



Effect of pressure on the superconducting critical temperature of $\text{La}[\text{O}_{0.89}\text{F}_{0.11}]\text{FeAs}$ and $\text{Ce}[\text{O}_{0.88}\text{F}_{0.12}]\text{FeAs}$

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ABSTRACT

We have performed several high-pressure resistivity experiments on the recently discovered superconductors $\text{La}[\text{O}_{0.89}\text{F}_{0.11}]\text{FeAs}$ and $\text{Ce}[\text{O}_{0.88}\text{F}_{0.12}]\text{FeAs}$. At ambient pressure, these materials have superconducting onset temperatures T_c of 28 K and 44 K, respectively. While the T_c of $\text{La}[\text{O}_{0.89}\text{F}_{0.11}]\text{FeAs}$ goes through a maximum between 10 and 68 kbar, in qualitative agreement with a recent report by Takahashi et al., the T_c of $\text{Ce}[\text{O}_{0.88}\text{F}_{0.12}]\text{FeAs}$ decreases monotonically over the measured pressure range. At 265 kbar, the T_c of the cerium-based compound has been suppressed below 1.1 K.

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1. Introduction

A new class of superconductors consisting of layered materials with the chemical formula LnOTPn , where Ln is a lanthanide element, T is a transition metal, and Pn is either P, As, or Bi, has recently emerged. The phosphorus-based versions of these compounds, LaOFeP and LaONiP have rather low superconducting critical temperatures, T_c of 3 [1] and 5 K [2], respectively. Much higher T_c values were achieved by fluorine doping the corresponding arsenic-based compound to produce $\text{La}[\text{O}_{1-x}\text{F}_x]\text{FeAs}$, where doping to $x \sim 0.11$ produces $T_c \sim 26$ K [3]. The T_c appears to pass through a maximum as a function of fluorine doping. Subsequently, it was found that under a modest pressure of 40 kbar, the T_c of $\text{La}[\text{O}_{0.89}\text{F}_{0.11}]\text{FeAs}$ increases to 43 K [4], becoming the first non-cuprate superconductor with a T_c higher than that of MgB_2 . Replacing lanthanum with heavier rare-earth elements also leads to high- T_c values, as in $\text{Ce}[\text{O}_{1-x}\text{F}_x]\text{FeAs}$ with T_c up to 41 K [5]. As of this writing, the highest T_c reported for this class of materials is about 55 K, which was achieved in the compound $\text{Sm}[\text{O}_{1-x}\text{F}_x]\text{FeAs}$ [6]. The T_c of optimally doped $\text{Sm}[\text{O}_{1-x}\text{F}_x]\text{FeAs}$ initially decreases with pressure [7].

In this letter, we report measurements of T_c as a function of pressure in the lanthanum- and cerium-based oxypnictide compounds to further probe the superconductivity in these interesting materials. In $\text{Ce}[\text{O}_{0.88}\text{F}_{0.12}]\text{FeAs}$, we found that T_c decreases monotonically from 47 K (resistivity onset) to 4.5 K at 190 kbar. In $\text{La}[\text{O}_{0.89}\text{F}_{0.11}]\text{FeAs}$, T_c appears to pass through a maximum between 10 and 68 kbar, in qualitative agreement with the results of Takahashi et al. [4].

2. $\text{La}[\text{O}_{0.89}\text{F}_{0.11}]\text{FeAs}$

We performed two separate high pressure experiments on polycrystalline samples of $\text{La}[\text{O}_{0.89}\text{F}_{0.11}]\text{FeAs}$. The samples were taken from the same batch described in Ref. [8]. The first experiment was performed in a Teflon capsule piston-cylinder cell and utilized a nearly hydrostatic 1:1 mixture of *n*-pentane:isomyl alcohol as the pressure medium. Pressure was increased at room temperature and determined at low temperature using the superconducting transition of a piece of Pb located next to the sample [9]. Electrical resistivity data were obtained using a 4-lead technique with a LR-700 AC resistance bridge at pressures of 0.5, 4.1 and 9.4 kbar. Fig. 1 (top) shows the temperature dependence of the resistance for each pressure measured in the hydrostatic cell. Upon attempting to increase the pressure beyond

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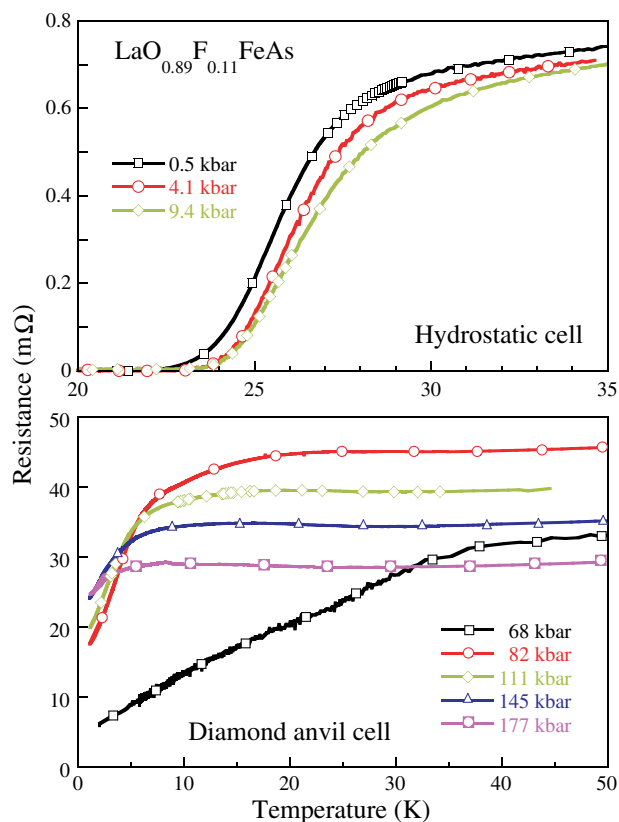


Fig. 1. Electrical resistance of $\text{La}[\text{O}_{0.89}\text{F}_{0.11}]\text{FeAs}$ for different pressures. Upper panel: curves corresponding to the hydrostatic clamp. Lower panel: diamond anvil cell experiment.

9.4 kbar, the cell failed and we continued the experiment in a diamond anvil cell (DAC).

The DAC is a mechanically loaded commercial model, manufactured by Kyowa Seisakusho Ltd. The diamond anvils are beveled from 500 to 250 μm tips. One of the diamonds contains six deposited tungsten microprobes encapsulated in high-quality homepitaxial diamond. The fabrication of “designer” diamonds is described in Ref. [10]. The gasket was made from a 200 μm thick MP35N foil preindented to 40–50 μm and a 100 μm diameter hole was drilled through the gasket using an electrical discharge machine (EDM). Several ~ 5 μm diameter ruby spheres were loaded into the hole in the gasket and the remaining space in the hole was filled with several small chunks of polycrystalline $\text{La}[\text{O}_{0.89}\text{F}_{0.11}]\text{FeAs}$. Pressure was adjusted and determined at room temperature, using the fluorescence spectrum of the ruby spheres and the calibration of Chijioke et al. [11]. Further details of the DAC technique are described in Ref. [12].

Fig. 1 (bottom) shows the temperature dependence of the resistivity as measured in the DAC. Following the initial measurement at 68 kbar, pressure was increased to 177 kbar and then decreased to 145, 111 and 82 kbar. Note that the sample is in direct contact with the metallic gasket so that the measured resistance results from a combination of the sample and gasket resistivity. However, such a configuration is sufficient for locating the sharp drop in resistance when the sample becomes superconducting. The critical temperature was determined by the temperature at which the sample resistance reached 90% of the normal state value just above T_c .

Fig. 2 illustrates the pressure dependence of T_c for $\text{La}[\text{O}_{0.89}\text{F}_{0.11}]\text{FeAs}$. For comparison, the results of Takahashi et al. [4] are plotted as a dashed line. While T_c initially increases and then decreases

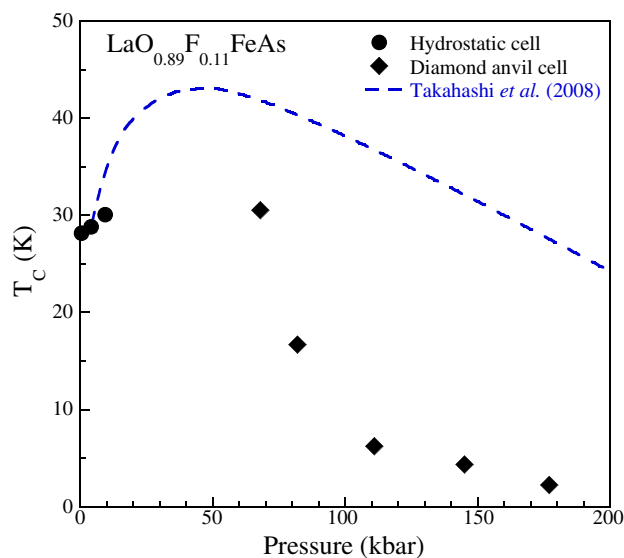


Fig. 2. Superconducting T_c versus pressure for $\text{La}[\text{O}_{0.89}\text{F}_{0.11}]\text{FeAs}$. Circles correspond to measurements in the hydrostatic cell, while diamonds correspond to the diamond anvil cell experiment. The dashed curve represents the data previously published by Takahashi et al. [4].

beyond ~ 68 kbar, bearing some resemblance to the previous measurements, the magnitude of the superconducting transition temperatures are quite different. The differing pressure dependencies could be due to differences in stoichiometry or sample purity. The reported fluorine concentrations are nominal concentrations determined by the stoichiometry of the unreacted mixtures. The final concentration of fluorine in the reacted material may depend strongly on the details of the high-temperature processing such as the annealing schedule.

3. $\text{Ce}[\text{O}_{0.88}\text{F}_{0.12}]\text{FeAs}$

We performed two high pressure experiments on polycrystalline samples of $\text{Ce}[\text{O}_{0.88}\text{F}_{0.12}]\text{FeAs}$ prepared at Oak Ridge National Laboratory. The compound was synthesized from CeAs, Fe_2O_3 , Fe, As, and a 1:1 mixture of Ce and CeF_3 , combined to produce a nominal composition of $\text{Ce}[\text{O}_{0.88}\text{F}_{0.12}]\text{FeAs}$. The reactants (3 g total mass) were intimately mixed and pressed into a pellet, sealed in a silica tube under about 1/3 atm of Ar, and heated for 36 h at 1200 $^\circ\text{C}$. Reaction with vapor in the tube produces a thin light gray coating on the surface of the pellet which was gently sanded away. The sample was then re-pelletized and heated for an additional 12 h under the same conditions. The thin surface-layer was sanded away prior to characterization. Powder X-ray diffraction analysis revealed two small impurity phases, FeAs and CeAs, present at the level of a few percent.

At ambient pressure, the sample displays T_c values of 40 and 44 K in magnetic susceptibility and resistivity, respectively. The resistive T_c value is determined by the temperature at which the resistivity drops to 90% of the normal state value just above T_c . The first high-pressure experiment was performed in a Bridgman anvil cell with 4 mm diameter anvil flats and utilized quasi-hydrostatic solid steatite as pressure medium. Pressure is applied at room temperature using a hydraulic press and clamped with a nut. At pressures up to 44 kbar, the pressure was determined using a Sn manometer located next to the sample and the calibration of Smith et al. [13]. Above 44 kbar, the wires connecting to the Sn manometer broke and pressure was determined from the applied load. Our previous experience with these Bridgman anvil cells indicates that the pressure determined from the applied load is accu-

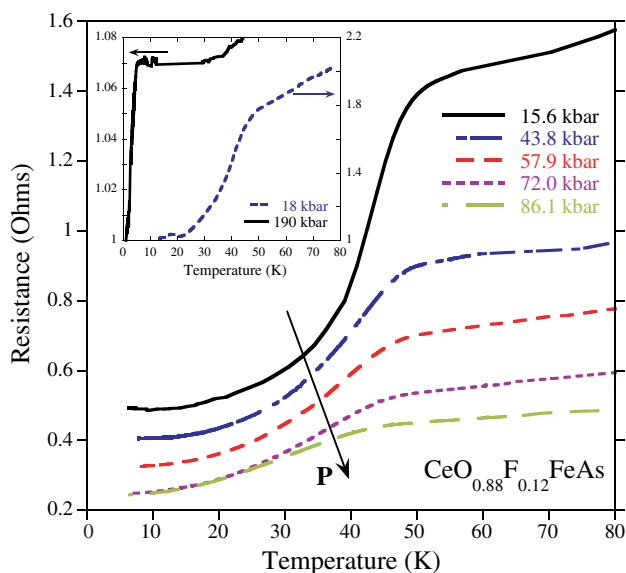


Fig. 3. Temperature dependence of the electrical resistance of $\text{Ce}[\text{O}_{0.88}\text{F}_{0.12}]\text{FeAs}$ for different applied pressures up to 86 kbar using the Bridgman anvil cell technique. Here we have also defined the superconducting T_c as the temperature at which the sample resistance reaches 90% of the normal state value. Inset: diamond anvil cell resistance curves for 18 and 190 kbar, normalized to their respective base temperature values.

rate to within $\pm 20\%$. Fig. 3 shows the results of the Bridgman cell measurements on $\text{Ce}[\text{O}_{0.88}\text{F}_{0.12}]\text{FeAs}$.

In order to verify the pressure dependence of T_c and to extend the results to higher pressure, we performed a second experiment on $\text{Ce}[\text{O}_{0.88}\text{F}_{0.12}]\text{FeAs}$ using a DAC. The technique used was the same as that described for the lanthanum-based compound. Fig. 3 (inset) shows resistance versus temperature obtained from the DAC measurements. Fig. 4 shows the T_c versus pressure for $\text{Ce}[\text{O}_{0.88}\text{F}_{0.12}]\text{FeAs}$ obtained from the Bridgman and DAC experiments. At the lowest measured pressures we find T_c values near 47 K, somewhat higher than the $T_c = 44$ K measured at ambient pressure. This small increase in the critical temperature is likely due to improvement in sample connectivity due to grain compac-

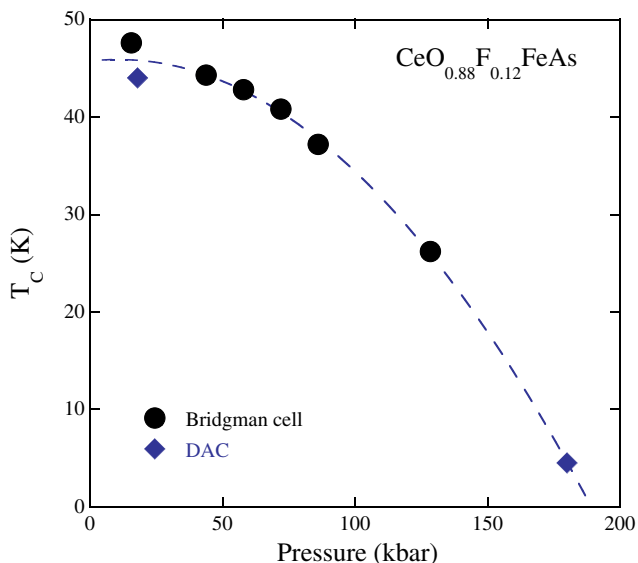


Fig. 4. Superconducting T_c versus pressure for $\text{Ce}[\text{O}_{0.88}\text{F}_{0.12}]\text{FeAs}$. The dashed curve is a guide to the eye given by a quadratic fit of the data, extrapolating to zero temperature at ~ 190 kbar.

tion under pressure, rather than the intrinsic pressure dependence of T_c . The T_c value decreases monotonically with pressure and is suppressed below 1.1 K at 265 kbar.

The strong dependence of T_c on pressure in these materials is rather remarkable. Shein and Ivanovskii [14] calculate that the bulk modulus of LaOFeAs is only 98 GPa, significantly smaller than that found for the cuprate superconductors. It is likely that the strong dependence of T_c on pressure for $\text{La}[\text{O}_{0.89}\text{F}_{0.11}]\text{FeAs}$ and $\text{Ce}[\text{O}_{0.88}\text{F}_{0.12}]\text{FeAs}$ is related to their high compressibility. Experiments to determine structural parameters under pressure would help to clarify the effect of lattice properties on T_c .

For the oxypnictides, it is likely that, as in the cuprates, increasing pressure leads to an increase in carrier concentration. The initial increase in T_c with pressure for $\text{La}[\text{O}_{0.89}\text{F}_{0.11}]\text{FeAs}$ may thus be due to the sample being underdoped. Indeed, Lu et al. [15] find that increased doping achieved through high-pressure synthesis raises T_c to 41 K in $\text{La}[\text{O}_{0.4}\text{F}_{0.6}]\text{FeAs}$. In the high- T_c cuprate superconductors, it is found that T_c generally increases with pressure in optimally doped samples, highlighting the fact that the effect of pressure is more complicated than simply changing the carrier concentration [16]. The negative pressure dependence of T_c that we find for apparently optimally doped $\text{Ce}[\text{O}_{1-x}\text{F}_x]\text{FeAs}$ combined with that previously reported for $\text{Sm}[\text{O}_{1-x}\text{F}_x]\text{FeAs}$ [7] points to a possible difference between the oxypnictide and cuprate superconductors. A systematic study of the effect of pressure on T_c across a wide range of dopings is clearly needed in order to obtain a better understanding of the optimal conditions for high- T_c values in the oxypnictide superconductors.

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References

- [1] T. Watanabe, Y. Yanagi, T. Kamiya, Y. Kamihara, H. Hiramatsu, M. Hirano, H. Hosono, *Inorg. Chem.* 46 (2007) 7719.
- [2] Y. Kamihara, H. Hiramatsu, M. Hirano, R. Kawamura, H. Yanagi, T. Kamiya, H. Hosono, *J. Am. Chem. Soc.* 128 (2006) 10012.
- [3] Y. Kamihara, T. Watanabe, M. Hirano, H. Hosono, *J. Am. Chem. Soc.* 130 (2008) 3296.
- [4] H. Takahashi, K. Igawa, K. Arii, Y. Kamihara, M. Hirano, H. Hosono, *Nature* 453 (2008) 376.
- [5] G.F. Chen, Z. Li, D. Wu, G. Li, Z. Hu, J. Dong, P. Zheng, J.L. Luo, N.L. Wang, 2008. <cond-mat/0803.3790>.
- [6] Z. Ren, W. Lu, J. Yang, W. Yi, X. Shen, Z. Li, G. Che, X. Dong, L. Sun, 2008. <cond-mat/0804.2053>.
- [7] B. Lorenz, K. Sasmal, R.P. Chaudhury, X.H. Chen, R.H. Liu, T. Wu, C.W. Chu, 2008. <cond-mat/0804.1582>.
- [8] A.S. Sefat, M.A. McGuire, B.C. Sales, R. Jin, J.Y. Howe, D. Mandrus, *Phys. Rev. B* 77 (2008) 174503.
- [9] B. Bireckoven, J. Wittig, *J. Phys. E: Sci. Instrum.* 21 (1988) 841.
- [10] S.T. Weir, J. Akella, C. Aracne-Ruddle, Y.K. Vohra, S.A. Catledge, *Appl. Phys. Lett.* 77 (2000) 3400.
- [11] A.D. Chijioke, W.J. Nellis, A. Soldatov, I.F. Silvera, *J. Appl. Phys.* 98 (11) (2005) 114905.
- [12] D.D. Jackson, J.R. Jeffries, W. Qiu, J.D. Griffith, S. McCall, C. Aracne, M. Fluss, M.B. Maple, S.T. Weir, Y.K. Vohra, *Phys. Rev. B* 74 (2006) 174401.

- [13] T.F. Smith, C.W. Chu, M.B. Maple, *Cryogenics* 9 (1969) 53–56.
- [14] I.R. Shein, A.L. Ivanovskii, 2008. <cond-mat/0804.0712>.
- [15] W. Lu, X.-L. Shen, J. Yang, Z.-C. Li, W. Yi, Z.-A. Ren, X.-L. Dong, G.-C. Che, L.-L. Sun, F. Zhou, Z.-X. Zhao, 2008. <cond-mat/0804.3725>.
- [16] J.S. Schilling, What High Pressure Studies have Taught us About High-Temperature Superconductivity. *Frontiers of High Pressure Research II: Application of High Pressure to Low-Dimensional Novel Electronic Materials*, Kluwer Academic Publishers, 2001. pp. 345–360.