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SUPERCONDUCTIVITY ABOVE 90 K AND BEYOND

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ABSTRACT

The discovery of high temperature superconductivity, first in 1986 at 35 K in $La_{2-x}Ba_xCuO_4$ and later in 1987 at 93 K in $YBa_2Cu_3O_7$, has been considered one of the most exciting developments in physics in the final decades of this century, with profound technological implications. In this 10th anniversary celebration, I shall begin by describing briefly two approaches adopted in the long and tortuous search for intermetallic superconductors with a higher transition temperature (T_c) that have had a significant bearing on our later work on the non-intermetallic superconductors. I shall then recall crucial steps we took in 1986, after the seminal observation made by Bednorz and Müller, which led to the exciting discovery in 1987 by the combined effort of our group in Houston and Wu's group in Huntsville. Efforts to raise the T_c over the last 10 years will be summarized, and the future prospects for T_c's above the current record of 134 K at ambient and 164 K at high pressure will be contemplated.

1. Introduction

It has always been an exhilarating experience to be a practitioner in the field of superconductivity, where intellectual challenge and technological promise coexist. This has been especially true over the past ten years, following the discovery of high temperature superconductivity (HTSy) [1,2]. HTSy is a rapidly evolving field, where records are shattered soon after their establishment by new discoveries, and models are made obsolete shortly after their proposition by new insights. The rapid pace of progress made in the field has been unprecedented. Voluminous exciting results in all areas of HTSy science and technology have been achieved. For instance, the transition temperature (T_c) has been quadrupled, several crucial aspects of HTSy have been understood, various models have been proposed, numerous material processing techniques have been developed, and a wide variety of prototype devices have been or are being constructed and tested.

It was said by Emerson that "there is no history; there is only biography." This is especially true when the events are recounted by a person who, himself, has been heavily involved and the line between history and autobiography can become blurred. To minimize possible injustices that may be done to researchers in the field, I plan to restrict myself to one small but important area of the HTSy research, i.e. the search for materials with higher T_c. Some of these events has been described elsewhere [3]. In this presentation, I summarize and discuss selected events that occurred: before 1986 that sowed the seeds in our group for later HTSy-development; in 1986, that were crucial to our discovery of 93 K-HTSy soon after the discovery of the 35 K high temperature superconductor (HTSr) [1]; in 1987 when the liquid nitrogen boiling temperature of 77 K barrier was finally conquered [2]; and from 1988 to 1996, during which time advancements [4-11] were achieved continuously in raising the T_c to the current records of 134 K at ambient [9] and 164 K at

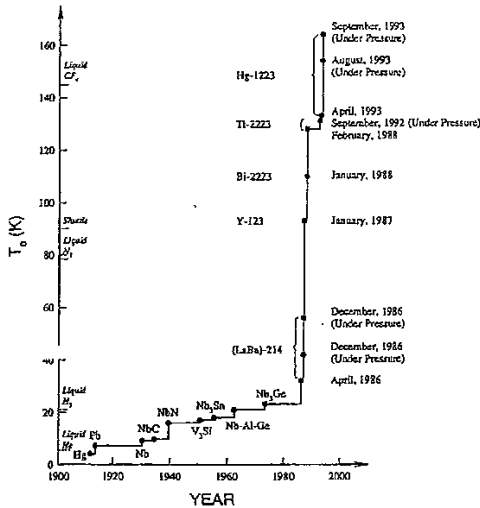high pressures [10,11]. The prospect for higher T_c's in the future will also be contemplated.

Figure 1. The evolution of T_c with time.

2. Before 1986

In spite of the enormous impact the search for novel HTSr has had on condensed matter physics research, the road to compounds with a higher T_c before 1986 was tortuous and slow, as shown in Figure 1. Until 1986, the record T_c remained at 23 K found in intermetallic Nb3Ge-films in 1972 [12], representing only a 19 K° increase since the discovery of the phenomenon in 1911. All superconductors with such a relatively high T_c then were intermetallic compounds. During this period of time, there were two general approaches adopted in the search for compounds with a T_c higher than the existing record: the BCS approach and the enlightened empirical approach. Although neither of the two approaches was able to lift the T_c above 23 K, studies by various groups including our own prior to 1986, give us the proper perspective on the high T_c problem, including: the possibility of a $T_c > 23$ K; the realization of the importance of optimization rather than maximization of parameters in raising T_c; the appreciation of the significance of instabilities and dimensionality to superconductivity at higher temperatures; skills in material synthesis and characterization; and knowledge of physics and chemistry of superconductors in general and of oxides in particular.

2.1. The BCS Approach

According to the BCS theory [13], T_c is given as

$$T_c = 1.14 \, \Theta_D exp[-1/N(E_F)V]$$

where Θ_D is the Debye tempera surface (E_F), and V the electron-

to increase with an increase in one

Many experiments on variou years, based on the BCS relati compounds [14], a higher N characteristic energy in lieu of th systems [15]. During these studie relation are not each independen structural and/or electronic inst structural collapse or an electron waves, etc.), before a really high instabilities and superconductivi the incipient instabilities associat To avoid catastrophic instabilitie superconductivity [16] were al: including oxides near their metal.

2.2. The Enlightened Empirical.

The most successful example of so-called "Matthias Empirical R ratio of valence electrons to num of a compound system usually of compounds and alloys were m While this correlation works v metal elements, it fails for non-superconductors.

3. 1986

The work on La-Ba-Cu-O (LB ushered in the era of HTSy. W excitement. We fabricated m technique that we acquired in observation immediately. It see to find a proper thermometer superconductivity researchers. resistance (R) drop by a factor of 2), suggesting the possibility above 60 K. Unfortunately, s: magnetic experiment to provide such high temperatures. How

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where Θ_D is the Debye temperature, $N(E_F)$ the electron-density of states at the Fermi surface (E_F), and V the electron-phonon interaction. In a simplistic sense, T_c is expected to increase with an increase in one or more of the three parameters Θ_D, $N(E_F)$, and V.

Many experiments on various compounds were made and analyzed in the ensuing years, based on the BCS relation. For instance, a large V was sought in unstable compounds [14], a higher N in low-dimensional compounds [15], and a greater characteristic energy in lieu of the conventional $k\Theta_D$ in one- or two-dimensional material systems [15]. During these studies, it was realized that the three parameters in the BCS T_c-relation are not each independent of the other. Unusually large N and/or V can trigger structural and/or electronic instabilities, which in some extreme cases, give rise to a structural collapse or an electronic ordering (such as charge-density waves, spin-density waves, etc.), before a really high T_c is achieved. By examining the competition between instabilities and superconductivity using the high pressure technique, we found [14] that the incipient instabilities associated with large N and/or V are not an obstacle to higher T_c. To avoid catastrophic instabilities, novel superconducting mechanisms such as interfacial superconductivity [16] were also proposed and explored in unusual material systems, including oxides near their metal/insulator boundaries [17].

2.2. The Enlightened Empirical Approach

The most successful example of the enlightened empirical approach before 1986 was the so-called "Matthias Empirical Rule" proposed in 1953 [18]. The rule correlates T_c with the ratio of valence electrons to number of atoms (e/a). According to the rule, the maximum T_c of a compound system usually occurs at e/a ~ 4.75 and ~ 6.4. Hundreds of intermetallic compounds and alloys were made with a T_c up to the 1972-record of 23 K in Nb3Ge. While this correlation works well for crystalline superconductors containing transition metal elements, it fails for non-transition metal compounds and alloys, or for amorphous superconductors.

3. 1986

The work on La-Ba-Cu-O (LBCO) with a T_c ~ 35 K in 1986 by Bednorz and Müller [1] ushered in the era of HTSy. We read their paper in early November 1986 with immense excitement. We fabricated multiphased samples of LBCO by the solid-state reaction technique that we acquired in the study of $(Ba_{1-x}Pb_x)BiO_3$ and reproduced their observation immediately. It seemed that the greatest experimental challenge at the time was to find a proper thermometer to measure in a temperature region alien to most superconductivity researchers. Even more exciting, in late November we detected a large resistance (R) drop by a factor of 80 at ~ 75 K in a multiphased sample of LBCO [19] (Fig. 2), suggesting the possibility of an even higher T_c. More R-drops were detected later above 60 K. Unfortunately, sample-aging problems prevented us from carrying out the magnetic experiment to provide more definitive evidence for a superconducting transition at such high temperatures. However, after reviewing all possible non-superconducting
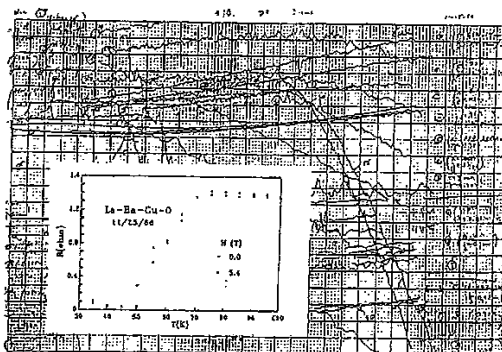
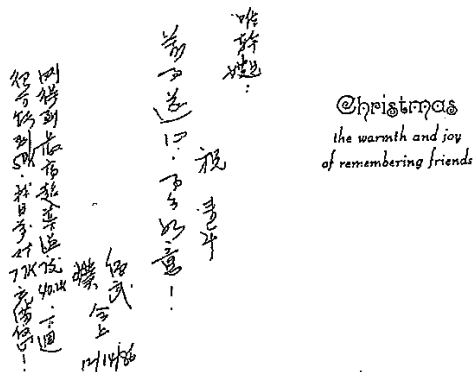Figure 2. The R(T)-curve of a multiphase LBCO sample obtained on November 25, 1986 (Ref. 3).

Figure 3. The Christmas card dated December 14, expressing our confidence of T_C's above 77 K. Translation: "Just obtained highest T_C at 40.2 K, next week very likely will reach 50 K. Presently, I am full of confidence of 77 K."

transitions in various compounds, I stated that "I am now full of confidence about the 77 K (for superconductivity)," in a Christmas card to Wei-Kan Chu dated December 14, 1986 (Fig. 3).

With LBCO-samples, even though multiphased, on hand, we examined the pressure effect on their superconducting transition in an attempt to determine if the nature of the superconductivity in this compound was similar to that of the superconductivity in the low temperature superconductors (LTSrs). We found its T_C to increase at a rate almost 10 times that observed in LTSrs without a structural transition to 40.2 K at 1.3 GPa [19], a temperature previously predicted to be impossible. This observation suggested to us that the superconductivity in LBCO was different from that in LTSrs, and that T_C may not have a ceiling, a faith that played an important role in our later work.

We presented our first LBCO-results at the Materials Research Society Meeting in Boston in early December, where I invited my former student Maw-Kuen Wu then of the University of Alabama at Huntsville to join our study. Koichi Kitazawa of Tokyo told me at the Meeting that they had identified the superconducting phase responsible in LBCO to be

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4. 1987

After destroying two of our three Pt-crucibles in an attempt to grow La-214 single crystals for a systematic study, we shifted our efforts to the R-drops in multiphased LBCO samples at high temperatures. While waiting for the Y, Yb and Lu we had ordered to arrive, we deliberately prepared LBCO samples with a composition distribution across them and heated them under different conditions. On January 12, 1987, a diamagnetic shift signaling the onset of superconductivity was unambiguously detected at ~ 90 K for the first time in one of the samples (Fig. 4). However, the insulating exte measurements. Since a large indicator than a R-drop, there v had finally been observed. Th 12, 1987 (Fig. 5) did displa $LaBa_2Cu_3O_7$ (La-123) for the was determined in early Mar disappeared the next day. The isolate the high temperature si we decided to publish the LBC superconducting phase, provi observation was made.

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4. 1987

After destroying two of our three Pt-crucibles in an attempt to grow La-214 single crystals for a systematic study, we shifted our efforts to the R-drops in multiphased LBCO samples at high temperatures. While waiting for the Y, Yb and Lu we had ordered to arrive, we deliberately prepared LBCO samples with a composition distribution across them and heated them under different conditions. On January 12, 1987, a diamagnetic shift signaling the onset of superconductivity was unambiguously detected at ~ 90 K for the first time in one of the samples (Fig. 4).

Figure 4. $\chi(T)$ for a multiphased LBCO-sample determined on January 12, 1987 (Ref. 3). Inset: Measurements after subtraction of the background.

However, the insulating exterior of the sample prevented us from doing the resistive measurements. Since a large diamagnetic signal (~ 26% at 4 K) is a more definitive indicator than a R-drop, there was no doubt in our mind that superconductivity above 77 K had finally been observed. The X-ray diffraction pattern of the sample taken on January 12, 1987 (Fig. 5) did display a structure different from La-214; but was indexed as $LaBa_2Cu_3O_7$ (La-123) for the major phase only after the structure of $YBa_2Cu_3O_7$ (Y-123) was determined in early March. Unfortunately, the diamagnetic signal in the sample disappeared the next day. The only questions that remained then were how to stabilize and isolate the high temperature superconducting (HTSg) phase. After careful consideration, we decided to publish the LBCO data so that others better equipped could stabilize the 90 K superconducting phase, provided that we stated clearly the conditions under which the observation was made.
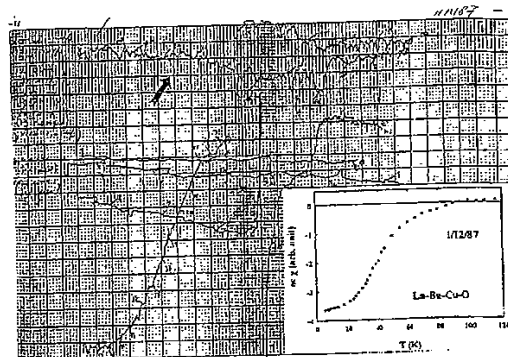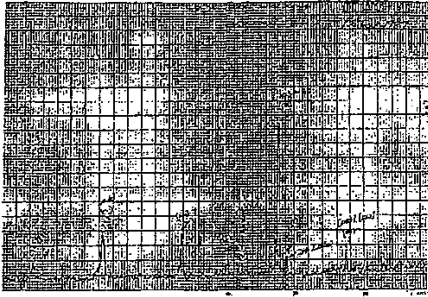
Figure 5. X-ray diffraction pattern for the LBCO-sample taken on January 12, 1987 and indexed later in March to be La-123 for the major phase (Ref. 3).
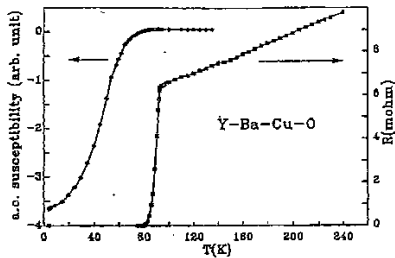

Figure 6. R(T) and χ(T) for a YBCO sample measured on January 30, 1987 (Ref. 2).

As I started to draft a paper on these results, Maw-Kuen called on January 29, 1987 and informed my former student Peiherng Hor and me that he and his students had just observed an R-drop to zero above 77 K. We were all ecstatic. Next day, Maw-Kuen and his student Jim Ashburn flew to Houston with their sample of Y-Ba-Cu-O (YBCO) for a definitive magnetic check. As shown in Figure 6, the R-drop between 80 and 93 K observed at Huntsville was reproduced and a diamagnetic signal indicative of a superconducting transition below 91 K was detected. Using the newly arrived Y, several superconducting samples were made and tested on the same day at Houston. The long sought stable and reproducible superconductivity above the 77 K-temperature barrier was finally established. Although we did not know how to determine the structure of the superconducting phase, the X-ray pattern of the sample and the pressure effect on its T_C [20] led us to conclude that the 90 K-superconducting phase must be structurally different from the 30 K La-214 phase.

The YBCO-results easily preempted my desire to write the paper on the unstable 90 K LBCO results. With the exciting YBCO results and the thought invested in the stillborn LBCO-paper, it did not take more than one evening for me to draft two papers on YBCO [2,20] which the LBCO-data was briefly included. After being reviewed by Mau-Kuen, Peiherng, and Ruling Meng, the papers were sent by express mail on February 5, 1987 to *Physical Review Letters* for publication. I was notified by Myron Strongin, editor of *Physical Review Letters*, of the acceptance of the papers on February 11.

I still vividly remember the sentence of the paper [2], "To ob and psychological temperature ba the greatest triumphs of scientific In spite of all my confidence, possibility, it might be too goc submission of the papers that my superconductivity we reported colleagues, "Can there be phenor for our observations? Please thir enormous and was relieved onl observation [21].

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I still vividly remember the extraordinary emotion I felt when I wrote the second sentence of the paper [2], "To obtain a superconductor reaching beyond the technological and psychological temperature barrier 77 K, the liquid nitrogen boiling point, will be one of the greatest triumphs of scientific endeavor of this kind," knowing that we had achieved it. In spite of all my confidence, deep down I still felt that, no matter how remote the possibility, it might be too good to be true. There were momentary scares after the submission of the papers that my career in superconductivity could end abruptly if the 90 K superconductivity we reported were to be proven untrue. More than once, I asked my colleagues, "Can there be phenomena other than superconductivity that are able to account for our observations? Please think and think hard!" The emotional burden at the time was enormous and was relieved only after news from other labs that they had reproduced the observation [21].

The structure of the superconducting phase was soon determined to be $YBa_2Cu_3O_7$ (Y-123) in collaboration with Bob Hazen and Dave Mao at the Geophysical Lab [22]. Other labs had also cracked the structure code at about the same time [23]. It is a layered structure with the stacking sequence of $(Y)(BaO)(CuO_2)(CuO)(CuO_2)(BaO)$, with two (CuO_2)-layers separated by a (CuO)-linear chain layer per unit cell.

Once the structure was determined, we set out to determine the role of Y in 90 K HTSy by partial replacement of magnetic rare-earth for Y. We found that, even with a large fraction of Y replaced by Gd and Eu, no T_c-depression was detected, suggesting that Y is electronically isolated from the superconducting carrier system and serves mostly as a stabilizer in the compound. A whole new series of $RBa_2Cu_3O_{7-\delta}$ (R-123) with R = Y, La, Nd, Sm, Eu, Gd, Ho, Er and Lu, with a $T_c \sim 90$ K was quickly synthesized [24] in our first trial. The series was synthesized in a reduced atmosphere which we used to significantly shorten the synthesis time and thus to give us a large advantage over other groups in the early days of HTSy. Our results prompted us to propose to attain higher T_c's by increasing the number of CuO_2-layers per unit cell [24]. Some of the R-123 were independently discovered at about the same time by other groups [25].

After submitting the paper on R-123, I departed for the special HTSy session of the 1987 March APS Meeting held on March 16 in New York. The special session was triggered by a "Dear Colleague" rejection letter from APS in the second week of December 1986, because our abstract on LBCO was half a line over the limit. By this time, a higher T_c was attained by pressure and R-drops at temperatures above 75 K were observed. I strongly felt that an exciting physics story was on the verge of unfolding. It did not take me long to convince the chairman of the Condensed Matter Physics Council of APS, Neil Ashcroft, and the other council members to agree to add a Special Session to the Meeting. I was asked to organize the special session. Alex Müller of IBM Zürich, Shiji Tanaka of the University of Tokyo, Paul Chu of the University of Houston, Zhong-Xian Zhao of the Physics Institute of the Chinese Academy of Sciences at Beijing, and Bertram Batlogg of AT&T Bell were invited to join a panel to address their work, in the same chronological order in which their respective work on La-214 appeared in journals. The dramatic events that took place within less than two months prior to the Meeting turned the Special Session on HTSy into the "Woodstock of Physics," a moniker coined by the late Mike Schlüter. I could not have dreamed that any such event would have happened when I first proposed it.

5.   1988-96

The years between 1988 and 1996 represent a period of solid advancement and many cuprate superconductors were discovered. They may be considered to belong to or be derivable from the layered compound systems of R_2CuO_4 [R-214 (1T), with R = La; or R-214(1T'), with R = Nd, Sm, Eu and Gd], $RBa_2Cu_3O_7$ (R-123, where R= rare earths except Ce, Pr, and Tb), $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ [Bi-22(n-1)n, with n = 1, 2, 3, ...], $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ [Tl-22(n-1)n, with n = 1, 2, 3, ...], $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ [Hg-12(n-1)n, with n = 1, 2, 3, ...], $CuBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ [Cu-12(n-1)n, with n = 1, 2, 3, ...]; and $A_{1-x}B_xCuO_2$ (with A = alkaline earth, B = alkaline earth or vacancy), and Sr_2CuO_4. They have also set new T_c-records and contributed to debates on the occurrence of HTSy. In this section I shall briefly comment on these systems except the first two, that have already been discussed.

5.1. Bi-22(n-1)n

As 1987 came to a close, T_c stagnated at 93 K. Some noted that the accumulated man-hours devoted to HTSy in 1987 probably exceeded all those devoted to low temperature superconductivity over the preceding 75 years, over-zealously concluding that $T_c > 93$ K could only be found in non-cuprate materials, if it existed at all. Their premature predictions were shattered by Maeda et al. who discovered [4] superconductivity above 100 K in the Bi-Sr-Ca-Cu-O (BSCCO) system in January 1988.

In the summer of 1987, Michel et al. reported [26] an important observation of superconductivity in Bi-Sr-Cu-O at ~ 8 K, which turned out to be the n = 1 member of the Bi-22(n-1)n system. Independently, in an attempt to expand the HTSg material base, Maeda et al. decided to replace the trivalent rare-earth element in R-123 by elements from the V-b group in the Periodic Table, such as Bi and Sb, which are trivalent and have ionic radii similar to the rare earths. They succeeded in detecting superconductivity above 105 K in multiphase samples of BSCCO [4]. The crystal structures of three members of the homologous series Bi-12(n-1)n with n = 1, 2, and 3 were soon determined [27], showing layered stacking sequence of $(BiO)_2(BaO)(CuO_2)(Ca)(CuO_2) ... (Ca)(CuO_2)(BaO)$ with n (CuO_2)-layers separated by n-1 (Ca)-layers, for Bi-22(n-1)n. The new record $T_c = 110$ K was attributed to the n = 3 members; and 22 and 80 K to members for n = 1 and 2, respectively. T_c clearly increased with n, as was predicted by us earlier [20]. Unfortunately, T_c was later shown to decrease with n > 3. It is interesting to note that it took Hazen et al. less than 48 hours to determine the Bi-1212 structure after receiving the samples from us. The acceleration of HTSy-research was clearly evident.

5.2. Tl-22(n-1)n

Following the similar rationale in forming R-123 [2,20], Sheng and Hermann started to substitute the trivalent nonmagnetic Tl for R by the end of 1987. After overcoming some problems associated with sample synthesis due to the low melting point and high volatility of Tl_2O_3, they detected superconductivity above 90 K in a multiphased sample with a nominal composition of TlBa$_2$ Ba by Ca, they discovered [5] (TBCCO) in February 1987. soon determined afterward to $(TlO)_2$-double layer [29]. T_c members, respectively. In Se enhanced to 131 K by the appli

5.3. Hg-12(n-1)n

As early as 1991, attempts we: Cu in the (CuO)-chain layer in the n = 1 member of Hg-12(n single-layered cuprate. It has Schilling et al. [9] succeeded ir 1)n with n = 2 and 3. Later sti 1)n possess T_c = 97, 127, and 12(n-1)n displays the stack: $(Ca)(CuO_2)(BaO)$, with n (C structure is similar to TlBa$_2$Ca concentration in the (HgO$_\delta$)-la: of the (HgO$_\delta$)-layers, unusually large T_c enhancement by pressure was achieved, pushing T_c first to ~ 154 K at ~ 16 GPa [10], and then to 164 K at ~ 30 GPa [11], setting new T_c-records (Fig. 7) in a temperature region attainable in the Space Shuttle on the side opposite to the sun or by air-conditioner technology. Hg-12(n-1)n serves as an excellent system to probe the physics of HTSy due to the unusually large doping-range associated with the large void concentration in the (HgO$_\delta$)-layer for oxygen.

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CuO4 [R-214 (1T), with R = La; or R-
13O7 (R-123, where R= rare earths
{Bi-22(n-1)n, with n = 1, 2, 3, ...],
2, 3, ...], HgBa2Can-1CunO2n+2+δ
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d [26] an important observation of
ned out to be the n = 1 member of the
: to expand the HTSg material base,
th element in R-123 by elements from
Sb, which are trivalent and have ionic
ecting superconductivity above 105 K
1 structures of three members of the
were soon determined [27], showing
)(CuO2) ... (Ca)(CuO2)(BaO) with n
2(n-1)n. The new record Tc = 110 K
80 K to members for n = 1 and 2,
was predicted by us earlier [20].
n > 3. It is interesting to note that it
Bi-1212 structure after receiving the
was clearly evident.

2,20], Sheng and Hermann started to
end of 1987. After overcoming some
low melting point and high volatility
0 K in a multiphased sample with a

nominal composition of TlBa2Cu3Ox in November 1987 [28]. By partially replacing the Ba by Ca, they discovered [5] a Tc ~ 120 K in the multiphase sample of Tl-Ba-Ca-Cu-O (TBCCO) in February 1987. The structures of members of the homologous series were soon determined afterward to be rather similar to Bi-2223 but with no modulation in the (TlO)2-double layer [29]. Tc = 90, 110, and 125 K were assigned to the n = 1, 2, and 3 members, respectively. In September 1992, the record Tc = 125 of Tl-2223 was further enhanced to 131 K by the application of pressure [30].

5.3. Hg-12(n-1)n

As early as 1991, attempts were made to substitute the linearly-coordinated Hg^{+2} for the Cu in the (CuO)-chain layer in R-123. Later, Putilin et al. [8] synthesized $HgBa_2CuO_{4+\delta}$, the n = 1 member of Hg-12(n-1)n, and found a Tc = 94 K, the highest Tc detected in a single-layered cuprate. It has been shown that Tc increases with n at least up to 3 or 4. Schilling et al. [9] succeeded in raising the Tc to 133 K in a multiphase sample of Hg-12(n-1)n with n = 2 and 3. Later studies demonstrated that n = 1, 2, or 3 members of Hg-12(n-1)n possess Tc = 97, 127, and 134 K, when optimally doped. The crystal structure of Hg-12(n-1)n displays the stacking sequence of $(HgO\delta)(BaO)(CuO_2)(Ca)(CuO_2)$ ... $(Ca)(CuO_2)(BaO)$, with n (CuO_2)-layers separated by n-1 (Ca)-layers. This layered structure is similar to $TlBa_2Ca_{n-1}Cu_nO_{2n+\delta}$, except Hg-12(n-1)n exhibits a large vacancy concentration in the $(HgO\delta)$-layer for oxygen to occupy. Due largely to the local structure

of the $(HgO\delta)$-layers, unusually large Tc enhancement by pressure was achieved, pushing Tc first to ~ 154 K at ~ 16 GPa [10], and then to 164 K at ~ 30 GPa [11], setting new Tc-records (Fig. 7) in a temperature region attainable in the Space Shuttle on the side opposite to the sun or by air-conditioner technology. Hg-12(n-1)n serves as an excellent system to probe the physics of HTSy due to the unusually large doping-range associated with the large void concentration in the (HgOδ)-layer for oxygen.
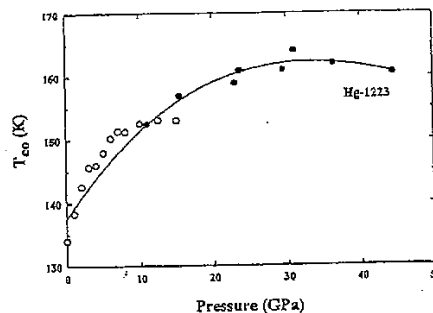

Figure 7. Tc(P) for Hg-1223. (Refs. 10,11)

26

5.4 $CuBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$

It has been observed that the T_c of the optimally doped homologous series $A_mX_2Ca_{n-1}Cu_nO_{2n+m+2+\delta}$, where m = 1 or 2; X = Ba or Sr; and n = 1, 2, 3, ... , increases as A changes progressively from the Group VB element Bi, through the Group IIIB element Tl, to the Group IIB element Hg. It may, therefore, be possible to raise the T_c by changing A further to the Group IB element Au, Ag, or Cu. Unfortunately, our attempt to synthesize $A_mX_2Ca_{n-1}Cu_nO_{2n+m+2+\delta}$ with A = Au or Ag failed due to the chemical inertness of Au and Ag. We have, therefore, tried Cu for A and discovered a 124 K superconducting phase in the system [31]. This becomes the highest T_c of cuprate without the toxic element, such as Tl or Hg.

In earlier studies, $CuBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ with n = 3 and 4 was formed under high pressure with a T_c of 60 and 117 K in the n = 3 and 4 members, respectively [32]. $Cu_2Ba_2Cu_2Cu_3O_{9+\delta}$ was also synthesized under high pressure to show a $T_c \sim 110$ K [33]. All $Cu_mBa_2Ca_{n-1}Cu_nO_{2n+m+\delta}$ made were layered cuprates with the Cu in the (CuO_δ)-layer partially replaced by C due to contamination from the high pressure graphite furnace used. The reported T_c-values are lower than the extrapolated value from T_c's of cuprates with A = Bi, Tl, and Hg. By varying the synthesis conditions, such as lower pressure (~ 5.5 GPa) and temperature (~ 870 °C) than those previously reported, we succeeded [31] in synthesizing Cu-Ba-Ca-Cu-O samples with or without C-contamination with a bulk
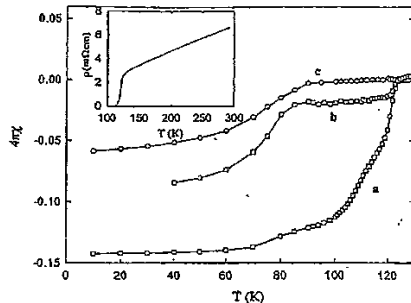

Figure 8. $\chi(T)$ and $\rho(T)$ for Cu-Ba-Ca-Cu-O at different ages: (a) < 3 days, (b) 2 weeks, and (c) 6 months.

superconducting transition up to 124 K, as shown in Figure 8. The T_c of this 124 K-phase degraded with age to ~ 80 K as the sample was kept in the desiccator for 2 months and 6 months, successively, as shown in the same Figure. These different T_c's displayed drastically different pressure effects. The structure of the 124 K-phase has yet to be determined. · However, Marezio et al. suggested in this Workshop [34] that the 124 K superconductivity might be associated with optimally-doped Cu-1223, although the maximum T_c of Cu-1223 achieved so far is 120 K [34].

5.5. R-214(1T')

In the beginning of 1989, Tokura et al., discovered [6] that the charge carriers in $Nd_{2-x}Ce_xCuO_4$ with a $T_c \sim 24$ K are electron-like, in contrast to almost all others HTSg

cuprates. The compounds have to the 1T-structure of $La_{2-x}Ba$ oxygen ions to each Cu in the (difference between 1T and 1T-] characters in the two phases ste in the compounds. By varying and Pr), an electron-hole sym appeared to exist [35], in co Unfortunately, the highest T_c o unusual normal state properties T_c, e.g. > 90 K, are absent from distinct group of their own, mc high T_c cuprates, remains unl insights to the understanding of

5.6. $A_{1-x}B_xCuO_2$

It was pointed out earlier that T per unit formula.. The homolo; form the center part of Bi-22(n- the study for quite a while.

In 1988, Siegrist et al. [38] member of $Ca_{n-1}Cu_nO_{2n-2}$ knov not superconducting. Three y $Sr_{1-y}Nd_yCuO_2$ under 2.4 GPa Takano et al. [40] detected sup; under 6 GPa. The nominal co excitements followed the obser doped infinite layered or the microstructure study revealed th the exact superconducting phase

Stoichiometric $SrCuO_2$ sam and found to be insulating. Thi: exactly +2. Recently, an altern the defective $SrCuO_2$ to be $CuSr_2Sr_{n-1}Cu_nO_{2n+2+\delta}$ [42]. A to act as a charge reservoir to ca R-123, (HgO_δ) in Hg-12(n-1)i propose a possible way to make through partial replacement of i such as Li, Na, K, etc.

mally doped homologous series
$K =$ Ba or Sr; and $n = 1, 2, 3, \ldots$,
p VB element Bi, through the Group
, therefore, be possible to raise the T_c
\g, or Cu. Unfortunately, our attempt
Au or Ag failed due to the chemical
l Cu for A and discovered a 124 K
mes the highest T_c of cuprate without

n = 3 and 4 was formed under high
and 4 members, respectively [32].
h pressure to show a $T_c \sim$ 110 K [33].
prates with the Cu in the (CuO_8)-layer
e high pressure graphite furnace used.
d value from T_c's of cuprates with A =
:, such as lower pressure (~ 5.5 GPa)
ly reported, we succeeded [31] in
t C-contamination with a bulk
superconducting transition up
to 124 K, as shown in Figure
8. The T_c of this 124 K-
phase degraded with age to ~
80 K as the sample was kept
in the desiccator for 2 months
and 6 months, successively,
as shown in the same Figure.
These different T_c's displayed
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Cu-1223 achieved so far is
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red [6] that the charge carriers in
in contrast to almost all others HTSg

cuprates. The compounds have a 1T structure distinctly different from but closely related to the 1T-structure of $La_{2-x}Ba_xCuO_4$. While the 1T-phase has two neighboring apical oxygen ions to each Cu in the (CuO_2)-layer, the 1T'-phase does not. The subtle structural difference between 1T and 1T'-phases, which lead to the subtle difference in charge carrier characters in the two phases stems from the stress induced by the different ionic radii of R in the compounds. By varying the doping (i.e. Ce) as well as R (i.e. R = Gd, Eu, Sm, Nd and Pr), an electron-hole symmetry in the induction of HTSy in cuprates by doping appeared to exist [35], in consistence with some models [36] but not others [37]. Unfortunately, the highest T_c of the 1T'-phase does not exist above 30 K and many of the unusual normal state properties characteristic of the hole-doped cuprates with a very high T_c, e.g. > 90 K, are absent from the 1T'-compounds. Whether the 1T'-compounds form a distinct group of their own, more similar to the conventional LTSrs than the hole-doped high T_c cuprates, remains unknown. A resolution of this issue may provide critical insights to the understanding of HTSy.

5.6. $A_{1-x}B_xCuO_2$

It was pointed out earlier that T_c appeared to increase with n, the number of CuO_2-layers per unit formula. The homologous series of layered $Ca_{n-1}Cu_nO_{2n-2}$ with large n, which form the center part of Bi-22(n-1)n or Tl-22(n-1)n had become an interesting candidate for the study for quite a while.

In 1988, Siegrist et al. [38] succeeded in stabilizing $(Ca_{0.85}Sr_{0.15})CuO_2$, the $n = \infty$ member of $Ca_{n-1}Cu_nO_{2n-2}$ known as the infinite layered compound. Unfortunately, it was not superconducting. Three years later, Smith et al. [39] synthesized electron-doped $Sr_{1-y}Nd_yCuO_2$ under 2.4 GPa and found it superconducting with a $T_c \sim 40$ K. Later, Takano et al. [40] detected superconductivity up to 110 K in $(Sr_{1-x}Ca_x)_{0.9}CuO_2$ prepared under 6 GPa. The nominal composition suggested hole-doped for the sample. Great excitements followed the observation, since one-model [41] seemed to suggest that hole-doped infinite layered or the 1T'-cuprate should have the highest T_c. The ensuing microstructure study revealed that the $(Sr_{1-x}Ca_x)_{0.9}CuO_2$ samples were full of defects and the exact superconducting phase is yet to be determined.

Stoichiometric $SrCuO_2$ samples were made by us recently in bulk and thin film forms and found to be insulating. This is not surprising since the Cu-valence in the compound is exactly +2. Recently, an alternative was proposed for the observed superconductivity in the defective $SrCuO_2$ to be $CuSr_2Sr_2Cu_3O_{8+\delta}$ or other homologous members of $CuSr_2Sr_{n-1}Cu_nO_{2n+2+\delta}$ [42]. A perfect structure of $SrCuO_2$ does not provide layer-block to act as a charge reservoir to carry out the so-called modulation doping such as the CuO in R-123, (HgO_8) in Hg-12(n-1)n, $(TlO)_2$ in Tl-22(n-1)n, or $(BiO)_2$ in Bi-22(n-1)n. We propose a possible way to make $ACuO_2$ superconducting and retain its structural integrity through partial replacement of the alkaline earth A by atomically small alkaline elements such as Li, Na, K, etc.

5.7. Sr_2CuO_4

Superconductivity up to 90's K has been reported in layered Sr_2CuO_4 synthesized under high pressures [43]. Sr_2CuO_4 so prepared exhibits a similar structure to that of R-214 (1T). Unfortunately, according to the Cu-valence effect on T_c, Sr_2CuO_4 is not expected to be superconducting. Recently, oxygen vacancies were also found [44] in the CuO_2-layers of $Sr_2CuO_{4-\delta}$, degrading the CuO_2-layer integrity which has been considered to be detrimental to HTSy. Furthermore, the superconducting volume faction in samples studied appears to be small compared with the volume-fraction of $Sr_2CuO_{4-\delta}$ present in these samples. A serious question concerning the identification of the reported superconductivity with the Sr_2CuO_4 phase has arisen.

We have recently succeeded in preparing samples with various volume fractions of Sr_2CuO_4 and $Sr_3Cu_2O_5$, under different conditions up to 10 GPa and 1200 °C. Some pure samples of Sr_2CuO_4 were obtained and found to be insulating and not superconducting. Superconductivity at ~ 90's K was detected in samples with the presence of the $Sr_3Cu_2O_5$ and the superconducting volume fraction increases as the $Sr_3Cu_2O_{5+\delta}$-content increases [45]. This demonstrates that the superconductivity at 90's K reported in the Sr_2CuO_4 is due to the impurity, such as $Sr_3Cu_2O_{5+\delta}$, present in the samples. Attempts to induce superconductivity in $Sr_2CuO_{4-\delta}$ by reduction have not yet been successful, perhaps, due to the O-defects in the CuO_2-layer previously reported.

VI. Prospects for a Higher T_c

There appears to be a lack of consensus as to the occurrence of HTSy at such high temperatures in such an unusual class of materials, not to mention the anomalous properties of the cuprate HTSrs in their normal state. The discovery of superconductors with a higher T_c's will no doubt pose new challenges to HTSy science and make applications more practical. Thermodynamically, the higher the T_c is, the more efficient operating a HTSg device becomes. Some of the target T_c's for applications can be determined by the coolants to be used, e.g. liquid nitrogen up to 77 K, passive cooling on the Space Shuttle in the space environment up to ~ 100 K, Freon (CF_4) up to 148 K, dry ice up to 198 K, and room temperature up to ~ 300 K. At present, there exists neither experimental nor theoretical reasons for T_c's not to reach these target temperatures.

It is my view that a T_c above the present record of 134 K at ambient or 164 K under pressure may still be found in the layered cuprate family by increasing the number of CuO_2-layers (n) per unit cell followed by proper doping. It has been shown that the T_c of a specific layered cuprate system increases with n up to 3 or 4 and that maximum T_c for all cuprates takes place at a carrier concentration (p) of ~ 0.16 holes per Cu-ion. The T_c drop for n > 3 or 4 has been attributed [46] to the possible depletion of p in the interior layers in a unit cell. We recently found [47] that p of cuprates with T_c > 3 or 4 indeed were underdoped with a p smaller than the optimal value of ~ 0.16 for maximum T_c to occur. Our attempt to enhance p by charging the sample with oxygen at high pressure was found to result in the decomposition of the n > 3 members of the homologous series to the n ≤ 3 ones. This may be understood in terms of the structural instability associated with large Coulomb repulsion that arises from the build up of excess charge as n increases, making doping the CuO_2-layers and doping them uniformly in all layers increasingly difficult. The suggestion is consistent with a small but noticeable decrease of the optimal p with

increasing n [47]. We believe to developing steps to overcome the CuO_2-layer integrity will enable Experiments are under way to tes

Suggestions that cuprate is : unequivocally. Therefore comp that catastrophic instabilities su charge density waves or spin possible novel mechanisms are p

Many reports of a sharp res small and always superimposed the last ten years [48]. Unfortur the existence of superconductiv: the compound has to be stable (e be reproducible (from sample observations can at best be call most recent reports in 1994-95 Ca-Cu-O, Bi-Sr-Ca-Cu-O, an category. Some of them s misinterpretation of data. Howe many by reputable laboratories, tantalizing to ignore although shortening of the coherence len compounds with increasing T_c superconductivity to exist, usin the very sensitive dependenc environment and thus not by a s be determined.

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f excess charge as n increases, making
r in all layers increasingly difficult. The
eable decrease of the optimal p with

increasing n [47]. We believe to properly dope cuprates with large n's to their optimal p by developing steps to overcome the doping instability described above without degrading the CuO_2-layer integrity will enable us to achieve a T_c higher than what we have presently. Experiments are under way to test this conjecture.

Suggestions that cuprate is necessary for HTSy have been made but not yet proven unequivocally. Therefore compounds other than cuprates should not be ignored, provided that catastrophic instabilities such as structural collapse, magnetic ordering, formation of charge density waves or spin density waves, *etc.* are avoided. Novel materials with possible novel mechanisms are promising candidates for higher T_c's.

Many reports of a sharp resistivity drop (but not to zero) or a diamagnetic shift (but small and always superimposed on a large paramagnetic background) have appeared over the last ten years [48]. Unfortunately, none could satisfy the four criteria I set in 1987 for the existence of superconductivity, *i.e.* in addition to zero resistivity and Meissner effect, the compound has to be stable (enough for definitive diagnosis) and the observation has to be reproducible (from sample to sample and from lab to lab). Therefore the reported observations can at best be called Unidentified Superconducting Objects (USO's). The most recent reports in 1994-95 of possible superconductivity above 200 K in the Hg-Ba-Ca-Cu-O, Bi-Sr-Ca-Cu-O, and Y-Ba-Cu-Se systems still belong to the same USO category. Some of them seem to be attributable to experimental artifacts or misinterpretation of data. However, the persistent sighting of USO's in multiphase oxides, many by reputable laboratories, in a similar temperature range over the last ten years, is too tantalizing to ignore although too fleeting to confirm. Could this be due to the ever shortening of the coherence length and the ever increasing of the compound stability for compounds with increasing T_c that make it more difficult to satisfy the four criteria for superconductivity to exist, using conventional diagnostic tools, or could this be caused by the very sensitive dependence of the electrical properties of many oxides on the environment and thus not by a superconducting transition? A definitive answer has yet to be determined.

VII. Acknowledgement

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