Superconductivity in layered iron Selenide induced by cobalt-and sodium-doping

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Abstract:

Superconductivity with zero resistance transition temperature ($T_c$) up to 8.4 K and 8.3 K can be obtained by doping cobalt and sodium in α-FeSe with the nominal composition of Fe₀.⁹₂Co₀.⁰₈Se and Na₀.₁FeSe, respectively. The electrical resistivity and AC magnetic susceptibility of the prepared samples, measured with physical property measurement system (PPMS), unambiguously consistent with each other to indicate that the samples are superconductive. The respective doping mechanisms for cobalt and sodium into the parent α-FeSe are the Fe-site substitution and the interlayer insertion. It is the first time that α-FeSe can be induced to be a superconductor with Na⁺ intercalated into the interlayers.
The pnictides containing the anti-PbO-like [FeAs] layered motifs have attracted much attention, since the superconductive transition temperature of 26 - 43 K was found in LaFe(O_{1-x}F_x)As [1, 2]. The other series of $M$Fe$_2$As$_2$ ($M =$ Ba, Sr and Ca) superconductors were also reported [3-8]. These materials show the obvious superconductivity by the aid of chemical doping in the positions of La, Fe, O and $M$, such as the Sr-doped LaFeOAs [9-10], F-doped LaFeOAs [1] and K-doped BaFe$_2$As$_2$ [3]. It is very interesting that Co is the only the $d$-block transition element for doping in the Fe position to induce the superconductivity in the literatures [11-17].

$\alpha$-FeSe, with the same space group P4/nmms and similar planar crystal sublattice just like LaFeOAs, has no superconducting. The very recent work showed that preparing $\alpha$-FeSe with intentional Se deficiency is one effective method to achieve it’s superconducting with $T_c$ equal to 8 K [18]. Then the question is whether the partial substitution of Fe by Co in $\alpha$-FeSe can induce the superconductivity except the Se deficiency? Furthermore, how about the sodium intercalation into the weakly-coupled FeSe layers to form Na$_x$FeSe, similar to the superconductors Na$_x$TaS$_2$ [19] and Cu$_x$TiSe$_2$ [20-22]? These questions initialize the motivation of the present work, and the superconductivity with $T_c$ up to 8.4 K and 8.3 K observed by Co-doping or Na-insertion in the $\alpha$-FeSe structure. The doping mechanisms for cobalt and sodium are also discussed in the context.

Polycrystalline samples with Fe$_{1-x}$Co$_x$Se ($x = 0.08$) and Na$_y$FeSe ($y = 0.1$) nominal compositions were prepared by conventional solid state reaction. The well-mixed stoichiometrically fine powders of Fe (99%), Co (99%), Se (99.99 %) and Fe, Se, Na$_2$Se (self-made) were cold-pressed into pellets, respectively. Then sealed in evacuated quartz tubes, placed in furnace and heated at the temperature of 750 °C twice with cooled down automatically and lastly annealed at the temperature of 400 °C for 30 hours. These samples were kept in a purified argon atmosphere glove box prior to each characterization.

X-ray diffraction (XRD) analysis was carried out to identify the samples, using an X-ray diffractometer (Rigaku D/Max 2550V, 40 kV 40 mA) with CuK$\alpha$ radiation in the 20 range from 20° to 70°.
The electrical resistivity was measured by the standard four-probe method with silver-paint contacts. The AC magnetic susceptibility was measured with a modulation field of 1 Oe and 333 Hz. And both of these measurements were carried out from 5 – 300 K on a Quantum Design physical property measurement system (PPMS, Model 6000).

The phases of polycrystalline samples Fe_{0.92}Co_{0.08}Se and Na_{0.1}FeSe were examined by X-ray powder diffraction patterns, as shown in Fig. 1. The XRD patterns indicate that α-FeSe (JCPDS no. 03-0533) was successfully synthesized with small amount of impurities, and the major impurity was identified to be element selenium, which are labeled as stars in the figure. The amount of impurity selenium in Na_{0.1}FeSe seems to be higher than that in Fe_{0.92}Co_{0.08}Se. The reason is that the home-made raw material Na_{2}Se used in the preparation of Na_{0.1}FeSe containing some extra Se. Though the doping amounts of Co and Na are as high as the designed 8 % and 10 %, respectively, the peak shift difference between Fe_{0.92}Co_{0.08}Se and Na_{0.1}FeSe is not very obvious.

Fig. 2 shows the temperature dependence of the electrical resistivity (ρ) of polycrystalline samples Fe_{0.92}Co_{0.08}Se and Na_{0.1}FeSe in zero magnetic field. The inset of the figure is the enlarged low temperature data. The superconducting transitions can be seen from the inset, and the $T_c$ temperatures of Fe_{0.92}Co_{0.08}Se and Na_{0.1}FeSe are 8.4 K and 8.3 K, higher than that of the reported Se deficient FeSe sample. The plot of Fe_{0.92}Co_{0.08}Se has a temperature-linear dependent resistivity observed from 300 K to 10 K. However, there is a small anomaly in Na_{0.1}FeSe for increase in resistivity at around 250 K.

In order to confirm the superconductivity, the AC magnetic susceptibility of the sample Fe_{0.92}Co_{0.08}Se was measured with the field amplitude of 1 Oe and the frequency of 333 Hz. The plot of the temperature dependence of AC magnetic susceptibility is shown in Fig. 3. It is obvious to see that there is a sudden abrupt drop at 8.4 K, which is coincident with the measurement of electrical resistivity in Fig. 2. The smooth line without any trace of background and the sudden abrupt drop indicate the superconductivity character of Fe_{0.92}Co_{0.08}Se, and the superconductivity is not
apparently affected by the impurities as exhibited in the XRD patterns. The similar result, which is not shown here, was also found for the sample Na0.1FeSe.

It is very necessary to firstly discuss here that, with an appreciate amount of Co2+ doping in the Fe2+ sites can be induced to be a superconductor without a big surprise, which was reported in the Co-doped compounds of LaFeOAs [15, 16], BaFe2As2 [14] and SrFe2As2 [13]. The superconductivities were achieved by introducing electron dope and the stronger effects of disorder with replacing Fe with Co. whereas there is only disorder effect produced by doping Co in the layered α-FeSe. Actually, Cu and Mn etc. were also used to replace Fe, but no superconductive phenomenon was found. Secondly, the Na-doping in α-FeSe with the Na0.1FeSe nominal composition is very different from that of Co. Na+ has the ability to be located in the interlayer of the layered [FeSe] structure. So the Na+ with appropriate molar ration, such as 0.1, can be intercalated into the weak coupled region between the anti-PbO-like [FeSe] layers to form NaFeSe. The similar results were reported in some layered transition-metal dichalcogenides, which, for example TaS2 [19] and TiSe2 [20-22], can be induced to be superconductors with specific ions (Na+ or Cu+) intercalation. So it can be inferred from Na0.1FeSe that layered transition-metal chalcogenides are also potential superconductors.

α-FeSe can be successfully induced to a superconductor with appropriate amount of cobalt doping or sodium doping. The two doped samples, Fe0.92Co0.08Se and Na0.1FeSe, have the similar zero resistance transition temperature 8.4 K and 8.3 K. The results of electrical resistivity and AC magnetic susceptibility are consistent with each other. The doping mechanisms for cobalt and sodium into parent α-FeSe are different and sodium doping follows the manner of Na+ intercalation into the interlayers of FeSe. Na0.1FeSe sends a message that layered transition-metal chalcogenides are potential superconductors.

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Figure captions:

Fig. 1: XRD patterns of samples Fe$_{0.92}$Co$_{0.08}$Se (A) and Na$_{0.1}$FeSe (B).

Fig. 2: Temperature dependence of electrical resistivity of samples Fe$_{0.92}$Co$_{0.08}$Se (A) and Na$_{0.1}$FeSe (B).

Fig. 3: Temperature dependence of AC magnetic susceptibility of samples Fe$_{0.92}$Co$_{0.08}$Se.
