Magnetic order in CaFe$_{1-x}$Co$_x$AsF ($x=0, 0.06, 0.12$) superconductor compounds

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A Neutron Powder Diffraction (NPD) experiment has been performed to investigate the structural phase transition and magnetic order in CaFe$_{1-x}$Co$_x$AsF superconductor compounds ($x=0, 0.06, 0.12$). The parent compound CaFeAsF undergoes a tetragonal to orthorhombic phase transition at 134(3) K, while the magnetic order in form of a spin-density wave (SDW) sets in at 114(3) K. The antiferromagnetic structure of the parent compound has been observed to coexist with superconductivity in the orthorhombic phase of the underdoped CaFe$_{0.94}$Co$_{0.06}$AsF with a reduced Fe moment (~0.15 $\mu_B$). Magnetic order is completely suppressed in optimally doped CaFe$_{0.88}$Co$_{0.12}$AsF. We argue that the coexistence of SDW and superconductivity might be related to mesoscopic phase separation.

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The recent discovery of superconductivity in the iron-arsenic-based system RFeAsO$_{1−x}$F$_x$ (with R = La, Ce, Pr etc.) has attracted tremendous amount of attention in the quest to understand the mechanism of high transition temperature superconductivity [1]. The superconducting transition temperature $T_c$ has been quickly raised to 55 K via electron and hole doping [2, 3, 4, 5]. The second family of the iron-arsenic-based superconductor system was discovered in Sr$_2$Fe$_x$AsF$_{2−x}$ (with $x$ = Ba, Sr, Ca, Cu etc., B = K, Na) with $T_c$ up to 38 K [6, 7]. The first family of the iron-arsenic-based superconductor system was discovered in A$_{1−x}$B$_x$Fe$_2$As$_2$ (A = Ba, Sr, Ca, Eu etc., B = K, Na) with $T_c$ up to 38 K [6, 7]. The second family of the iron-arsenic-based superconductor system was discovered in A$_{1−x}$B$_x$Fe$_2$As$_2$ (A = Ba, Sr, Ca, Eu etc., B = K, Na) with $T_c$ up to 38 K [6, 7]. The first family of the iron-arsenic-based superconductor system was discovered in A$_{1−x}$B$_x$Fe$_2$As$_2$ (A = Ba, Sr, Ca, Eu etc., B = K, Na) with $T_c$ up to 38 K [6, 7].
diffraction experiment on the CaFe$_{1-x}$Co$_x$AsF ($x = 0, 0.06, 0.12$) superconductor compounds. The magnetic and crystal structures of the CaFeAsF parent compound have been determined via the Rietveld refinement. The evolution of magnetic order and crystal structure in the Co-doped CaFeAsF compounds has been described in Ref [19] with impurity phases ($\text{CaF}_2$ and $\text{Fe}_2\text{O}_3$) of less than 1%. The neutron powder diffraction measurements were performed on the high flux powder diffractometer D20 at Institut Laue Langevin (Grenoble, France). A pyrolitic graphite PG (002) monochromator was used to produce a monochromatic neutron beam of wavelength 2.42 Å. The sample was loaded in a vanadium sample holder and then installed in the liquid helium cryostat. The program FULLPROF [25] was used for the Rietveld refinement of the crystallographic data. The program was used for the Rietveld refinement of the crystal structures of the CaFeAsF parent compound has been determined via the Rietveld refinement. The evolution of magnetic order and crystal structure in the Co-doped CaFeAsF compounds has been described in Ref [19] with impurity phases ($\text{CaF}_2$ and $\text{Fe}_2\text{O}_3$) of less than 1%. The neutron powder diffraction measurements were performed on the high flux powder diffractometer D20 at Institut Laue Langevin (Grenoble, France). A pyrolitic graphite PG (002) monochromator was used to produce a monochromatic neutron beam of wavelength 2.42 Å. The sample was loaded in a vanadium sample holder and then installed in the liquid helium cryostat. The program FULLPROF [25] was used for the Rietveld refinement of the crystal structures of the compounds.

The CaFeAsF crystallizes in tetragonal structure with space group $P4/nmm$ at 150 K as shown in Fig. 1a. With decreasing temperature the CaFeAsF undergoes an orthorhombic distortion (space group $Cmma$) as revealed by the NPD pattern measured at 2 K (Fig. 1b). The splitting of the (112)$_T$ reflection (inset of Fig. 1a and Fig. 1b) could not be resolved due to the limited resolution and the small difference in lattice parameters $a$ and $b$. However the splitting is obvious from the observed peak broadening. In order to clarify the structural transition, the peak intensity and full width at half maximum (FWHM) of (112)$_T$ reflection are plotted in Fig. 2a. The sharp decrease of the intensity and the significant broadening of FWHM of (112)$_T$ reflection reveal the occurrence of the tetragonal to orthorhombic structural transition. From the onset of the broadening of the (112)$_T$ reflection, we estimate the phase transition temperature to be in the range of 131 K to 137 K.

Compared with the NPD pattern at 150 K, the magnetic reflections appear at lower temperature for CaFeAsF. The temperature evolution of the magnetic reflection between 33.6° and 37.4° is shown in Fig. 3a, which indicates the appearance of long range magnetic order. The integrated intensity of the magnetic reflection at Q = 1.583 Å$^{-1}$ is plotted in Fig. 3b. The solid curve is a power law fit to estimate a Neel temperature of 114(3) K. A series of magnetic peaks can be noticed clearly as shown in Fig. 3c by subtracting the NPD pattern measured at 150 K from the pattern measured at 2 K. By indexing the magnetic Bragg peaks, we find that the magnetic ordering of CaFeAsF at 2 K can be described within an antiferromagnetic model where the magnetic unit cell is dou-
FIG. 3: (a) Temperature evolution of the reflection at $Q = 1.583 \, \text{Å}^{-1}$ indicating the onset of long range magnetic ordering in CaFeAsF. (b) Temperature dependence of the integrated intensity of magnetic Bragg reflection. (c) The magnetic reflections obtained by subtracting the NPD pattern measured at 150 K from the pattern measured at 2 K. The asymmetric peak shape is due to neighboring reflections. (d) Comparison of NPD patterns for CaFeAsF measured at 2 K (black) and 150 K (blue), respectively. The red and green curves are the calculated patterns of (103)$_M$ and (013)$_M$ reflections, respectively. The magnetic peak at $Q = 1.583 \, \text{Å}^{-1}$ can be indexed as the (103)$_M$ properly within the magnetic unit cell.

bled along the $c$-axis. The Fe moments are coupled antiferromagnetically along the $c$ direction, while in the $ab$ plane, the Fe moment ordered antiferromagnetically along one axis and ferromagnetically along another axis. This antiferromagnetic model is exactly the same as the magnetic structure found by neutron powder diffraction for LaFeAsO [10], and NdFeAsO [26]. However, for both LaFeAsO and NdFeAsO the precise Fe moment direction in the $ab$ plane of the orthorhombic structure could not be determined due to the weak magnetic intensity and small difference of the respective magnetic peaks position corresponding to the Fe moment aligned along the $a$ or $b$ direction. In the present work, the high intensity diffraction data that we collected from D20 allows us to determine the exact propagation vector and the iron moment direction within the $ab$ plane. For those configurations in which $k$ is perpendicular to the moment direction, i.e. $k = (1,0,1)$ with the Fe moment along the $b$ direction or $k = (0,1,1)$ with the Fe moment along the $a$ direction, the intensity ratio between (101)/(011), (103)/(013) and (121)/(211) was expected to be $32:17:2$ due to the difference of the Fe magnetic form factor in the corresponding Q-position(Table I). However, based on our NPD results, the intensity of (121)/(211) reflection is observed to be stronger than (101)/(011) reflection (Fig. 3c and Table I). Therefore, these configurations can be ruled out. As shown in Fig.3 d, the reflection at $Q = 1.583 \, \text{Å}^{-1}$ can be fitted properly as (103) magnetic reflection with the moment along the $a$ direction whereas the position of (013) reflection is slightly shifted to a higher $Q$-position at $Q = 1.589 \, \text{Å}^{-1}$. Therefore, the magnetic structure of CaFeAsF can be unambiguously determined as antiferromagnetic structure with Fe moment along the long $a$-axis in orthorhombic unit cell as shown in Fig. 2b. The Fe moment derived from NPD result is $0.49(5) \mu_B$, which is considerably larger than the moment observed in LaFeAsO ($0.35 \mu_B$) and NdFeAsO ($0.25 \mu_B$) but smaller than the moment observed in BaFe$_2$As$_2$ ($0.8 \mu_B$) and SrFe$_2$As$_2$ ($0.94 \mu_B$). Note that the origin of the observed large difference of the Fe moment in iron pnictides is still not clear, while the same antiferromagnetic structure due to SDW instabilities of a nested Fermi surface have been observed among all compounds.

Both the structural and magnetic phase transition have thus been determined for parent compound CaFeAsF. Recently, Zhao et al. found that the highest $T_c$ of FeAs-based compound can be obtained when the Fe-As-Fe bond angle is close to the ideal value of 109.47° expected from a perfect FeAs tetrahedron. The effective way to increase $T_c$ in FeAs-based systems is to optimize the Fe-As-Fe angle. It can be noticed that the Fe-As-Fe bond angle in CaFeAsF is 108.55°, which is relatively close to the ideal value compared with LaFeAsO.

**TABLE I: The observed intensity of magnetic reflections and the calculated value for different magnetic models.**

| Reflection | $I_{obs}$ | $I_{Cal}[(1,0,1), a]$ | $I_{Cal}[(0,1,1), a]$ |
|------------|-----------|----------------------|----------------------|
| (103)$_M$/ (011)$_M$ | 396(93) | 301 | 3173 |
| (103)$_M$/ (013)$_M$ | 830(87) | 825 | 1697 |
| (121)$_M$/ (211)$_M$ | 739(88) | 766 | 210 |

*The propagation vector and the moment direction are shown in brackets.
and BaFe$_2$As$_2$. Therefore the CaFeAsF is suggested to be a promising system for maximizing $T_c$. In addition, it should be emphasized that the two phase transitions in CaFeAsF occur at different temperatures, 134(3) K for structural and 114(3) K for magnetic phase transition. Separated phase transitions are also observed in LaFeAsO [10] and CeFeAsO [17]. However, for the LaFeAsO, the anomaly in resistivity is associated with the structural transition, but according to the resistivity measurement on CaFeAsF (Fig. 4a), the anomaly in resistivity takes place at around 120 K which is closer to the magnetic phase transition. Therefore, the decrease of resistivity is likely associated with the SDW transition in CaFeAsF.

In order to investigate in detail the change of the crystal structure and the variation of SDW across the superconducting boundary, the NPD measurement was also carried out on the Ca(Fe$_{1-x}$Co$_x$)$_2$AsF with $x = 0.06$ and 0.12. For the superconductor Ca(Fe$_{0.88}$Co$_{0.12}$)$_2$AsF, the tetragonal structure persists down to 2 K and no evidence of SDW is observed (Fig. 1c). This would indicate that the SDW in Ca(Fe$_{1-x}$Co$_x$)$_2$AsF system is totally suppressed in superconducting state with an optimal Co doping level. For the slightly underdoped Ca(Fe$_{0.94}$Co$_{0.06}$)$_2$AsF compound, the SDW survives at 2 K as show in Fig. 4b and the Fe moment is reduced to 0.15(5) $\mu_B$. To determine the structural phase transition of Ca(Fe$_{0.94}$Co$_{0.06}$)$_2$AsF, the conventional lab X-ray diffractometer was used to collect X-ray powder diffraction patterns under different temperatures as shown in Fig. 4c. Based on the splitting of the (220)$_T$ reflection, the tetragonal to orthorhombic phase transition temperature is determined to be around 85(3) K, which is lower than that of parent compound CaFeAsF. The orthorhombic distortion parameter $P=(a-b)/(a+b)$ is deduced to be 0.17% for the 6% Co-doped compound at 2 K, while it is 0.34% for the parent compound. It seems that there exists a close relation between the order parameter $P$ and the Fe moment value, in other words, the smaller orthorhombic splitting will lead to a weaker SDW ordering.

Fig. 4d shows the temperature dependence of ac susceptibility of Ca(Fe$_{0.94}$Co$_{0.06}$)$_2$AsF, the strong diamagnetic signal exhibits below 20 K, which corresponds to the anomaly observed in resistivity-temperature curve. The temperature dependence of magnetization also supports the existence of the Meissner state as shown in the inset of Fig. 4d. Therefore, the coexistence of SDW and superconductivity can be confirmed in Ca(Fe$_{0.94}$Co$_{0.06}$)$_2$AsF. Moreover, the superconductivity can occur in either the tetragonal (with $x = 0.12$) or orthorhombic (with $x = 0.06$) structure in Ca(Fe$_{1-x}$Co$_x$)$_2$AsF system. Presently, several phase diagrams have been constructed for different FeAs-based superconductor systems. However, the different systems always exhibit different behaviors around the phase boundary between the antiferromagnetic and superconducting regimes. For example, there is no overlap between those two phases in the LaFeAsO [28] and the CeFeAsO [17] systems, while a slightly overlap was observed in SmFeAsFO [29, 30] system and broad overlap composition range in Ba$_{1-x}$K$_x$Fe$_2$As system [31, 32]. Although the mechanism of such coexistence is still not clear, the phase separation on macroscopic scale can be ruled out since the single orthorhombic phase was clearly revealed by synchrotron X-ray for Ba$_{1-x}$K$_x$Fe$_2$As [28] and by lab X-ray for our Ca(Fe$_{0.94}$Co$_{0.06}$)$_2$AsF case. Recently, mesoscopic phase separation was suggested by Park et al. [33] in slightly underdoped Ba$_{1-x}$K$_x$Fe$_2$As superconductor. Therefore, such mesoscopic phase separation might be considered as an intrinsic property and it may explain the coexistence of antiferromagnetic and superconducting states in some FeAs-based superconducting system.

In summary, by using high flux neutron powder diffraction we have observed the tetragonal to orthorhombic structural transition at 134(3) K followed by the magnetic structure transition at 114(3) K in CaFeAsF. Below $T_c$, long range antiferromagnetic ordering with a propagation vector $k = (1,0,1)$ and an Fe moment of 0.49(5) and of 0.15(5) for parent compound and 6% Co-doped compound, respectively. With increasing Co doping on the Fe site the SDW is weakened in the 6% Co-doped compound and completely suppressed in the 12% Co-doped compound. The observed coexistence of antiferromagnetic and superconducting states might be explained as due to the mesoscopic phase separation.
[34] P. A. Lee et al., Rev. Mod. Phys. 78, 17 (2006).