Physica C: Superconductivity and its applications 549 (2018) 61–65

Contents lists available at ScienceDirect

Physica C: Superconductivity and its applications

journal homepage: www.elsevier.com/locate/physc

Fe-vacancy and superconductivity in FeSe-based superconductors

C.H. Wang[a], T.K. Chen[a], C.C. Chang[a], Y.C. Lee[a], M.J. Wang[b], K.C. Huang[a], P.M. Wu[a], M.K. Wu[a,*]

[a] Institute of Physics, Academia Sinica, Taipei, Taiwan
[b] Institute of Astronomy and Astrophysics, Academia Sinica, Taipei, Taiwan

ARTICLE INFO

Keywords:
Superconductivity
Fe-chalcogenide
Fe-vacancy
X-ray diffraction
Rietveld refinement
Structural distortion

ABSTRACT

This review summarizes recent advancements in FeSe and related systems. The FeSe and related superconductors are currently receiving considerable attention for the high Tcs observed and for many similar features to the high *Tc* cuprate superconductors. These similarities suggest that understanding the FeSe based compounds could potentially help our understanding of the cuprates. We shall first review the common features observed in the FeSe-based system. It was found that with a careful control of material synthesizing processes, numerous rich phases have been observed in the FeSe-based system. Detailed studies show that the Fe-vacancy ordered phases found in the FeSe based compounds, which are non-superconducting Mott insulators, are the parent compounds of the superconductors. Superconductivity emerges from the parent phases by disordering the Fe vacancy order, often by a simple annealing treatment. Recent high temperature X-ray diffraction experiments show that the degree of structural distortion associated with the disorder of Fe-vacancy is closely related to volume fraction of the superconductivity observed. These results suggest the strong lattice to spin coupling are important for the occurrence of superconductivity in FeSe based superconductors.

1. Introduction

Ever since the discovery of FeSe superconductor, several key issues remain unresolved. One is the exact chemical stoichiometry of the compound. Previous studies showed that the superconducting property of β-$Fe_{1+\delta}Se$ is very sensitive to its stoichiometry [1,2], bulk superconductivity was observed in samples with δ close to 0.01 [3]. Another fact that higher superconducting transition temperature can be found in monolayer FeSe on $SrTiO_3$ substrate suggesting that the commonly accepted phase diagram, which derived from assuming the FeTe is the non-superconducting parent compound of FeSe [4], is plausible. We have demonstrated the presence of superconducting-like feature with T_c close to 40 K in samples of nano-dimensional form [5]. We have also reported the discovery of iron vacancies with at least three types of vacancy orders in tetragonal β-$Fe_{1-x}Se$, characterized by analytical transmission electron microscopy [6].

The alkali/alkaline-intercalated iron selenide ($A_{1-x}Fe_{2-y}Se_2$) superconductors with rich superconducting phases, where A = K, Rb, Cs, Tl, attracted great attention not only due to its high superconducting transition temperature (T_c, up to 46 K) [7], but also because of their dissimilar characteristics as compared to other iron-based superconductors, especially its seemingly intrinsic multiphase nature, and the presence of iron vacancies, which orders with $\sqrt{5} \times \sqrt{5} \times 1$ superstructure, in the non-superconducting regime [8–12]. The most frequently observed Fe-vacancy order phase has a chemical stoichiometry of $A_2Fe_4Se_5$. $A_2Fe_4Se_5$ has been identified as an insulator with a blocked checkerboard AFM ordered at a temperature above 550 K by neutron scattering [13].

The complexity of phases and phase separation in $A_{1-x}Fe_{2-y}Se_2$ make it difficult to conclusively verify the phase-property relationship, even for the superconducting phases. We have recently developed a novel synthesis approach to combine the mechanical ball milling and high temperature calcination processes to the formation of polycrystalline $K_{2-x}Fe_{4+y}Se_5$ samples with homogenous chemical composition and crystal phase. Our studies on $K_{2-x}Fe_{4+y}Se_5$ phase have settled two issues: 1) the Fe-vacancy ordered $K_2Fe_4Se_5$ is the insulating parent compound (Mott insulator) of the superconducting state and 2) superconductivity in $K_{2-x}Fe_{4+y}Se_5$ originates from the Fe-vacancy order to disorder transition.

In this report, we summarize recent studies on the Fe-Chalcogenide superconductors, focusing on FeSe system including the alkaline-metal intercalated FeSe system. FeSe is shown to be a material with strong correlation, and it is sensitive to the change of the crystal modifications. Observation of various Fe-vacancy orders in β-$Fe_{1-x}Se$ suggests that the rich-phases similar to those in $A_{1-x}Fe_{2-y}Se_2$ may be more prevalently found in Fe-chalcogenide superconductors. Non-superconducting Fe_4Se_5 becomes a superconductor after high temperature annealing, strongly indicating that one of the Fe-vacancy ordered β-$Fe_{1-x}Se$ is the

* Corresponding author.
E-mail address: mkwu@phys.sinica.edu.tw (M.K. Wu).

https://doi.org/10.1016/j.physc.2018.02.047
Received 15 July 2017; Accepted 28 February 2018

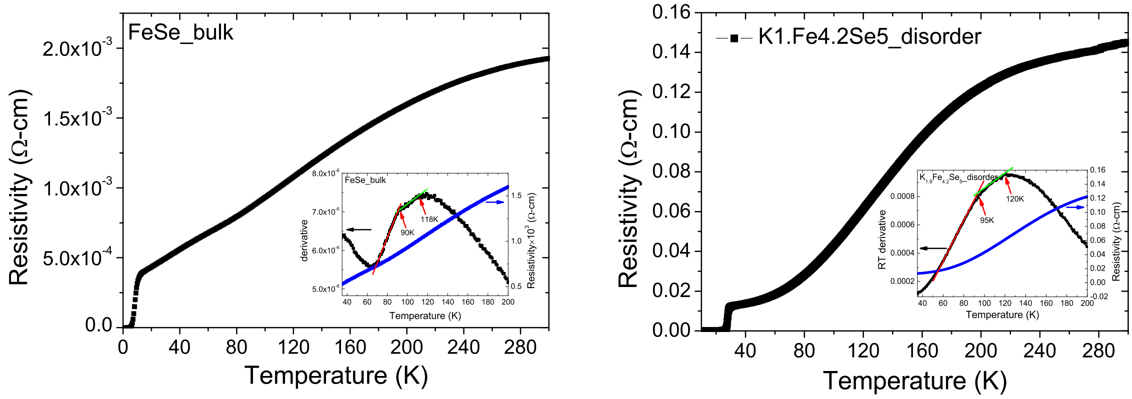

Fig. 1. Temperature-dependent resistivity of (a-left) FeSe superconductor and (b-right) $K_{1.9}Fe_{4.2}Se_5$ superconductor. The insets are the temperature derivative of the resistive curve as a function of temperature.

insulating parent compound of the superconducting state. Similarly $K_2Fe_4Se_5$ compounds prepared using ultra-fine powder are also found to change from the non-superconducting state, which exhibit strong Fe-vacancy order, to a superconducting state, in which Fe-vacancy order is completely suppressed after annealing. These results strongly suggest the Fe-vacancy order to disorder transition is associated with the presence of superconductivity.

2. Structure-property correlations of superconducting Fe-chalcogenides

Fig. 1(a, b) are the temperature dependent resistivity of superconducting FeSe single crystal and polycrystalline $K_2Fe_{4.2}Se_5$, respectively. More detailed analysis of the data, as shown in the inset of Fig. 1, which displays the temperature derivative of the resistivity as a function of temperature, shows anomalies with onset at about ~120 K and ~90 K (*Ts*). The lower temperature anomaly at ~90 K has been identified in FeSe material as the signature for a structural distortion from tetragonal (P4/nmm) to orthorhombic symmetry with space group *Cmma*. This structural deformation correlates closely with the occurrence of superconductivity at low temperature [14]. For the $K_2Fe_{4.2}Se_5$ sample, no such a low temperature distortion has yet been reported in literature. However, as we'll show later, there is a similar fine structural distortion present in the sample at much higher temperature.

Fig. 2(a, b) are the temperature dependence of magnetoresistance (MR) of FeSe and $K_2Fe_{4.2}Se_5$, respectively at temperature ranges between 100 K and 200 K. In this temperature regime, both samples show linear B-dependence of MR and the magnitude MR increases as temperature decreases. However, below the structural distortion temperature, the MR gradually becomes non-linearly dependent on B-field and the magnitude decreases with temperature, as shown in Fig. 3, indicating the influence of magnetic field becomes less. Such a picture is consistent with the suggestion of spin-fluctuation below the structural distortion as has been shown in NMR experiment (bot at ambient and under high pressure) on FeSe. It is also noted that the low temperature thermoelectric power of both superconducting FeSe and $K_2Fe_{4.2}Se_5$ exhibits a local maximum at the structural distortion temperature [15,16].

Several optical properties characterizations have provided the insights into the understanding of the origin for the resistive anomaly that observed at the temperature (~120 K) above the structural distortion temperature. Symmetry analysis of FeSe shows four Raman active modes in this phase [$G_{Raman} = A_{1g}(Se) + B_{1g}(Fe) + 2E_g(Se, Fe)$]. There were reports [15] showing the frequency of E_g mode saturates below 90 K, which is consistent with the observation of the structural distortion at that temperature. The temperature-dependent frequency shifts of the Raman modes at 182 cm^{-1} (A_{1g}(Se) mode) and 206 cm^{-1} (B_{1g}(Fe) mode) show below ~140 K a large (~6.5%) hardening of the B_{1g}(Fe) mode and can be attributed to the suppression of local fluctuations of the iron spin state with a gradual decrease of the iron paramagnetic moment [17]. This observation was attributed to the opening of an energy gap between low ($S = 0$) and higher spin states, which prevents magnetic order in FeSe.

Another consistent results comes from the quasiparticle dynamics measurements on FeSe [18]. It was found the sub-ps relaxation is absent at high temperatures and emerges below 130–140 K, reflecting the appearance of new electronic structure near the Fermi level. This temperature dependency allows for attributing this process to the

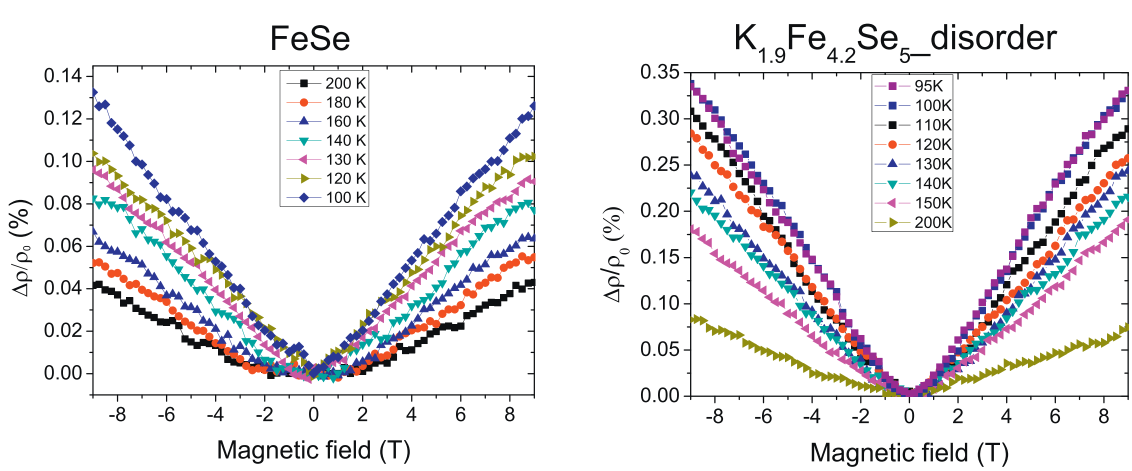

Fig. 2. Magnetic field dependent of change in magnetoresistance (MR) of (a-left) FeSe, and (b-right) $K_{1.9}Fe_{4.2}Se_5$ superconductor in the temperature range from 200 K to 100 K.