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Effect of 3d transition metal doping on the superconductivity in quaternary fluoroarsenide CaFeAsF

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Abstract. We examined the doping effect of 3d transition metal (TM) elements (Cr, Mn, Co, Ni and Cu) at the Fe site of a quaternary fluoroarsenide CaFeAsF, an analogue of 1111-type parent compound LaFeAsO. The anomaly at $\sim$120 K observed in resistivity ($\rho$) versus temperature ($T$) plot for the parent compound is suppressed by the doping of each TM element. Furthermore, Co and Ni doping (CaFe$_{1-x}$TM$_x$AsF, TM = Co, Ni) induces superconductivity with a transition temperature maximized at the nominal $x = 0.10$ for Co (22 K) and at $x = 0.05$ for Ni (12 K). These optimal doping levels may be understood by considering that Ni$^{2+}$ (3d$^8$) adds double electrons to the FeAs layers compared with Co$^{2+}$ (3d$^7$). Increased $x$ for Co or Ni breaks the superconductivity, while metallic nature $d\rho/dT > 0$ is still kept. These observations indicate that Co and Ni serve as electron donors. In contrast, Cr, Mn and Cu doping does not induce superconductivity, yielding $d\rho/dT < 0$ below the $\rho$--$T$ anomaly temperature, indicating that these TM ions act as scattering centers. The two different types of behavior of TM replacing the Fe site are discussed in relation to the changes in the lattice constants with doping.

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1. Introduction

The discovery of superconductivity in fluorine-doped LaFeAsO with transition temperature $T_c = 26$ K [1] triggered intensive studies of FeAs-based and related layered compound systems including RFeAsO (R = rare earth) [2]–[8], BFe$_2$As$_2$ (B = alkali earth) [9]–[11], AFeAs (A = alkali) [12] and FeCh (Ch = chalcogen) [13]–[15], with the hope of realizing higher-$T_c$ superconductors. These efforts lead to raising $T_c$ up to 56 K in Th-doped GdFeAsO [8]. These superconductors belong to ZrCuSiAs type (space group P4/nmm), ThCr$_2$Si$_2$ type (I4/mmm), Cu$_2$Sb type (P4/nmm) or PbO type (P4/mmm) consisting of an alternating stack of a basal Fe layer (FeAs)$^{\delta-}$ and a blocking layer (RO)$^{\delta+}$, B$^{\delta+}$ or A$^{\delta+}$ layers except the FeCh without a blocking layer. They experience a crystallographic transition from the tetragonal to the orthogonal, accompanied by an antiferromagnetic transition yielding an anomaly in electrical resistivity at 140–200 K [1, 3], [7]–[11], [16]–[18]. There is now a consensus that superconductivity in all the compounds is induced as a result of electron or hole doping to the (FeAs)$^{\delta-}$ layer, which simultaneously suppresses both transitions from occurring. Thus, explorations in material studies have been focused on the synthesis of ZrCuSiAs- and related-type compounds containing the square iron lattice as well as on the carrier-doping technique [19].

Four types of doping methods have been reported to date, i.e. (i) indirect electron doping by an introduction of fluorine into the O sites and oxygen-vacancy formation in insulating layers (RO)$^{\delta+}$ in RFeAsO [20, 21], (ii) indirect hole doping by alkali-metal doping to the B$^{\delta+}$ layer in BFe$_2$As$_2$ [9]–[11] and formation of a vacancy at the A site in AFeAs [12], (iii) electron doping by partial replacement of Fe with Co in RFeAsO and AFe$_2$As$_2$ [22]–[26], and (iv) direct electron doping by formation of a vacancy at the Se or Te sites in FeCh [13]–[15]. The direct hole doping has not been achieved yet.

Recently, we reported the synthesis of a new FeAs containing ZrCuSiAs-type compounds, BFeAsF (B = Ca, Sr), in which the (FeAs)$^{\delta-}$ layer is sandwiched by the (AF)$^{\delta+}$ layer in place of the (RO)$^{\delta+}$ layer in RFeAsO compounds (figure 1(a)) and their superconductivity is induced by partial substitution of Fe with cobalt [27, 28]. Following these reports, the existence of the BFeAsF (B = Ca, Sr and Eu) system was reported by a few groups [29, 30] and superconductivity induced by lanthanide metal doping with $T_c$ up to 56 K has been posted on the arXiv/condmat preprint server [31, 32]. For the case of partial substitution of Fe with Co, the optimal $T_c$ is 22 K for 10% Co substituted CaFeAsF (CaFe$_{0.9}$Co$_{0.1}$AsF) and 4 K for SrFe$_{0.875}$Co$_{0.125}$AsF. $T_c$ in the former is comparable to those in Co substituted FeAs-based compounds ($T_c = 14$ K for LaFeAsO, 17 K for SmFeAsO, 20 K for SrFe$_2$As$_2$ and 22 K for BaFe$_2$As$_2$) [22]–[26]. Our discovery indicates that the Co doping technique is a universal way of converting the FeAs-based layered compounds to superconductors. Further, the effectiveness of
Co doping suggests that the square Fe lattice in the FeAs layer is much more robust to impurities than CuO$_4$ planes in high-$T_c$ cuprate [33].

In this study, we examined the substitution of a series of 3d transition metals (TMs) to the Fe site on the emergence of superconductivity in CaFeAsF. Temperature dependence of electrical resistivity and lattice parameter changes upon substitution were measured. As a consequence, it was revealed that Ni substitution induces superconductivity similar to Co, whereas Cr, Mn or Cu substitution does not induce superconductivity. The optimal concentration of Ni was almost half that of Co, suggesting that both ions with excess 3d electrons serve as electron donors.

2. Experimental

Samples were prepared by a solid-state reaction of CaF$_2$ (99.99%), CaAs, Fe$_2$As and TM$_2$As (TM = Cr, Mn, Co, Ni, or Cu): CaF$_2$ + CaAs + (1 − x)Fe$_2$As + xTM$_2$As → 2CaFe$_{1−x}$MnxAsF. CaAs was synthesized by heating a mixture of Ca shots (99.99 wt.%) and As powder (99.9999 wt.%) at 650 °C for 10 h in an evacuated silica tube. Fe$_2$As and TM$_2$As were synthesized from the powders of respective elements at 800 °C for 10 h (Fe: 99.9 wt.%; Cr: 99 wt.%, Mn: 99.99 wt.%, Co: 99.9 wt.%, Ni: 99.99 wt.%, Cu: 99.9 wt.%). These products were then mixed in stoichiometric ratios, pressed and heated in evacuated silica tubes at 1000 °C for 10 h to obtain sintered pellets. All the procedures until the sealing into silica glass tubes were carried out in an Ar-filled glove box (O$_2$, H$_2$O < 1 ppm).

The crystal structure and lattice constants of the materials were examined by powder x-ray diffraction (XRD; Bruker D8 Advance TXS) using Cu Kα radiation from a rotating anode.
with the aid of Rietveld refinement using Code TOPAS3 [34]. The temperature dependence of dc electrical resistivity ($\rho$) at 2–300 K was measured by a four-probe technique using platinum electrodes deposited on samples.

3. Results and discussion

Figure 1(b) shows the powder XRD pattern of non-doped CaFeAsF. Except for several weak peaks arising from the impurity phase (Fe$_2$As, the volume fraction being 2% at most), each of the major peaks was assigned to the CaFeAsF phase and room temperature lattice constants were evaluated as $a = 0.3879$ nm and $c = 0.8593$ nm. Figure 1(c) shows the temperature dependence of the electrical resistivity of CaFeAsF. With a decrease in temperature, $\rho$–$T$ curves exhibit sudden decreases at $\sim 120$ K ($T_{\text{anom}}$). This anomalous behavior is quite analogous to those in RFeAsO and BFe$_2$As$_2$, implying that the crystallographic transition takes place at $T_{\text{anom}}$. CaFeAsF also likely suffers magnetic ordering in a similar temperature region.

Figures 2 and 3 show the powder XRD patterns of CaFeAsF doped with Cr (figure 2(a)), Mn (figure 2(b)), Co (figure 3(a)), Ni (figure 3(b)) and Cu (figure 3(c)). Except for the small peaks attributable to those of impurity phases, most of the peaks in all the patterns are assigned to originate from the CaFeAsF phase (volume fraction: >97% for Cr doping, >79% for Mn, >83% for Co, >88% for Ni and 80% for Cu). FeAs (<10%) and CaF$_2$ (<12%) were mainly observed as impurity phases, and their volume fractions were not dependent on the TM substitution level. This indicates that these impurity phases may result from the loss of
Ca elements due to vaporization from the starting mixture during the heating process. For cases of Mn, Co and Ni doping, oxide impurities CaO and Fe₂O₃ (volume fraction: <7%) were observed, indicating oxygen contamination of calcium or TM reagents during the heating process. Mn substitution over 15% leads to the segregation of the CaMn₂As₂ phase, indicating that the Mn concentration exceeds the solubility limit. Since all the samples contain impurity phases, practical doping level $x$ is not obvious. Therefore, we used the molar fractions of TMs in the starting mixture as nominal $x$ hereafter.

Figure 4 shows $a$- and $c$-axis lengths of CaFe$_{1-x}$TM$_x$AsF (TM = Cr, Mn, Co, Ni and Cu) as functions of nominal $x$. The $a$-axis length evidently increases with Mn and Cu substitution (+0.10% for Mn and +0.23% for Cu doping for nominal $x = 0.05$), whereas it decreases with Cr substitution (−0.09% for nominal $x = 0.05$). Since the $a$-axis length directly corresponds to the distance between first neighboring irons in the iron squares lattice ($r_{Fe−Fe} = a/\sqrt{2}$; see figure 1(a)), these results indicate that Cr, Mn and Cu substitution introduces lattice distortion, yielding a change in the Fe–Fe distance. In contrast, the increment of $a$-axis length due to Co and
Ni substitution is smaller than that for the above cases (+0.04% for Co and +0.03% for Ni doping for nominal $x = 0.05$), indicating that Co and Ni substitution do not induce large distortion in the iron lattice. As shown in the lower column of figure 4, the $c$-axis length increases with Cr and Mn doping and decreases with Co and Ni doping. This may be understood as a consequence of the reduction or enhancement in Coulombic interaction between the (CaF)$^{δ+r}$ and (FeAs)$^{δ−}$ layers upon doping, providing evidence that the Cr/Mn and Co/Ni substitutions respectively decrease and increase the effective electron population, i.e. hole/electron doping in the FeAs layers.

Figure 5 shows $ρ−T$ curves for Cr and Mn doped samples. With an increase of nominal $x$ for both Cr and Mn, the $ρ−T$ anomaly shifts to lower temperatures (see the shoulder below 60 K for nominal $x = 0.05$ for Cr and 0.10 for Mn) and is eventually suppressed for nominal $x > 0.14$ for Cr and $> 0.1$ for Mn. However, the Cr and Mn substitutions enhance the resistivity and change the temperature coefficient at low temperature from positive to negative. These observations indicate that Cr and Mn form a scattering center, possibly magnetic, disturbing the electron conduction in the FeAs layer. Especially, the Mn doping induces higher resistivity, presumably corresponding to larger structural changes in the FeAs layers.

Figure 6 shows the temperature dependences of resistivity for CaFe$_{1−x}$Co$_x$AsF and CaFe$_{1−x}$Ni$_x$AsF. It is clearly demonstrated that the $ρ−T$ anomaly temperature is lowered with an increase in Co and Ni content and superconductivity is induced for nominal $x > 0.07$ for the Co doping and nominal $x > 0.05$ for Ni doping. In contrast, the Cu doping never induces superconductivity and the electrical resistivity at low temperatures is enhanced by $\sim 10^3$ times than that of the non-doped sample. Cu apparently acts as a strong scattering center for the itinerant electrons.

Figures 7(a) and (b) show close-up views of $ρ−T$ curves around onset superconducting transition temperatures ($T_{onset}$) for Co and Ni substituted CaFeAsF samples. $T_{onset}$ values as a
Figure 5. Temperature dependence of electrical resistivity in \( \text{CaFe}_{1-x} \text{TM}_x \text{AsF} \) with 3d TM (TM = Cr and Mn) substitution. (a) \( \text{CaFe}_{1-x} \text{Cr}_x \text{AsF} \) (nominal \( x = 0.05, 0.10, 0.14 \) and 0.20). (b) \( \text{CaFe}_{1-x} \text{Mn}_x \text{AsF} \) (nominal \( x = 0.05, 0.10 \) and 0.15).

Figure 6. Temperature dependence of electrical resistivity in \( \text{CaFe}_{1-x} \text{TM}_x \text{AsF} \) with 3d TM (TM = Co, Ni and Cu) substitution (a) \( \text{CaFe}_{1-x} \text{Co}_x \text{AsF} \) (nominal \( x = 0.05, 0.07, 0.10, 0.15, 0.20 \) and 0.26), (b) \( \text{CaFe}_{1-x} \text{Ni}_x \text{AsF} \) (nominal \( x = 0.05, 0.10, 0.15 \) and 0.20) and (c) \( \text{CaFe}_{0.95} \text{Cu}_{0.05} \text{AsF} \).

function of nominal \( x \), obtained from the \( \rho-T \), plots are summarized in figure 7(c). It is evident that the optimal Ni doping level yielding maximum \( T_{\text{onset}} \) (nominal \( x \sim 0.05 \)) is nearly half that for the Co doping (nominal \( x \sim 0.1 \)). This suggests that Co\(^{2+}\) with 3d\(^7\) electronic configuration gives an additional electron, whereas Ni\(^{2+}\) with 3d\(^8\) gives two electrons to the FeAs layer.
It is noteworthy that Co acts as a non-magnetic donor for small values of nominal \( x \) although LaCoAsO exhibits ferromagnetism [35]. It is also of interest to note that the threshold and optimal electron-doping level (~0.1 electron/Fe) is close to that in the RFeAs(O\(_{1-x}\)F\(_x\)) system notwithstanding that the impurity-doped layer is different.

Finally, we stress the practical importance of Co/Ni doping in the fabrication of epitaxial thin films of FeAs-based superconductors. Carrier doping is a requisite for the emergence of superconductivity in this system. Several methods have been reported to be effective to date such as electron doping via the formation of the oxygen vacancy for the 1111 system and hole doping via substitution of alkaline earth ion sites with an alkali ion for the 122 system. However, both of these were practically hard to dope into the thin films by vapor phase deposition processes due presumably to the weak chemical bonding strength of these species with the host lattice. Using Co as dopant, the first demonstration of epitaxial thin films of Sr(Fe, Co)\(_2\)As\(_2\) exhibiting a \( T_c = 22 \) K have been realized recently [36].

4. Summary

We examined the partial replacement of the Fe site in CaFeAsF with 3d TMs (Cr, Mn, Co, Ni and Cu) and obtained the following conclusions:

1. Only Co or Ni doping was effective for the emergence of superconductivity. The optimal doping level for Ni was close to half that for Co doping.

2. Cr, Mn or Cu doping led to enhanced resistivity at low temperatures, without inducing superconductivity, indicating that these ions act as scattering centers.

3. The spacing between CaF and FeAs layers changed with TM doping and the sign of the change was opposite between Co/Ni and Cr/Mn groups. This result was understood due to the different polarity of carriers (hole or electron) doped into the FeAs layer.

**Figure 7.** Magnified \( \rho-T \) curves of CaFe\(_{1-x}\)Co\(_x\)AsF (a) and CaFe\(_{1-x}\)Ni\(_x\)AsF around \( T_{\text{onset}} \). (b). (c) \( T_{\text{onset}} \) as a function of nominal \( x \).
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