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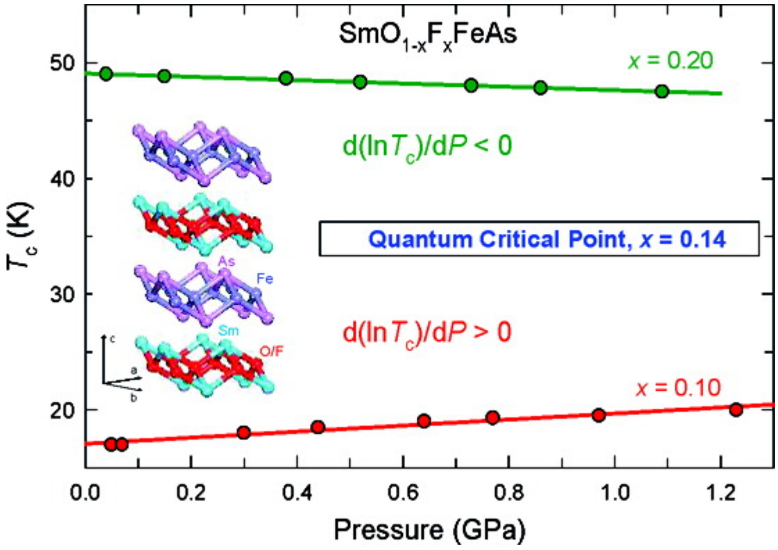

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Doping Dependence of the Pressure Response of T_c in the $SmO_{1-x}F_xFeAs$ Superconductors

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The discovery of superconductivity in the family of fluorine-doped rare-earth iron oxyarsenides, $REO_{1-x}F_xFeAs$ (RE = La, Ce, Pr, Nd, Sm, Gd) with transition temperatures, T_c as high as 55 K is currently generating considerable interest.[1,2] These systems adopt tetragonal crystal structures (ZrCuSiAs-type, space group $P4/nmm$),[1] comprising interleaved two-dimensional RE(O,F) and FeAs layers (Figure 1 inset) with the latter providing the carrier conduction pathway. The appearance of high T_c superconductivity in these materials is generating exciting arguments on the possible mechanism of superconductivity and has led to considerable optimism for raising T_c to even higher values. In particular, it appears that superconductivity emerges at some critical value of F-doping when a competing spin-density-wave (SDW)-type long-range antiferromagnetic (AFM) order collapses; T_c increases smoothly with increasing doping level x until it reaches a maximum and then it decreases. This phenomenology together with the presence of magnetic interactions is reminiscent of the long established behavior of the high T_c cuprate superconductors and has led to suggestions of an unconventional non-BCS origin of the pairing mechanism.

A key experimental observation that can provide crucial information in differentiating between competing models of superconductivity in these oxyarsenides relates to the effect of applied pressure on T_c. Specifically it has been suggested that applied P should enhance the charge transfer between the insulating RE(O,F) and conducting FeAs slabs, thereby raising the value of T_c.[3] Experimental data on the $LaO_{0.89}F_{0.11}FeAs$ superconductor appear to support this picture with T_c increasing with P at a rate of 1−2 K GPa^{-1}.[3,4] Here we report an investigation of the magnetic response of the $SmO_{1-x}F_xFeAs$ ($0.05 \leq x \leq 0.20$) family of superconductors as a function of pressure up to 1.2 GPa. We find that at low F-doping levels ($x \leq 0.12$), the pressure coefficient, dT_c/dP is positive with T_c rapidly increasing with applied pressure. However, the sign of dT_c/dP sharply switches over and becomes negative as x increases beyond 0.15.

Polycrystalline samples with nominal composition $SmO_{1-x}F_xFeAs$ ($0 \leq x \leq 0.20$) were synthesized by conventional solid state reaction using high-purity SmAs, SmF_3, Fe, and Fe_2O_3, as described elsewhere.[5] The samples were characterized by powder X-ray diffraction and temperature-dependent resistivity and *dc* magnetization measurements at ambient pressure. Bulk superconductivity is observed for $x = 0.10$ at ~12 K. T_c increases monotonically with increasing F content and reaches a maximum value of ~54 K (from resistivity measurements) at the optimal doping, $x = 0.20$ (Figure 1). This composition also represents the current upper limit of F doping in SmOFeAs.[5] Magnetization measurements were carried out at 20 Oe on about 10-mg samples in the temperature range 1.8−60 K under both zero-field-cooling (ZFC) and field-cooling (FC) protocols with a Quantum Design SQUID magnetometer. Hydrostatic external pressure to ~1.2 GPa was applied with a piston−cylinder high-pressure cell (easyLab Technologies Mcell10) using high-purity Sn as an in situ manometer. The error in the pressure determination is on the order of 0.01−0.02 GPa. Daphne mineral oil was used as the pressure transmitting medium. Magnetization data were collected both on increasing and decreasing P.

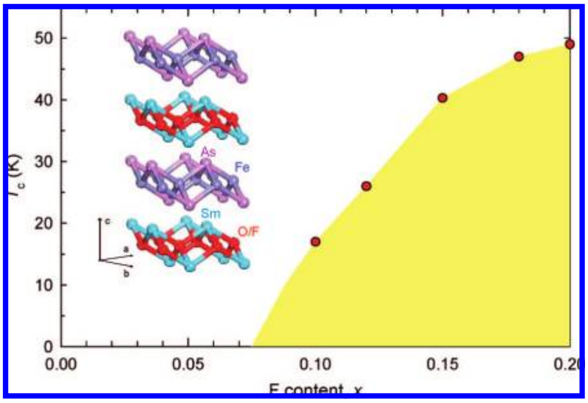

Figure 1. Doping dependence of the superconducting transition temperature T_c in $SmO_{1-x}F_xFeAs$; (inset) schematic diagram of the tetragonal crystal structure of rare-earth iron oxyarsenides.

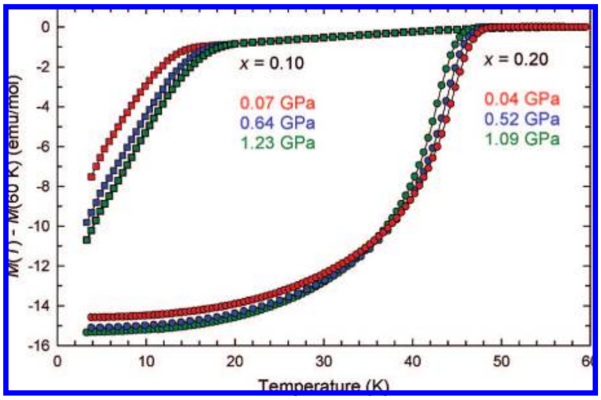

Figure 2. Temperature dependence of the magnetization, M (ZFC, 20 Oe) at selected pressures for $SmO_{0.90}F_{0.10}FeAs$ (squares) and $SmO_{0.80}F_{0.20}FeAs$ (circles).

Figure 2 shows the temperature dependence of the ZFC magnetization, M at various pressures for the $SmO_{0.90}F_{0.10}FeAs$ and $SmO_{0.80}F_{0.20}FeAs$ samples. Close to ambient pressure, bulk super-

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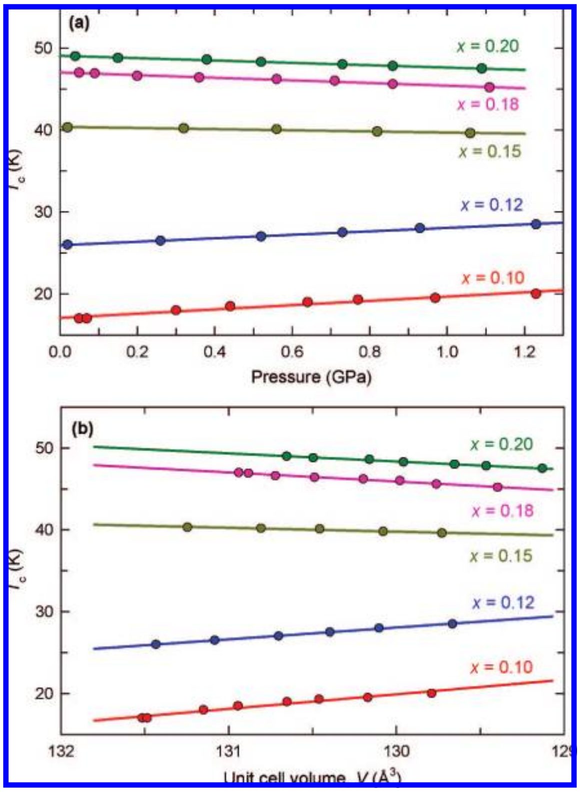

Figure 3. Superconducting transition temperature, T_c vs (a) applied pressure P and (b) unit-cell volume V for $SmO_{1-x}F_xFeAs$ ($0.10 \leq x \leq 0.20$). The lines through the points are linear fits to the data.

conductivity with onset T_cs of 17 and 49 K and shielding fractions of 12% and 23% (at 3.8 K) is observed for $x = 0.10$ and 0.20, respectively (Figure 2). However, the superconducting response of the samples to increasing external hydrostatic pressure is found to be drastically different. Although in both cases, T_c responds to pressure very sensitively, it shifts quasi-linearly to higher temperatures (at a rate of 2.6(2) K GPa^{-1}) for $SmO_{0.90}F_{0.10}FeAs$ and to lower temperatures (at a rate of −1.44(5) K GPa^{-1}) for $SmO_{0.80}F_{0.20}FeAs$. Unlike earlier measurements,[3,4,6] no broadening of the transitions is observed with increasing P implying the absence of sample inhomogeneities. The relation between T_c and pressure for $SmO_{1-x}F_xFeAs$ ($0.10 \leq x \leq 0.20$) is summarized in Figure 3a, which clearly shows that the change in sign of the pressure coefficient, dT_c/dP occurs for compositions with F doping levels between 0.12 and 0.15. We also note that low-field magnetization measurements on a $SmO_{0.95}F_{0.05}FeAs$ sample revealed the presence of only pressure-independent trace (~0.1%) superconductivity below 5 K and no pressure-induced transition to a superconducting state up to 1.2 GPa.

Of paramount importance is the determination of the underlying mechanism for superconductivity in the $REO_{1-x}F_xFeAs$ phases, and experimental data are rapidly being accumulated. Specifically for the $SmO_{1-x}F_xFeAs$ series, resistivity and Hall effect measurements[5] have been interpreted in terms of the occurrence near $x \approx 0.14$ of a quantum critical point (QCP) owing to the competition of SDW order and superconductivity. Then it is indeed remarkable that the change in sign of dT_c/dP from positive to negative is observed in our experiments precisely at doping levels that straddle the putative QCP. Our experimental results are therefore not in agreement with theoretical models[7] which have proposed that dT_c/dP should change sign from positive to negative when the compounds cross from the so-called underdoped (T_c increases with x) to the overdoped (T_c decreases with x) region.

The absolute values of the normalized pressure coefficient, $d(\ln T_c)/dP$ also vary significantly across the $SmO_{1-x}F_xFeAs$ series. Close to the critical composition at which the superconducting state emerges, $d(\ln T_c)/dP$ assumes a maximum value of 0.15(1) GPa^{-1}. As the doping level increases further, $d(\ln T_c)/dP$ reaches a value of 0.081(2) GPa^{-1} at $x = 0.12$. Following the reversal in sign of the pressure coefficient, $d(\ln T_c)/dP$ is much smaller in magnitude at −0.017(3) GPa^{-1} for $x = 0.15$; as x increases further and approaches optimal doping, $d(\ln T_c)/dP$ remains essentially constant at −0.03 GPa^{-1}. Of particular importance will be also to establish the doping dependence of the volume coefficients of T_c. At present, there are no experimental data available for the volume compressibility of $REO_{1-x}F_xFeAs$ phases but theoretical calculations[8] provide a value of the bulk modulus B on the order of 90 GPa. Taking this into account, we estimate $|d(\ln T_c)/dV|$ to be 0.104(8) Å^{-3} at $x = 0.10$, implying a very sensitive dependence of the superconducting properties of $SmO_{1-x}F_xFeAs$ to the interatomic distances in the underdoped regime. The results of converting the $T_c(P)$ data in Figure 3a to $T_c(V)$ are shown in Figure 3b. As the doping level exceeds that of the QCP, $|d(\ln T_c)/dV|$ is strongly suppressed and the dependence of the superconductivity onset to the interatomic distances is almost an order of magnitude smaller (0.012(2) Å^{-3} at $x = 0.15$). By the time optimal doping is reached the volume coefficient of T_c is somewhat larger but still about five times smaller ($|d(\ln T_c)/dV| = 0.020(1)$ Å^{-3} at $x = 0.20$) than for that in the underdoped regime.

In conclusion, the observed doping dependence of the pressure coefficients in the $SmO_{1-x}F_xFeAs$ ($0.10 \leq x \leq 0.20$) superconductors reveals a sharp change in sign from positive to negative in the vicinity of the QCP proposed by resistivity and Hall effect measurements.[5] In the underdoped region, the compounds display an extremely sensitive dependence of T_c on the interatomic distances. However, beyond the QCP and as optimal doping is approached, this sensitivity is strongly suppressed by a factor of 5−10. These results should form a stringent test of competing models for the interpretation of the superconducting pairing mechanism in fluorine-doped rare-earth iron oxyarsenides.

Supporting Information Available: Pressure-dependent magnetization measurements of the $x = 0.12$, 0.15, and 0.18 samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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