Pressure effect of superconducting oxypnictide LaFeAO$_{1-x}$F$_x$ and related materials

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Abstract. Pressure dependence on superconducting transition temperature ($T_c$) has been investigated for iron-based superconductor LaFeAsO$_{1-x}$F$_x$, SmFeAsO$_{1-x}$F$_x$ and Ca(Fe$_{1-x}$Co$_x$)AsF. The $T_c$ increases largely for LaFeAsO$_{1-x}$F$_x$ with a small increase of pressure, and decreases with further compression. In SmFeAsO$_{1-x}$F$_x$ the $T_c$ decreases with increasing pressure. The increase of $T_c$ in LaFeAsO$_{1-x}$F$_x$ seems to be related to the suppression of magnetic ordering phase. Pressure-induced superconductivity was observed for these materials. The common features on 1111 type superconductors are discussed.

1. Introduction

Discovery of the high-$T_c$ superconductivity in Fe-based LaFeAsO$_{1-x}$F$_x$ [1] had a significant impact in the field of condensed matter physics because of including a magnetic iron atom. Moreover, applying pressure on optimally doped LaFeAsO$_{1-x}$F$_x$ increased $T_c$ to 43 K, which is the significantly large enhancement of $T_c$ compared with the cuprate high-$T_c$ superconductors [2]. In this way, these results suggest that the compression is an advantageous route to investigate superconductivity in this system. Indeed, substitution of smaller rare earth elements, such as Nd, Sm etc. for La raised the $T_c$ above 50 K [3,4]. This fact indicates that the chemical pressure affects $T_c$ in a similar manner to the external pressure.
The crystal structure of LaFeAsO$_{1-x}$F$_x$ is tetragonal (space group P4/nmm), which is composed of a stack of alternating LaO and FeAs layers as shown in Fig.1. Undoped LaFeAsO exhibits an orthorhombic to tetragonal transition at 165 K [5] and a paramagnetic to antiferromagnetic (SDW) transition at 140 K [6] successively. The electrical resistivity shows large decrease at around 150 K accompanied by these transitions. The conductive carriers have a two-dimensional feature due to the crystal structure, whose concentration can be controlled by atomic substitution of O$^{2-}$ by F$^{-}$ in the LaO layer. With increasing F substitution, the structural and the magnetic transitions are suppressed and superconductivity appears. The $T_c$ increases with F substitution, and suppressed by further F substitution. This situation is similar to the case of cuprate high-$T_c$ superconductors. In the cuprate superconductors, superconductivity appears in doped Mott insulator. The $T_c$ shows a dome-shape curve as a function of the carrier concentration. Concerning high-pressure properties for the cuprate superconductors, anisotropic compression was revealed by x-ray and neutron diffraction measurements. This anisotropic compression often increases the carrier concentration in the CuO$_2$ plane through changing the charge distribution. Then the $T_c$ of optimum-doped cuprate tends to decrease it with increasing pressure. However, in LaFeAsO$_{1-x}$F$_x$ system, the material with the highest $T_c$ (optimally doping) exhibited steep increase of $T_c$ with increasing pressure.

In this work, high-pressure studies for three kinds of 1111 type iron oxypnictide, LaFeAsO$_{1-x}$F$_x$, SmFeAsO$_{1-x}$F$_x$, and Ca(Fe$_{1-x}$Co$_x$)AsF$^-$, were carried out to examine the pressure effect on $T_c$ for several kinds of doping level. SmFeAsO$_{1-x}$F$_x$ (x=0) exhibits the structural and magnetic transitions, as observed in the LaFeAsO$_{1-x}$F$_x$ system. With increasing F doping, these transitions are suppressed and superconductivity emerges. The highest $T_c$ of SmFeAsO$_{1-x}$F$_x$ is 55 K [4], which is strikingly high temperature compared with LaFeAsO$_{1-x}$F$_x$. It is quite interesting to compare the pressure dependence of $T_c$ for both systems. Ca(Fe$_{1-x}$Co$_x$)AsF(x=0) also exhibits the structural and magnetic transitions [7]. The electron doping was performed by substituting Co for Fe in FeAs layer. With increasing Co doping, these transitions are suppressed and superconductivity emerges, whereas the magnetic properties of this material is not affected by Co doping. It is interesting to compare the material having FeAs layer doped with Co atom with F-doped 1111 type superconductors under high pressure. These results are compared with the cuprate high-$T_c$ superconductors. Pressure-induced superconductivity was discovered in undoped LaFeAsO and SmFeAsO. Although only the spin-ladder material Sr$_{14}$Ca$_2$Cu$_{22}$O$_{41}$ exhibited the pressure-induced superconductivity in the cuprate superconductors [8], several materials exhibit it in the iron oxypnictide. This fact suggests that the electronic state of iron oxypnictide superconductors is easily affected by pressure. The x-ray diffraction measurements for LaFeAsO$_{1-x}$F$_x$ at room temperature at P < 10 GPa reveal the anisotropic compression [9], like as the cuprate superconductors. The pressure effects on the lattice constants are also presented.

2. Experimental

Polycrystalline LaFeAsO$_{1-x}$F$_x$, SmFeAsO$_{1-x}$F$_x$, and Ca(Fe$_{1-x}$Co$_x$)AsF were prepared by a solid-state reactions reported previously [1,2,7]. The values of F content x in LaFeAsO$_{1-x}$F$_x$ and SmFeAsO$_{1-x}$F$_x$ were determined by the lattice constants using Vegard’s volume rule. Electrical resistivity
measurements under high pressure were performed by means of a standard dc four-probe method. A piston cylinder device was used up to 3 GPa and a cubic anvil press was used up to 12 GPa, using a liquid pressure-transmitting medium (Fluorinert FC70:FC77 = 1:1) to maintain hydrostatic conditions. A diamond anvil cell (DAC) was used for electrical resistance measurements at pressures up to 30 GPa using NaCl as a pressure transmitting medium. The high-pressure x-ray diffraction measurements were performed using synchrotron radiation at PF-BL18C at High Energy Accelerator Research Organization (KEK) with the wavelength of 0.061642 nm and the DAC with a liquid pressure-transmitting medium (methanol:ethanol = 4:1).

3. Results and discussion

High pressure experiments were carried out for the compounds x = 0, 0.05, 0.11 and 0.14 of LaFeAsO$_{1-x}$F$_x$. The pressure dependence of onset $T_c$ for these compounds is shown in Fig. 2. The onset $T_c$ was determined from the intersection of the two extrapolated lines; one is drawn through the resistivity curve in the normal state just above $T_c$, and the other is drawn through the steepest part of the resistivity curve in the superconducting state. The increase of onset $T_c$ from 19 to 43 K is significantly large for x=0.14, compared with other superconductors. The enhancement of $T_c$ with pressure is also quite large in LaFeAsO$_{0.86}F_{0.14}$ [2], which has the highest $T_c$ at atmospheric pressure in LaFeAsO$_{1-x}$F$_x$. The peak value of $T_c$ for x=0.11 under pressure is the comparable value to LaFeAsO$_{0.84}F_{0.14}$. The dome-shaped pressure dependence of $T_c$ is a common feature in LaFeAsO$_{1-x}$F$_x$, as shown in Fig. 2. Although zero resistivity was observed below 2 GPa using the piston cylinder device, the $T_c$ determined at zero resistivity increased more slowly than the onset $T_c$, resulting in a broadening of the superconducting transition with increasing pressure for both materials [10]. This is unlikely to be due to a distribution of pressure in the pressure cell, and is more probably caused by sample inhomogeneity, because the hydrostatic conditions were kept unchanged during the measurements. For higher pressures using the DAC a clear zero resistance was not observed. The failure to observe the zero resistance was caused by a distribution in the non-hydrostatic compressive stress as a result of the use of a solid pressure-transmitting medium.

![Figure 2. Superconducting phase diagram of LaFeAsO$_{1-x}$F$_x$ (x=0, 0.05, 0.11 and 0.14). Arrows indicate the $T_c$ maximum. The solid curves are guides for eyes.](image1)

![Figure 3. $T_c$ as a function of F content(x) for LaFeAsO$_{1-x}$F$_x$. The maximum $T_c$ under high pressure at each x is shown. The pressure where the material exhibits maximum $T_c$ was indicated.](image2)
In case of undoped LaFeAsO, electrical resistivity was measured up to 12 GPa using cubic anvil press [11]. A rapid decrease in electrical resistivity at around 150 K due to the structural and magnetic phase transitions becomes broader with applying pressure. The characteristic temperature $T_0$ which is defined at a peak in the $d\rho/dT$ vs. $T$ curve decreases monotonously with applying pressure. The $T_0$ seems to correspond to the magnetic transition. The resistivity loss associated with superconductivity emerges at 2 GPa. A zero resistivity was observed at 12 GPa. The superconductivity was confirmed by the current effect and diamagnetic signal obtained by AC susceptibility measurements under high pressure. The high-pressure resistivity measurements were performed up to 29 GPa, using the DAC. The $T_c$ shows the maximum of 21 K, and decreases monotonously above 16 GPa. Thus, $P$-$T$ phase diagram of LaFeAsO is similar to $x$-$T$ phase diagram of LaFeAsO$_{1-x}$F$_x$. Fig. 3 shows the maximum value of $T_c$ obtained under high pressure as a function of $F$ concentration, together with the $T_c$ at atmospheric pressure. The pressures at which the maximum $T_c$ was obtained are also shown. While the highest $T_c$ was observed for the highly doped compounds ($x=0.11$ and 0.14), rather lower $T_c$’s were observed for the lightly doped and undoped ones, which is in contrast to the cuprate superconductors. For LaFeAsO$_{1-x}$F$_x$, the materials with $x=0.11$ and 0.14 correspond to optimum-doped and over-doped one in case of cuprate superconductor, respectively. In fact, the $T_c$ of over-doped cuprate superconductor Tl$_2$Ba$_2$CuO$_4$ decreases with increasing pressure [12]. Therefore, it is noted that the pressure does not simply correspond to the $F$ doping. The one reason why the maximum $T_c$ is so low in the lightly doped one may be that the superconductivity is affected by the magnetic interaction existing close the superconducting phase. Recently, Mössbauer spectrum measurements under high pressure revealed that the magnetic ordering phase was completely suppressed under high pressure at about 25 GPa. This result is consistent with this study.

![Figure 4](image)

Figure 4. Superconducting phase diagram of SmFeAsO$_{1-x}$F$_x$ ($x=0$ and 0.07). The dotted curves are guides for eyes.

High pressure experiments were carried out for the compounds $x=0$ and 0.07 of SmFeAsO$_{1-x}$F$_x$. For undoped SmFeAsO, the structural and magnetic transitions at around 150 K are also observed and suppressed by $F$ substitution, similar to LaFeAsO. The $T_c$ of more than 50 K has been reported in SmFeAsO$_{1-x}$F$_x$ system or oxygen deficient SmFeAsO$_{1-\delta}$. Although the large enhancement of $T_c$ was expected for the high-pressure experiments for SmFeAsO$_{1-x}$F$_x$, like as LaFeAsO$_{1-x}$F$_x$, small increase of the $T_c$ was observed for the lightly doped SmFeAsO, whereas a large decrease of the $T_c$ was observed for the highly doped one under high pressure [14-16]. Pressure dependence of $T_c$ of SmFeAsO$_{0.95}$F$_{0.07}$ is shown in Fig. 4, which was obtained from the electrical resistivity measurements. The $T_c$ decreased at a ratio of -6 K/GPa, which is larger than the data obtained by other groups [14,15]. Although several groups have reported the pressure effect on $T_c$ for Sm-based system, it is noted that there is inconsistency in the $x$-$T$ phase diagram of SmFeAsO$_{1-x}$F$_x$ because of the difficulty to decide the doping concentration $x$. For undoped SmFeAsO, the $T_0$, determined by the same manner as LaFeAsO,
decreased with pressure at a rate of -6 K/GPa, which is consistent with ref.[14] qualitatively. On the other hand, pressure-induced superconductivity, which was confirmed by the current effect, was observed above 9 GPa. The pressure dependence of $T_c$ is also shown in Fig. 4, where the $T_c$ of 11 K at 9 GPa decreases gradually up to 29 GPa. The maximum $T_c$ of SmFeAsO is not as high as one of pressure-induced superconductivity in LaFeAsO. However, the SmFeAsO$_{1-x}$F$_x$ or SmFeAsO$_{1-\delta}$ system has much higher $T_c$ than LaFeAsO$_{1-\delta}$ system. The magnetic transition temperature ($T_m$) is suppressed by pressure at the initial rate of -13.7 K/GPa and -6 K/GPa for LaFeAsO and SmFeAsO, respectively. The superconductivity of SmFeAsO may emerge at much higher pressure than LaFeAsO. Since the pressure-induced superconductivity seems to emerge after the magnetic ordered phase is adequately suppressed, it is likely that the magnetic ordering phase in SmFeAsO may survive at higher pressure than the case of LaFeAsO. The lower maximum $T_c$ observed in SmFeAsO under high pressure may be also due to rest of surviving magnetic phase. However, the whole mechanism for pressure effect on $T_c$ has not been clear yet.

Recently electrical resistivity measurements were carried out for the superconducting compounds $x = 0.10, 0.15$ and 0.20 of Ca(Fe$_{1-x}$Co$_x$)AsF under high pressure. For undoped CaFeAsF, the structural and magnetic transitions at around 120 K are also observed, similar to LaFeAsO and SmFeAsO. These transitions are suppressed by Co substitution and superconductivity appears above $x = 0.05$ and the highest $T_c$ was 24 K at $x = 0.10$. Although the doping of Co to FeAs layer is effective to obtain superconductivity for LaFeAsO and SmFeAsO, the optimum values of $T_c$ are 13 K and 15 K for La(Fe$_{1-x}$Co$_x$)AsO$_{17}$ and Sm(Fe$_{1-x}$Co$_x$)AsO$_{18}$, respectively. However, F-doping or applying pressure increases $T_c$ much higher than Co-doping as described before. Thus, it is expected to have higher $T_c$ for Ca(Fe$_{1-x}$Co$_x$)AsF system under high pressure, since the $T_c$ of 24 K in Co-doped CaFeAsF is much larger than other Co doped 1111 type superconductors. For $x = 0.10, 0.15$ and 0.20 of Ca(Fe$_{1-x}$Co$_x$)AsF, no structural and magnetic transitions are observed and superconductivity occurs at 24, 20 and 16 K at 1 atm, respectively. These $T_c$’s increase slightly under high pressure below 1 GPa and decrease with further compression. Then the highest $T_c$ under high pressure decreases with increasing Co concentration from $x = 0.10$ to 0.20. The results of suppression of $T_c$ under pressure remind us the over-doped cuprate superconductors. On the other hand, these results suggest that the Co doping to FeAs layer is not necessarily useful route to realize higher $T_c$ material. It is noted that the carrier doping through the AsF layer in CaFeAsF may be more effective to increase $T_c$, because F-doped 1111 type superconductors have much higher $T_c$ than Co-doped ones.

From the x-ray diffraction measurements for LaFeAsO$_{0.89}$F$_{0.11}$ at room temperature under high pressure below 10 GPa, an anisotropic compression was observed. Compressibility $\kappa$, linear compressibilities $\kappa_a$ and $\kappa_c$, bulk modulus $B_0$ and $B_0^0$ (= $dB_0/dP$) are 3.98x10$^{-3}$GPa$^{-1}$, 7.25x10$^{-3}$GPa$^{-1}$, 15.1x10$^{-3}$GPa$^{-1}$, 66GPa, 7.0GPa, respectively. The $c/a$ ratio is more compressible than the $a/a_0$ and the value of $c/a$ decreases linearly with applying pressure, which is usually observed in the layered compounds. For example, $\kappa_c$ is almost twice as $\kappa_a$ in YBa$_2$Cu$_3$O$_{7-\gamma}$ [19] and HgBa$_2$CaCu$_2$O$_{6+\delta}$ [20]. These values are similar to the present results. From the neutron diffraction measurement for YBa$_2$Cu$_3$O$_8$ [21], it was indicated that the anisotropic compression enhances the charge transfer and carrier concentration in the conductive CuO$_2$ layer by calculation of pressure effect on charge distribution.

4. Summary

Pressure dependence of $T_c$ for LaFeAsO$_{1-x}$F$_x$, SmFeAsO$_{1-x}$F$_x$ and Ca(Fe$_{1-x}$Co$_x$)AsF were obtained from the electrical resistivity measurements under high pressure. These materials have the magnetic ordering phase as a parent phase, and superconductivity appears by suppressing the magnetic phase. However, even if the magnetic phase is not completely suppressed, superconductivity could be observed. This behavior is quite different from cuprate superconductors. From the high-pressure experiment for LaFeAsO$_{1-x}$F$_x$, it seems reasonable to suppose that the magnetic phase existing in the lightly doped region affected the pressure dependence of $T_c$. For undoped SmFeAsO, it is likely that the magnetic phase may survive under high pressure more than LaFeAsO. Thus the magnetic phase is
unfavourable to the high-$T_c$ superconductivity in iron pnictide materials. However, it is believed that magnetic interaction plays an important role for iron-based superconductivity from many experimental and theoretical works. As another common property of iron pnictide materials, pressure-induced superconductivity is observed in several materials, in contrast to the cuprate superconductors.

From the x-ray diffraction measurements for LaFeAsO$_{1-x}$F$_x$ up to 10 GPa, it was revealed that the lattice constant $c$ is more compressible than $a$. This is one reason why the electronic state is modified significantly by an application of pressure. Anisotropic compression can cause to change the charge distribution, which was often observed in the cuprate superconductors. However, detailed structural parameters are necessary to estimate the electronic state under high pressure from the theoretical calculation. Precise refinements for crystal parameters under pressure are in progress.

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