The Rise of $T_c$: A Promising Paradigm via Interfacial Mechanism

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A tribute to those with courage in the search for higher $T$, in the last 25 years:

Ralph Waldo Emerson once said “Whatever course you decide upon, there is always someone to tell you that you are wrong. There are always difficulties arising that tempt you to believe that your critics are right. To map out a course of action and to follow it to the end requires courage.”

Abstract. Following the seminal detection of superconductivity at 35 K in the first cuprate high temperature superconductor Ba-doped ternary LCO (La214) by Mueller and Bednorz in 1986, the discovery of the first liquid nitrogen superconductor quaternary YBCO (Y123) with a transition temperature $T_c$ of 93 K by Chu, Wu, and colleagues in 1987 has ushered in the modern era of high temperature superconductivity (HTS). In the ensuing 25 years, great progress has been made in all areas of HTS research and development, from materials to physics to devices. However, the $T_c$ remains at 134 K in quaternary HBCCO (Hg1223) at ambient pressure achieved in 1993 by Schilling et al. and at 164 K in the same compound under high pressure in the same year by Gao et al. A holistic multidisciplinary enlightened empirical approach has been proposed to search for superconductors with higher $T_c$, which includes the discovery of new compounds empirically and the realization of novel mechanisms proposed by theorists. Recently, we have observed nonbulk superconductivity in single crystalline rare-earth doped Ca122 samples with an onset $T_c$ of 49 K, higher than the $T_c$ of any known compounds formed of the constituent elements at ambient or under high pressures. Subsequent systematic structural, electrical, magnetic, and calorimetric investigations suggest that the observation may be attributed to an interface-induced $T_c$, thus suggesting a possible new paradigm for higher $T_c$. In this presentation, our results will be presented and discussed, following a brief recollection of a few events in our lab in the continuing search for higher $T_c$, even though a number of review articles have appeared.
1. Introduction

Superconductivity is intellectually challenging and technologically promising. It provides the never-ending lure to scientists and technologists and the never-ending inspiration to those in the frontiers of science from quarks to Majorana fermions. As a result, superconductivity is considered a subject of pursuit only 101 years young. One of the major driving forces for its vitality is the continued quest for superconductivity at higher $T_c$.

The $T_c$-rise with time is shown in figure 1. $T_c$ was 4 K in Hg when superconductivity was first discovered by Kamerlingh Onnes at Leiden in 1911 after liquefying gas helium [1], rose steadily but only slowly to 23 K in Nb$_3$Ge thin film by Gavaler et al. of Westinghouse and Testardi et al. of Bell Labs in 1973 [2], after improving the stoichiometry of the compound, and stayed there until 1986. However, it jumped to 35 K in the mixed-phase La-Ba-Cu-O samples when Mueller and Bednorz (MB) at Zurich decided to dive into the new path of perovskite oxides for a higher $T_c$ in 1986 [3]. The genie of this seminal discovery was formally let out of the bottle on December 4 at the 1986 Fall MRS meeting in Boston when I announced our reproduction at Houston of the Zurich result at the end of my formal presentation on the oxide BPBO superconductor and, during the ensuing Q&A, Kitazawa of Tokyo immediately revealed their identification of the superconducting phase as La$_2$14 in MB’s samples [4]. The world caught fire afterward, busily working around the clock on the new La214 superconductor, in spite of the initial skepticism expressed by many except for a lucky few, including my group.

In an attempt to understand the cause of the observation and to explore the possibility of further raising the $T_c$, we decided to determine the effect of the inter-atomic distance on the 35 K superconductivity in the La-Ba-Cu-O samples by the application of pressure. To our great surprise, the $T_c$ increases rapidly at a rate about ten times that observed in previously known superconductors to a new record first at 40.2 K [5], and then at 52.5 K [6], exceeding the $T_c$-ceiling of ~ 30s K predicted by theory [7] and thus raising the prospect that higher $T_c$ is possible through high pressure and/or chemical replacement. It should be noted that unstable resistive and ac magnetic anomalies were also detected above 77 K before the MRS meeting in some mixed-phase samples of La-Ba-Cu-O of ours [8], suggestive of superconductivity above the liquid nitrogen temperature for the first time. I shared

![Figure 1. $T_c$-rise with time (*—under pressure).](image-url)
the preliminary data at the MRS meeting at Boston with my former student M. K. Wu and invited him to join the search.

Like many in the field who believe that the best way to study the physics of materials is to use single-crystal samples, we tried but failed to grow single crystals of La214 following Kitazawa’s phase identification. Unfortunately, two-thirds of our Pt-crucibles for crystal growth were destroyed. However, during this period of time, we found that as the polycrystalline samples were made purer with La214, the appearance of the high temperature resistive anomalies became less frequent. We decided to skip the study of single-crystalline La214 and tried to achieve higher Tc directly by stabilizing the resistive and magnetic anomalies detected sporadically by us above 77 K via chemical replacement and pressure application [9]. Replacements of Ba by the smaller isovalent Ca and Sr and of La by the smaller non-magnetic rare-earth (R) elements, Y, Yb, and Lu (thinking to avoid the magnetic ones, based on the conventional wisdom but finding out later that this was unnecessary as shown below), were proposed and attempted. Substitution of Ba by Sr indeed leads to a Tc increase but not by Ca. A resistive drop in the Y-Ba-Cu-O above 77 K was observed on January 28, 1987, and the superconducting state in these samples was firmly established by detecting the Meissner effect in these samples the very next day. Stable superconductivity with a Tc of 93 K above the liquid nitrogen temperature of 77 K was finally achieved in YBCO [10]. A subsequent high pressure test demonstrated that the newly discovered 93 K Tc YBCO belongs to a new material family different from that of La214 [11]. The crystal structure of YBCO was quickly determined in collaboration with Hazen et al. of Geophysical Laboratories at Washington DC to be YBa2Cu3Oy (Y123) [12]. To probe the role of Y+3 in YBCO, a standard technique was employed by examining the effect of a small replacement of the Y+3 by a magnetic R+3 element such as Gd. We found the Tc was hardly affected and concluded that the role of Y in YBCO is to stabilize the crystal structure and not to participate in the superconducting process. We therefore replaced the Y in YBCO completely by R and obtained the new superconducting family of RBCO (RBa2Cu3Oy or R123) for all Rs except Ce and Pr, with a Tc up to 98 K [13]. Extending the replacement of Y with the trivalent ions beyond the R+3’s, two more superconducting families BSCCO [Bi2Sr2CaCu2Oy for n = 1, 2, 3, … or Bi22(n-1)n] with a Tc up to 105 K for n = 3 and TBCCO [Tl2Ba2Ca2Cu3Oy for n = 1, 2, 3, … or Tl22(n-1)n] with a Tc up to 125 K for n = 3 were discovered by Maeda et al. in Tsukuba [14] and Sheng and Hermann in Arkansas [15], respectively, in 1988. Five years later in 1993, Schilling et al. [16] in Zurich replaced the trivalent R with Hg and raised the Tc to the current record of 134 K in HBCCO [HgBa2Ca2Cu3Oy for n = 1, 2, 3, … for n = 3 at ambient, which was subsequently raised by the application of pressure at ~ 30 GPa to 164 K by Gao et al. of Houston and Mao et al. at Geophysical Laboratories at Washington DC [17].

In the last 25 years, a large number of cuprate HTSs has been discovered. They belong to the above families and their derivatives. These cuprate HTSs display a layered structure and can be represented by a generic formula, AmE2Rn-1Cu2O2n+m+2, with m = 1 or 2; n = 1, 2, 3, …; 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 AmE2Rn-1Cu2O2n+m+2 = [(EO)(AO)m(EO)] + [(CuO2)Rn-1(CuO2)y] that consists of two main alternately stacked blocks, namely the active block [(CuO2)Rn-1(CuO2)y], where supercurrent flows along the CuO2-planes, and the charge-reservoir block [(EO)(AO)m(EO)], where doping takes place to introduce charge-carriers without defects to the CuO2-planes. The active block comprises n (CuO2)-layers interleaved by (n-1) R-layers, while the charge-reservoir block consists of m (AO)-layers bracketed by 2 (EO)-layers, as shown in figure 2. Almost every cuprate HTS can be designated as Am2(n-1)n with the (AO)-layer or 0m2(n-1)n without the (AO)-layer. Their parents are an antiferromagnetic Mott-insulator and made superconducting through doping. Tc increases with n up to 3 and decreases beyond due to the inhomogeneous doping and proximity effect for n > 3. In spite of the large number and their higher Tc, YBCO remains to be the choice HTS for science and application due to its higher Jc in high field, higher chemical stability and physical robustness, ease in epitaxial film growth and lower cost. As a result, it has been included in the 2000 White House Millennium Time Capsule “to honor the past
and imagine the future” as a tribute to the ingenuity of the Americans in the 20th century. Hope the full potential of YBCO can be realized long before our grandchildren open the time capsule in 2100.

In 2008, the layered Fe-based superconductor F-doped LaFeAsO (1111) with a $T_c \sim 26$ K was discovered by Hosono et al. at Tokyo [18], leading to the second explosion of superconductivity research activities in the hope of raising the $T_c$ further because of the existence of a large number of compounds with similar structure and the unraveling of the role of magnetism due to the existence of a large amount of the magnetic Fe in them. Indeed, a new class of Fe-based pnictide and chalcogenide superconductors has been found with a maximum $T_c$ of 56 K in the ensuing years. They all possess the FeAs or FeSe-layers and may be grouped into the following families as shown in figure 3: the RFeAsO (1111) with $R =$ rare-earth elements and a maximum $T_c$ of 56 K [19]; the AFe$_2$As$_2$, A'Fe$_2$As$_2$, and AFe$_2$Se$_2$ (122) with $A =$ alkaline and $A' =$ alkaline-earth elements and a maximum $T_c$ of 38 K [20] in general and 49 K in special cases [21] (see below); AFeAs (111) with $A =$ Li and Na and a maximum $T_c$ of 25 K [22]; and FeSe (11) with a maximum $T_c$ of 10 K [23] and 46 K [24] in bulk and single-layer form, respectively (see below).

2. Search for superconductors of higher $T_c$

Indeed, in the last 25 years, $T_c$ has undergone a dramatic rise to the current record of 134 K at ambient [16] and 164 K under pressure [17]. Unfortunately, it has stagnated at these values since 1993. However, the intrinsic scientific lure and potential technological implication of superconductivity at a higher $T_c$ have kept its search unabated. The ultimate goal is to discover a superconductor with a higher $T_c$, preferably at room temperature. It should be pointed out that the term of room temperature superconductor (RTS) can be a relative one. A superconductor is an RTS if its $T_c$ is equal to the ambient temperature of the environment where a superconductor is tested and used, i.e. it can be the liquid nitrogen boiling point, the liquid natural gas boiling point, or 300 K around which we live. Therefore, there are two ways to achieve RTS: one is to increase the $T_c$ and the other is to lower the ambient temperature. For practitioners in the HTS-field, we would like to raise the $T_c$ to 300 K. Three questions immediately follow: the first is whether it is possible to achieve 300 K superconductivity. My answer is a simple “yes,” because we have learned the following over the past 25 years: there is no evidence, experimental or theoretical, to show that room temperature superconductivity is impossible; whatever physics law doesn’t say won’t happen will happen; and history repeats itself always. The second is whether the effort to search for RTS is worth it in view of the potential challenge to use RTS
for power or large current applications because of its possible small current carrying capability due to the small flux pinning force associated with its short coherence length $\xi \approx 1/T_c$ as a result of the high $T_c$. This is particularly true for a highly anisotropic superconductor, which has generally been considered to favor high $T_c$. However, a reduction in the anisotropy of an RTS can provide relief to such an impasse to a large extent. In addition, small-current applications of HTS can have equal, if not more, impacts on lives in this increasingly electricity-dependent society. The third question is how to find it. We believe a holistic multidisciplinary enlightened empirical approach, where knowledge and experience in different fields, insight, imagination, courage, and even luck play important roles, can be most fruitful [25].

In the general approach mentioned above, two paths have been adopted to raise $T_c$: to realize novel mechanisms inspired by theoretical models and to discover new compounds guided by experience and insight empirically. Among the many theoretical mechanisms proposed for higher $T_c$, interfacial mechanism in different forms has been the one most explored theoretically and experimentally since 1964 when Little and Ginzburg [26] first proposed it. However, an analytic study was not made until 1973 when Allender, Bray, and Bardeen (ABB) [27] considered a model system that consists of an interface between a thin metal-layer and a semiconductor. Their realistic estimations showed that a substantial $T_c$-enhancement is possible via the exchange of excitons with a higher characteristic energy should the stringent requirements on the interfaces and materials be met, although questions have also been raised [28]. As was pointed out by ABB, the realization of interfacial mechanism might not only lead to a substantial $T_c$-enhancement but would also be a notable achievement by itself. Numerous experiments inspired by the general concept of interface-induced $T_c$-enhancement have subsequently been carried out on samples with heterostructures that consist of insulating, semiconducting, metallic, and superconducting bilayers, trilayers, or superlattices [29]. Some have reported the observation of interfacial superconductivity with enhanced $T_c$. However, evidence for its existence remains elusive due to the technical difficulties in direct diagnoses. Interfacial superconductivity has often been inferred from the higher $T_c$ detected in the artificially made layered samples as compared to that in the starting materials of the layers under ambient conditions without detailed information about the superconducting state. Even the $T_c$ reported in these heterostructural samples appears to be often achievable in the original materials through either doping or straining.

Figure 3. The schematic crystal structures of the four families of Fe-pnictide (green) and Fe-chalcogenides (blue) superconductors with their maximum $T_c$s.
3. Possible evidence for interface-enhanced $T_c$ in rare-earth doped Ca122

Recently, non-bulk superconductivity was detected in Pr-doped single-crystalline CaFe$_2$As$_2$ [(Ca$_{1-x}$Pr$_x$)Fe$_2$As$_2$ or (Ca,Pr)122] with an onset-$T_c$ ($T_{c\text{on}}$) up to ~ 49 K [21]. Such a $T_{c\text{on}}$ is much higher than the $T_c$ previously known for compounds at ambient or high pressure that contain one or more of the constituent elements Pr, Ca, Fe, and As. In addition, it exceeds what expected from the phonon-mediated superconductor [7]. These authors, therefore, conjectured that the enhanced $T_{c\text{on}}$ of 49 K may have occurred at the interfaces associated with strains and/or defects without further elaboration.

We have therefore examined systematically the rare-earth (R) doped single crystals of (Ca$_{1-x}$R$_x$)Fe$_2$As$_2$ [(Ca,R)122] with R = La, Ce, Pr, and Nd to determine whether the enhanced-$T_c$ is a mere effect of doping in small segregated regions of the sample and, if not, what the morphology of the superconducting body is. Quality crystals with x up to their solubility limits were subsequently grown by the self-flux technique in an Ar inert atmosphere. Wavelength-dispersive-spectrometry (WDS) analysis shows they are chemically homogeneous. All (Ca,R)122 crystals display a $T_{c\text{on}}$ between 42 K for R = Nd and 49 K for R = Pr and show similar transport and magnetic behavior. They also display two sequential superconducting transitions resistively in the otherwise homogeneous single-crystalline

![Figure 4](image-url)

**Figure 4.** (a) $\rho$(T) at ambient and 3 mA and (b) $\chi_{dc}$(T) at 1 Oe of single-crystalline (Ca,Nd)122, where arrows in (a) show the two superconducting transitions.
samples: one with a $T^c_{on}$ at $\sim 42$ K and the other with a $T^c_{on}$ $\sim 12$ K, as exemplified by the resistance $\rho(T)$ and low field dc magnetic susceptibility $\chi_{dc}(T)$ for Ca$_{0.93}$Nd$_{0.07}$Fe$_2$As$_2$, shown in figures 4a and 4b, respectively. A dc magnetic field was found to broaden the $\rho(T)$-transition and shifts it toward lower temperature but cannot suppress it completely down to 4 K at 5 T, indicating a Type-II characteristic for the superconducting state, while the diamagnetic transition in $\chi_{dc}(T)$ was observed to disappear in less than 1 kOe, suggesting a large magnetic background of the sample, similar to [21]. Because of the slightly higher $T^c_{on}$ at 49 K and 24 K for the two transitions, respectively, for R = Pr, we shall discuss only (Ca,Pr)122 hereafter. The two transitions were recovered in the ac-susceptibilities in an ac field $H_{ac}$ of 0.5 Oe along the c-axis ($\chi_{ac}^c$) and the ab-direction ($\chi_{ac}^{ab}$) shown in figure 5. The two transitions exhibit drastically different responses to the magnetic fields as previously reported for R = Pr. This is clear from the rapid suppression of the diamagnetic transition at 47 K to below 20 K by a dc-bias field $H_{dc}$ of only $\sim 300$ Oe (figure 5), suggesting that the superconducting body consists of Josephson Junction Arrays (JJAs). The magnetic anisotropy $\eta = \chi_{ac}^c/\chi_{ac}^{ab}$ is large and exhibits a drastic drop at $\sim 20$ K, coinciding with the entering into the low temperature phase, as displayed in the inset of figure 5.

We have determined the x-dependence of $T^c_{on}$ on (Ca$_{1-x}$Rx)$_2$Fe$_2$As$_2$ single crystals for x up to its maximum solubility of 0.13. $T^c_{on}$ is found to be x-insensitive to within $\pm 2$ K throughout the superconducting region of x = 0.06–0.13, as shown in figure 6. In contrast to $T^c_{on}(x)$, the upper-limit of the superconducting volume-fraction $f$, estimated as the zero-field-cooled dc diamagnetic $4\pi\chi_{dc}^{ab}$ at

![Figure 5](https://via.placeholder.com/150)

**Figure 5.** The temperature dependences of the magnetic susceptibilities for single-crystalline Ca$_{0.87}$Pr$_{0.13}$Fe$_2$As$_2$: red triangles — $10 \times 4\pi\chi_{ac}^{ab}$ at $H_{ac} = 0.5$ Oe and $H_{dc} = 0$; blue circles — $4\pi\chi_{ac}^{ab}$ at $H_{ac} = 0.5$ Oe and $H_{dc} = 300$ Oe; and black triangles — $4\pi\chi_{ac}^c$ at $H_{ac} = 0.5$ Oe and $H_{dc} = 0$. Inset: $\eta = \chi_{ac}^c/\chi_{ac}^{ab}$.}
5 K and $H_{dc} = 2 \text{ Oe}$, was also obtained and shown in the same figure. $f$ increases rapidly with $x$ but, even at the solubility limit of $x = 0.13$, is still far below 10% of that of a perfect superconductor, demonstrating that the superconducting state is indeed non-bulk, consistent with the previous report [21] and the negligible specific heat anomaly at the transition detected by us. The combined observations of the $x$-independent $T_c^\text{on}$ and the rapidly increasing $f$ with $x$ in contrast to the large $x$-range of $0.06 < x \leq 0.13$ for superconductivity and the excellent chemical homogeneity of the samples suggest that the non-bulk superconductivity in (Ca,RE)$_{122}$ cannot be caused by local chemical-doping, i.e. small inclusions of a bulk superconducting phase in the sample. These unusual observations, however, can be attributed to an $x$-dependent defect morphology, consistent with the picture of interface superconductivity.

To elucidate the morphology of such an unusual superconducting body in the single-crystalline (Ca,R)$_{122}$, we have examined the field effects on $\chi_{ab}^{\text{ac}}$ in a total field $H_t = H_{ac} + H_{dc}$ between $10^{-3}$ and $10^3 \text{ Oe}$ on another crystal. $4\pi\chi_{ab}^{\text{ac}}(H_t)$ and $4\pi\chi_{ac}^{\text{ac}}(H_t)$ at 25 K without the interference of the low $T_c^\text{on}$-phase is shown in figure 7. It is evident that as $H_t$ increases, the magnitude of the diamagnetic $4\pi\chi_{ab}^{\text{ac}}$ or $f_{ab}$ remains constant at $f_{1,ab}^{\text{ab}} \sim 1.6 \times 10^{-3}$ for $H_t \leq H_{t1} \sim 10 \text{ Oe}$; decreases for $H_t > H_{t1}$, representing the beginning of flux penetration into the sample along the $ab$-direction; and finally levels off at $f_{2,ab}^{\text{ab}} \sim 2 \times 10^{-4}$ for $H_{dc} \geq 500 \text{ Oe}$, presumably < $H_{c1}$. The much larger $4\pi\chi_{ac}^{\text{ac}}(H_t)$ or $f_c \sim 63 \times 4\pi\chi_{ab}^{\text{ac}}(H_t)$ exhibits a similar behavior: a constant $f_{1,c}^{\text{ab}} \sim 100 \times 10^{-3}$ for $H_t \leq H_{t1} \sim 0.4 \text{ Oe}$ that decreases linearly until $H_t \sim 5 \text{ Oe}$ and nonlinearly beyond. An unusually large magnetic anisotropy $\eta \sim 63$ at low field and 25 K is thus evident, in contrast to the geometric anisotropy $\sim 4$ of the sample, suggesting that the superconducting body must be composed of sparsely populated domains made of Josephson-coupled thin superconducting platelets, which have a large aspect ratio $\sim \eta$. This is consistent with the low superconducting screening and flux penetration threshold $H_{t1}$ observed along both directions. Similar

Figure 6. The $x$-dependences of $T_c^{\text{on}}$: black triangles—for the high $T_c^{\text{on}}$ transition; and red triangles—for the superconducting volume-fraction, for $x = 0-0.13$ of (Ca$_{1-x}$Pr$_x$)Fe$_2$As$_2$ single crystals.
field effects on $4\pi\chi_{ac}^{ab}$ ($H_t$) and $4\pi\chi_{ac}^{c}$ ($H_t$) at lower temperatures have also been observed.

The above field-dependences of $4\pi\chi_{ac}^{ab}$ ($H_t$) and $4\pi\chi_{ac}^{c}$ ($H_t$) are reminiscent of field-penetration into granular ceramic superconductors [30] and can thus be so understood in terms of a superconducting morphology in the sample proposed in figure 8. In such a sample, penetration occurs in two stages of vortex creation: first the Josephson vortices within the weak-links between the superconducting platelets in low field and then Abrikosov vortices at a higher field within the individual platelets. In our samples, as $H_t$ increases, $f$ is initially a constant for $H_t < H_t1 \sim 10$ Oe when the sample is shielded by the JJAs; decreases as $H_t > H_t1$ when the Josephson vortices form and enter the sample; and finally stops decreasing at $H_t2 \sim 500$ Oe when all weak-links between the superconducting platelets are decoupled and before the Abrikosov vortices can enter the platelets when $H_t2$ is smaller than the effective lower critical field $H_{c1}$ of the platelet, as presumably is the case.

In an attempt to estimate the thickness of the superconducting platelets, we examined the suppression of the superconducting screening in a thin long sample with the field parallel to the $ab$-

Figure 7. The field effects on $4\pi\chi_{ac}^{ab}$ at 25 K between $10^{-3}$ and $10^3$ Oe.

Figure 8. The proposed morphology for the non-bulk highly anisotropic superconducting body in the $(Ca_{0.87}Pr_{0.13})Fe_2As_2$ single crystal, which is composed of interfaces between alternately stacked perfect and defected $Fe_2As_2$ layers.
axis from that of an ideal sample. The expected suppression factor is \( S = \left[ 1 - \frac{\lambda}{d} \cdot \tanh \left( \frac{d}{\lambda} \right) \right] \) for a thin sheet with a thickness \( d \), where \( \lambda \) is the penetration depth [31]. The large \( S \sim \frac{f(H_{1})}{f(H_{2})} = 8 \) for the superconducting platelets offers a model-insensitive way to estimate the thickness of the platelets \( d \), leading to an upper limit of \( d < 1.3 \lambda \). For known bulk Fe-pnictide superconductors, the reported \( \lambda \) varies between 0.2 and 0.6 \( \mu \)m. The estimated \( d \) for the superconducting platelets is thus on the order of sub-microns, consistent with the dimension-induced, unusually large \( H_{1} > 500 \) Oe along the ab-direction suggested by figure 7. Dense interfaces may also exist within the platelets that consist of alternately stacked perfect and defect-infested \( \text{Fe}_{2}\text{As}_{2} \) layers, similar to the case of the \( \text{K}_{x}\text{Fe}_{2-y}\text{Se}_{2} \) system. This is in agreement with our preliminary finding that \( f \) is proportional to the superparamagnetic cluster density in the samples investigated [32]. It is therefore rather natural for us to attribute the enhanced \( T_{c}^{in} \) observed to the interfaces between the closely packed perfect and defect-infested \( \text{Fe}_{2}\text{As}_{2} \) layers. The defects may arise from As-deficiencies that usually occur in pure or slightly doped \( \text{AeFe}_{2}\text{As}_{2} \) samples for \( \text{Ae} = \text{alkaline earth elements} \) [32].

4. Conclusion
In the present study we have provided the most convincing evidence for interface-enhanced \( T_{c} \) to date. This may also be able to account for the non-bulk superconductivity previously observed in the undoped \( \text{Ba}_{122} \), \( \text{Sr}_{122} \), and \( \text{Ca}_{122} \) single crystals below \( \sim 20 \) K and other systems. The full deployment of the interface mechanism in other artificially made or naturally assembled material systems may lead to higher \( T_{c} \). Detailed investigations on the nature of these defects will help further reveal the working of interfaces and are currently underway in our lab.

Acknowledgments
The work in Houston is supported in part by U.S. Air Force Office of Scientific Research contract FA9550-09-1-0656, U.S. Air Force Research Laboratory subcontract R15901 (CONTACT) through Rice University, the T. L. L. Temple Foundation, the John J. and Rebecca Moores Endowment, and the State of Texas through the Texas Center for Superconductivity at the University of Houston.

References
[1] Onnes H K 1911 *Leiden Comm.* 120b; Onnes H K 1911 *Leiden Comm.* 122b; Onnes H K 1912 *Leiden Comm.* 124c
[2] Gavaler J R, Janocko M A and Jones C K 1974 *J. Appl. Phys.* 45 3009; Testardi L R, Wernick J H and Royer W A 1974 *Solid State Commun.* 15 1
[3] Bednorz J G and Müller K A 1986 Z. *Phys. B.* 64 189
[4] Takagi H, Uchida S, Kitazawa K and Tanaka S 1987 *Jpn. J. Appl. Phys.* 26 L123
[5] Chu C W, Hor P H, Meng R L, Gao L, Huang Z J and Wang Y Q 1987 *Phys. Rev. Lett.* 58 405
[6] Chu C W, Hor P H, Meng R L, Gao L and Huang Z J 1987 *Science* 235 567–569
[7] McMillan W L 1968 *Phys. Rev.* 167 331–344
[8] Chu C W 1988 *Physics in a Technological World*, ed A P French (New York: American Institute of Physics) p 211
[9] See for example, Chu C W 1987 (January 12) Patent application; Chu C W 1996 *History of Original Ideas and Basic Discoveries in Particle Physics (NATO Advanced Study Institute, Series B: Physics)* vol 352 ed. H. B. Newman and T. Ypsilantis (New York: Plenum) p 793
[10] Wu M K, Ashburn J R, Torng C J, Hor P H, Meng R L, Gao L, Huang Z J, Wang Y Q and Chu C W 1987 *Phys. Rev. Lett.* 58 908
[11] Hor P H et al. 1987 *Phys. Rev. Lett.* 58 911
[12] Hazen R M, Finger L W, Angel R J, Prewitt C T, Ross N L, Mao H K, Hadadiacos C G, Hor P H, Meng R L and Chu C W 1987 *Phys. Rev. B* 35 7238(R)
[13] Hor P H, Meng R L, Wang Y Q, Gao L, Huang Z J, Bechtold J, Forster K and Chu C W, *Phys. Rev. Lett.* 58 1891
[14] Maeda H, Tanaka Y, Fukutomi M and Asano T 1988 *Jpn. J. Appl. Phys.* 27 L209
[15] Sheng Z Z and Hermann A M 1988 *Nature* 332 138
[16] Schilling A, Cantoni M, Guo J D and Ott H R 1993 *Nature* 363 56
[17] Gao L, Xue Y Y, Chen F, Xiong Q, Meng R L, Ramirez D, Chu C W, Eggert J H and Mao H K 1994 *Phys. Rev.* B 50 4260(R)
[18] Kamihara Y, Watanabe T, Hirano M and Hosono H 2008 *J. Am. Chem. Soc.* 130 3296
[19] Chen X H, Wu T, Wu G, Liu R H, Chen H & Fang D F 2008 *Nature* 453 761; Ren Z A et al. 2008 *Phys. Lett.* 25 2215
[20] Rotter M, Tegel M and Johrendt D 2008 *Phys. Rev. Lett.* 101 107006; Sasmal K, Lv B, Lorenz B, Guloy A M, Chen F, Xue Y Y and Chu C W 2008 *Phys. Rev. Lett.* 101 107007; Guo J G, Jin S F, Wang G, Wang S C, Zhu K X, Zhou T T, He M and Chen X L 2010 *Phys. Rev.* B 82 180520(R)
[21] Lv B, Deng L Z, Gooch M, Wei F Y, Sun Y Y, Meen J, Xue Y Y, Lorenz B and Chu C W 2011 *Proc. Nat. Acad. Sci. USA* 108 15705–15709
[22] Tapp J H, Tang Z J, Lv B, Sasmal K, Lorenz B, Chu C W and Guloy A M 2008 *Phys. Rev.* B 78 060505(R); Wang X C, Liu Q Q, Lv Y X, Gao W B, Yang L X, Yu R C, Li F Y and Jin C Q 2008 *Solid State Comm.* 148 538; Chu C W, Chen F, Gooch M, Guloy A M, Lorenz B, Lv B, Sasmal K, Tang Z J, Tapp J H and Xue Y Y 2009 *Physica C* 469 326; Parker D R, Pitcher M J, Baker P J, Franke I, Lancaster T, Blundell S J and Clarke S J 2009 *Chem. Commun.* 2189–2191; Sasmal K, Lv B, Tang Z J, Chen F, Xue Y Y, Lorenz B, Guloy A M and Chu C W 2009 *Phys. Rev.* B 79 184516.
[23] Hsu F C et al. 2008 *Proc. Natl. Acad. Sci. USA* 105 14262
[24] Wang Q Y et al. 2012 *Chin. Phys. Lett.* 29 037402
[25] Chu C W 2008 *AAPPS Bulletin* 18 9
[26] Little W A 1964 *Phys. Rev.* 134 A1416; Ginzburg V L 1964 *JETP* 47 2318
[27] Allender D, Bray J and Bardeen J 1973 *Phys. Rev.* B 7 1020
[28] Inkson J C and Anderson P W 1973 *Phys. Rev.* B 8 4429–4432; Allender D, Bray J and Bardeen J 1973 *Phys. Rev.* B 8 4433–4434; Inkson J C 1975 *J. Phys. C: Solid State Phys.* 8 L164–L168
[29] For a review, see Pereiro J, Petrovic A, Panagopoulos C and Božović I 2011 Interface superconductivity: History, development and prospects *Physics Express* 1 208–241
[30] Müller K H, Nikolo M and Driver R 1988 *Phys. Rev.* B 43 7976; Clem J R 1988 *Physica C* 153–155 50
[31] See for example, Porch A, Cooper J R, Zheng D N, Waldram J R, Campbell A M and Freeman P A 1993 *Physica C* 214 350
[32] Y. Y. Xue et al., unpublished