What have we learned from high-pressure experiments on Cu-oxide and Fe-based superconductors?

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Abstract. High-pressure experiments have made many important contributions to the field of superconductivity, including studies on the Cu-oxide and Fe-based high-temperature superconductors (HTS). However, for detailed quantitative understanding, the nature of the high-pressure environment acting on the sample must be well defined, a requirement often not met. Since HTS are quasi-2D, all properties are anisotropic. As a result, only a combination of fully hydrostatic and uniaxial pressure experiments are capable of providing the detailed information required. Unfortunately, very few such experiments have been carried out. For both Cu-oxide and Fe-based HTS at optimal doping, $T_c$ is found to be enhanced by either increasing the separation of the superconducting planes or decreasing their area. Future experiments will extend such hydrostatic/uniaxial studies over the entire doping range.

1. Introduction

Since the discovery of the high-$T_c$ cuprates in 1986 [1] and the Fe-based pnictides in 2008 [2], an enormous volume of experimental and theoretical work has been carried out. Unfortunately, the essential question – why these materials superconduct at such high temperatures in the first place – has yet to be resolved. Besides varying the crystal structure and stoichiometry of the materials, experimentalists have availed themselves of the thermodynamic variables temperature, magnetic field, and high pressure in an effort to further understanding.

In this paper we will attempt to illustrate a few examples of what high-pressure studies have, and have not, taught us about high-temperature superconductors (HTS). But first we would like to outline five different ways high-pressure experiments have advanced our understanding of the superconducting state in general.

(i) Create new superconductors. Many materials only superconduct under high pressure. Of the 92 naturally occurring elements in the periodic table, more than half (53) are known to superconduct as elemental solids – 30 at ambient pressure and 23 more under high pressure, as illustrated in Fig 1 below [3]. A number of distinct mechanisms may prompt a material to become superconducting under pressure, for example:

(a) an insulator- or semiconductor-to-metal transition, as in O, Si or Ge;
(b) a weakening or complete suppression of magnetism, as in Fe, Ce or Eu;
(c) a substantial change in the character of the conduction electrons, as in Ca, Sr, Ba, Sc, Y and the alkali metal Cs.

(ii) **Expose new phases, reveal new phenomena.** In 1999 Neaton and Ashcroft [4] pointed out that subjecting the highly compressible alkali metal Li to extreme pressures would bring neighboring atoms so close together that their core electrons begin to overlap, thus trapping the conduction electrons in interstitial sites. The result is a strong deviation in the conduction electrons from nearly-free-electron behavior and highly anomalous electronic properties, including possible superconductivity at relatively high temperatures, followed by a metal-insulator transition at higher pressure. Indeed, as seen in Fig 2, Li metal exhibits a superconducting transition temperature $T_c$ which increases to a temperature as high as 14 K at 30 GPa [5]. This alone is a clear indication that Li’s conduction electrons are no longer free-electron-like since, for all known simple-metal superconductors, $T_c$ decreases under pressure [6]. At 67 GPa it is seen in Fig 2 that superconductivity abruptly disappears. Matsuoka et al. [7] demonstrated that this disappearance of superconductivity is the result of the fact that Li suffers a metal-to-semiconductor transition. A transition back to metallic behavior has been predicted at even higher pressures [8]. In our opinion these highly anomalous properties constitute some of the most interesting physics ever explored using the high pressure technique.

![Figure 1](https://example.com/figure1.jpg)

**Figure 1.** Periodic Table from Ref. [3] listing elements which superconduct at ambient pressure (yellow) or only under high pressure (light green). For each element the upper position gives the value of $T_c(K)$ at ambient pressure; middle position gives maximum value $T_c^{\text{max}}(K)$ in a high-pressure experiment at the pressure $P(GPa)$ (lower position). If $T_c$ decreases under pressure, only the ambient pressure value of $T_c$ is given.
With reference to HTS: (a) Sun et al. [9] have recently reported that in the iron chalcogenides a second superconducting phase suddenly reemerges near 12 GPa after $T_c$ decreases in monotonic fashion from 32 K to 0 K at 10 GPa. In this reemergent phase $T_c$ reaches values as high as 49 K. In addition, in resistivity studies on Ba$_{1-x}$K$_x$Fe$_2$As$_2$ Hassinger et al. [10] find evidence for a new phase between the antiferromagnetic and the superconducting states, possibly a second spin-density-wave phase, which appears to compete with superconductivity. Further studies are required to identify the nature of this new phase.

(iii) **Synthesize at high-pressure/temperature.** As pointed out by Iimura et al. [11], the $T_c$ versus $x$ phase diagram for LnFeAsO$_{1-x}$F$_x$, where Ln = lanthanide, is limited to $x \leq 0.2$ by the low solubility of F. Substituting instead H for O in this compound allows one to extend the $T_c(x)$ phase diagram to the much higher doping level $x \leq 0.5$. To synthesize these hydrogen-doped superconductors, simultaneous pressures/temperatures as high as 5 GPa/1200°C are necessary [11, 12]. The results of these studies are of considerable significance.

(iv) **Help push $T_c$ to higher temperatures at ambient pressure.** Here we only outline three of the many examples.

(a) The $T_c$-value of the original HTS LaBaCuO, discovered by Bednorz and Müller [1] in 1986, was soon found to increase rapidly with pressure. Soon thereafter Wu et al. [13] availed themselves of chemical pressure by substituting the smaller cation Y for La, whereupon they discovered the 123-compound YBa$_2$Cu$_3$O$_7$, the first superconductor with a $T_c$ value above liquid nitrogen temperatures.

(b) With the rapid increase in $T_c$ with pressure for LaBaCuO and LaSrCuO in mind, Locquet et al. [14] grew a film of LaSrCuO epitaxially on a suitable substrate which compressed the CuO$_2$ basal plane, whereupon the separation between these planes increased. As a result the value of $T_c$ nearly doubled to 49 K, a record high value for this cuprate.

(c) Early high-pressure studies on the Fe-based superconductor LaFeAsO$_{1-x}$F$_x$ by Takahashi et al. [15] showed that $T_c$ initially increases rapidly with pressure. Ren et
al. [16] increased the chemical pressure in this compound by substituting the smaller Sm cation for La and found that $T_c$ nearly doubled to 55 K, the highest known value for any Fe-based superconductor.

(v) **Use high pressure as a quantitative tool to further understanding and test theory.** Compressing a superconducting solid through high pressure changes its lattice, electronic and magnetic properties, and thus also the interactions responsible for the attractive interaction binding the two electrons together in a Cooper pair. The universal decrease in $T_c$ under pressure observed in simple-metal superconductors comes about because the electron-phonon interaction weakens as the crystal lattice stiffens under pressure, the change in electronic properties playing only a minor role [6]. In this way high-pressure studies serve to test the suitability of the BCS theory of superconductivity where the lattice vibrational modes form the basis for the pairing interaction. The isotope effect constitutes a more direct probe; however, in contrast to the isotope effect, the changes generated by high pressure are relatively large since they occur in the exponent of the BCS expression for $T_c$. In the cuprate and Fe-based superconductors it appears likely that magnetic or electronic interactions lead to the pairing. In these quasi-2D materials a basic question is whether the superconducting state is strengthened or weakened as the planar area or the separation between planes decreases under pressure. In one theoretical model it is predicted that $T_c$ should increase as the separation between the CuO$_2$ planes is reduced [17].

2. **High Pressure as a Variable**
In contrast to the ‘clean’ thermodynamic variables temperature $T$ and magnetic field $H$, pressure is often relatively poorly defined. The reason for this is that some type of pressure medium is necessary when applying pressure to a solid. This pressure may be a gas, liquid, solid or perhaps even the sample itself. For cubic solids the ideal pressure medium is a gas or liquid which exerts hydrostatic pressure. A solid pressure medium, on the other hand, is unable to exert purely hydrostatic pressure but also subjects the sample to shear stresses which can cause nonuniform compression and even plastic deformation and extensive defect formation, i.e. the sample gets squashed. These shear stresses themselves may drastically change the way the sample’s properties change compared to if hydrostatic pressure is applied. Helium is by far the most satisfactory hydrostatic pressure medium since it only becomes solid (freezes) above 27 bar at 0 K, 0.18 GPa at 20 K, 2.2 GPa at 100 K or 12 GPa at room temperature. All other fluids freeze at much lower pressures.

If the sample is noncubic, as for the cuprate and Fe-based superconductors, which are quasi-2D, then all properties, including the compressibility, are anisotropic. In this case hydrostatic pressure experiments alone are insufficient. Both hydrostatic and uniaxial pressures must be applied to single-crystalline samples to gain full, unequivocal, quantitative information on the response of the sample to changes in the respective lattice parameters. Unfortunately, uniaxial pressure measurements are normally restricted to pressures sufficiently weak as to not destroy the sample, i.e. approximately 0.1 GPa. Unequivocal hydrostatic/uniaxial information is, therefore, confined to a relatively narrow pressure range.

3. **Cuprate Superconductors**
The parent compounds for the high-$T_c$ cuprates are antiferromagnetic insulators. As a function of either doping level or pressure, the cuprates becomes metallic as the antiferromagnetic phase is suppressed in favor of the superconducting phase, as represented in Fig 3; thus far the entire phase diagram has been traversed only through doping. In the superconducting phase $T_c(P)$ typically follows a bell-shaped curve. In the hole-doped cuprates, the carrier concentration in
the CuO$_2$ planes normally increases with pressure [6]. Were this the only effect, one would then expect $T_c$ to increase (decrease) with pressure for underdoped (overdoped) samples, but remain constant at optimal doping, as indicated by the respective black arrows in Fig 3.

This is not the behavior obtained in experiment, as seen in Fig 4(a), where the initial pressure dependence $T_c(P)$ is seen to be positive with an identical slope to 0.9 GPa for the one- (HgBa$_2$CuO$_4$ (Hg-1201)), two- (HgBa$_2$CaCu$_2$O$_6$ (Hg-1212)), and three-layer (HgBa$_2$Ca$_2$Cu$_3$O$_8$ (Hg-1223)) mercury cuprates at optimal doping [19]. The parallelism of $T_c(P)$ continues to pressures above 40 GPa, as illustrated in Fig 4(b) where $T_c$ is seen to reach values near 160 K at 30 GPa for Hg-1223 [20]. From these data and those on other systems it is clear that for the cuprates the measured change in $T_c$ under pressure is a function of both ‘intrinsic’ and doping dependent terms, i.e.

$$
\left(\frac{dT_c}{dP}\right)_{measured} = \left(\frac{dT_c}{dP}\right)_{doping} + \left(\frac{dT_c}{dP}\right)_{intrinsic},
$$

as illustrated in Fig 3 by the black and red arrows. At optimal doping $(dT_c/dP)_{doping} = 0$. For a wide range of optimally doped cuprates with $T_c$ values above 90 K it is found that $(dT_c/dP)_{measured} = (dT_c/dP)_{intrinsic} = +1$ to $+2$ K/GPa, consistent with the data in Fig 4.

![Figure 3.](image-url) Generic phase diagram for cuprates and Fe-based pnictides, adapted from Ref [18].

![Figure 4(a).](image-url) $T_c$ versus pressure to 0.9 GPa [19].

![Figure 4(b).](image-url) $T_c$ versus pressure to 45 GPa [20].
The question remaining is: why does $T_c$ here initially increase under pressure at the relatively modest rate of approximately 1-2 %/GPa? Since the cuprates are quasi-2D (planar) compounds, the first step in obtaining a quantitative answer to this question is to carry out parallel uniaxial pressure experiments on single crystalline samples. Hardy et al. [21] have determined the uniaxial pressure derivatives along the tetragonal $a$- and $c$-axes for the nearly optimally doped single-layer cuprate Hg-1201 and obtain $dT_c/dP_a = +2.3(2)$ K/GPa and $dT_c/dP_c = -3.6(3)$ K/GPa. Bringing the CuO$_2$ planes closer together through pressure along the $c$-axis is thus seen to rapidly decrease the value of $T_c$ whereas it is increased by reducing the area of the CuO$_2$ plane. This contradicts the prediction of the theoretical model of Anderson referred to above [17].

A consistency check can be carried out by comparing the anticipated hydrostatic pressure derivative $dT_c/dP = 2dT_c/dP_a + dT_c/dP_c \simeq +1.0(5)$ K/GPa to the value obtained in a direct He-gas hydrostatic pressure experiment on the same single crystal, $dT_c/dP = +1.48(5)$ K/GPa, which is in reasonable agreement.

In Fig 5 these values of the partial pressure derivatives are compared to those for several other optimally doped cuprates. The main result remains, namely, that $T_c$ increases both by increasing the separation between the CuO$_2$ planes and decreasing their area. In addition, the partial pressure derivatives are seen to be much larger than the hydrostatic derivative because they are opposite in sign and nearly cancel. It would be interesting to determine to what extent these results hold for the high-$T_c$ cuprates in the over- and underdoped regions.

![Figure 5. Partial pressure derivatives for several optimally doped cuprates from Ref [21].](image)

Perhaps the first study which took advantage of the above results were by Locquet et al. [14] who grew an epitaxial film of La$_{1-x}$Sr$_x$CuO$_4$ (La-214) on a suitable substrate which compressed the CuO$_2$ planes and, by virtue of the Poisson effect, expanded the lattice in the $c$-direction, both effects serving to increase $T_c$. As a result, $T_c$ was found to almost double in value from 25 K to 49 K in the epitaxially grown thin films!

4. Fe-Based Superconductors

Following the discovery in 2008 of high-temperature superconductivity in the Fe-based compound LaFeAsO$_{1-x}$F$_x$ [2], a veritable avalanche of research has been carried out, including many studies under high pressure conditions which have been extensively reviewed [22, 23, 24, 25, 26, 27],
the most recent being the excellent review by Athena Sefat [18]. As indicated in Fig 3, the antiferromagnetic phase of the parent compound is suppressed through doping $x$ or high pressure $P$, making way for a superconducting phase. $T_c$ as a function of $x$ or $P$ exhibits a dome-like dependence, similar to that for the cuprates. Very recently Hosono’s group has utilized temperatures to 1200$^\circ$C and pressures to 5 GPa to synthesize the H-doped compounds $LnFeAsO_{1-x}F_x$ ($Ln = La, Ce, Sm, Gd$) [11]. The advantage is that a significantly higher doping level $x = 0.5$ can be reached with hydrogen, whereas only $x = 0.2$ is possible with fluorine. Remarkably, a double-dome $T_c(x)$ dependence is obtained to $x = 0.5$ for the La-compound, but only a single, broad dome appears for $Ln = Ce, Sm,$ and Gd. High pressure has also successfully induced superconductivity in hydrogen substituted CaFeAsF$_{1-x}H_x$ [28].

The first high-pressure experiments on the Fe-doped superconductors were carried out by Takahashi et al. [15] on LaFeAsO$_{0.59}$F$_{0.11}$ who found that the ambient-pressure value $T_c \approx 25$ K initially increases sharply with pressure, passing through a maximum of 43 K at 5 GPa before decreasing gradually to 8 K at 30 GPa. As pointed out extensively in the reviews cited above for the Fe-based superconductors, however, the dependence of $T_c$ on pressure differs widely from one experimental group to another, depending to a considerable extent on the pressure medium used and whether the sample is single- or polycrystalline. This situation is brought out clearly by high-pressure experiments on non-crystalline and single-crystalline LaFePO samples where $T_c \approx 6$ K. In piston-cylinder studies to 1.5 GPa by Igawa et al. [29] using Fluorinert pressure medium $T_c$ is observed to rise sharply with pressure and pass through a maximum near 9 K at 0.8 GPa. Hamlin et al. [30] studied LaFePO in a diamond-anvil cell without pressure medium and found $T_c$ to pass through a maximum of 10 K at 5 GPa. From these results one might conclude that a determination of $T_c(P)$ under purely hydrostatic pressure in a He-gas system would find that $T_c$ rises very rapidly with pressure, perhaps passing through a maximum at a pressure below 0.8 GPa.

That this is not at all the case is seen for the He-gas measurements in Fig 6 where $T_c$ is seen to decrease rapidly with pressure, irrespective of whether single- or polycrystalline LaFePO samples are studied, nor whether resistivity or magnetic susceptibility measurements are used to determine $T_c$; only when a polycrystalline sample was crushed in a diamond-anvil cell without pressure medium is a dome-shaped $T_c(P)$ dependence found for LaFePO with a $T_c$-maximum near 0.6 GPa [31].

The sensitivity of Fe-based HTS to strain also means that high-pressure studies should preferably be carried out only on samples in single-crystalline form rather than polycrystalline. The reason for this is that the compressibility of these materials is highly anisotropic; since the individual crystallites in a polycrystalline material are ‘glued’ together at the grain boundaries, applying even a completely hydrostatic pressure to a polycrystalline sample may result in a significant change in the strain field within the sample. This induced strain field may depend on the temperature at which the pressure is changed since the sample’s elastic properties are temperature dependent. This may be the reason that Bi et al. [32] observed significant pressure/temperature history effects in He-gas $T_c(P)$ studies on polycrystalline LaO$_{1-x}$F$_x$FeAs.

The unusually strong dependence of the pressure dependence $T_c(P)$ on the pressure medium used is also exhibited by other Fe-doped systems. In an experiment using Daphne Oil 7373 or Fluorinert FC-75 pressure medium, Alireza et al. [33] find that superconductivity is induced under pressure in CaFe$_2$As$_2$ near 0.3 GPa pressure and in SrFe$_2$As$_2$ and BaFe$_2$As$_2$ near 3 GPa, all single crystals. However, in a later experiment on a CaFe$_2$As$_2$ single crystal using a He-gas pressure system, Yu et al. [34] can find no superconductivity to 0.7 GPa!
Comparing three different pressure media, two fluid at room temperature (Daphne 7474, Daphne 7373) and one solid (Stycast 1266), Kotegawa et al. [35] find that for SrFe$_2$As$_2$ crystals that the less hydrostatic the pressure medium, the lower the pressure needed to suppress the antiferromagnetism and the associated tetragonal-to-orthorhombic phase transition, thus allowing the superconducting state to appear.

Kirshenbaum et al. [36] find that some SrFe$_2$As$_2$ single crystals show evidence for superconductivity near 21 K at ambient pressure if they are measured before a strain-relieving anneal is carried out; they find the superconductivity disappears after annealing. Cleaving or quenching the crystal in liquid nitrogen is not able to resurrect the superconductivity, but severe deformation of the crystal does reinstate superconductivity near 21 K.

Saha et al. [37] suggest that there exists “an intimate relationship among superconductivity, magnetism, and crystallographic strain in this system of materials” and Duncan et al. [38] state that “an increasing uniaxial pressure component in BaFe$_2$As$_2$ quickly reduces spin-density-wave order and favors the appearance of superconductivity, similar to what is seen in SrFe$_2$As$_2.”

It thus seems clear for these Fe-based systems that the more highly strained the sample is, the more likely it is that the sample is superconducting! In fact, the strains and disorder associated with doping into the Fe$_2$As$_2$ planes, for example with Co, may make superconductivity more likely, in contrast to the situation with the high-$T_c$ cuprates where in-plane doping quickly quenches the superconductivity.

To get a quantitative handle on the mechanisms behind the extreme sensitivity of the properties of the Fe-based superconductors to strain, uniaxial pressure experiments are essential. Hardy et al. [39] find the uniaxial pressure derivatives for a nearly optimally doped Ba(Fe$_{0.92}$Co$_{0.08}$)$_2$As$_2$ crystal to be $dT_c/dP_a = +3.1$ K/GPa and $dT_c/dP_c = -7.0$ K/GPa using an ultrahigh resolution dilatometer. A direct uniaxial pressure measurement along the c-axis of a crystal with the same composition yields the surprisingly large negative value $dT_c/dP_c = -15$ K/GPa [40]. Note that the sign of the uniaxial pressure derivatives is the same as for the optimally doped cuprates.

For a Ba(Fe$_{0.92}$Co$_{0.074}$)$_2$As$_2$ single crystal, Bud’ko et al. [41] find the derivatives $dT_c/dP_a = +3$ K/GPa and $dT_c/dP_c = -26$ K/GPa, confirming the sign of the uniaxial derivatives reported by Hardy et al. [39]. However, for Ba(Fe$_{0.962}$Co$_{0.038}$)$_2$As$_2$, Bud’ko et al. find $dT_c/dP_a = -41$
K/GPa and $dT_c/dP_t = +17$ K/GPa, revealing that the uniaxial pressure derivatives of $T_c$ both change sign at the lower doping level [41].

Recent extensive dilatometer experiments by the Meingast group [42] over the Co concentration range from 4% to 12% confirm this sign change, finding, in fact, that both derivatives $dT_C/dP_a$ and $dT_C/dP_t$ abruptly change sign at the 6% Co doping level; interestingly, this is the doping level above which the orthorhombic-to-tetragonal phase transition is fully suppressed.

5. Conclusions
With regard to the Cu-oxide and Fe-based superconductors, the high-pressure technique has proven to be a valuable resource to: (a) synthesize new materials, (b) induce normal-to-superconductor transitions, (c) expose new phases and reveal new phenomena, and (d) help develop strategies to push $T_c$ to higher temperatures at ambient pressure. However, the high-pressure variable has not yet lived up to its potential to make substantial contributions as a quantitative tool to further our understanding and test theoretical models. The difficulty is that ‘not all pressures are created equal’ since the nature of high-pressure to which the sample is subjected (degree of hydrostaticity, size and direction of shear stresses, etc) depends on many factors, particularly the pressure medium used and the temperature at which the pressure is changed. This uncertainty is particularly worrisome for the Fe-based materials since they appear to be exquisitely sensitive to shear stresses which are, surprisingly, found to favor superconductivity.

To make substantial contributions to our quantitative understanding, high-pressure experiments on both the Cu-oxide and Fe-based superconductors should ideally be carried out under both fully hydrostatic and uniaxial pressure conditions, or perhaps both combined. Helium is the hydrostatic pressure medium of choice since it does not solidify at room temperature until pressures exceeding 12 GPa have been reached. Even as a solid helium is relatively soft, able to exert only minor shear stresses on the sample embedded in it. However, due to the quasi-2D nature of both the cuprate and Fe-based HTS, the changes in the normal and superconducting state properties under hydrostatic pressure do not provide sufficient information for quantitative interpretation. In fact, since the uniaxial pressure dependences are large and opposite in sign, the dependence of $T_c$ on hydrostatic pressure alone has no direct physical significance! Uniaxial pressure experiments are thus absolutely essential. Only through combined hydrostatic/uniaxial pressure experiments can the most basic questions be answered, such as whether superconductivity is weakened or strengthened as the relevant quasi-2D planes are compressed or brought closer together. Such information would allow definitive tests of theoretical models. Ultimately, such quantitative experiments on the Cu-oxide and Fe-based superconductors have the potential to reveal the nature of the pairing mechanism, much as the universal suppression of $T_c$ in simple-metal superconductors along with measurements of the lattice Grüneisen parameter clearly point to the importance of the electron-phonon interaction.

Clearly, carefully controlled hydrostatic AND uniaxial pressure experiments on high quality, high-$T_c$ single crystals over a wide doping range are necessary to further our quantitative understanding. The uniaxial pressure experiments carried out thus far have concentrated on optimally doped samples and have, as we have discussed above, revealed that the superconducting state is strengthened ($T_c$ increases) in one of two ways: (1) by reducing the area of the superconducting planes, or (2) by increasing the separation between these planes. Whether or not this result also holds for under- or overdoped samples is the subject of future experimentation.

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