

Anomalous He-gas high-pressure studies on superconducting $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$

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Abstract. Ac susceptibility measurements have been carried out on superconducting $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ for $x = 0.07$ and 0.14 under He-gas pressures to ~ 0.8 GPa. Not only do the measured values of dT_c/dP differ substantially from those obtained in previous studies using other pressure media, but also the $T_c(P)$ dependences observed depend on the detailed pressure/temperature history of the sample. A sizeable sensitivity of $T_c(P)$ to shear stresses provides a possible explanation.

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1. Introduction

The discovery of superconductivity at temperatures as high as 26 K in $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ [1], a layered compound devoid of CuO_2 planes, has rekindled interest in high-temperature superconductivity. As for the cuprates⁵, high-pressure experiments can potentially play an important role in furthering our understanding of the new Fe-based pnictides [3, 4]. High-pressure experiments to 30 GPa by Takahashi *et al* [5] on this compound for $x = 0.11$ using a solid (NaCl) pressure medium reveal that the superconducting onset in electrical resistivity reaches temperatures as high as 46 K. The initial slope dT_c/dP appears to increase with the fluorine content, at least for concentrations $x \leq 0.14$ [3]. Resistivity and magnetic susceptibility studies by several groups [3], [5]–[7] using various fluid pressure media agree that dT_c/dP is positive initially, but differs widely in its magnitude. As in previous studies on the high- T_c cuprates [2] and the binary compound MgB_2 [8], it would be of interest to carry out benchmark determinations of $T_c(P)$ in magnetic susceptibility measurements on $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ using the most hydrostatic pressure medium known, He gas.

One notable result is that the non-superconducting, undoped pnictides LaOFeAs [3], CaFe_2As_2 [9], SrFe_2As_2 [10] and BaFe_2As_2 [10] reportedly become superconducting under pressure when pressure media such as Fluorinert, methanol–ethanol and silicone oil were used, superconductivity in CaFe_2As_2 appearing at a relatively low pressure ≤ 0.4 GPa. However, recent dc susceptibility and electrical resistivity measurements by Yu *et al* [11] on CaFe_2As_2 using He-gas pressure medium fail to detect any sign of superconductivity to 0.7 GPa and 2 K. These authors suggest that not only in CaFe_2As_2 , but also in SrFe_2As_2 and BaFe_2As_2 , non-hydrostatic stress components may have been responsible for the reported pressure-induced superconductivity. In addition, very recently Matsubayashi *et al* [12] carried out parallel ac susceptibility and electrical resistivity measurements on BaFe_2As_2 and SrFe_2As_2 single crystals to 8 GPa pressure in a relatively hydrostatic cubic anvil pressure apparatus and found no trace of superconductivity in the former compound; in SrFe_2As_2 , bulk superconductivity, as evidenced by full shielding in ac susceptibility, is only found in a rather narrow (2 GPa) pressure region centered about 6 GPa, whereas non-bulk (filamentary) superconductivity is revealed in the resistivity that falls to zero over a much wider pressure region. Extensive mechanical deformation studies on SrFe_2As_2 single crystals indicate that internal strain originating from *c*-axis-oriented planar defects plays a central role in the appearance of superconductivity at ambient pressure [13]. The potentially important role that shear stresses play in the superconductivity of Fe-based pnictides is emphasized in the recent review of Chu and Lorenz [4]. Indeed, shear-stress effects on $T_c(P)$ are well known from studies on diverse superconducting materials such as organic metals [14], high- T_c oxides [2], MgB_2 [8] and Re metal [15].

To our knowledge, the measurements of Yu *et al* [11] on CaFe_2As_2 are the only He-gas high-pressure studies of superconductivity carried out to date on an Fe-based pnictide. It would be of obvious interest to extend such studies to the $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ system to ascertain whether $T_c(P)$ differs from the findings of earlier studies, where less hydrostatic pressure media were employed. Using He as the pressure medium brings a further benefit: it allows one to change the hydrostatic pressure at relatively low temperatures, thus permitting studies of phenomena impacting superconductivity that are both pressure and temperature dependent. An example of such phenomena in the cuprates is the well-known oxygen ordering effect, which

⁵ For recent reviews of high-pressure studies on cuprates, plus references to earlier reviews, see [2].

has been shown in some systems to be the dominant factor determining the dependence of T_c on pressure [2].

To throw some light on these issues, we have determined $T_c(P)$ using He-gas pressure medium to 0.78 GPa for the original Fe-based superconducting pnictide, $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$, where $x = 0.07$ and 0.14 . For these doping levels, we find the initial pressure derivative dT_c/dP to be positive, but markedly less than the published values using other pressure media; in addition, the dependence of T_c on pressure is not reversible but depends on the detailed pressure/temperature history of the sample. Possible origins for this behavior are discussed.

2. Experiment

Polycrystalline $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ samples are prepared by solid-state reaction as described in previous publications [1, 5]. For $x = 0.14$ both the previous resistivity measurements [3] and the present ac susceptibility studies are carried out on pieces taken from the same mother sample. The fluorine content in the present samples, $x = 0.07$ and 0.14 , is determined from the lattice constant using Vegard's law; these samples have densities 6.704 and 6.739 g cm^{-3} [1] and masses 1.54 and 8.69 mg (or 5.65 mg), respectively.

To generate hydrostatic pressures as high as 0.8 GPa , a He-gas compressor system (Harwood Engineering) was used in combination with a CuBe pressure cell (Unipress). Ac susceptibility measurements at 0.1 Oe rms and 1023 Hz were carried out under pressure to the same high accuracy as measurements at ambient pressure by surrounding the sample with a primary/secondary compensated coil system connected to a Stanford Research SR830 digital lock-in amplifier via an SR554 transformer preamplifier. A two-stage closed-cycle refrigerator was used to cool the pressure cell to temperatures as low as $5\text{--}6 \text{ K}$; measurements were carried out on warming up slowly through the transition at the rate $\sim 0.3 \text{ K min}^{-1}$. All susceptibility measurements were repeated at least once to verify that the reproducibility of the transition temperature was within 20 mK . Unless otherwise stated, the sample was cooled down to measure T_c $30\text{--}60 \text{ min}$ after a given change in pressure/temperature. Further details of the He-gas techniques are given elsewhere [16].

3. Experimental results

3.1. $\text{LaO}_{0.93}\text{F}_{0.07}\text{FeAs}$ sample

For the $x = 0.07$ sample at ambient pressure, the $80\text{--}20$ transition width in ac susceptibility is $\sim 1 \text{ K}$, where $T_c \simeq 21.7 \text{ K}$ from the transition onset and $T_c \simeq 21 \text{ K}$ from the midpoint (see figure 1(a)). These values of T_c are several degrees kelvin less than those estimated from the resistivity onset at comparable fluorine concentrations [3].

Previous high-pressure resistivity measurements with Fluorinert pressure medium on $\text{LaFeAsO}_{1-x}\text{F}_x$ for $x = 0.05$, 0.08 and 0.11 yielded the following positive values of the initial derivative $dT_c/dP \simeq 2$, 2 and 8 K GPa^{-1} , respectively, where T_c was determined from the resistivity onset [3]. From these results, one would anticipate that $dT_c/dP \simeq 2 \text{ K GPa}^{-1}$ for $x = 0.07$. On the other hand, if T_c is determined from the temperature at which the resistivity ρ drops to 0 , one finds for $x = 0.08$ the initial pressure dependence $dT_c/dP \simeq 0.54 \text{ K GPa}^{-1}$, a value approximately $4\times$ smaller than that from the resistivity onset (for $x = 0.05$ and 0.11 , it was not possible to reliably estimate the temperature at which $\rho \rightarrow 0$). In resistivity

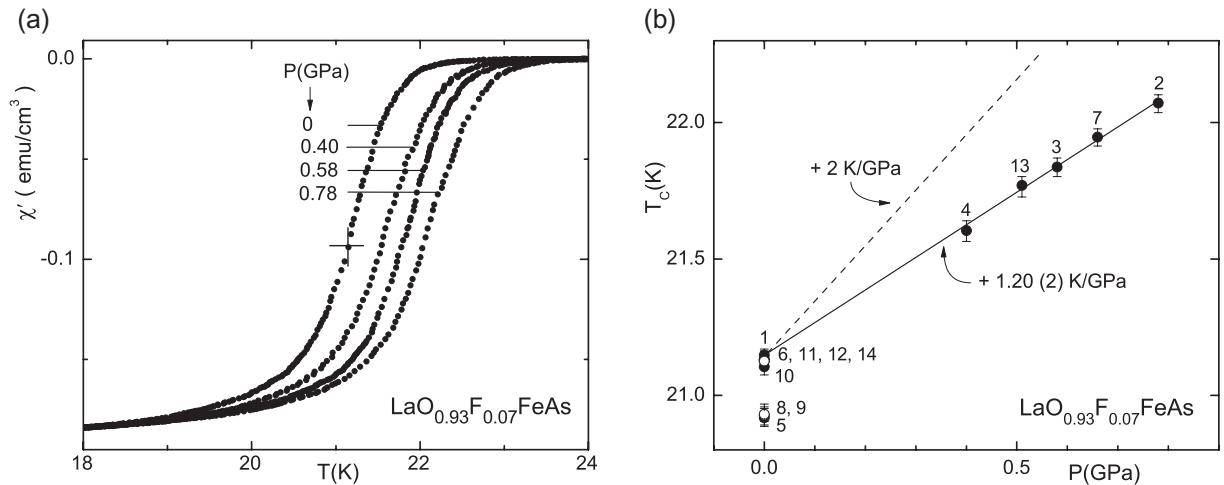


Figure 1. $\text{LaO}_{0.93}\text{F}_{0.07}\text{FeAs}$ sample (mass 1.54 mg). (a) Real part of the ac susceptibility versus temperature at four selected He-gas pressures. Order of measurement given by pressure values from top to bottom. Large cross (+) marks midpoint of superconducting transition for initial measurement at ambient pressure (0 GPa). (b) T_c versus pressure for all data taken. Numbers give order of measurement (see text for details). Closed and open circles used for clarity. Solid straight line is to guide the eye and dashed line gives slope inferred from resistivity onset data in [3].

measurements, therefore, the value of dT_c/dP obtained evidently depends on the criterion used to determine T_c .

We now compare the values of dT_c/dP obtained from the present ac susceptibility measurements using hydrostatic He-gas pressure on $\text{LaFeAsO}_{1-x}\text{F}_x$ with those obtained in the above resistivity studies. Figure 1(a) shows our results for the F concentration $x = 0.07$. The large magnitude of the superconducting transition is consistent with bulk superconductivity; in fact, the shielding effect is approximately twice that expected for perfect diamagnetism. No correction is made here for diamagnetization effects. Under increasing He-gas pressure to 0.78 GPa, the superconducting transition is seen to shift monotonically to higher temperatures. Here T_c is defined by the transition midpoint (see figure 1(a)); however, since the shape $\chi'(T)$ of the transition does not change with pressure, the shift in T_c with pressure is the same irrespective of whether T_c is defined from the transition midpoint or onset.

In figure 1(b) the dependence of T_c on pressure is shown for all measurements on the $x = 0.07$ sample, the numbers giving the order of measurement. After the ambient pressure measurement (point 1), 0.78 GPa pressure is applied at room temperature (RT) to yield point 2. T_c is seen to increase under pressure at the rate $+1.20 \text{ K GPa}^{-1}$, clearly less than the value $+2 \text{ K GPa}^{-1}$ inferred from the resistivity onset but greater than the value using the $\rho \rightarrow 0$ criterion at nearly the same F concentration ($x = 0.08$) [3]; in the resistivity studies, the pressure was always changed at RT. The pressure was then successively reduced at low temperatures (62, 52 and 45 K for points 2 → 3, 3 → 4 and 4 → 5, respectively) before cooling down further to measure T_c . Up to and including point 4, the $T_c(P)$ dependence is reversible; however, at ambient pressure (point 5) T_c lies $\sim 220 \text{ mK}$ lower than the initial value at ambient pressure (point 1). Interestingly, after warming the sample back to RT and holding for 1.5 h, T_c is seen to revert (point 6) back to its initial value. This behavior bears some resemblance to that observed

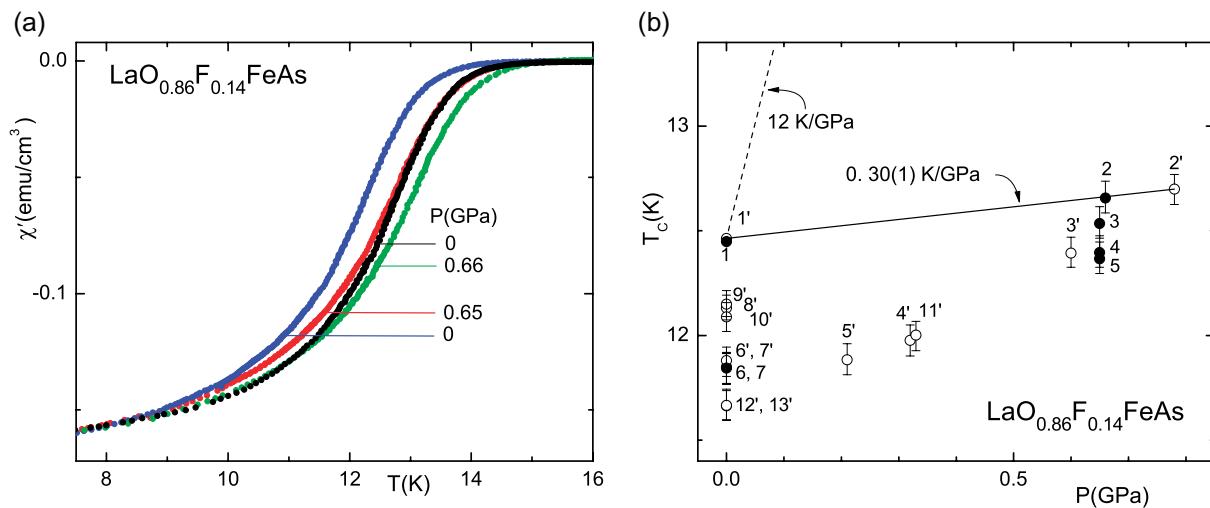


Figure 2. $\text{LaO}_{0.86}\text{F}_{0.14}\text{FeAs}$ sample. (a) Real part of the ac susceptibility versus temperature at four selected He-gas pressures for sample with mass 8.69 mg. Order of measurement given by pressure values from top to bottom (corresponds to points 1, 2, 5 and 6 in figure 2(b)). (b) T_c versus pressure for all data taken. Numbers give order of measurement (see text for details). Data for primed and unprimed numbers (open and closed circles) taken on different samples with masses 5.65 and 8.69 mg, respectively. Solid straight line is to guide the eye and dashed line gives slope from resistivity onset data in [3].

previously from oxygen-ordering effects in the cuprates, where $T_c(P)$ may differ strongly depending on whether the pressure is changed at RT or low temperatures [2]; there is, however, one notable difference—when pressure is reduced at low temperature in a cuprate with oxygen ordering, all values of T_c would differ, and not just those below a certain pressure threshold.

To examine whether, as in the cuprates, there exists a particular (sub-RT) temperature above which such T_c -relaxation occurs, we applied 0.66 GPa pressure at RT (point 7) and then released pressure at 60 K (point 8), reproducing exactly the previous results. Holding the sample at 100 K for 90 min resulted in no change in T_c (point 9). However, after holding the sample at 200 K for 100 min, T_c returned to its initial value (point 10). Warming back to RT for 1 h (point 11) and then for one week (point 12) resulted in no further change in T_c . A pressure of 0.51 GPa was then applied at 60 K (point 13) and released at 50 K (point 14); these T_c values faithfully track the $+1.2 \text{ K GPa}^{-1}$ straight line in figure 1(b).

3.2. $\text{LaO}_{0.86}\text{F}_{0.14}\text{FeAs}$ sample

For the $x = 0.14$ sample at ambient pressure, the 80–20 transition width in ac susceptibility is ~ 2 K, where $T_c \simeq 13.7$ K from the transition onset and $T_c \simeq 12.5$ K from the midpoint (see figure 2(a)). This onset value is several degrees kelvin less than from the resistivity onset (~ 19 K); however, the temperature of the susceptibility midpoint is comparable to the resistivity zero point (~ 12 K) [3].

Previous high-pressure resistivity measurements on $\text{LaO}_{0.86}\text{F}_{0.14}\text{FeAs}$, where pressure was always changed at RT, revealed that T_c from the resistivity onset increases rapidly with pressure in Fluorinert pressure medium at the rate $+12 \text{ K GPa}^{-1}$ [3]. At a pressure of 0.66 GPa, therefore,

T_c would be expected to increase by approximately 8 K. In figure 2(a), however, the application of 0.66 GPa He-gas pressure at RT is seen to slightly broaden the transition in ac susceptibility and shift it only slightly (~ 0.2 K) to higher temperatures (point 2 in figure 2(b)), a shift 40 \times less than the 8 K expected! This difference in dT_c/dP decreases to 15 \times if the resistivity zero point is used (4.4 K GPa $^{-1}$).

The sample was then allowed to remain at RT for various cumulative lengths of time (20 h for point 3, 68 h for point 4 and 112 h for point 5) for a total of 112 h, during which time the pressure at RT decreased only slightly to 0.65 GPa; surprisingly, T_c is seen in figure 2(b) to decrease by ~ 0.3 K (point 5)! Releasing the pressure then at 55 K to 0 GPa results in T_c shifting further downwards to a temperature (point 6) ~ 0.5 K less than its initial value at ambient pressure (point 1), the transition recovering its original sharpness. After the release of pressure at 55 K (point 6), holding the sample at 270 K for 1 h did not result in a further change in T_c (point 7). The superconducting transition appears to be stuck at this lower value. Such a feature was not observed in oxygen ordering phenomena in the cuprates [2].

A second sample from the same synthesis batch was then studied to check these highly anomalous results, yielding the data points (open circles) labeled with primed numbers in figure 2(b). The value of T_c at ambient pressure was identical to that of the previous sample. Applying 0.78 GPa He-gas pressure at RT shifted T_c upward by only 0.23 K (point 2'), yielding a slope $dT_c/dP \simeq +0.30(1)$ K GPa $^{-1}$ in excellent agreement with the results for the first sample (closed circles), but far less (40 \times) than that (dashed line) observed in resistivity studies by Takahashi *et al* [3] using Fluorinert pressure medium. The pressure was then reduced successively at low temperatures to $P = 0$ (2' \rightarrow 3' at 60 K, 3' \rightarrow 4' at 55 K, 4' \rightarrow 5' at 40 K and 5' \rightarrow 6' at 35 K). At ambient pressure, T_c now lies 0.62 K lower than the initial value (point 1'). Holding the sample for 1 h at 100 K caused no further change in T_c (point 7'). T_c was observed to shift upwards by 0.33 K after holding at 200 K for 1.3 h (point 8'), but no further shift in T_c occurred after holding at 250 K for 1 h (point 9') or at RT for 30 h (point 10'). A pressure of 0.33 GPa was then applied at 60 K (point 11') and released again at 50 K (point 12'), yielding a value of T_c approximately 0.8 K lower than the initial value (point 1'). The ambient pressure value of T_c did not change further, even after holding at RT for 170 h (point 13')!

4. Discussion

In all previous high-pressure studies on superconducting pnictides, pressure was changed at RT. We first compare the results of those studies with the present He-gas results for pressure change at RT. To our knowledge, the only measurements of $T_c(P)$ under pressure on $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ for fluorine concentrations near those ($x = 0.07$ and 0.14) used in the present study are the resistivity measurements to 1.5 GPa with Fluorinert pressure medium by Takahashi *et al* [3] for $x = 0.05$, 0.08, 0.11 and 0.14. As discussed above, if the pressure is changed at RT, the values obtained for dT_c/dP from resistivity studies depend sensitively on the criterion used to determine T_c ; the resistivity onset or $\rho \rightarrow 0$ point gives $dT_c/dP \simeq 2$ or 0.54 K GPa $^{-1}$, respectively, in contrast to the present ac susceptibility studies using He-gas pressure where the intermediate value $dT_c/dP \simeq 1.2$ K GPa $^{-1}$ is observed. The difference in the value of dT_c/dP is much larger at the higher fluorine concentration $x = 0.14$, where Takahashi *et al* [3] find $dT_c/dP \simeq 12$ K GPa $^{-1}$ (onset) or 4.4 K GPa $^{-1}$ ($\rho \rightarrow 0$ point), the respective values being 40 \times or 15 \times higher than the 0.30 K GPa $^{-1}$ found in the present He-gas experiments (see figure 2(b)). The fact that the anomalous temperature/pressure effects are most dramatic for the $x = 0.14$

sample, which lies near the substitution limit of F for O, suggests that the application of pressure may cause an irreversible phase separation. This would explain why the value of T_c does not recover in our experiments after a pressure cycle, as seen in figure 2(b).

We note that at the lower concentration $x = 0.11$, Takahashi *et al* [3] report $dT_c/dP \approx 8 \text{ K GPa}^{-1}$. On the other hand, at the same F concentration the much lower value $dT_c/dP \approx 1.2 \text{ K GPa}^{-1}$ is obtained in a dc susceptibility measurement by Lu *et al* [6] to 1 GPa pressure using an unspecified fluid pressure medium and in resistivity (onset) studies by Zocco *et al* [7] using *n*-pentane: iso-amyl alcohol pressure medium to 0.94 GPa. It appears, therefore, that in the 1111 Fe-pnictides the pressure dependence of T_c depends sensitively not only on the dopant concentration but also on which physical property is measured, how the value of T_c is determined and the type of pressure transmitting medium used. This would appear to support the view of Yu *et al* [11] that shear-stress effects play an important role in determining $T_c(P)$ in the oxypnictides, large shear stresses generating significant changes in T_c . The marked temperature/pressure history effects seen in figures 1(b) and 2(b) may be indicative of important shear-stress effects between grains in polycrystalline samples, even when purely hydrostatic He-gas pressure is applied. Parallel measurements on high-quality single crystals would test this hypothesis. It is also possible that the short-range diffusion of oxygen or fluorine anions within the crystal structure may occur in response to a change in pressure at RT, much as the ‘oxygen ordering effects’ observed in the cuprate oxides [2].

In order to check whether the temperature/pressure history effects seen here might result from the penetration of the He pressure medium into the crystal lattice, we heated a 3.3 mg portion of the $x = 0.14$ sample used in the present He-gas experiments to 100 °C while connected to a sensitive mass spectrometer. We were unable to detect the slightest trace of He escaping from the sample. Subsequent vaporization of this sample in an ultra-sensitive mass spectrometer set the He impurity level at $\sim 1 \text{ ppm}$, an amount far too small to effect the dramatic changes observed in T_c .

An alternative scenario is conceivable. The undoped compound LaOFeAs exhibits a spin-density-wave (SDW) and structural phase transition (tetragonal \rightarrow orthorhombic) below 150 K [1, 17]. Substituting O with F or applying pressure is believed to suppress this transition and allow a superconducting ground state to appear. Competition between an SDW instability and superconductivity is also observed in CeO_{1-x}F_xFeAs [18]. Perhaps shear-stress effects result in superconducting and non-superconducting SDW regions in the sample, which lead to the complex temperature/pressure history effects found in the present studies.

Whatever the explanation for the anomalous behavior of $T_c(P)$, it is likely that in the oxypnictides, as in the cuprates, a full understanding of the manner in which T_c changes under pressure may be difficult to obtain since it almost certainly depends on several factors simultaneously, including the strength of shear-stress effects as well as changes in the carrier concentration and the separation and area of the superconducting planes. Further experimentation that focusses on pressure-induced changes in superconductivity and crystal structure on global and local scales is clearly needed here.

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