A Possible Path to RTS

C. W. Chu

University of Houston, 4800 Calhoun Road, Houston, Texas, USA
Hong Kong University of Science and Technology, Clear Water Bay, Kowlong, Hong Kong
Lawrence Berkeley National Laboratory, One Cyclotron Road, Berkeley, California 94720, USA

C. W. Chu

Great progress has been made in high temperature superconductivity (HTS) science, material and technology in the 20 years since its discovery. The next grand challenge will be room temperature superconductivity (RTS). Room temperature superconductivity, if achieved, can change the world both scientifically and technologically. Unfortunately, it has long been considered by some to belong to the domain of science fiction and to occur only "at an astronomical temperature and at an astronomical distance." With the advent of HTS in 1987, the outlook for RTS has become much brighter. Currently, there appears to be no reason, either theoretical or experimental, why room temperature superconductivity should be impossible. BCS theory has provided the basic framework for the occurrence and understanding of superconductivity, but, since its inception, it has failed to show where and how to find superconductivity at higher temperatures. To date, empiricism remains the most effective way to discover superconductors with high transition temperatures. In this paper based on the talk given at the Professor Yang's 85th birthday celebration on October 31, 2007 in Singapore, I shall summarize the search for superconductors of higher T_c prior to and after the discovery of HTS, list the common features of HTS and describe some approaches toward RTS that we are currently pursuing.

1. INTRODUCTION

It is rather fitting for us to discuss the possibility of achieving room temperature superconductivity (RTS) in this auspicious year (2007). During 2007, we are celebrating the 50th anniversary of the BCS theory of superconductivity [1], the 50th anniversary of the proposition of parity nonconservation [2] (this is particularly so as we are celebrating Professor Yang's 85th birthday here in Singapore) and the 20th anniversary of the discovery of the first liquid nitrogen superconductor $YBa_2Cu_3O_7$ [3]. It is also interesting to note that the discovery of the first cuprate high temperature superconductor (HTS) Ba-doped La_2CuO_4 in 1986 [4] was exactly 300 years after Newton published his Principia Mathematica [5] that had formally ushered in the era of modern science.

Ever since the discovery of superconductivity in 1911 [6], the search for superconductors with higher superconducting transition temperatures (T_c) has been one of the major driving forces in the long sustained research effort on superconductivity. The rise of T_c with time is summarized in Fig. 1. Before 1986, through mainly Matthias's effort, a generation of superconducting inter-metallic alloys and compounds was born, giving rise to the then-record T_c of 23.2 K in Nb_3Ge in 1973 [7] attainable in a liquid hydrogen environment. Mueller and Bednorz inaugurated the new era of high temperature superconductivity (HTS) by discovering the new generation of superconducting perovskite-like cuprates with a T_c up to a new record of 35 K in Ba-doped La_2CuO_4 in 1986 [4]. Twenty-one years later, people can easily accept the report as matter-of-factly. However, when their seminal discovery when first appeared in September 1986, it was met with skepticism except by a very few groups, since oxides are mostly insulators, and are not even metallic, let alone superconducting at high temperature. Our group in Houston was among these very lucky few non-skeptics [8]. This is because we had been actively investigating the unstable perovskite and related oxide systems, such as $BaPb_xBi_{1-x}O_3$ and $Li_{1+x}Ti_{2-x}O_4$, since the mid-70s, from which

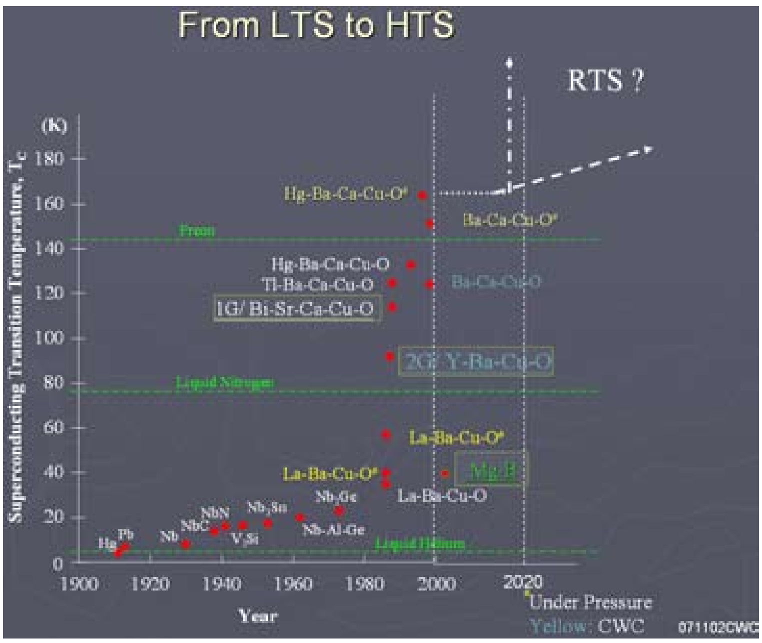

Fig. 1: The T_c-evolution with time.

not only did we learn that superconductivity is possible in oxides, but also mastered the oxide synthesis skill crucial for later HTS studies. Our previous extensive studies on the correlation of lattice instabilities with T_c using the high pressure technique had convinced us that lattice instabilities should not be the absolute deterrence to higher T_c, in contrast to the then-prevailing theoretical prediction, and that higher T_c was possible [9]. Therefore, we took the results of Mueller and Bednorz seriously and reproduced them soon afterward. We quickly raised the T_c to 40 K [10] and then 52 K [11] by the application of pressures at a rate more than ten times that on the inter-metallic superconductors. Our observation of a T_c higher than 40 K shattered the then-theoretical T_c-limit of 30's K [12] and raised serious doubts about the validity of the assumptions on which the prediction was made. The unusually large positive pressure effect on T_c suggested to me right away that higher T_c may be achievable through chemical pressures by replacing elements in the compound with smaller ones of the same valence, such as Ba by Sr or Ca; or La by Y or Lu. The Ba-Sr replacement to raise T_c was quickly confirmed by us and others, but the Ba-Ca substitution was unfortunately found to suppress T_c. The effect of other proposed replacements to enhance T_c was not carried out until a month later. The unusually large positive pressure effect on T_c observed also suggested that these oxide superconductors may belong to a new class of materials that warranted further studies, in contrast to some who thought that the Ba – doped La_2CuO_4 was not unusual since its T_c of 35 K at ambient pressure fell within the range predicted by the theory [13].

At the 1986 Fall MRS Meeting in Boston on December 4, I made an oral presentation on our work on $BaPb_xBi_{1-x}O_3$ and, before concluding the talk, I disclosed our duplication of the results of Mueller and Bednorz. During the question-and-answer portion of my talk, Kitazawa from Tokyo announced that the phase responsible for the 35 K superconductivity in the mixed-phase La-Ba-Cu-O samples of Mueller and Bednorz had been identified as the Ba-doped La_2CuO_4 or $La_{2-x}Ba_xCuO_4$ known as the 214 phase. With this piece of information on hand, it was quite natural for people, including ourselves, to focus on making single 214-phase samples and to examine the origin of the unusually high T_c in this unusual compound. We determined that to get 214 single crystals would be ideal. Unfortunately, we failed to grow 214 single crystals. So, following the destruction of two of our three crystal-growing Pt-crucibles, I decided to focus instead on stabilizing the high temperature resistivity drops, then indicative but not a proof of superconductivity, that were detected sporadically in the multiphase samples based on the nominal compositions of Bednorz and Mueller by replacing La with Y and Lu for the reason mentioned earlier. It should be noted that the first sign of superconductivity as evidenced by a resistivity drop at a temperature above 70 K was detected in mid-November, although it was too fleeting to make a definitive characterization due to the unstable nature of the samples. However, I showed the preliminary data to M. K. Wu of Alabama at the Boston meeting and successfully convinced him to join the search. In mid-January 1987, we observed a large diamagnetic shift or Meissner signal in one of our mixed-phase La-Ba-Cu-O samples up to ~ 96 K, representing the first definitive superconductivity signal detected above the liquid nitrogen temperature of 77 K [Fig. 2]. Unfortunately, the sample degraded and the signal was lost the following day. Nonetheless, the X-ray pattern of the fresh sample was taken and later identified to possess the 123 structure (see below). In late January 1987, the 93 K superconductivity was stabilized [3] in mixed-phase Y-Ba-Cu-O samples, almost tripling the T_c of the 214 compound. The discovery broke the liquid nitrogen temperature barrier of 77 K and posed serious challenges to physicists concerning the cause for the observation. It also brought superconductivity technology a giant step closer to applications that could use the practical liquid nitrogen as their coolant. In less than a month, the superconducting phase $YBa_2Cu_3O_7$ (known as123 or YBCO) was identified and its structure resolved with Bob Hazen *et al.* from the Carnegie Geophysical Laboratory in Washington [14]. With the structure information on hand, we quickly found that Y in YBCO is electronically isolated from the superconducting component of the compound and discovered the whole cuprate series

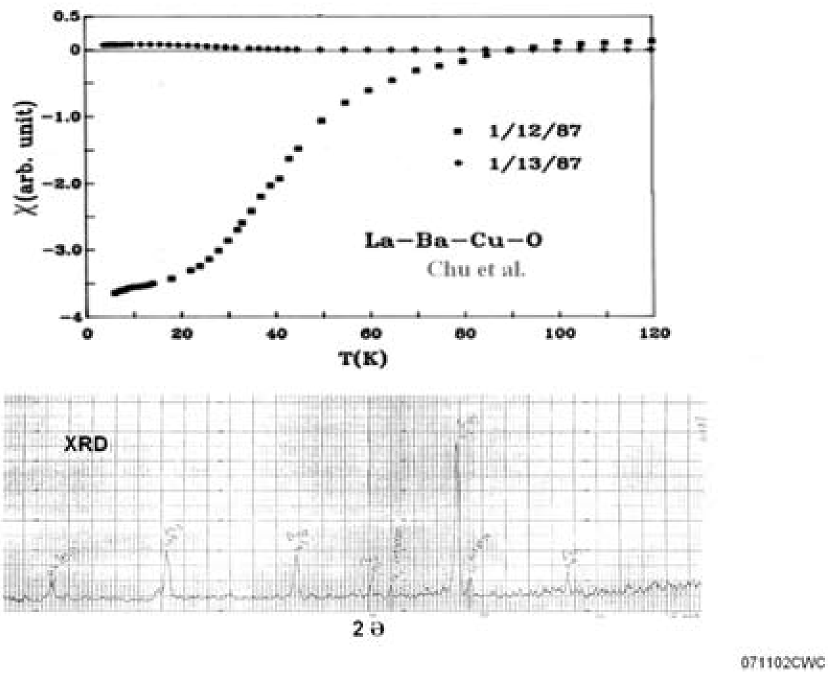

Fig. 2: The first definitive sign of superconductivity above 77 K.

of $RBa_2Cu_3O_7$ (RBCO or R123)with $T_c \sim$ 90s K where R = Y and rare-earth elements [15]. The T_c has since been advanced first in 1988 to 115 K in $Bi_2Sr_2Ca_2Cu_3O_{10}$ and to 125 K in $Tl_2Ba_2Ca_2Cu_3O_{10}$ by Maeda *et al.* [16] and Herman and Sheng [17], respectively, and then in 1993 to 134 K in $HgBa_2Ca_2Cu_3O_9$ by Schilling *et al.* [18]. The T_c of $HgBa_2Ca_2Cu_3O_9$ was further advanced to 164 K by us by the application of pressures up to 30 GPa [19]. This is the record T_c to date, albeit under pressure, and can be attained through household air-conditioning technology using Freon (CF_4) with a boiling point of 148 K.

In the last 20 years, many theoretical models have been advanced to account for numerous unusual observations in high temperature superconductors (HTS) and many superconducting prototype devices have been constructed and demonstrated successfully with superior performance to their non-superconducting counterparts. To take advantage of the full prowess of superconductivity for our daily lives, room temperature superconductivity (RTS) will be a natural target in order to avoid completely the inconvenience of cooling. Even before the discovery of superconductivity, people had already been fascinated by the concept of perpetual motion machines and RTS, because the flow of a persistent electric current in a superconducting ring is the closest thing to a perpetual machine that we have. Therefore, room temperature superconductors (RTS) have long found their way into popular culture through from science-fiction and cinema before entering into serious science. RTS, if achieved, could profoundly change the world scientifically and technologically as well.

2. A PRACTICAL ROOM TEMPERATURE SUPERCONDUCTOR

I remember that when I was a graduate student in the late 1960s, I asked my thesis advisor, the late Professor Bernd T. Matthias, whether there existed a RTS and if yes, where. His answer was brief and direct, "Yes, just go to the edge of the universe." At the time, T_c was 21 K found by him in the pseudoternary intermetallic compound, $Nb_3(Al, Ge)$ [21] and the ambient temperature at the edge of the universe is 3 K, due to the cosmic microwave background radiation resulting from the residue of Big Bang. A 21 K superconductor is thus a room temperature superconductor at the edge of the universe. However the edge of the universe is more than 13 billion light years away from us, an astronomical distance indeed that can be reached by us only in our dream.

Therefore, strictly speaking, RTS is a relative term, depending on the environment of the superconductor. It denotes a superconductor with a T_c equal to or above the ambient temperature of the environment in which the superconductor is located and used. In principle, one can thus achieve RTS either by raising the T_c of a superconductor or by lowering the ambient temperature of the environment so that the two temperatures can meet. In this presentation, I shall focus on raising the T_c.

Over the years, various target T_cs have been set at different time, e.g. 77 K (liquid nitrogen boiling point), 100 K (inside the cargo bay of the space shuttle or on the moon's surface, opposite to the sun), 120 K (liquid natural gas boiling point), 148 K (liquid Freon boiling point), 198 K (dry ice temperature) and 300 K (temperature of our living environment). With the superconductors we have, many of these target temperatures have been reached. Unfortunately, they are still not readily practical for the ubiquitous applications of superconducting devices envisioned. For instant, $HgBa_2Ca_2Cu_3O_9$ with the current record T_c of 164 K [19] under high pressure can be considered a RTS in a liquid Freon environment, achievable by an air conditioner. However, the high pressure required renders it impractical not to mention the undesirable effect of Freon on the protective ozone layer in our upper atmosphere. If one could enhance the T_c to 198 K, the simple dry ice cooling would suffice. Unfortunately, for the environmentally conscious generation, such a superconductor is not acceptable due to the greenhouse carbon dioxide gas released from the dry ice.

As a result, the practical and desirable RTS that we want today is one that has a T_c of 300 K, high enough so that its superconducting state can be achieved in our living environment without the burden of using any cryogenic cooling. On the other hand, in order to take advantage of 90% of the maximum current-carrying capacity of a superconductor, the operating temperature usually should be kept at ~ 70% of its T_c or lower. For an operating temperature of 300 K of our living environment, the T_c required therefore will be ~ 430 K.

The discovery of such a superconductor will have an all-encompassing impact on our lives whenever we use electricity and a new industrial revolution will follow. According to our current theoretical understanding and experimental data, there exists no reason why RTS should be impossible. It is therefore not surprising to find that the 2006 DoE Workshop on Basic Science Needs for Superconductivity Report has identified the discovery of RTS together with the unraveling of the mechanism of HTS as two grand challenges in our future superconductivity research. Last summer, the US Air Force Office of Scientific Research, NATO and the Texas Center for Superconductivity at the University of Houston had jointly held in Norway a very successful "Workshop on the Road to RTS." For simplicity in later discussions, I shall take RTS to be possession of a T_c at or above 300 K.

3. SOME INTERESTING CLAIMS

The long and tortuous path in the search for superconductors with higher T_c has been dotted with triumphs of success and agonies of failure, including extravagant claims. Successes have been reported in various articles and books; and failures are too many to document and are often unreported. Being an optimist and a strong believer that whatever is not prohibited by the laws of physics will happen, I often give the benefit of the doubt to many claims of RTS, even the extravagant ones.

I would not dismiss them outright until they are proven false by reasoning or by testing them experimentally to the best I can. Consequently, I have been contacted by many such claimers. Unfortunately, so far, to find them not superconducting is the norm let alone superconducting at room temperature. Examples are abundant, but let me just cite just a few for amusement. A few years ago, a California based company (which may still exist) that was raising capital to commercialize its alleged RTS based on a modified polymer material supposedly developed in the former Soviet Union with published references. The head of the company contacted me and asked me to test the materials. I did but found them to be insulating. In another example, the anchorwoman of a reputable TV program asked me to test a piece of material which was allegedly to have been left by an extraterrestrial vehicle in an Arizona desert and determined by a few reputable labs to be superconducting at room temperature in the presence of a strong microwave. I found it to be a rather ordinary metal containing elements such as Fe, Mn, In etc. and not superconducting. Yet another example was a call several years ago from a Croatian physicist who asked me to sign a disclosure agreement before faxing me information about his RTS claim. After seeing his faxed message, I had some doubts but still repeated what was described in the message, When told of our negative test results, he attributed them to our alleged poor sample quality. Still giving him the benefit of doubt, I asked for a piece of his sample, but he wanted me to purchase it when he started to mass produce it and put it on the market before Easter the following year. Unfortunately I have yet to hear from him since that Easter.

While many of the claims can be ignored outright due to experimental artifacts or dismissed after cursory examinations, others are interesting and may be worth further investigation. Revisiting these may lead to new understanding of HTS and new mechanisms for HTS, in addition to higher T_c. I shall briefly describe three of these other reports of very high T_c, occasionally exceeding 300 K below:

3.1. In 1946, Ogg Reported [22] a large drop in resistance and the presence of persistent current in their sodium-ammonia solution at temperatures as high as 180 K upon rapid cooling but not on slow cooling. He attributed the observations to superconductivity. According to him the superconductivity detected was due to Bose-Einstein condensation of Bosons of electron-pairs in vacancies that resulted from dissolution of Na in NH_3 [23]. It should be noted that Ogg was the first to suggest electron pairing for superconductivity. Later in the same year, conflicting reports appeared [24]: some disputed Ogg's results, some saw resistance drop but not to zero, yet another found corroboration for Ogg's observation. Interest in this material system resurged [25] in the earlier 1970's mostly in the former Soviet Union but waned in the late 1970's. However, the topics has been picked up by some recently in the West [26]. Unfortunately, the issue concerning the existence of superconductivity in the solution remains unresolved. On the other hand, the phase separation takes place in the Na-NH_3 solution separating the metallic from the insulating ones, a reflection of the presence of some kind of instabilities in the system that are reminiscent of all high temperature superconductors known today. If electron pairs do form in the vacancies in the insulating NH_3-background prior to the onset of phase coherence as initially proposed by Ogg, this may be another similarity to what takes place in the HTS cuprates below the pseudo-gap temperature, not to mention the possible pairing in real space proposed in cuprates. Given the tremendous improvement in experimental techniques today compared with those used by Ogg and his contemporaries and the possible resemblance between the known HTSs and the Na-NH_3 solution, a revisit may be warranted.

3.2. A Large Drop of Resistivity associated with a small ac diamagnetic susceptibility shift in CuCl at ~ 40 kbar and 300 K was reported in 1975 [27]. A series of pressure-induced phases was also proposed, although without any X-ray diffraction structural change under pressure to 90 kbar [28]. Later in 1978, Brandt *et al.* claimed the observation of superconductivity up to 170 K in CuCl under pressures based on the large resistive and magnetic anomalies detected and attributed the observation to electron pairing via the exchange of excitons [29]. This was in contrast with the earlier failed search for the metallic phase in CuCl under pressure in a thermal equilibrium condition below room temperature [30]. However, for samples in their thermally non-equilibrium state during rapid warming, an ac susceptibility anomaly above 90 K over a temperature range of 10-20 K was detected [30], corresponding to a paramagnetic-diamagnetic-paramagnetic transition. The magnitude of the diamagnetic shift was estimated to be about 7% that of a bulk superconductor. In the temperature region where the diamagnetic shift occurred, the resistivity was also observed to undergo a sharp decrease. The simultaneous transient appearance of the resistive and magnetic anomalies upon rapid warming is rather intriguing and consistent with, although not proof of, a possible superconducting transition in a minute part of the sample. Unfortunately, no definitively confirmation or refutation has been reported. Ginzburg proposed that a possible new state of superdiagmanetism might have existed in CuCl [31]. The transient nature of the anomalies reported [30] may result from a temperature induced strain/stress relaxation which in turn gives rise to a disproportionation of the CuCl compound, creating a rather complex metastable metal/insulator or insulator/insulator composite material system rather different from its simple parent CuCl that was originally examined. The proposed role of interfaces in these composite material systems for superconductivity is encouraged by the recent observation of superconductivity at the interface of two insulating compounds [32]. Disproportionation also represents the presence of instabilities that commonly occur in high T_c and related oxide materials. Furthermore, given the important role of Cu in cuprate HTS, reexamination of CuCl may be warranted. (I still remember that Phil Anderson dropped me a short note "Cu rises again!" immediately after the discovery of the 93 K superconductivity in YBCO was announced in 1987.) To develop a proper experimental environment to simulate the transient effects induced by rapid warming of CuCl under pressure, one may be able to turn the transient anomalies into steady ones for definitive characterization. For example, one may be able to simulate the pressure gradient induced by the rapid warming by steady physical means.

3.3. Before 1986-87, physicists in the field of superconductivity research were very pessimistic about high T_c due to the long stagnation of T_c at 23.2 K coupled with the prevailing belief of the existence of the then-theoretical T_c-ceiling of 30's K [20]. I still remember the extremely emotional burden in writing the YBCO paper to make the first claim of 93 K superconductivity [3]. Even after the acceptance of the paper, I continued to repeatedly ask myself and my students "Could there be phenomena other than superconductivity that are able to account for our observations? Please think and think hard," knowing that a mistake of this magnitude could send me into life time exile from my superconductivity career. However, the discovery and the immediate confirmation of YBCO with a T_c at 93 K in the early 1987 drastically changed the mental state of people in the field. Physicists were suddenly in a state of euphoria and became extremely bullish about T_c, thinking that only the sky was the limit. For exemple, J. T. Chen *et al*. reported in May 1987 the observation of a two-step resistive transition in the Y-Ba-Cu-O compounds with one transition beginning at 240 K [33]. They attributed the transition to superconductivity in the yet-to-be identified unstable Y-Ba-Cu-O compound in its granular form based on the ac Josephson-effect they claimed to have detected. Many other similar reports of anomalies indicating superconductivity at very high temperatures in cuprates appeared in the ensuing years. They include the observation of superconductivity above 200 K in BSCCO [34] and HBCCO [35]. All reports share some but not all of the following features: a sharp resistive drop (but not to zero), a diamagnetic shift (but small and superimposed on a large paramagnetic background), and poor reproducibility (not just from lab to lab and from sample to sample, but also from run to run of the same sample). They definitely cannot satisfy simultaneously the four criteria I set in 1987 for a serious claim of superconductivity, i.e. zero resistivity, large diamagnetic shift decisively showing the Meissner effect, stability high enough for a definitive diagnosis and good reproducibility from sample to sample and from lab to lab. Therefore in 1987, I dubbed these fleeting anomalies at best Unidentified Superconducting Objects (USOs) to be parallel to the Unidentified Flying Objects (UFOs) or Unidentified Superconducting Anomalies (USAs) to be patriotic. Later Koichi Kitazawa told me that he had already coined the name USO for anomalies of this kind and that "uso" sounds like "a big lie" in Japanese. Some of the USOs have been shown to arise from experimental artifacts or from misinterpretation of the data, while the cause for others remains unclear. The high frequency of the reports, the similar high temperature range (between ~ 240-300 K) for the sightings of USOs and the many reputable labs from which the reports originated make these USOs too tantalizing to ignore. This is especially true for the low reproducibility of the USOs in view of the extremely unstable chemical nature of the cuprates, and for the possibly missing Meissner effect in view of the ever-decreasing of coherence length as the T_c increases.

3.4. The Great Majority of the USOs Reported have been in cuprates as described above. One exception is the report by Reich *et al*. in Jerusalem of the detection of a superconducting transition with a T_c of 91 K in the Na-doped surface of WO_3, as evidenced by the diamagnetic signal and the drop of resistance below the transition temperature [36]. Careful characterization of the samples and examination of the transition were performed later by groups in Jerusalem and Zurich, using the XDR, XPS, EPR, STM and STS techniques in the ensuing two years [37]. All observations appear to be consistent with the existence of superconductivity in the Na-doped surface of WO_3. Unfortunately, all reports were done on samples from the same source, i.e. Reich's lab, and no other confirmations have appeared. Recognizing the chemically sensitive nature of the Na/WO_3 interface, the difficulty in producing the observation is not unexpected. The implication of a high T_c in this non-cuprate material system would be profound, if its existence is proven and the possibility of contamination by cuprate HTS can excluded.

4. SOME VISIONARY PREDICTIONS

The discovery of YBCO in 1987 changed the outlook for higher T_c. Unfortunately T_c has stopped rising since 1994 and the feeling of gloom and doom has started to return in recent years. This seems to have been epitomized by the recent appearance of the article by Barth and Max titled "Mapping High Temperature Superconductors: A Scientometric Approach"[38]. According to their scientometric analysis of the time-dependence of the overall number of articles and patents and the time-variation of publications related to specific compound subsets and subject categories, they showed beautiful figures that predicted the death of the field of HTS between 2010 and 2015 by linear extrapolation. While people in database collection and research consider the analysis accurate and sound, many scientists point out the blindness of "bean counters" in scientific research. In fact by applying the same approach, many fields of science should have been dead long ago. For example, atomic physics and superconductivity would have been over long before Bose-Einstein condensation and HTS entered the stage of exciting research, scientific breakthrough goes beyond statistics. I often resonate with the statement by Mark Twain about figures – "there are three kinds of lies: lies, damned lies and statistics.” Fortunately, Barth and Marx also pointed out that the situation can drastically change if a breakthrough were to take place, such as when superconductors are found to work at a higher temperature or in a new class of materials, or a theory is found to explain the HTS. To discover a RTS would definitely be such a breakthrough and more. Since the 1960s, some visionary theorists have already proposed that RTS may be achievable through a variety of schemes. A few examples are given below:

4.1. In 1964, Little examined the question originally posed by London, whether superconductivity occurs in organic macromolecules within the framework of the BCS theory and concluded that superconductivity above room temperature is not only possible but also expected in organic macromolecules of a special design [39]. The proposed model macromolecule consists of a long spine and a series of side chains. The long spine may or may not be a conducting system. By choosing the molecules in the side chains with proper oscillation of charges, the electrons in the spine can be polarized to form pairs via the exchange of excitons with the side chain molecules. According to Little’s estimation of the matrix elements and density of states in his model polymer, a superconductivity transition should occur at temperature well above room temperature from an insulating, a semiconducting or a metallic state of the spine. He also pointed out the challenges in establishing electric contacts for resistive measurements and in determining the Meissner effect. While superconductivity has been discovered [40] in organic metals often under pressure, the T_c remains low but in materials with structures different from that suggested by Little and due to different mechanisms. One of the challenges in realizing Little’s vision is in synthesizing the macromolecules with the proposed design. With the great advancement in material synthesis and diagnostic techniques for nanomaterials made in recent years, an attempt to produce macromolecules including the model macromolecule proposed by Little may be worthwhile and timely. The suggested transition directly from a localized state to the superconducting state reminiscent of what takes place in cuprate HTS in the presence of a high field at low temperature [41] and of field-induced superconductivity in λ-$(BETS)_2FeCl_2$ is intriguing.

4.2. In 1964, Ginzburg noticed the possible drawbacks of the one-dimensional organic macromolecule superconductor proposed by Little, such as fluctuations, instabilities and lack of Coulomb screening, and therefore focused instead on two-dimensional materials that might alleviate the impasse in part. He proposed that surface superconductivity could occur in the surface of a metal, especially when covered by a dielectric material and suggested a possible T_c of 10^2-10^3 K after making a few estimations [42]. This is different from the surface superconductivity in the surface of a bulk homogeneous superconductor existing slightly above H_{c2} proposed by Saint-James and de Gennes a year earlier. Ginzburg wrote that $T_c \sim \Theta\exp(-1/g)$ with Θ being the characteristic temperature of the excitation energy spectrum responsible for electron pairing and g the effective attraction between electrons. He argued that for electron-phonon interaction the characteristic temperature is the Debye temperature Θ_D, which is ~ 10^2 K. In the weak coupling approximation of BCS, the maximum T_c was estimated to be below 40 K. He proposed a novel mechanism to enhance T_c within the weak limit of BCS, i.e. to increase T_c by taking advantage of the high characteristic temperature Θ_e of the electron-electron interaction via the exchange of excitons, which can be as high as 10^5 K. By taking a realistic value of g ~ 1/4, Ginzburg obtained a $T_c \sim 1.8 \times 10^3$ K for a $\Theta_e \sim 10^5$ [43]. In order to facilitate the so-called exciton mechanism, he conjectured that one should consider the following material systems: metallic thin films, metal surfaces covered by dielectrics, metal sandwiches with dielectrics in between and two-dimensional layer compounds. Many experiments were done following the suggestion. For example, in the early 1970’s, the layered compounds of transition-metal dichalcogenides were considered to be the natural candidate and extensive research was conducted. Unfortunately, the T_c remained low and the superconductivity observed could be explained by the conventional electron-phonon mechanism. In spite of the disappointing outcome, the study led to the discovery of charge density waves in 1973, which became one of the most studied topics in the ensuing decades [44]. It may not be surprising if there exists a connection between the layered materials Ginzburg proposed and the cuprates in which HTS was discovered a little more than three decades later in view of the common metal-semiconductor layer sequence present. For the two-dimensional materials proposed by Ginzburg to work, close coupling between the layers is needed and the metallic and semiconducting layers in cuparate HTSs happen to assemble themselves naturally. The new development in thin-film deposition may provide another avenue to synthesize these layers with better coupling to test the proposal.

4.3. In 1968, Ashcroft proposed that metallic hydrogen could have a T_c of a few hundred degrees Kelvin based on the standard BCS formula [45]. Assuming that metallic monatomic hydrogen could be achieved by compressing hydrogen under high pressure, he pointed out that metallic hydrogen could be considered as an element of the alkaline metal group but rather different from other members of the group. While all alkali metal elements (except Li with a T_c = 0.0004 K) are not superconducting at ambient pressure due to the complete cancellation of the electron – phonon attraction by the electron – electron repulsion, metallic hydrogen has instead: a high Debye temperature Θ_D as the prefactor in the BCS formula due to its low ionic mass; a strong electron-phonon coupling λ due to the absence of the inner core structure; and a relatively large density of states N(0) at the Fermi energy due to its high electron density, all contributing to a high proposed T_c. By using reasonable estimated values of Θ_D,

λ, N(0) and the Coulomb pseudopotential, Ashcroft obtained a lower bounded T_c on the order of 10^2 K. In the ensuing years, numerous analyses of metallic hydrogen with different sophistications point to the same temperature range for T_c. In 1997, Ashcroft and Richardson showed that the correlated fluctuations between electrons and holes in the metallic modification of diatomic hydrogen through band-overlap under high pressure will reduce the Coulomb pseudopotential and result in an enhanced T_c higher than its monatomic counterpart [46]. Recently, Ashcroft further suggested that metallic group IVa hydrides with hydrogen as the major constituent would be high T_c superconductors under pressure, following the similar approach that predicts metallic hydrogen to be a high temperature superconductor [47]. He also suggested that the group IVa hydrides have the possible added advantage of requiring a lower critical pressure to achieve their metallic state. It should be pointed out that, in spite of the extensive studies of hydrogen under pressures in the 100s GPa-range over the past few decades, the existence of the metallic state of hydrogen remains elusive, and superconductivity has yet to be detected. However, in view of the great advancements made in computational science and high pressure techniques in recent years, it is time to tackle this exciting problem head-on.

4.4. Although Several Complex Material Systems

Although Several Complex Material Systems were suggested for raising the T_c by taking advantage of the possibly high characteristic temperatures of their exciton energy spectra after Ginzburg's 1964 proposition, detailed analyses of the feasibility of superconductivity due to the exciton mechanism were lacking. By 1973, Allender, Bray and Bardeen had carried out a more rigorous analysis on a simple model system to explore the existence of the exciton mechanism and its impact on T_c, if it exists [48]. Their model material consists of a metal thin film of Fermi energy E_F on a semiconductor of a narrow gap of E_g. When the metal thin film is in perfect contact with the semiconductor to form a chemical bond at the interface and the Fermi level of the metal thin film lies in the middle of the semiconductor gap, the electron wave function will have maximum penetration into the semiconductor without localization or the detrimental effect due to band bending in the semiconductor. These electrons that tunnel into and spend enough time inside the semiconductor gap will form pairs via the exchange of excitons. They concluded that T_c can indeed be enhanced by adding the exciton mechanism to the phonon mechanism when the material conditions are optimized and that the exciton mechanism is a promising vehicle for higher T_c. While the exciton mechanism may be as promising as they have shown, they also point out the difficulty in creating the model material system with the proper metal/semiconductor interfaces that satisfy the stringent requirements so that the full effectiveness of the exciton mechanism can be realized. Several experimental attempts had been made until the late 80s but with no success reported. With the recent advancement in multi-thin-film synthesis, one should be able to artificially prepare samples satisfying the stringent criteria specified for the exciton mechanism. Naturally occurring metal/semiconductor layered compounds may be a good alternative if the E_F is adjusted to be located in the middle of E_g.

5. COMMON FEATURES OF SUPERCONDUCTIVITY WITH HIGH T_c

Many superconductors of various material families have been found: Some have higher T_c than others and some are easier to be shaped into practical forms for applications than others. However, superconductors with a relatively high T_c appear to share some common features, independent of the compound families to which they belong.

At the moment, we do not yet know enough about a RTS other than that it has a $T_c > 300$ K, as we have chosen, to ask intelligent questions with answers to which will lead us to the promised land of RTS. It is also not unlikely that a RTS to be discovered may turn out to be a very different material from the HTSs to which we are accustomed to. However, being a superconductor, RTS has to have the basic superconducting characteristics and very likely has to share at least some features with the HTSs we have. A review of these features is considered most helpful and can serve as a launching pad for our attempt to look for RTS.

5.1. Electron-pairing and Phase-coherence

According to the BCS theory, electron-pairing and phase-coherence are the very basic features of a superconducting state that exhibits zero resistivity ($\rho = 0$) and perfect diamagnetism (magnetic induction B = 0). Electrons in the presence of an attraction, no matter how small, will form pairs, lower the energy and result in an energy gap (Δ) immediately below the Fermi energy [40], although nodes or lines of nodes occur in superconductors with non-s symmetric pairing orders. Electron pairing takes place in the k-space via the virtual exchange of bosons, although in cuprate HTS, pairing of electrons in the real-space has also been proposed [50]. When the wave functions of the electron pairs overlap, phase coherence is established and the compound undergoes a bulk phase transition to the macroscopic superconducting state at T_c. It has been long accepted that electron-pairing and phase-coherence occur at the same temperature, T_c for the conventional low temperature superconductors. However, suggestions have been made that electron-pairing may procede phase-coherence at a temperature higher than T_c in the cuprate high temperature superconductors [51]. If true, the feature provides a new degree of freedom for the search for superconductors of higher T_c.

5.2. Strongly Correlated Electron Systems

The current HTSs with a T_cs above 77 K are cuprate oxides with a strong interaction between electrons due to the incompletely filled 3d-shell. They can therefore be considered to belong to the class of materials of transition metal oxides where strongly correlated electrons exist. This is further evidenced by the failure of band calculations which neglect the correlations between electrons to predict the physical properties of the undoped parent compound of the 214 HTS, La_2CuO_4. It is an antiferromagnetic insulator with a sensitive dependence on doping, in contrast to predictions by band calculations. Strongly correlated electron systems are rich in electronically induced phase transitions with a wide range of transition temperatures and therefore may provide various avenues to HTS. Fig. 3 shows schematically the linkages between magnetism and superconductivity and between magnetism and ferroelectricity in strongly correlated electron systems. In contrast to the original thinking that magnetism is detrimental to superconductivity, we now find that magnetism can help superconductivity [52] and that magnetic field can induced superconductivity [53]. Similarly, magnetism and ferroelectricity had been considered to be antithetic to each other until recent experiments showed that they can help each other under the proper conditions [54]. I believe that if the missing link between ferroelectricity and superconductivity is found, higher T_c can be achieved.

5.3. Instabilities

In the strongly correlated electron systems, there exist various electronically or phononically induced transitions of different kinds, e.g. superconducting, structural, antiferromagnetic, ferromagnetic, ferroelectric, antiferroelectric, metal-insulator, charge-density-waves, spin-density-waves, charge-order, orbital-order, etc. [55]. They arise from instabilities due to the proximity of their Fermi levels to the singularities in their respective energy spectra, such as phonon, electron, spin, exciton and charge. The dominant instability will win over the weaker ones and determines the nature of the transition. The transition can be induced by variation in temperature, pressure, chemical doping, magnetic field and/or electric field. In other words, there can be more than one type of interactions in a solid and the strengths (absolute or relative) of these interaction can be adjusted by changing the above physical or chemical parameters (see e.g. Fig. 3).

Apparently, superconductors with high T_c are intrinsically unstable, physically or chemically due to the strong attractive interaction involved whether they are intermetallic or non-intermetallic. A case in point is the A15 system of inter-metallic compounds with relatively high T_cs prior to 1986, such as V_3Si (17 K) and Nb_3Sn (18 K), which undergo a structural transformation at T_m due to the softening of the phonons prior to entering the superconducting state on cooling. When pressure brings T_m closer to T_c, T_c increases as for the case of V_3Si; whereas when T_m is moved away from T_c by pressure, T_c decreases as in the case of Nb_3Sn, demonstrating a significant positive role of phonons in superconductivity of these compounds [56]. HTS cuprates exhibit a magnetically driven pseudogap opening at T_p that decreases while the T_c increases in the underdoped region [57], reminiscent of the relationship between T_m and T_c for the A15 intermetallic compounds under pressure. It suggests a significant role of magnetic fluctuations in HTS. In addition to the physical instabilities discussed above, instabilities can be chemical in nature. For example Nb_3Ge cannot achieve its optimal Nb:Ge = 3:1 stoichiometry in bulk synthesized under the ambient condition. A similar situation occurs for the HTS cuprates, i.e. YBCO can loose its oxygen easily, and doping in the $HgBa_2Ca_{n-1}Cu_nO_{2n+3-\delta}$ tends to reduce n for n > 3, while for n > 4 high pressure synthesis is required usually. Instabilities will be perhaps the most serious challenge for achieving RTS. One way to alleviate the impasse in part is to develop a complex material structure and to utilize the extreme conditions.

5.4. Fluctuations

As has been pointed out above, HTSs are strongly correlated electron systems that can possess interactions of different nature. Instabilities in the energy spectra of these interactions result in transitions of different types. Near the phase transition, fluctuations set in. In some compounds, instabilities associated with a transition result in fluctuations prior to its formation of a long-rage order, such as magnetic-order, charge-density-waves, spin-density-waves, or charge-order. These fluctuations may become a source of electron pairing or superconductivity, especially when the superconducting transition gets close to the transitions for the above orders to take advantage of the associated fluctuations. Various experiments have shown that many of these interactions or transitions are tunable by both physical and chemical means. They can be coupled to one another

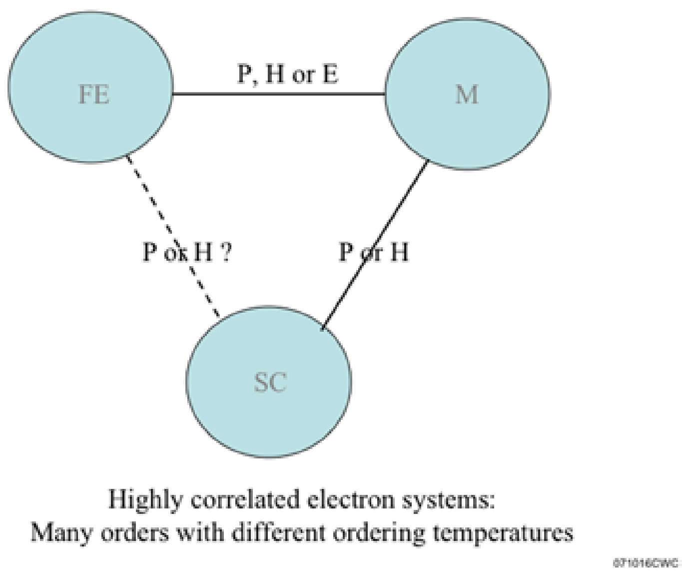

Fig. 3: The relationship between superconductivity, magnetism and ferroelectricity.

with one being able to enhance or suppress the other. Such a coupling becomes most effective through the fluctuations near the phase transition. For instance, the soft phonon modes associated with a structural transition have been observed to enhance superconductivity as evident, for example, from the detection of higher T_c in the A15 intermetallic compounds [56] when the structural and superconducting transitions that occur simultaneously in these compounds are brought closer to one another by pressures, and from the observation of the highest T_c near the alkaline-doping-induced metal-insulator transition in WO_3 [58]. The ever-presence of magnetic fluctuations associated with the antiferromagnetic transition that takes place in the undoped parent compounds of cuprate HTSs or associated with the spin-density-waves transition that occurs in the insulator parent of the organic superconductors have strongly demonstrated the significant positive role of magnetic fluctuations in superconductivity [52].

5.5. Layered Structure with Two Different Blocks

Reduced dimensionality has been shown to facilitate the enhancement of T_c, generally due to the relatively large density of states and the stronger electron-electron interaction associated with a 2D system. For instance, all HTS cuprates exhibit a layered structure as shown in Fig. 4 [59]. They can be represented by a generic layered formula $A_mE_2R_{n-1}Cu_nO_{2n+m+2}$, where A = Bi, Tl, Pb or Cu; E = Ca, Sr or Ba, and R = Ca or a rare-earth element. The generic formula can be rewritten as $A_mE_2R_{n-1}Cu_nO_{2n+m+2}$ = $[(EO)(AO)_m(EO)]+[(CuO_2)R_{n-1}(CuO_2)_{n-1}]$, consisting of two main blocks, namely the active block $[(CuO_2)R_{n-1}(CuO_2)_{n-1}]$ and the charge reservoir block $[(EO)(AO)_m(EO)]$. The former consists of *n* (CuO_2)-layers interleaved by *n-1* R-layers and the latter comprises *m* (AO)-layers bracketed by 2 (EO)-layers. Superconducting current flows in the CuO_2-layers in the active block while the charge reservoir block enables the introduction of carriers to the CuO_2-layers without affecting the layer-integrity (also known as modulation doping in multilayered structures of semiconductors).

The above appears also to be true for transition metal nitrides. For example, ß-HfNCl has a structure related to the $CdCl_2$-type with the [Hf-N-N-Hf] layers occupying the Cd-positions and sandwiched between the loosely packed Cl-layers. When $Li_x(THF)_y$-layers which act as a charge-reservoir, are intercalated into the HfN-layers between the Cl-layers, ß-HfNCl/$Li_x(THF)_y$ becomes superconducting with a T_c reaching 25.5 K [60]. This is in strong contrast to the T_c = 8.8 K of the cubic HfN.

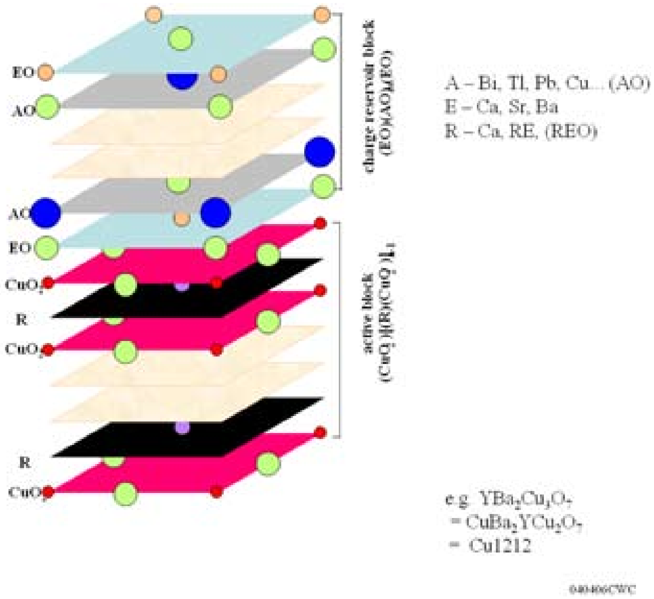

Fig. 4: The layered structure of HTS cuprates.

5.6. Near the Metal-insulator Phase Boundary, Low Carrier Density and High Degree of Covalence

The metal-insulator transition represents one of the electronically or phononically induced extreme instabilities associated with HTS as discussed above. For instance, superconductivity evolves from an antiferromagnetic Mott insulator for the cuprates with a T_c up to 134 K, from a charge-density-wave insulator for $Ba_{1-x}K_xBiO_3$ and $BaPb_{1-x}Bi_xO_3$ with a T_c up to 30 K and 13 K [61], respectively, from a yet-unknown insulating phase near x ~ 0.1 and for $Li_{1+x}Ti_{2-x}O_4$ with a T_c up to 14 K [62] and from a ferroelectric insulator for A_xWO_3 with a T_c up to 7 K, where A = alkaline elements [58]. A similar situation is found in the organic salts when the spin-density-wave (SDW) gap is quenched by pressure they become superconducting. [59] Although the T_c*s* of the non-cuprates is not high compared with those of the cuprate HTSs, they are high within their own material groups. As a result, the carrier concentrations of the HTS and related compounds are low, and the degree of covalency is high for carriers in the conduction band. As a precursor with doping, these superconducting compounds usually exhibit a large temperature-independent Pauli susceptibility at room temperature indicative of a large density of states near the Fermi surface.

5.7. Mixed Valence

Mixed valence states are often found in superconductors with a relatively high T_c. The appearance of mixed valence states in a compound also represents an example of the electron-induced instabilities discussed earlier. This is evident, e.g. in (Cu^{+2} & Cu^{+3}) in cuprate HTSs, (Bi^{+3} & Bi^{+4}) in $Ba_{1-x}K_xBiO_3$ and $BaPb_{1-x}Bi_xO_3$, (Ti^{+3} & Ti^{+4}) in $Li_{1+x}Ti_{2-x}O_4$ and (W^{+4} & W^{+6}) in A_xWO_3. It is interesting to note that doping into the Ba-site of $BaBiO_3$ by K gives a maximum T_c of ~ 34 K while doping into the Bi-site by Pb leads to a maximum T_c of only 13 K. This observation suggests that in addition to changing the carrier concentration, doping in $BaPbBiO_3$ must affect other factors that are important to T_c. Determining the cause of this observation will also provide insights into the occurrence of high T_c in oxide superconductors.

5.8. High Polarizability

The crucial role of the active block of HTS cuprates has long been recognized but not of the charge reservoir block. However, different cuprate systems with identical active blocks but different charge reservoir blocks display different T_cs. For example, the maximum T_c's of $HgBa_2Ca_2Cu_3O_{9-\delta}$ and $Bi_2Sr_2Ca_2Cu_3O_{10}$ are 134 K and 115 K, respectively, although both have the same active block of *[(CuO₂)Ca(CuO₂)Ca(CuO₂)]*. The charge reservoir blocks must play a role in their T_cs. It is interesting to note that HTS cuprates with Ba in their charge reservoir blocks, i.e. $[(BaO)(AO)_m(BaO)]$, usually exhibits a higher T_c than their iso-electronic and iso-structural counterpart with Sr containing reservoir blocks, i.e. $[(SrO)(AO)_m(SrO)]$. For instance, $YBa_2Cu_3O_7$ = $[(BaO)(CuO)(BaO)]+[(CuO_2)Y(CuO_2)]$ possesses a $T_c \sim 93$ K whereas $YSr_2Cu_3O_7$ displays a $T_c \leq 60$ K. A similar observation is found in ferroelectrics, e.g. $BaTiO_3$ becomes ferroelectric at a Curie temperature $T_c = 393$ K while $SrTiO_3$ remains non-ferroelectric down to 1 K in its unstrained state. This has been attributed to the larger polarizability of the Ba-ion. It may not be surprising to see a similar reason for the case of superconductivity although it has not yet been included in any theoretical model. Phenomenologically, a general correlation between superconductivity and ferroelectricity has been previously suggested by Jim Phillips.

5.9. Magnetic Interactions

Many have demonstrated that the conventional electron-phonon interaction derived from the normal state properties of the cuprates is not sufficient to produce a T_c as high as those observed in these superconductors. Magnetic interactions have therefore been proposed. This is certainly consistent with the fact that all superconductors known to date with a T_c above 77 K, liquid nitrogen temperature, are cuprates whose Cu^{2+}-ions with a spin S = ½ may provide the suggested antiferromagnetic fluctuations needed for the attractive interaction for the high T_c. The question whether the Cu^{2+}-ion with S = ½ is synonymous to a high temperature superconductivity remains unanswered. Given the ubiquitous nature of superconductivity and magnetism, it is not unthinkable that high temperature superconductivity can be found in materials containing other types of magnetic ions with possibly different S that can generate the needed antiferromagnetic or ferromagnetic fluctuations.

6. THE ENLIGHTEND EMPIRICAL APPROACH

In philosophy, "Empiricism or Rationalism" has been debated among scholars for a long time. The difference between the two lies mainly in the different relationships between reason and knowledge and between experience and knowledge: whether reason or experience is the source of knowledge and whether knowledge can be gained independent of experience. Empiricists consider experience to be the source of knowledge and to be independent of knowledge, while rationalists claim that reason is the source of knowledge and is independent of experience. In the long search for superconductors of higher T_c, Matthias, Geballe and Mueller reminded us at different times of the effectiveness of the empirical approach.

I think the most effective empirical approach toward RTS is better conceptualized as an enlightened empirical approach that embodies both experience and reason. Looking back at the history of superconductivity or of science in general, the line has always blurred between empiricists and rationalists, or between Edisonians and Einsteinians, i.e. between experimentalists and theorists. Synergistic effect between the two has long been recognized as was well illustrated, for example, by Bardeen in the development of the BCS theory *[J. Bardeen, Impact of Basic Research on Technology, ed. B. Kursunoglu and A. Perlmutt (Plenum Press, 1973), p.15]*. Even when Matthias said "don't listen to theorists," he reminded people that "I do have good theorist friends."

In Sections 3, 4 and 5, I have summarized what we have learned from past experiments and theories. They can serve as a guide to project enlightened-empirically into the future paths that may be most fruitful to achieve HTS with higher T_c or even RTS. The summaries include some of the interesting claims that may warrant further tests, some visionary predictions that may be pursued and the common features of superconductors with high T_c that may provide directions for the search for novel superconductors. The worldwide extensive studies on HTS cuprates and related materials over the last two decades have given us unusual physical insight to materials, powerful computational capabilities for materials, sensitive material characterization techniques and new material synthesis tools. Time is ripe to bring all these skills to bear in the search for novel superconductors with higher T_c, preferably at room temperature. If history is any guide, I strongly believe that, in the process, in addition to higher T_cs, new physics will be discovered and novel materials found with both scientific and technological significance.

While the exact path to be taken depends on the style and taste of the practitioner, to paraphrase of Professor Yang's statement on doing physics, I would like to list some of my thoughts below.

6.1. Some Interesting Claims That may Be Worth Revisiting

- The Na-NH_3 system reported to display persistent current suggestive of superconductivity at temperatures up to 180 K may bear a certain possible resemblance to the cuprate HTS system, namely, phase separation, pseudo-gap and real-space pairing. Given the tremendous improvement in diagnostic tools today, a revisit may be worthwhile.

- The large resistive and diamagnetic anomalies suggestive of superconductivity at temperatures up to 160 K reported in CuCl during rapid warming reported may be associated with some of the common features of HTS, such as instability, disproportionation, and interface effect. The role of Cu in the cuprate HTS era is particularly intriguing. It will make easier a definitive diagnosis of the nature of the anomalies by developing a technique to transform the transient nature of the anomalies to a steady one.

- The frequent report of resistive anomalies in cuprates suggestive of superconductivity in the similar temperature range of 230-350 K by different reputable labs in different countries is too tantalizing and does not seem to be pure coincident. With the recent development of ultra-sensitive diagnostic tools such as microwave spectrometry and of powerful synthesis technique, a systematic revisit is worthwhile.

- The resistive, magnetic, and microwave anomalies and magneto-optical imaging data suggestive of superconductivity at temperatures up to 91 K reported in WO_3 surface-doped by Na remain a puzzle. In spite of the relatively low temperature of the anomalies, the system appears to be simple and represents the first noncuprate system to display such a high T_c, if proven to be superconducting and not due to contamination by cuprate HTS. Controlled surface doping can be deployed to resolve the puzzle easily.

6.2. Some Visionary Predictions That may Be Worth Testing

- The organic macromolecules that consist of a long spine and a series of side chains were predicted to superconduct above room temperature. They may be designed using powerful computational skills, and synthesized and characterized by advanced techniques acquired over the last two decades. At the same time we should keep in mind how to overcome several serious challenges for a one-dimensional electron system: i) the inherent fluctuations associated with a one-dimensional system that prevents long-range order and a coherent phase transition; ii) the inherent Peierls instability that will result in the opening of a gap and a transition to an insulating state; and iii) the lack of screening of the Coulomb repulsion that will overwhelm the attractive interaction for electron pairing.

- The surface superconductivity at high T_cs above room temperature was predicted to take place in the surface of a metal, especially when covered by a dielectric material. This may be realized today by the powerful molecular beam epitaxial technique now available to grow samples with desired interfaces in a controlled atmosphere available.

- Superconductivity with a T_c above room temperature was predicted to take place in light ionic mass materials such as H, Li and group IVa hydrides with H as a major constituent under very high pressures. With the advancement in ultrahigh pressure and characterization techniques, the theoretical conditions are now within reach of experiments.

- The interfacial superconductivity with enhanced T_c through the exchange of excitons was predicted to take place in a materials system that consists of a metallic thin film on a semiconductor with Fermi energy E_F and energy gap E_g, respectively. The stringent requirements on the coupling between the metal film and the semiconductor and on the E_F -E_g relation can now be achieved with advanced experimental and computational techniques.

6.3. Common Features of High T_c Superconductivity as a Guide

Besides what has been pointed out in the above two sub-sections, I shall list the general directions that are most likely to yield results in our search for novel superconductors with higher T_c or even RTS.

- Pay attention to layered strongly correlated two-dimensional electron systems displaying multiple interactions and instabilities, and seek ways, physical and chemical, to optimize the multiple interactions and to control the instabilities.

- Pay particular attention to layered strongly correlated material systems that exhibit antiferromagnetic or ferromagnetic fluctuations and strong covalent bonding.

- Pay attention to multi-component layered strongly correlated material systems.

- Pay attention to multi-scale material systems.

- Examine materials that may show the appearance of psudo-gap at high temperature signaling the onset of electron pairing.

- Pay more attention to noncuprate layered materials systems.

- Design and synthesize layered inorganic/organic hybrid systems.

- Develop conventional or nonconventional doping techniques for the above systems.

- Take advantage of pressure, fields, and chemical and physical means in the search.

- Improve the cuprate HTS.

7. CONCLUSION

To date, there exists neither theoretical nor experimental evidence to exclude the existence of novel superconductors with a T_c exceeding room temperature. Due to the past two decades of extensive work on HTS worldwide, we have acquired better insight into materials, achieved powerful material computational methods and developed powerful materials characterization and diagnostic tools, and novel material synthesis techniques. What we have learned in the study of HTS over the last 20 years may now bear fruits in our search for novel superconductors of higher T_c, especially in layered strongly correlated electron systems with multi-subcomponents and magnetic fluctuations, and by using different pressure, fields, and chemical and physical means of tuning, I think that the approaches listed above will yield significant results in our search for RTS based on my strong belief that whatever the law of physics do not say will not happen will happen.

Note added: After the delivery of the above presentation in Singapore in October 2007, the exciting news of the discovery by Hosono *et al.* in Japan of a new class of superconductor at a relatively high temperature reached me a few months later. Guided by the rule that high temperature superconductivity usually occurs in the strongly correlated electron layered systems as the case of cuprates, they examined the layered rare-earth transition-metal oxypnictides (ROTPn, where R = rare-earth element, T = transition-metal element, and Pn = pnictogen) and discovered superconductivity in several of these compounds with a T_c as high as 26 K in the doped La(O,F)FeAs. The presence of the large concentration of magnetic Fe appears to be consistent with the suggested important role of magnetism in superconductivity with high T_c. In the few weeks following the news, the T_c was raised to 52 K by replacing La by rare-earth elements of smaller radii. Pressure was also found to raise the T_c of La(O,F)FeAs. Euphoria permeated in the community such that as far as T_c is concerned, only the sky would be the limit. By carrying out a systematic pressure study and analyzing the data, we concluded that the maximum T_c of the doped ROFeAs(R1111) can only be in the 50s K and almost independent of R, similar to the cuprates (R123). Later a similar layered A'Fe_2As_2(A'122) where A' = alkaline-earth element Ba or Sr was found superconducting with a T_c up to 38 K when it is hole-doped by partial replacement of A' by alkaline metal A = K or Cs. Subsequently, we found that K122 and Cs122 were superconducting at 2.8 and 3.7 K, respectively and form complete phase diagrams of (A,Sr)Fe_2As_2 with A = K and Cs, showing that a continued evolution from a superconducting state at A122 to a spin-density-wave (SDW) state at A'122 with an intermediate region where the SDW state coexists with the superconducting state through continuous electron doping by partial replacement of A with A'. Later, yet another FeAs-layered compound system AFeAs (or A111) with A = Li and Na was discovered by us to be superconducting at 20 and 17 K, respectively. The above three new compound systems, R1111, A'122 and A111, can be considered to belong to a homologous compound series with FeAs-layers, similar to the cuprates with the CuO_2-layers. A111 may then be the equivalent of the infinite-layered cuprate, $SrCuO_2$. We have therefore recently proposed that higher T_c may be achievable by designing and synthesizing more complex compounds that consist of TPn-layers.

REFERENCES

[1] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **106**, 162 (1957).

[2] T. D. Lee and C.N. Yang, *PR* **105**, 1671 (1957).

[3] M. K. Wu *et al.*, *Phys. Rev. Lett.* **58**, 908 (1987).

[4] J. G. Bednorz and K. A. Müller, *Z. Phys. B* **64**, 189 (1986).

[5] Sir Isaac Newton, Philosophiæ Naturalis Principia Mathematica (1686).

[6] H. K. Onnes, *Leiden Comm.* 120b, 122b, 124c (1911).

[7] J. R. Gavaler *et al.*, *J. Appl. Phys.* **45**, 3009 (1974); L. R. Testardi *et al.*, *Solid State Comm.* **15**, 1 (1974).

[8] Tokyo, Houston and Beijing groups.

[9] C. W. Chu and L. R. Testardi, *Phys. Rev. Lett.* **32**, 766 (1974); C. W. Chu, *Phys. Rev. Lett.* **33**, 1283 (1974); C. W. Chu and V. Diatschenko, *Phys. Rev. Lett.* **41**, 572 (1978).

[10] C. W. Chu *et al.*, *Phys. Rev. Lett.* **58**, 405 (1987).

[11] C. W. Chu *et al.*, Science **235**, 567 (1987).

[12] W. L. McMillan, *Phys. Rev.* **167**, 331 (1968).

[13] R. J. Cava *et al.*, *Phys. Rev. Lett.* **58**, 408 (1987).

[14] R. M. Hazen *et al.*, *Phys. Rev. B (RC)* **35**, 7238 (1987).

[15] P. H. Hor *et al.*, *Phys. Rev. Lett.* **58**, 1891 (1987).

[16] H. Maeda *et al.*, *Jpn. J. Appl. Phys.* **27**, L209 (1988).

[17] Z. Z. Sheng and A. M. Hermann, *Nature* **332**, 138 (1988).

[18] A. Schilling *et al.*, *Nature* **363**, 56 (1993).

[19] L. Gao *et al.*, *Phys. Rev. B (RC)* **50**, 4260 (1994).

[20] For a review, see for example Superconductivity, by C. P. Poole Jr., H. A. Farach, R. J. Creswick, and R. Prozorov, Academic Press (2008); - Appl.

[21] B. T. Matthias, T. H. Geballe, L. D. Longinotti, E. Corenzwit, G. W. Hull (1966).

[22] R. A. Ogg, *Phys. Rev.* **69**, 243 (1946).

[23] R. A. Ogg, *J. Am. Chem. Soc.* **68**, 155 (1946).

[24] H. W. Boore *et al.*, *Phys. Rev.* **70**, 72 (1946); J. G. Daunt *et al. Phys. Rev.* **70**, 219 (1946); and J. W. Hodgins, *Phys. Rev.* **70**, 568 (1946).

[25] D. A. Kirzhnitz and Yu. V. Kopaev, *JETP Lett.* **17**, 270 (1973); I. M. Dmitrenko and I. S. Shchetkin, *JETP Lett.* **18**, 292 (1974).

[26] For example, P. Edwards *et al.*, *Chem. Phys. Chem.* **7**, 2015 (2006).

[27] A. P. Rusakov *et al.*, *Phys. Status Solid B* **75**, K191 (1975).

[28] C. W. Chu *et al.*, *J. Phys. C: Solid State Phys.* **8**, L241 (1975); A. P. Rusakov *et al.*, *Sov. Phys.: Solid State* **19**, 680 (1977).

[29] N. B. Brandt *et al.*, *JETP Lett.* **27**, 37 (1978).

[30] C. W. Chu *et al.*, *Phys. Rev. B* **18**, 3116 (1978).

[31] V. L. Ginzburg, *S. S. Comm.* **50**, 339 (1984).

[32] N. Reyren *et al.*, *Science* **317**, 1196 (2007).

[33] J. T. Chen *et al.*, *Phys. Rev. Lett.* **58**, 1972 (1987).

[34] M. Lagues *et al.*, *Science* **262**, 1850 (1993).

[35] J. L. Tholence *et al.*, *Phys. Lett. A* **184**, 215 (1994).
[36] S. Reich and Y. Tsabba, *Eur. Phys. J. B* **9**, 1 (1999).
[37] See for example, S. Reich *et al.*, *J. Superconductivity: Incorporating Novel Magnetism* **13**, 855 (2002).
[38] H. Barth and W. Marx, Cond.-Mat/0609114 (2006).
[39] W. A. Little, *Phys. Rev.* **164**, A1416 (1964).
[40] M. Lang and J. Müller, Cond.-Mat/0302157 (2003).
[41] Y. Ando *et al.*, *Phys. Rev. Lett.* **77**, 2065 (1996).
[42] V. L. Ginzburg, *JETP* **47**, 2318 (1964).
[43] V. L. Ginzburg, *Soviet Phys., Uspekhi* **13**, 335 (1970).
[44] J. A. Wilson *et al.*, *Phys. Rev. Lett.* **32**, 882 (1974).
[45] N. W. Ashcroft, *Phys. Rev. Lett.* **21**, 1748 (1968).
[46] C. F. Richardson and N. W. Ashcroft, *Phys. Rev. Lett.* **78**, 119 (1997).
[47] N. W. Ashcroft, *Phys. Rev. Lett.* **92**, 187002 (2004).
[48] D. Allender, J. Bray, and J. Bardeen, *Phys. Rev. B* **7**, 1020 (1973).
[49] L. N. Cooper, *Phys. Rev.* **104**, 1189 (1956).
[50] M. Rice and L. Sneddon, *Phys. Rev. Lett.* **47**, 689 (1981).
[51] Z. A. Xu *et al.*, *Nature* **406**, 486 (2000).
[52] K. S. Bedell and D. Pines, *Phys. Rev. B* **37**, 3730 (1988).
[53] H. W. Meul *et al.*, *Phys. Rev. Lett.* **53**, 497 (1984).
[54] R. P. Chaudhury *et al.*, *Phys. Rev. B*, in press (2008).
[55] M. Rice, *Physica C* **282-287**, xix (1997).
[56] C. W. Chu and V. Diatschenko, *Phys. Rev. Lett.* **41**, 572 (1978).
[57] C. Y. Huang *et al.*, *J. Korean Phys. Soc.* **31**, 16 (1997).
[58] R. G. Sweedler *et al.*, *Phys. Lett.* **15**, 108 (1965).
[59] C. W. Chu, *History of Original Ideas and Basic Discoveries in Particle Physics*, ed. H. B. Newman and T. Ypsilantis (Plenum Press, New York, 1996), p. 793.
[60] S. Yamada *et al.*, *Nature* **239**, 530 (1998).
[61] L. F. Mattheiss *et al.*, *Phys. Rev. B* **37**, 3745 (1988); A. W. Sleight *et al.*, *Solid State Comm.* **17**, 27 (1975).
[62] D. C. Johnston *et al.*, *Mater. Res. Bull.* **8**, 777 (1973).
[63] D. Jérome *et al.*, *J. Physique Lett.* **41**, 95 (1980).