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Pressure dependence of the superconductor transition temperature of Ca($Fe_{1-x}Co_x$)AsF compounds: A comparison with the effect of pressure on $LaFeAsO_{1-x}F_x$

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We performed systematic investigation of pressure effect on superconductivity in Ca($Fe_{1-x}Co_x$)AsF. Pressure-induced superconductivity was observed for $x=0.0$ after suppression of the antiferromagnetically ordered orthorhombic phase at the critical pressure $P_c \sim 5$ GPa. Unlike the pressure effect on T_c in F-doped LaFeAsO, all the Co-doped superconductors show no marked enhancement, which is less than 1 K. Consequently, the highest T_c among Ca($Fe_{1-x}Co_x$)AsF was obtained in parent compound. These results suggest that Co doping suppresses superconductivity. The maximum T_c observed in parent compound is higher than that in LaFeAsO, suggesting that CaFeAsF is considered as a candidate parent compound for realizing higher T_c.

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High-pressure experiments play a significant role in the field of superconductivity and provide important information for realizing higher transition temperature T_c as well as for understanding the mechanism of superconductivity.[1,2] In particular, external pressure has been powerful tool in the recently discovered iron-based superconductors. Soon after the discovery of superconductivity in LaFeAs(O,F),[3] the onset T_c was increased from 26 to 43 K by application of external pressure.[4] This suggests that the lattice contraction is effective in the enhancement of T_c of iron-based superconductors. Actually, the chemical pressure via the lanthanide contraction by the substitution of La with heavier rare earth atoms raised the onset T_c over 50 K at atmospheric pressure.[5–10] Moreover, T_c of FeSe, which exhibits superconductivity with $T_c=8$ K at atmospheric pressure,[11] shows marked pressure sensitivity and reaches ~37 K at 7–9 GPa.[12–14] Even parent compounds of iron-based superconductors have been found to be superconductor under high pressure in 122-type compounds AFe_2As_2 (A=Ca, Sr, Ba, and Eu) and 1111-type compound LaFeAsO.[15–20]

A new oxygen-free iron-based compound CaFeAsF has a ZrCuSiAs-type tetragonal structure,[21] in which LaO layers in LaFeAsO are replaced by CaF layers. Similarly to LaFeAsO,[22,23] the compound has an antiferromagnetically ordered orthorhombic phase at a low temperature.[24,25] Electrons doped into FeAs layers by partial replacement of Fe with Co suppress both the orthorhombic structure and the antiferromagnetic state, leading to the emergence of superconductivity with $T_c=22$ K for Co concentration of 10%.[21] Superconductivity induced by Co substitution has also been reported in other iron pnictides.[26–28] Compared with the Co-doped iron pnictides, Ca($Fe_{0.9}Co_{0.1}$)AsF shows higher T_c. Therefore, it is expected that further high T_c is realized with marked enhancement by pressure in Ca($Fe_{1-x}Co_x$)AsF. Also, considering the same crystal structure to $LaFeAsO_{1-x}F_x$ and the emergence of superconductivity by electron doping, it is interesting to compare with pressure effect on T_c in F-doped LaFeAsO. Here, we report on pressure effect on superconductivity in Ca($Fe_{1-x}Co_x$)AsF; we observed no marked enhancement of T_c but found that parent compound exhibits pressure-induced superconductivity with higher T_c than that in LaFeAsO, suggesting that CaFeAsF is considered as a candidate parent compound for iron-based superconductor with higher T_c.

Polycrystalline Ca($Fe_{1-x}Co_x$)AsF samples were synthesized by a solid state reaction method. The samples were confirmed to be mostly single phase with ZrCuSiAs-type tetragonal structure and the volume fraction of the impurity phase was estimated to be less than 2%.[21] Electrical resistivity measurements under hydrostatic pressures were performed by a standard four-probe method. External pressures of up to 2.5 and 8 GPa were generated by using a piston-cylinder-type pressure cell and a cubic anvil press,[29] respectively. A liquid pressure-transmitting medium (Daphne 7474) was used to maintain hydrostatic conditions.[30] A diamond anvil cell (DAC) was utilized for electrical resistivity measurements under high pressures of up to 20 GPa. The sample chamber equipped with a stainless-steel gasket was filled with powdered NaCl as a pressure-transmitting medium.

Figures 1(a) and 1(b) show the temperature dependence of the electrical resistivity $\rho(T)$ for parent compound CaFeAsF obtained using the piston-cylinder-type cell and the cubic anvil press. The compound exhibits a resistive anomaly due to the structural and magnetic transitions at 0 GPa. The derivative with respect to temperature ($d\rho/dT$) shows maximum at $T_0=112$ K, which corresponds to the magnetic transition rather than the structural phase transition.[24,25] T_0 is suppressed by pressure and the resistive anomaly disappears above 5 GPa. Instead, we observed a resistivity loss at 29 K under 4 GPa. Although the resistivity at 4 GPa showed a

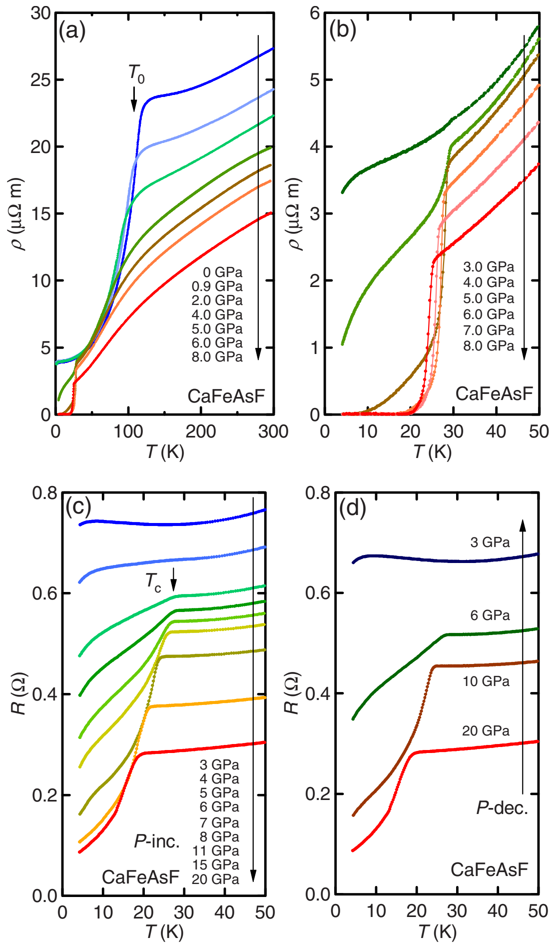

FIG. 1. (Color online) (a),(b) Temperature dependence of the electrical resistivity under hydrostatic pressures of up to 8 GPa for CaFeAsF below 300 and 50 K obtained using piston-cylinder-type pressure cell and cubic anvil press. (c),(d) The resistivity data below 50 K obtained using diamond anvil cell in the pressure-increasing and pressure-decreasing processes.

finite value at 4.2 K, zero resistivity was detected above 5 GPa, where a pressure-induced superconductivity was confirmed. The onset T_c appears at 29 K under 5 GPa and decreases with increasing pressure. As shown Fig. 1(c), the resistivity loss was also detected by measurements using the DAC. The superconducting transition was not detected below 4 GPa, but a kink was observed at 29 K under 5 GPa. The resistivity loss just below the kink becomes larger and the kink shifts to low-temperature side with increasing pressure. This kink is considered as the onset of superconducting transition. In this measurement, no zero resistivity was observed even in the highest pressure, but we confirmed current effect on the resistivity loss. The failure to observe zero resistivity is probably caused by a minor resistivity in the contact between sample and electrodes and/or a nonhydrostatic pressure condition arising from the use of a solid pressure-transmitting medium.

After the measurement at 20 GPa, external pressure was decreased to 10, 6, and 3 GPa and the resistivity was measured at each pressure [Fig. 1(d)]. The onset T_c increases with decreasing pressure, then the superconducting transition vanishes at 3 GPa. The obtained data in the pressure-decreasing process are in excellent agreement with those in the pressure-increasing process shown in Fig. 1(c). Therefore, the pressure-induced superconducting transition of CaFeAsF is reversible and no pressure-induced degradation of the sample occurs.

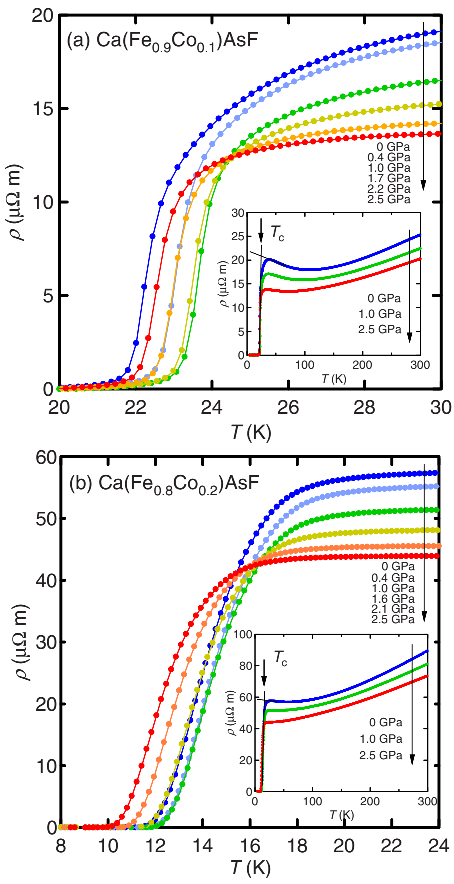

FIG. 2. (Color online) Electrical resistivity under high pressure of (a) Ca(Fe$_{0.9}$Co$_{0.1}$)AsF and (b) Ca(Fe$_{0.8}$Co$_{0.2}$)AsF in the vicinity of T_c. The insets show the data below 300 K. These data were obtained using piston-cylinder-type cell.

Figures 2(a) and 2(b) show the temperature dependence of the electrical resistivity for Ca(Fe$_{0.9}$Co$_{0.1}$)AsF and Ca(Fe$_{0.8}$Co$_{0.2}$)AsF under various pressures of up to 2.5 GPa, respectively. As shown in the insets of Figs. 2(a) and 2(b), the anomaly due to the structural and magnetic transitions is completely suppressed by Co substitution over $x=0.1$ and superconductivity is realized at 0 GPa at the onset $T_c=23.8$ and 16.4 K for $x=0.1$ and 0.2, respectively. T_c increases initially to 24.7 K at 1.0 GPa for $x=0.1$ and to 16.7 K at 0.4 GPa for $x=0.2$, but decreases upon increasing applying pressure. We also observed similar pressure dependence of T_c for $x=0.15$; T_c increases from 20.4 K at 0 GPa to 20.7 K at 0.4 GPa and then decreases.

The pressure dependence of T_0 and T_c for Ca(Fe$_{1-x}$Co$_x$)AsF are summarized in Fig. 3. T_0 at which $\rho(T)$ shows anomaly linearly decreases with increasing pressure at a rate of 12.3 K/GPa and then vanishes at a critical pressure $P_c \sim 5$ GPa. The pressure-induced superconductivity emerges with $T_c=29$ K after suppression of the anomaly at

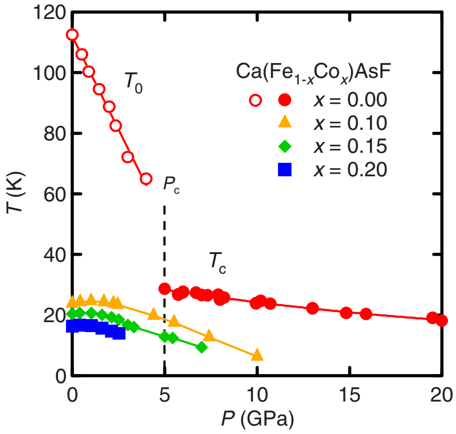

FIG. 3. (Color online) Pressure dependence of T_0 and T_c for $Ca(Fe_{1-x}Co_x)AsF$. The open and closed symbols indicate the characteristic temperature T_0, at which the resistivity shows anomaly and the onset T_c, respectively. The dashed lines indicate the critical pressures P_c. The solid curves are guides to the eye.

T_0. T_c shows maximum value at P_c and monotonically decreases upon increasing applying pressure. Similar pressure effects on T_0 and T_c have been reported in $SrFe_2As_2$ and $BaFe_2As_2$; the antiferromagnetically ordered orthorhombic phase is suppressed and superconductivity with maximum T_c emerges at P_c.[31,32] Pure LaFeAsO has also been found to be superconductor under high pressure.[20] In case of LaFeAsO, T_0 is suppressed by pressure and zero resistivity is detected at 12 GPa, where the maximum T_c is observed. It seems that a critical pressure in LaFeAsO exists at ∼12 GPa. Here, the onset T_c shows a dome-shaped pressure dependency and the critical pressure is not observed clearly. The discrepancy between the results of CaFeAaF and LaFeAsO may be attributed to the inhomogeneity of the sample and/or external pressure because the transition in LaFeAsO is gradual.

All the Co-doped superconductors show no marked increase of T_c. The onset T_c increases initially but the enhancement is less than 1 K, which is quite small compared with that in $LaFeAsO_{1-x}F_x$. The maximum T_c ($T_{c,max}$) of each sample decreases with increasing Co concentration.

Figures 4(a) and 4(b) show $T_{c,max}$ obtained under high pressure and the onset T_c at 0 GPa in $Ca(Fe_{1-x}Co_x)AsF$ and $LaFeAsO_{1-x}F_x$ as a function of x, respectively. Both systems exhibit superconductivity at 0 GPa by Co or F substitution. Also, both parent compounds show pressure-induced superconductivity. In $Ca(Fe_{1-x}Co_x)AsF$ system, the highest T_c is observed for parent compound. The enhancement of T_c by pressure is small for $x=0.1$, 0.15, and 0.2. As a result, $T_{c,max}$ monotonically decreases with increasing Co concentration. In contrast, $LaFeAsO_{1-x}F_x$ shows marked enhancement of T_c in heavily doped region.[4,20] In particular, T_c of $LaFeAsO_{0.86}F_{0.14}$ increases from 19 K to $T_{c,max}=43$ K. This value is equivalent to $T_{c,max}$ of $LaFeAsO_{0.89}F_{0.11}$, although T_c at 0 GPa is lower than that of $LaFeAsO_{0.89}F_{0.11}$ by 9 K. In lightly doped region ($x=0.05$ and 0.08), T_c is increased by pressure but its enhancement of ∼5 K is small compared with that in heavily doped region. Consequently, $T_{c,max}$ in $LaFeAsO_{1-x}F_x$ shows marked enhancement by F substitution.

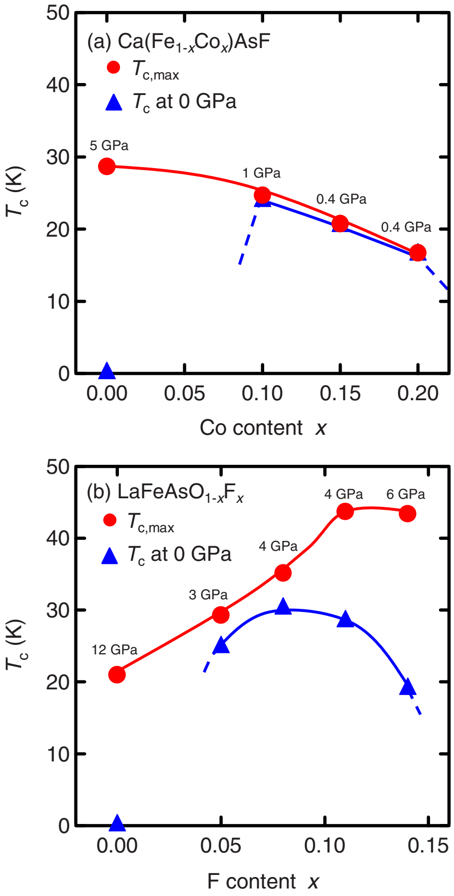

FIG. 4. (Color online) Maximum T_c ($T_{c,max}$) obtained under high pressure and T_c at atmospheric pressure as a function of (a) Co content for $Ca(Fe_{1-x}Co_x)AsF$ and (b) F content for $LaFeAsO_{1-x}F_x$. The pressures at which the maximum T_c was observed are shown for each compound. The solid and dashed lines are guides to the eye. The data of $LaFeAsO_{1-x}F_x$ were reported in Refs. 4 and 20.

It is thought that both the Co substitution in CaFeAsF and the F substitution in LaFeAsO introduce electrons in FeAs layers. However, electrons are directly doped into FeAs layers by partial replacement of Fe with Co, whereas the F substitution is regarded as indirect electron doping via LaO layers. The Co substitution leads randomness of superconducting (Fe,Co)As layers.[33] That is, the replacement of Fe introduces scattering centers in superconducting layers. Indeed, the resistivity shows upturn in lower temperatures by small amount of Co. This is one of the reasons for the suppression of $T_{c,max}$ in $Ca(Fe_{1-x}Co_x)AsF$. It has been considered that iron-based superconductor is robust against the replacement of Fe compared with the replacement of Cu in cuprates because superconductivity is realized by substituting Co for Fe. Although the antiferromagneticlly ordered orthorhombic phase is suppressed, the results of pressure effect indicate that Co substitution also suppresses superconductivity. Therefore, from the viewpoint of pressure effect, it suggests that direct doping into FeAs layers is not useful for realizing higher T_c in iron-based superconductor. Actually, iron-based superconductors induced by Co doping show lower T_c than those induced by indirect carrier doping.[26–28] Also, it has been reported that the substitution of Ca with *R*

(R=rare earth), which is regard as indirect electron doping, can cause superconductivity.[34] Note that the maximum T_c of 29 K of parent compound CaFeAsF is higher than that of 21 K of LaFeAsO. Therefore, CaFeAsF can be considered as a candidate parent compound of iron-based superconductor with higher T_c. The rare-earth substitution is known to suffer from oxygen contamination of sample. Hence, we expect that higher T_c is realized in CaFeAsF if indirect carrier doping by substitution for F or F deficiency is successful.

In summary, we performed systematic investigation of pressure effect on T_c in Ca(Fe$_{1-x}$Co$_x$)AsF. The parent compound exhibits pressure-induced superconductivity with onset T_c=29 K at 5 GPa, after suppression of the resistive anomaly due to the structural and magnetic transitions. Unlike the pressure effect on T_c in LaFeAsO$_{1-x}$F$_x$, the Co-doped superconductors show no marked enhancement of T_c. The maximum T_c of each sample monotonically decreases with increasing Co concentration. This is probably due to randomness of superconducting layers caused by direct doping into FeAs layers. As a result, the highest T_c among Ca(Fe$_{1-x}$Co$_x$)AsF was obtained in the parent compound. The maximum T_c of 29 K in parent compound is higher than that in LaFeAsO. Therefore, we expect that higher T_c is realized if indirect doping such as substitution for F or F deficiency is successful in CaFeAsF.

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