

Effect of pressure on the superconducting and spin-density-wave states of $\text{SmFeAsO}_{1-x}\text{F}_x$ B. Lorenz,¹ K. Sasmal,¹ R. P. Chaudhury,¹ X. H. Chen,² R. H. Liu,² T. Wu,² and C. W. Chu^{1,3,4}¹*Department of Physics and TCSUH, University of Houston, Houston, Texas 77204, USA*²*Hefei National Laboratory for Physical Science at Microscale and Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China*³*Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720, USA*⁴*Hong Kong University of Science and Technology, Hong Kong, China*

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High-temperature superconductors with a T_c above 40 K have been found to be strongly correlated electron systems and to have a layered structure. Guided by these rules, Kamihara *et al.* [J. Am. Chem. Soc. **130**, 3296 (2008)] discovered a T_c up to 26 K in the layered $\text{La}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$. By replacing La with trivalence rare-earth (RE) elements of smaller ionic radii, T_c has subsequently been raised to 41–52 K. Many theoretical models have been proposed that emphasize the important magnetic origin of superconductivity in this compound system and a possible further T_c enhancement in $\text{RE}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$ by compression. This later prediction appears to be supported by the pressure-induced T_c increase in $\text{La}(\text{O}_{0.89}\text{F}_{0.11})\text{FeAs}$ observed. Here we show that, in contrast to previous expectations, pressure can either suppress or enhance T_c , depending on the doping level, suggesting that a T_c exceeding 50 K may be found only in the yet-to-be discovered compound systems related to but different from $\text{RE}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$ and that the T_c of $\text{La}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$ and $\text{Sm}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$ may be further raised to about 50 K.

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There exists in nature a large class of equiatomic quaternary layered compounds REOTPn (RE=La, Nd, Sm, Gd; T =Mn, Fe, Co, Ni, Cu; Pn=P, As, Sb) with a tetragonal structure of the ZrCuSiAs type.¹ The rare-earth transition oxy-pnictides REOTPn consist of transition-metal pnictide (TPn) layers sandwiched by rare-earth oxide (REO) layers. Similar to the cuprate high-temperature superconductors, the charge carriers are supposed to flow in the TPn layers, while the REO layers inject charge carriers to the former via the so-called modulation doping while retaining the layer integrity of the TPn layers. However, the coordination structure of REOTPn is different from that of the high- T_c cuprates: The divalent T is tetrahedrally coordinated with four Pn ions, whereas the divalent Cu forms the fourfold square plane. Based on the above analysis, superconductivity was first discovered in LaOFeP with a $T_c \sim 4$ K.² By increasing the carrier concentration through the partial replacement of O with F, the T_c was raised to ~ 9 K. Shortly afterward, LaONiP was found to exhibit a $T_c \sim 3$ K.³ However, immense excitement did not arise until the very recent discovery of the 26 K superconductivity in the F-doped LaOFeAs .⁴ The refined x-ray diffraction data show that the oxidation numbers of REOFeAs are $\text{RE}^{3+}\text{O}^{2-}\text{Fe}^{2+}\text{As}^{3-}$, where the conducting iron arsenide (FeAs)¹⁻ layers are stacked alternately with the less conducting rare-earth (REO)¹⁺ layers.¹

Immediately after the discovery of a T_c of 26 K in $\text{La}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$,⁴ T_c was drastically raised to 43 K in $\text{Sm}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$,⁵ followed by reports of a T_c of up to 41 K in $\text{Ce}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$,⁶ 52 K in $\text{Pr}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$,⁷ and 50 K in $\text{Nd}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$.⁸ These are the first instances that T_c 's above 40 K, the theoretical T_c limit prior to the discovery of the 93 K $\text{YBa}_2\text{Cu}_3\text{O}_7$ superconducting cuprate,⁹ have been found outside the layered cuprate compound system. The recent discoveries have generated great enthusiasm about the future of high-temperature superconductivity. These Fe-based rare-earth oxyarsenides $\text{RE}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$ are expected

to provide an alternative material base for studying the origin of high-temperature superconductivity and to offer a different avenue to achieving superconductivity at a temperature surpassing the record T_c of the cuprates. Indeed, the crucial role of the magnetic Fe element in the occurrence of the relatively high T_c in these compounds is unexpected, since the presence of magnetic ions tends to be antagonistic to the conventional s -wave superconductivity. Unconventional superconductivity has been proposed by many.^{10–18} Much higher T_c has also been suggested in this class of compounds by fine-tuning through doping and/or applying pressure.^{14,15,19} The suggestion appears to be consistent with the initial observation of the T_c increase of $\text{La}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$ due to the possible internal pressure induced by the replacement of La by the smaller rare-earth elements.^{5–8} It seems also to be corroborated by the T_c enhancement of $\text{La}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$ by external pressures at a rate of $dT_c/dP \sim 1.2$ K/GPa.¹⁹ This compound system is expected to have a softer characteristic¹⁵ and, when an enhanced T_c is achieved, may thus alleviate some of the burdens in high-temperature superconducting wire fabrication encountered for the second-generation superconducting wires that use $\text{YBa}_2\text{Cu}_3\text{O}_7$. However, it is not clear whether such a positive pressure effect on T_c is true for all other superconducting rare-earth Fe oxyarsenides, whether the reported rapid saturation of T_c at ~ 50 K with x is intrinsic, and whether pressure can further raise the T_c of those compounds with their T_c already over 50 K.

Band calculations show that the electronic structure of REOFeAs is quasi-two-dimensional and semi-metal-like at the verge of instabilities, suggesting the possible existence of different competing states against the superconducting state, such as spin-density wave (SDW), antiferromagnetism, and ferromagnetism.^{10–13} Indeed, magnetic, resistive, and optical measurements of REOFeAs display anomalies at ~ 150 K,^{4,12} indicative of the opening of a SDW gap on

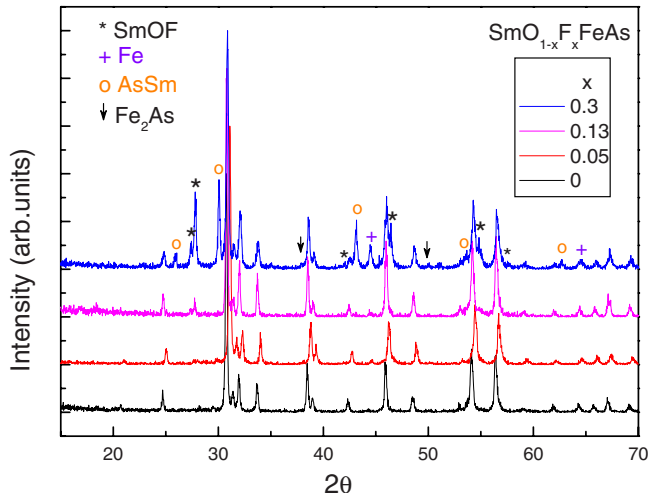


FIG. 1. (Color online) X-ray spectra of $\text{SmO}_{1-x}\text{F}_x\text{FeAs}$ for $x = 0, 0.05, 0.13,$ and 0.3 (bottom to top). Several impurity phases are indicated by different symbols.

cooling and partial reduction of the Fermi surface due to Fermi-surface nesting between the electrons and holes.¹² Doping through the partial replacement of O by F or application of external pressure is thus suggested to narrow and eventually eliminate the SDW gap, leading to the appearance of superconductivity. This appears to be supported by the experimental observations that superconductivity takes place as soon as the 150 K resistive anomaly is suppressed by F doping. However, the rapid rise in T_c of $\text{RE}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$ to its x -insensitive maximum plateau is different from the cuprates and not yet understood. The complexity in sample preparation of $\text{RE}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$ may be able to account, at least partially, for the observation. The exact effect of SDW on superconductivity in these compounds remains unclear. Examining the pressure influence on SDW may provide an insight into the relationship between the two phenomena without chemical complications in doping. To address some of the questions raised above, we have chosen to investigate the pressure effect on the $\text{Sm}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$ samples with nominal $x=0, 0.05, 0.13,$ and 0.3 , covering the nonsuperconducting and the superconducting regions.

All samples were prepared by solid-state reaction with the precautions described previously.^{4,5} X-ray spectra show the typical diffraction profile for $\text{Sm}(\text{O}/\text{F})\text{FeAs}$ (Fig. 1). Various impurity phases are detected in particular for $x=0.3$ as indicated in Fig. 1. The dc magnetization for the superconducting samples was measured in a superconducting quantum interference device (SQUID) at ambient pressure. Samples used for resistivity measurements had a typical size of 3 mm length and an area of 1 mm². The resistance was measured using the standard four-lead technique. The electrical contacts were made by attaching platinum wires using silver paint. The contact resistance was on the order of a few ohms. The low-frequency (19 Hz) resistance bridge (LR700) was employed for resistivity measurements. High-pressure measurements were carried out employing the Be-Cu clamp method with the pressure determined by the Pb-pressure gauge.²⁰ A mixture of Fluorinert 70 and 77 liquid was used as the pressure transmitting medium.

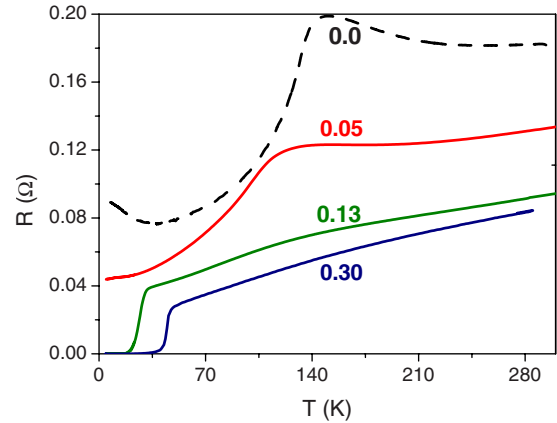


FIG. 2. (Color online) R vs T of $\text{Sm}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$ at various doping levels. The doping levels are noted next to the curves.

The magnetic susceptibility of the superconducting samples was measured at ambient pressure in 5 Oe. The diamagnetic shielding signal corresponds to $>30\%$ of superconducting volume fraction for both samples. This value is reasonable in view of the nonsuperconducting impurity phases present in the samples. The resistance (R) variations with temperature in our samples are in agreement with previous reports. A R maximum at T_{SDW} indicative of the onset of magnetic order (SDW) is evident in the $x=0$ and 0.05 nonsuperconducting samples with T_{SDW} decreasing from 150 to 125 K at ambient pressure but not in the $x=0.13$ and 0.3 superconducting samples with an onset T_c increasing from ~ 30 to ~ 48 K (Fig. 2), consistent with the F-doping effects expected from theoretical predictions.

Under pressure, the room temperature R of the $x=0.3$ sample decreases rapidly with initial pressure increase and continues to decrease, but only slowly, at higher pressures during the pressure-increase cycle, perhaps due to an initial pressure-induced compaction of the sample. However, pressure reduction results in an irreversible R increase, attributed to the pressure-induced degradation of the sample. To define the superconducting T_c consistently, we have taken the inflection point temperature of the R - T curve or the peak temperature of the dR/dT vs T plot as our T_c . A T_c defined as such is expected to be lower than the previously reported T_c 's, most of which referred to the onset temperatures. The T_c of the $x=0.3$ sample is suppressed by pressure at a rate of $dT_c/dP \sim -2.3$ K/GPa (Fig. 3), in contrast to previous suggestions. It should be noted that the T_c of 42.5 K upon the complete release of pressure is slightly lower than the starting value, probably due to the combination effect of sample degradation and the residual pressure locked in the high-pressure cell. On the other hand, for the $x=0.13$ sample, T_c increases with pressure from 24.7 to 25.55 K at 0.94 GPa at a rate of ~ 0.9 K/GPa and then stays at 25.55 K at higher pressures (Fig. 4), while the room temperature R varies with pressure as in the $x=0.3$ sample. The T_c after the complete release of pressure became higher, attributable to the sample change and the residual stress. Therefore, pressure effects on the T_c of the two samples examined are reversible except when the pressure is finally removed. The latter can be due to the polycrystallinity and low density of the samples, which

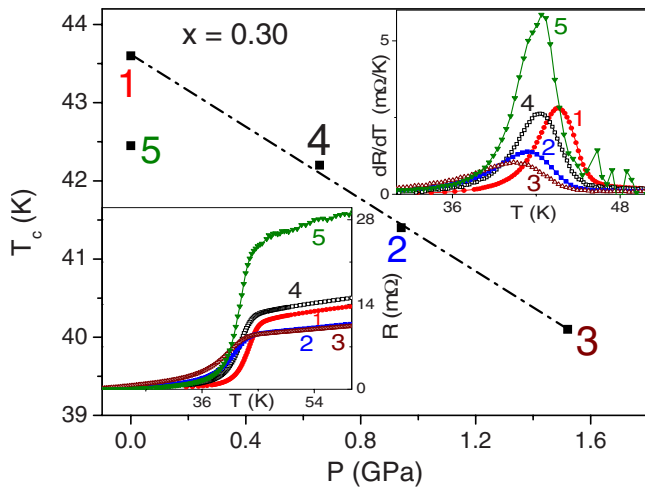


FIG. 3. (Color online) T_c vs P of $\text{Sm}(\text{O}_{0.7}\text{F}_{0.3})\text{FeAs}$. The numbers denote the sequential order of the experimental runs. Lower left inset: R vs T at $P=0$ (1), 0.94 (2), 1.52 (3), 0.66 (4), and ~ 0 + GPa (5). Upper right inset: $R' = dR/dT$ vs T .

raises the possibility that the release of pressure may weaken the interactions between grains. The unusual pressure dependence of T_c of this sample observed may be a reflection of the fine electronic structure near the Fermi surface. To study the behavior of the SDW state under pressure, we measured only the $x=0.05$ nonsuperconducting sample. It is evident that the R peak is suppressed by pressure (Fig. 5). For better definition, we take T_{SDW} as the peak temperature of dR/dT ; the suppression of the SDW state by pressure is shown in Fig. 5.

In contrast to theoretical predictions that F doping and pressure would have the same effect in suppressing the SDW state and enhancing the superconducting state of $\text{Sm}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$,^{12,15,19} we found that pressure can either promote or suppress the superconducting state, depending on the doping level of x , whereas pressure always suppresses the SDW state. It has been shown that the T_c of the cuprate

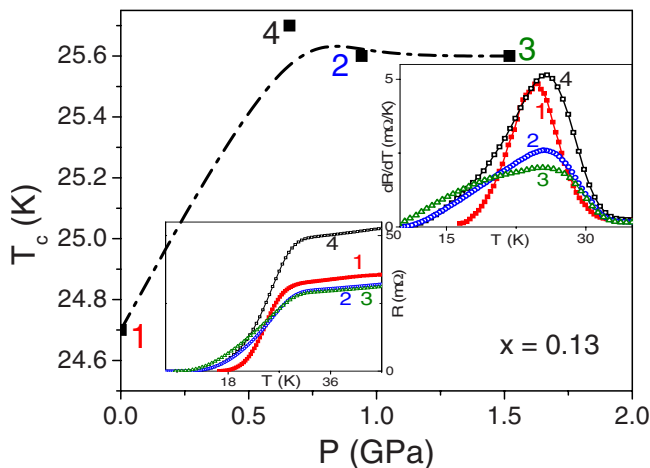


FIG. 4. (Color online) T_c vs P of $\text{Sm}(\text{O}_{0.87}\text{F}_{0.13})\text{FeAs}$. The numbers denote the sequential order of the experimental runs. Lower left inset: R vs T at $P=0$ (1), 0.94 (2), 1.52 (3), 0.66 (4), and ~ 0 + GPa (5). Upper right inset: $R' = dR/dT$ vs T .

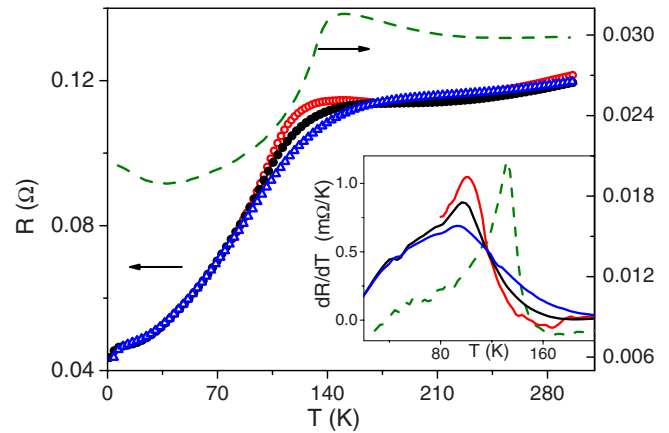


FIG. 5. (Color online) R vs T for $\text{Sm}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$ at various doping levels and pressures. $x=0$ at $P=0$ GPa (dashed line); $x=0.05$ at $P=0$ GPa (open circles), 0.94 GPa (solid circles), and 1.51 GPa (open triangles). Inset: $R' = dR/dT$ vs T for the data shown in the main panel.

high-temperature superconductors varies with carrier concentration (n) following a universal parabolic rule with T_c peaks at a carrier concentration n_0 .²¹ T_c increases with n in the so-called underdoped region where $n < n_0$ but decreases with n when the compound is in the so-called overdoped region where $n > n_0$. It has also been demonstrated²² that dT_c/dP is negative when $n \geq n_0$ and positive when $n < n_0$. The $\text{Sm}(\text{O}/\text{F})\text{FeAs}$ system seems to be similar to the high- T_c cuprates, although the current doping levels achieved do not reveal the expected decrease in T_c yet.²³ Further increase in the electron number in the FeAs layers by improved methods of doping should therefore result in a decrease in T_c . With this conjecture in mind, one can conclude that the $x=0.30$ sample with a negative dT_c/dP must lie close to the overdoped region and the $x=0.13$ sample with a positive dT_c/dP in the underdoped region. This suggests that the T_c of $\text{Sm}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$ should peak between nominal $x=0.13$ and 0.3 and within a T_c range of 50–60 K. Indeed, a systematic control of x in $\text{Sm}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$ has just led to an enhanced T_c of 53 K. Furthermore, in the cuprate high-temperature superconductors $\text{REBa}_2\text{Cu}_3\text{O}_7$ (REBCO), where $\text{RE}=\text{Y}$ and rare-earth elements, RE controls the stability of the crystal structure but is electronically isolated from the superconductivity of the compound because the density of states of RE lies deep below the Fermi level.²⁴ Therefore, the T_c of REBCO has been observed to vary with n universally and the maximum T_c falls into the narrow range around 90 K independent of RE. Similarities between the layered structures of $\text{RE}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$ and REBCO led us to conjecture that, like REBCO, $\text{RE}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$ will have a similar T_c variation with x and a narrow maximum T_c range in ~ 50 K for all RE provided that the ZrCuSiAs layered structure can be stabilized in spite of the great variation from 26 to 52 K of the maximum T_c of $\text{RE}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$ reported for different RE's.^{4–8} A systematic study on the doping effect is warranted and should yield a nonmonotonic T_c - x relation instead of those previously reported. To increase the maximum T_c of $\text{La}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$ from 26 to around 50 K is a strong possibility. On the other hand, several cuprate high- T_c compound

systems similar to REBCO exist with T_c up to 134 K at ambient pressure²⁵ and 164 K at 30 GPa.²⁶ It is not unlikely that T_c above 50 K will be found in a yet-to-be-discovered compound system similar to but different from REOFesAs with proper doping.

The suppression of the SDW state is clearly evidenced by the shifting of the resistance peak at T_{SDW} to a lower temperature by F doping and also by the diminishing of the resistance peak near T_{SDW} upon the application of pressure, in general agreement with the band calculations (Fig. 5). Questions of whether the appearance of superconductivity requires the complete disruption of the SDW gap, as many of

the published results suggest, and whether a direct interaction exists between the superconducting and the SDW states remain unanswered. A systematic high-pressure study on compounds very close to the border between the superconducting and SDW states should help address these questions.

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