barium-copper-oxide system" and submitted it at *Science*, eventually published on 30 January 1987 (*since then it has received 266 citations*). It was at this point that the whole research fervor went public. New York Times published a front-page article, written by Walter Sullivan on 30 December 1986. Despite the fact that the article was mistakenly giving the lead of research to Bell Labs, it did raise public awareness on the incipient breakthrough in the field of superconductors.

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Serendipity

Chu's submission to *Physical Review Letters* was accepted, but, due to the Christmas holidays that intervened, there was a slight delay of two weeks for its publication. In the meantime, the administration of the University of Houston realized that something with potential economic benefit was coming into being at Chu's laboratory. Roy Weinstein, Dean of the School of Natural Sciences of University of Houston, convinced Chu to submit for a patent, before his article would appear at *Physical Review Letters*. The lawyer of the University of Houston insisted that such a patent should have been accepted before any publication had reached the academic libraries. The patent was submitted on 12 December 1986.

However, all these events did not really matter; Chu was on the verge of making the discovery of his life. By combining high pressure results, which indicated that T_C was increasing with an increase in pressure, and pure intuition, having to do with structural considerations (please keep in mind that the crystallography of Chu's La-Ba-Cu-O was mostly unknown), Chu and his research team produced a superconductor with a T_C close to 100 K! That meant that cheap liquid nitrogen could be used, instead of expensive liquid helium, to transform *this* material to a superconductor. This was a discovery with potential momentous implications. A really high T_C superconductor could create a multibillion dollar market and could lead to applications with beneficial societal impact. *This* material, created on 29 January 1987, did not contain lanthanum but yttrium instead; the "miracle" material was based on the Y-Ba-Cu-O system.

The time to really apply the full experimental protocol had come: Chu had to make the delicate measurement for the occurrence of the "Meissner Effect", so he sent to Chao-Yuan Huang of Los Alamos laboratories in New Mexico the precious samples. He also had to isolate and fully characterize the structure of the superconductive phase. Then problems started. At the beginning, for the sake of confidentiality, Chu tasked one of his coworkers to characterize the superconductive phase; that proved to be a tantalizing undertaking, since this coworker was not an expert in XRD analysis. Chu had to trust again Moss's experimental hardware and Forster, who was eager to put his hands on the new sample. In order to cover his back, Chu did NOT reveal the exact composition to Moss and Forster. As soon as the preliminary analysis was concluded, Chu was pushing Moss to publish. Both men seemed to realize that the stakes were extremely high. However their approach was fundamentally different. Moss refused to publish until a complete crystallographic analysis was made; that meant learning the composition and exact stoichiometry of the "miracle" sample. Chu refused. Moss literally kicked Chu out of his laboratory and forbade Forster to have any other involvement with Chu's "hocus-pocus".

The dark gatekeepers

Chu started writing again a manuscript entitled "Superconductivity at 93 K in a new mixed-phase Y-Ba-Cu-O compound system at ambient pressure" to *Physical Review Letters*. He knew that the two experts assigned to review the manuscript could be scientific competitors of Chu. Despite the fact that they were bound by confidentiality agreement, Chu was suspicious that they would try to take advantage since they would have access to cutting edge information. Chu tried to convince Myron Strongin, chief editor of *Physical Review Letters*, to

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publish his manuscript WITHOUT going through the peer review process; Strongin refused. Chu, then, suggested putting asterisks at the place of the chemical composition of his “miracle” material; Strongin refused again. The two men agreed on the following “breach” of reviewing process, due to the extraordinary significance of the manuscript: the reviewers were selected by both Chu and Strongin AND their names would remain undisclosed to everyone else. The manuscript was submitted on 6 February 1987 and, in just 4 days, was accepted for publication.

A triumph of scientific integrity? Let’s not jump into conclusions yet. Chu’s manuscript contained two inaccuracies:

- Instead of yttrium (Y) the manuscript contained ytterbium (Yb)[2]
- Instead of $Y_{1.2}Ba_{0.8}CuO_4$ the manuscript contained another stoichiometry: $Yb_{1.2}Ba_{0.8}CuO$

Right after the submission of the manuscript, rumors of a new Yb-based superconductor had spread among the scientific community dealing with superconductivity. The news had leaked. This is the darkest point of the “race for the superconductor”.

Chu, on 18 February 1987, AFTER his manuscript was accepted, sent the corrections on the Yb and stoichiometry. The article was published on 2 March 1987 and shook the superconductor community; the citation is: “Superconductivity at 93 K in a new mixed-phase Y-Ba-Cu-O compound system at ambient pressure” M.K. Wu, J.R. Ashburn, C.J. Torng, P.H. Hor, R.L. Meng, L. Gao, Z.J. Huang, Y.Q. Wang, and C.W. Chu, *Phys. Rev. Let*. **58**(9) (1987) 908 (*since then it has received 8730 citations*).


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

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(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.

PACS numbers: 74.70.Ya

The search for high-temperature superconductivity and novel superconducting mechanisms is one of the most challenging tasks of condensed-matter physicists and material scientists. To obtain a superconducting state reaching beyond the technological and psychological temperature barrier of 77 K, the liquid-nitrogen boiling point, will be one of the greatest triumphs of scientific endeavor of this kind. According to our studies,[1] we would like to point out the possible attainment of a superconducting state with an onset temperature higher than 100 K, at ambient pressure, in compound systems generically represented by $(L_{1-x}M_x)_aA_bD_y$. In

sharper transition. A transition width[10] of 2 K and an onset[11] T_c of 48.6 K were obtained at ambient pressure.

Pressure[8,12] was found to enhance the T_c of the La-Ba-Cu-O system at a rate of greater than 10^{-3} K bar^{-1} and to raise the onset T_c to 57 K, with a “zero-resistance” state[13] reached at 40 K, the highest in any known superconductor until now. Pressure reduces the lattice parameter and enhances the Cu^{+3}/Cu^{+2} ratio in the compounds. This unusually large pressure effect on T_c has led to suggestions[8,12] that the high-temperature superconductivity in the La-Ba-Cu-O and La-Sr-Cu-O systems may be associated with interfacial effects arising

Figure 4: First page of the famous publication of Chu.

The darker gatekeepers

Such an important scientific advance, with even greater technological implications, could not be left unnoticed by people outside the scientific community. Chu was summoned to Washington by a panel of high rank officials responsible for the Strategic Defense Initiative (SDI),[3] commonly known as “Star Wars”. Chu had already elaborated a number of potential applications for military applications of his discovery. For example, the new high T_C superconductor could store huge amounts of energy, could be used for the production of hyper sensitive sensors for infra-red radiation, to lightweight computers. High T_C superconductors could be a key

[2] An interesting twist of fate is that Yb-based compounds did actually revealed superconductivity! Universities of Tokyo and Tohoku (Japan), as well as IBM and Bell Laboratories (USA), at the beginning of March 1987 “confirmed” the manipulated manuscript of Chu.

[3] A program initiated on 23 March 1983, under USA President Ronald Reagan. The aim was to develop a sophisticated anti-ballistic missile system in order to prevent missile attacks from other countries, specifically the Soviet Union.

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discovery for the SDI, in which Chu saw an opportunity for vast amounts of funding. Chu presented himself in front of four people on 13 February 1987 (i.e. BEFORE his famous paper was published).

The meeting very quickly took a grim character. These four people asked Chu to give them all the results of his publicly funded research. Chu refused to give any details. Chu was almost bullied; he was told that he may have to give explanations about his refusal to Erich Bloch (president of the National Science Foundation) and William Graham (consultant of President Reagan in scientific issues). When the Chair of the conversation, James Ionson – head of the Innovative Science and Technologies Office of SDI, was convinced that Chu would not reveal details of his discovery, he just stormed out of the meeting room saying to Chu “*You are wasting my time!*”.

One thing was clear to Chu: he was neither going to ask nor receive financial support from SDI.

The aftermath

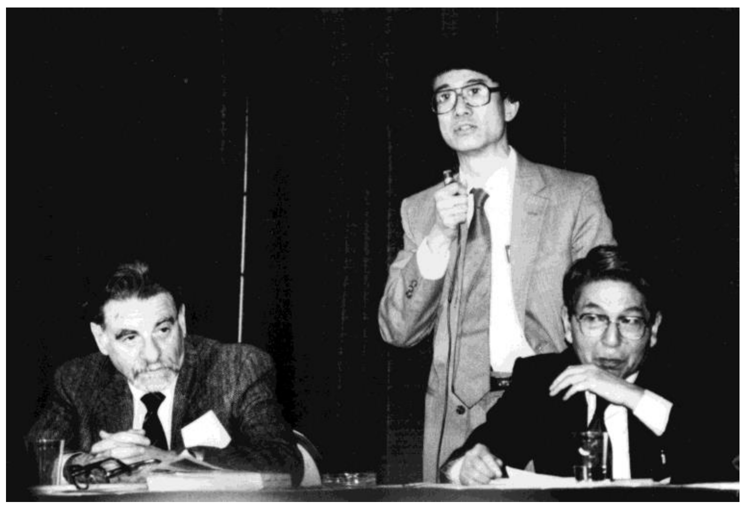

Figure 5: Three “stars” of the Woodstock of Physics. From left to right: Karl A. Müller, Paul Chu and Zhongxian Zhao.

All important scientists that took part in the discovery of high T_C superconductors participated in the so-called "*Woodstock of Physics*"; this refers to the marathon session of the American Physical Society’s meeting on 18 March 1987, which featured 51 presentations concerning the science of high T_C superconductors. Bednorz and Müller were there, as well as Chu, Kitazawa, Zhao and several other scientists that played a crucial or not so crucial role in the discovery and interpretation of the phenomenon of superconductivity in oxide systems. There were, also, scientists from industrial laboratories who had already succeeded not only in producing a high T_C superconductor, but also in producing actual demonstrators for the computer industry. There, in front of an enthusiastic audience, all recent and current advances, covered until then under a cloud of secrecy, were openly presented to the scientific community and the public, since the event was, also, covered by the mass media.

Chu was acknowledged as one of the main players of the progress that had just taken place. However, the path to glory did not reach the heights he had perhaps dreamt of. The Nobel Prize in Physics 1987 was awarded jointly to Bednorz and Müller "*for their important break-through in the discovery of superconductivity in ceramic materials*", as described in the press release of the Swedish Academy of Sciences. For some critics, this decision was based on the wish of the Swedish Academy of Sciences not to be involved in the competition of who was the first to discover high T_C superconductivity and, perhaps, a delicate way to avoid the complications with publication ethics where Chu had been involved, intentionally or unintentionally.

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Guide to discussion

Below, a list questions to guide the discussion has been categorized according to the sections of this document.

The prelude	1. Why Bednorz and Müller followed such a low-profile approach to the publication of their research? 2. Was the replication study of Chu complete, taking into account that he had not followed the experimental protocol for recognizing superconductivity?
The unfolding drama	3. Do you think that Chu was "cherry picking" for his papers? 4. Do you think that Chu should not allow his team working around the clock, since this causes serious safety risks in the laboratory?
Serendipity	5. Do you think that there should be instances, where a scientist should trust her/his instinct, when the timing for announcing important results is crucial, without necessarily following the experimental Standard Operating Procedures of her/his discipline? 6. How can a scientist decide when to protect a discovery by a patent, instead of openly announcing her/his findings?
The dark gatekeepers	7. Was the reference to "Yb" a typographic error, as Chu says? 8. Who leaked the original (manipulated) Chu's manuscript? 9. Do you think that Chu knew that the Yb compound or the mistaken stoichiometry was not producing a superconductor? 10. Does it make any difference? 11. Were researchers that tested Yb justified to accuse Chu of scientific fraud? 12. Were Chu's incentives malevolent, assuming that he intentionally changed the formula? 13. Should the scientists that "confirmed" Yb superconductivity be held responsible for plagiarism or scientific fraud? 14. Should *Physical Review Letters* held responsible for scientific fraud? 15. Should *Physical Review Letters* expose the two reviewers? 16. Do you think that the protection of Chu's original (manipulated) manuscript would be better protected if he was working for a prestigious University?
The darker gatekeepers	17. Do you agree with the way SDI people approached Chu? Why? 18. Do you agree with their demands? Why? 19. Do you think that a scientist should safeguard the results of his research from any kind of possible misuse? 20. How should scientists approach claims of "National Security"?
The aftermath	21. Do you think that the decision of the Swedish Academy of Sciences was correct? 22. Do you think that it was based on other criteria not mentioned in the official rationale?

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