Superconducting Fe-based compounds $(A_{1-x}Sr_x)Fe_2As_2$ with A=K and Cs with transition temperatures up to 37 K

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New high- T_c Fe-based superconducting compounds, AFe₂As₂ with A = K, Cs, K/Sr and Cs/Sr, were synthesized. The T_c of KFe₂As₂ and CsFe₂As₂ is 3.8 and 2.6 K, respectively, which rises with partial substitution of Sr for K and Cs and peaks at 37 K for 50-60% Sr substitution, and the compounds enter a spin-density-wave state (SDW) with increasing electron number (Sr-content). The compounds represent p-type analogs of the n-doped rare-earth oxypnictide superconductors. Their electronic and structural behavior demonstrate the crucial role of the (Fe₂As₂)-layers in the superconductivity of the Fe-based layered systems, and the special feature of having elemental A-layers provides new avenues to superconductivity at higher T_c .

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Guided by the rule that high-temperature superconductivity usually occurs in strongly correlated electron layered systems as in the copper oxides [1], Hosono's group started a few years ago to search for superconductivity in quaternary equiatomic rare-earth transitionmetal oxypnictides, ROTPn, where R = rare-earth, T = transition-metal and Pn = pnictogen. Indeed, superconductivity was found in ROTPn, where R = La, T = Niand Fe, Pn = P and As, with transition temperatures (T_c) up to 26 K in F-doped LaOFeAs [2]. The observation generated immense excitement due to the high T_c , and the significantly large amount of a magnetic component, Fe, which is considered antithetic to conventional s-wave superconductivity. In the ensuing few weeks, after the initial report of $T_c = 26$ K in La(O,F)FeAs, the T_c was quickly raised to 41-52 K in other F-doped samples, R(O,F)FeAs, replacing La with other trivalent R with smaller ionic radii [2, 3, 4, 5, 6, 7]. This is consistent with the reported positive pressure effect on the T_c of Ce(O,F)FeAs [8]. Thus, a new class of materials with a promising potential for high T_c that may rival the well-known cuprate high-temperature superconductors was born. Intensive studies followed to further raise their T_c , and to unravel the underlying mechanism for superconductivity in R(O,F)FeAs. A subsequent high pressure study shows that the pressure effect on the T_c of Sm(O,F)FeAs depends on F-doping, i.e. positive when the sample is under-doped but negative when over-doped, similar to the cuprates [9]. The results suggest that the maximum T_c of R(O,F)FeAs is around ~ 55 K and higher T_c 's (>55 K) may yet be discovered in compounds that are chemically different, but physically related to R(O,F)FeAs. We therefore examined the structurally related layered system AFe_2As_2 , with A = K, Cs, Sr, (K/Sr) or (Cs/Sr). We found KFe₂As₂ and CsFe₂As₂ exhibit superconducting transitions at 3.8 K and 2.6 K,

respectively. Furthermore, with Sr substitution, the T_c of $(K_{1-x}Sr_x)Fe_2As_2$ and $(Cs_{1-x}Sr_x)Fe_2As_2$ increases to a maximum T_c of 36.5 K and 37.2 K, respectively, at $x\sim0.5$ -0.6. A new family of Fe-based layered compounds with a relatively high T_c is thus discovered. Given that elemental K, Cs, (K/Sr) or (Cs/Sr)-layers separate the (Fe_2As_2) -layers, this class of superconducting materials may provide new ways to raise T_c .

ROFeAs crystallize in the tetragonal ZrCuSiAs-type structure [2, 3] that consists of transition-metal pnictide (Fe_2As_2) -layers sandwiched by rare-earth oxide (R_2O_2) layers, as shown in Fig. 1a. Similar to the cuprate high temperature superconductors, the charge carriers are supposed to flow within the (Fe₂As₂)-layers, and the (R₂O₂)-layers act as "modulation doping" layers while retaining the structural integrity of the (Fe₂As₂)-layers. However, details of the layered structure of ROFeAs are different from the high T_c cuprates: the formally divalent Fe is tetrahedrally coordinated to four As-atoms, whereas the divalent Cu in cuprates is coordinated to four oxygens in a square planar manner. AFe₂As₂ (A=K and Cs) crystallize in the ThCr₂Si₂ structure type [10, 11]. It features identical (Fe₂As₂)-layers as in ROFeAs, but separated by single elemental A-layers, as shown in Fig. 1b. In stacking the (Fe₂As₂)-layers in AFe₂As₂, the layers are oriented such that the As-As distances between adjacent layers are closest. Nevertheless, interlayer As-As distances in AFe₂As₂ are effectively nonbonding. In ROFeAs, adjacent (Fe₂As₂)-layers are stacked parallel, with identical orientations, and the (Fe₂As₂)-layers are further isolated by more complex (La_2O_2) -slabs.

We have undertaken a systematic study of the $(K_{1-x}Sr_x)Fe_2As_2$ for $x=0, 0.1, 0.3, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0. In addition, representative superconducting phases of <math>(Cs_{1-x}Sr_x)Fe_2As_2$ with x=0.5 and 0.6, as well as $CsFe_2As_2$, were studied. All ternary com-

pounds were prepared by high-temperature solid state reactions of high purity K, Cs and Sr with FeAs. Phasepure FeAs powder was prepared from the reaction of pure elements in sealed quartz containers at 600-800 °C. Polycrystalline samples of the title compounds were prepared and handled under purified Ar atmosphere. Samples were prepared as follows: stoichiometric amounts of the starting materials were mixed and pressed into pellets. The pellets were sealed in welded Nb tubes under Ar. The reaction charges were jacketed within sealed quartz containers, and then heated for 20-24 hrs at 1000, 950, and 700 °C for SrFe₂As₂, KFe₂As₂, and CsFe₂As₂, respectively. In addition, SrFe₂As₂ was preheated at 1200 °C for 1.5 hours, and CsFe₂As₂ was preheated at 550 $^{\circ}\mathrm{C}$ for 12 hours. For the mixed-metal samples, (K,Sr)Fe₂As₂ and (Cs,Sr)Fe₂As₂, stoichiometric amounts of the ternary iron arsenides were thoroughly mixed, pressed and then annealed within welded Nb containers (jacketed in quartz) at 900 °C for 20-30 hours. The SrFe₂As₂ and the mixed metal, (K-Sr) and (Cs-Sr), compounds are stable to air and moisture. However, KFe₂As₂ and CsFe₂As₂ are air- and moisture-sensitive. The resulting polycrystalline samples were investigated by powder X-ray diffraction. XRD data of the end compounds (i.e. x = 0.0 and 1.0), shown in Fig. 2, can be completely indexed to the tetragonal $ThCr_2Si_2$ structure. The refined tetragonal cell parameters of the isostructural mixed-metal phases show a trend in cell volume that agrees with the atomic radii of the metals, i.e. cell volumes increase with increasing alkali metal content. In addition, the c/a ratios changes significantly with Srincorporation in that the ratio decreases with increasing Sr-content, while the a-parameter nearly remains unchanged. The contraction in the c/a ratio is most significant in the Cs-compounds. This implies that the interlayer distance between the (Fe₂As₂)-layers and the relevant As-As distances decrease with Sr content. $\rho(T)$ was measured by employing a standard 4-probe method using a Linear Research LR-700 ac bridge operated at 19 Hz and the magnetic field effect on ρ was measured using a Quantum Design PPMS system for temperatures down to 1.8 K and magnetic fields up to 7 T. The temperature dependence of the dc-magnetic susceptibility $\chi(T)$ was measured using Quantum Design SQUID magnetometer at fields up to 5 T. The Seebeck coefficient was measured using a very low frequency ac two-heater method [12].

The resistivities $\varrho(T)$, as a function of temperature and magnetic field; magnetic susceptibilities $\chi(T)$ as a function of temperature; and Seebeck coefficients of the title compounds were measured. The $\varrho(T)$ s of all samples investigated exhibit metallic behavior. Fig. 3a shows that the ϱ of SrFe₂As₂ decreases from room temperature and undergoes a rapid drop at ~200 K, indicative of the onset of a SDW state, similar to the isoelectronic BaFe₂As₂ [13, 14]. The observed noise near room temperature is associated with the condensation of moisture in the sam-

ples. Fig. 3a also shows ϱ of KFe₂As₂ decreasing with temperature, but with a strong negative curvature, suggesting strong electron-electron correlation. The ϱ finally drops to zero below ~ 3.8 K, indicating a transition to the superconducting state (Fig. 3a inset).

All samples, except SrFe₂As₂ and K_{0.1}Sr_{0.9}Fe₂As₂, display bulk superconductivity as evidenced by the drastic drop of ϱ to zero and a large Meissner effect at T_c . The $\chi(T)$ for KFe₂As₂ and CsFe₂As₂ show superconducting transitions at ~ 3.8 K and ~ 2.6 K as shown in Fig. 4a (inset), respectively. The $\chi(T)$ of the samples with highest T_c , $(K_{0.4}Sr_{0.6})Fe_2As_2$ and $(Cs_{0.4}Sr_{0.6})Fe_2As_2$, are also shown in Fig. 4a. As expected, the magnetic field is observed to suppress the superconducting transitions of $(K_{0.4}Sr_{0.6})Fe_2As_2$ and $(Cs_{0.4}Sr_{0.6})Fe_2As_2$, as shown in Fig. 3b. Using the Ginzburg-Landau formula on Figs. 3b and 3c, and defining T_c as the temperature at which ϱ drops by 50%, a high $H_{c2}(0)$ of 140 T and 190 T can be deduced for $(Cs_{0.4}Sr_{0.6})Fe_2As_2$ and $(K_{0.4}Sr_{0.6})Fe_2As_2$, respectively. Even at the 90 % resistivity drop the extrapolated $H_{c2}(0)$ is still high, 110 T for $(Cs_{0.4}Sr_{0.6})Fe_2As_2$ and 153 T for $(K_{0.4}Sr_{0.6})Fe_2As_2$. It is remarkable that these values exceed the critical fields of the fluorine-doped LaOFeAs compound [15]. The superconducting and the SDW transitions, evident from the $\varrho(T)$ and $\chi(T)$, is further confirmed by the measured Seebeck coefficients presented in Fig. 4b. The significant positive thermoelectric power of $(K_{0.4}Sr_{0.6})Fe_2As_2$ indicates the major carriers in this system are hole-like (p-type), in contrast to the electron-like large negative thermoelectric power in the superconducting $CeO_{0.84}F_{0.16}FeAs$.

The results of $\rho(T)$ and $\chi(T)$ for phases with varying Sr content can be summarized by a phase diagram of T_c vs. Sr content (x), constructed for $(K_{1-x}Sr_x)Fe_2As_2$, in Fig. 5. A similar phase diagram for $(Cs_{1-x}Sr_x)Fe_2As_2$ is also observed. The diagram shows that the T_c 's of KFe₂As₂ and CsFe₂As₂ are enhanced continuously by Sr-doping and peak at ~ 37 K for Sr substitution levels of 50-60%. In view of the valence counts of $[(K)^{1+}]_{0.5}(FeAs)^{0.5-}$ in KFe_2As_2 and $[(Sr)^{2+}]_{0.5}(FeAs)^{1-}$ compared to (RO)¹⁺(FeAs)¹⁻ in ROFeAs, KFe₂As₂ exhibits significant electron deficiency, whereas SrFe₂As₂ is isoelectronic to ROFeAs. Partial substitution of K by Sr corresponds to electron counts approaching the electron count of ROFeAs, and the T_c crests at doping levels corresponding to $(FeAs)^{(0.75-0.8)-}$. In contrast, the formal electron count corresponding to the superconducting phase, $RO_{1-x}F_xFeAs$ (x = 0.15-0.20), is $(\text{FeAs})^{(1.15-1.20)}$. Therefore, we conclude that the superconductivity in the (Fe₂As₂) layers almost symmetrically peaks at two different types of carrier densities: p-type in (K/Cs,Sr)Fe₂As₂, and n-type in R(O,F)FeAs. These observations demonstrate that Cooper pairs in the Fe₂As₂ layers can be formed by both holes and electrons, similar to the behavior of the high-T_c cuprates. The evolution of superconducting state to a SDW state

by electron-doping in AFe_2As_2 and the induction of a superconducting state from the SDW state in ROFeAs effectively demonstrates the symmetry in the extended phase diagram (hole and electron carriers) and the unique role of (Fe_2As_2) -layers for superconductivity at relatively high temperature. Our results and conclusions prove the significant role of the (Fe_2As_2) -layers in superconductivity of the Fe-based layer superconductors, and as the primary cause for non-conventional superconductivity in these compounds. The simple AFe_2As_2 family of compounds also provides a basis from which T_c may be raised. This may be achieved by constructing more complex homologues of the layered Fe-pnictides, similar to what has been carried out in the high- T_c cuprates.

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- See for example, C. W. Chu, in Emerging Materials ed. D. Shaw, In Handbook of Superconducting Materials, eds. D. Cardwell and D. Ginley, Characterization, Applications, and Cryogenics (IOP, Bristol, 2003), vol 2, chap.
- [2] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. 130, 3296 (2008).
- [3] H. Takahashi, K. Igawa, K. Arii, Y. Kamihara, M. Hirano, and H. Hosono, Nature 453, 376 (2008).
- [4] X. H. Chen, T. Wu, G. Wu, R. H. Liu, H. Chen, and D. F. Fang, Nature 453, 761 (2008).
- [5] G. F. Chen, Z. Li, D. Wu, G. Li, W. Z. Hu, J. Dong, P. Zheng, J. L. Luo, and N. L. Wang, Phys. Rev. Letters 100, 247002 (2008).
- [6] Z. A. Ren, J. Yang, W. Lu, W. Yi, G. C. Che, X. L. Dong, L. L. Sun, and Z. X. Zhao, Mater. Sci. Innov. 12, 1 (2008).
- [7] Z. A. Ren, J. Yang, W. Lu, W. Yi, X. L. Shen, Z. C. Li, G. C. Che, X. L. Dong, L. L. Sun, F. Zhou, and Z. X. Zhao, Europhys. Letters 82, 57002 (2008).
- [8] W. Lu, J. Yang, X. L. Dong, Z. A. Ren, G. C. Che, and Z. X. Zhao, New J. Phys. 10, 063026 (2008).
- [9] B. Lorenz, K. Sasmal, R. P. Chaudhury, X. H. Chen, R. H. Liu, T. Wu, and C. W. Chu, Phys. Rev. B 78, 012505 (2008).
- [10] S. Rozsa and H. U. Schuster, Z. Naturforsch. B: Chem. Sci. 36, 1668 (1981).
- [11] A. Czybulka, M. Noak, and H.-U. Schuster, Z. Anorg. Allg. Chem. 609, 122 (1992).
- [12] F. Chen, J. C. Cooley, W. L. Hults, and J. L. Smith, Rev. Sci. Instru. 72, 4201 (2001).
- [13] M. Rotter, M. Tegel, D. Johrendt, I. Schellenberg, W. Hermes, and R. Pöttgen, Phys. Rev. B 78, 020503(R) (2008).

- [14] Near the completion of our work, the observation of a SDW state in pure SrFe₂As₂ was reported by C. Krellner, N. Caroca-Canales, A. Jesche, H. Rosner, A. Ormeci, and C. Geibel, arXiv:0806.1043 [cond-mat.supr-con] (2008), unpublished. Also superconductivity has been reported in the related compound K_{0.4}Ba_{0.6}Fe₂As₂ by M. Rotter, M. Tegel, and D. Johrendt, arXiv:0805.4630 [condmat.supr-con] (2008), unpublished.
- [15] F. Hunte, J. Jaroszynski, A. Gurevuch, D. C. Lar-balestier, R. Jin, A. S. Sefat, M. A. McGuire, B. C. Sales, D, K, Christen, and D. Mandrus, Nature 453, 903 (2008).

(a)

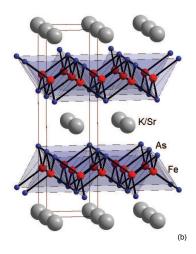
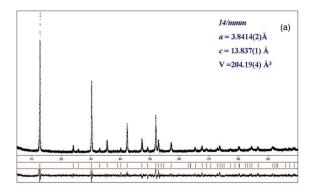


FIG. 1: (Color online) a) Crystal structure of LaOFeAs; b) crystal structure of (K/Sr)Fe₂As₂ and (Cs/Sr)Fe₂As₂.



(b)

(c)

FIG. 2: a) Powder diffraction data/Rietveld refinement: a) $\rm KFe_2As_2,$ b) $\rm SrFe_2As_2,$ c) $\rm CsFe_2As_2.$

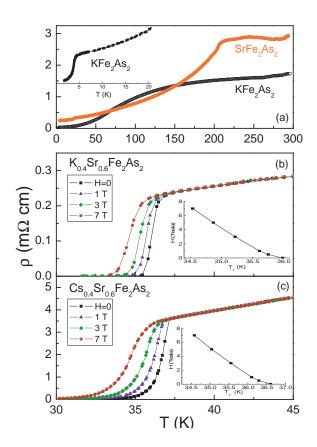


FIG. 3: (Color online) a) Resistivity of the two end members, $\rm SrFe_2As_2$ and $\rm KFe_2As_2$. The inset shows the superconducting transition of $\rm KFe_2As_2$ on an enlarged scale; b) Resistivity at different fields of $\rm K_{0.4}Sr_{0.6}Fe_2As_2$; c) Resistivity at different fields of $\rm Cs_{0.4}Sr_{0.6}Fe_2As_2$. The insets in b) and c) show the T-dependence of the critical fields as determined from the midpoint of the resistivity drop.

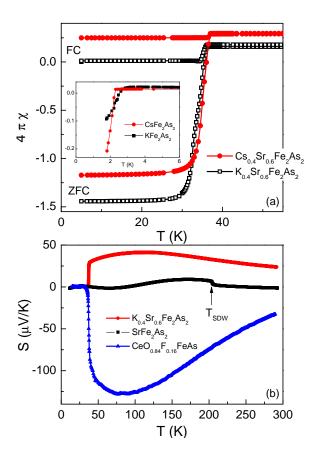


FIG. 4: (Color online) a) Magnetic susceptibilities of $K_{0.4}Sr_{0.6}Fe_2As_2$ and $Cs_{0.4}Sr_{0.6}Fe_2As_2$ measured at 10 Oe. The inset shows the magnetic susceptibilities of KFe_2As_2 and $CsFe_2As_2$ near T_c ; b) Seebeck coefficients of $K_{0.4}Sr_{0.6}Fe_2As_2$ (top curve), $SrFe_2As_2$ (middle) and $CeO_{0.84}F_{0.16}FeAs$ (bottom).

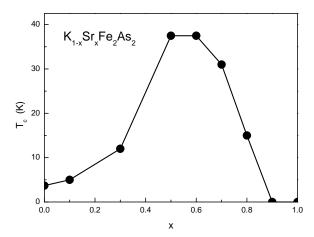


FIG. 5: Superconducting phase diagram of $K_{1-x}Sr_xFe_2As_2$.