Coexistence of superconductivity and antiferromagnetism in single crystals A$_{0.8}$Fe$_{2-x}$Se$_2$ (A = K, Rb, Cs, Tl/K and Tl/Rb): Evidence from magnetization and resistivity

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received 16 February 2011; accepted in final form 21 March 2011
published online 19 April 2011

PACS 74.70.xa – pnictides and chalcogenides
PACS 74.25.F- – Transport properties
PACS 74.25.Ha – Magnetic properties including vortex structures and related phenomena

Abstract – We measure the resistivity and magnetic susceptibility in the temperature range from 5 K to 600 K for the single crystals AFe$_{2-x}$Se$_2$ (A = K$_{0.8}$, Rb$_{0.8}$, Cs$_{0.8}$, Tl$_{0.5}$K$_{0.3}$ and Tl$_{0.4}$Rb$_{0.6}$). A sharp superconducting transition is observed in low-temperature resistivity and susceptibility, and the fully shielding fraction shows bulk susceptibility for all the crystals, while an antiferromagnetic transition is observed in susceptibility at Néel temperature ($T_N$) as high as 500 K to 540 K depending on A. This indicates the coexistence of superconductivity and antiferromagnetism in these intercalated iron selenides. A sharp increase in resistivity arises from the structural transition due to Fe vacancy ordering at temperature slightly higher than $T_N$. Occurrence of superconductivity in an antiferromagnetic ordered state with so high $T_N$ may suggest new physics in this type of unconventional superconductors.

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One of the most amazing issues in the correlated electronic system is that usually there are the coexistence and competition of several electronic or magnetic orders. High-transition-temperature ($T_c$) superconducting cuprates have kept being the central topics in condensed-matter physics in the past 25 years as a result of the multi-orders, which induced extremely complicated physics. Especially, the correlation between superconductivity and antiferromagnetic or spin-density-wave (SDW) order has puzzled the scientists for decades and has been thought to be related to the origin of high-$T_c$ superconductivity in the cuprates. The newly discovered high-$T_c$ superconducting iron pnictides attracted worldwide attention immediately after the discovery of superconductivity [1–3] because it occurs in proximity to the magnetically ordered state or, more than that, because of the coexistence of the superconductivity with antiferromagnetic order [4–6]. Naturally, one takes the iron pnictides to compare with cuprates, and believes that they may have the same origin of high-$T_c$ superconductivity, which could be closely related to the antiferromagnetism. However, no consensus has been reached on this issue so far.

Recently, another newly discovered iron-based superconductors with A$_x$Fe$_{2-y}$Se$_2$ (A = K, Rb, Cs, Tl) with $T_c$ around 30 K are reported [7–12]. Antiferromagnetic transition can be clearly observed in magnetization for non-superconducting Ti- or (Tl, K)-intercalated compounds [12,13]. Muon-spin rotation/relaxation (µSR) experiments indicate that superconductivity below $T_c = 28$ K microscopically coexists with a magnetic ordering state with transition temperature $T_m = 478$ K in Cs$_{0.8}$(Fe$_{0.98}$Se$_{0.02}$)$_2$ [14]. Very recently, Bao et al. reported an antiferromagnetism with Néel temperature ($T_N$) as high as 559 K with iron magnetic moment of 3.31$\mu_B$, and a structural transition at $T_S = 578$ K due to iron vacancy ordering in superconducting K$_{0.8}$Fe$_{1.4}$Se$_2$ [15]. Iron vacancy superstructure at $T_S = 500$ K and possible antiferromagnetic ordering with Fe magnetic moment of 2$\mu_B$ is also reported in Cs$_x$Fe$_{2-y}$Se$_2$ ($y = 0.29$ and $x = 0.83$) [16]. It is well known that there exists a response in resistivity to the magnetic transition, and the magnetic transition can be detected by the susceptibility in iron pnictides superconductors [17]. In order to directly study

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The resistivity measurements above 400 K were carried out with an alternative current resistance bridge (LR700P) by using the a Type-K Chromel-Alumel thermocouples as thermometer in a home-built vacuum resistance oven. Magnetic susceptibility was measured using the Quantum Design SQUID-MPMS. A high-temperature oven was used in the SQUID-MPMS for magnetic-susceptibility measurements above 400 K.

Five systems of superconducting AFe$_{2-y}$Se$_2$ crystals (A = K$_{0.8}$, Rb$_{0.8}$, Cs$_{0.8}$, Tl$_{0.5}$K$_{0.3}$ and Tl$_{0.5}$Rb$_{0.4}$) were investigated in this study. The superconducting transition temperatures ($T_c$) for all the superconducting samples are listed in table 1. As shown in fig. 1, the superconducting transition width lies between 0.5 and 3 K. Especially, the transition width for K$_{0.8}$Fe$_{2-y}$Se$_2$, Rb$_{0.8}$Fe$_{2-y}$Se$_2$ and Tl$_{0.4}$Rb$_{0.4}$Fe$_{2-y}$Se$_2$ is less than 1 K. The susceptibility measured in the zero-field–cooled process at 10 Oe with the field applied within the ab-plane shows fully shielding at 5 K for the crystals with A = K$_{0.8}$, Rb$_{0.8}$, Cs$_{0.8}$, and Tl$_{0.4}$Rb$_{0.4}$, and 90% shielding fraction for the crystal with A = Tl$_{0.5}$K$_{0.3}$.

Figure 2 shows the temperature dependence of the resistivity in the temperature range from 5 K to 600 K for the single crystal AFe$_{2-y}$Se$_2$ with A = K$_{0.8}$, Rb$_{0.8}$, Cs$_{0.8}$, Tl$_{0.5}$K$_{0.3}$, and Tl$_{0.5}$Rb$_{0.4}$. All of the samples display common features. They show superconducting behavior at $T_c \sim 30$ K, and $T_c$ is listed in table 1. Resistivity shows a broad hump in the temperatures range from 70 K to 300 K.
is observed in the resistivity. An arrow points out a kink in the susceptibility, and a similar kink above superconductors \[17–19\] and the FeSe single crystals \[20\]. So high for all the samples compared to the iron pnictide so high for all the samples compared to the iron pnictide.

\[T_0\] as a function of temperature for the crystals \(\text{AFE}_2\text{Se}_2\) \((\text{A}=\text{K}, \text{Rb, Cs}, \text{Tl}_0,5\text{KO}_3, \text{and Tl}_0,4\text{Rb}_0,4)\). The black arrow points out a kink in the susceptibility, and a similar kink is observed in the resistivity.

\((T_{\text{bump}})\) for all crystals. The magnitude of the resistivity is so high for all the samples compared to the iron pnictide superconductors \[17–19\] and the FeSe single crystals \[20\]. Above \(T_{\text{bump}}\), the resistivity shows a semiconductor-like behavior. A sharp increase in resistivity can be observed above 500 K for all samples, indicating the existence of a phase transition. The temperature \((T_S)\), at which the resistivity starts to sharply increase, varies from 512 to 551 K with changing A. Above \(T_S\), the resistivity shows a weak temperature dependence. \(T_S\) is listed in table 1 for all the samples.

In order to detect the magnetic transition and make clear what transition is inferred by the kinks in the resistivity, we measured the magnetic susceptibility at 5 T with the field applied within the \(ab\)-plane in the temperature range up to 600 K, as shown in fig. 3. A pronounced drop is observed in the magnetic susceptibility at a temperature above 490 K for all the samples. This indicates the antiferromagnetic transition at these temperatures \((T_N)\). \(T_N\) is 540, 534, 504, 500, and 496 K for the crystals with \(\text{A}=\text{K}_0,8, \text{Rb}_0,8, \text{Cs}_0,8, \text{Tl}_0,5\text{KO}_3, \text{and Tl}_0,4\text{Rb}_0,4, \) respectively. The antiferromagnetic transition has also been observed in the \(\text{C}_0,8(\text{FeSe}_0,98)_2\) by \(\mu\text{SR}\) with \(T_N \approx 478.5\) K \[14\]. And an antiferromagnetic transition has also been observed in \(\text{K}_0,8\text{Fe}_{1,6}\text{Se}_2\) at \(T_N\) as high as 559 K from neutron diffraction experiments \[15\]. Here, magnetic-susceptibility data indicate the existence of the antiferromagnetic transition above 490 K for all the single crystals, and all \(T_N\) are listed in table 1. It is worth noting that the temperature of the kink in resistivity is slightly higher than those of \(T_N\) observed in the magnetic susceptibility. Actually, \(T_N\) locates in the middle of the transition observed in the resistivity. This suggests that the sharp increase in the resistivity at high temperature does not correspond to the antiferromagnetic transition. Indeed, the neutron diffraction results indicate that a structural transition takes place at a temperature \((T_S)\) just above \(T_N\) due to the ordering of the iron vacancy, \(T_N\) and \(T_S\) are 559 K and 578 K for the sample \(\text{K}_0,8\text{Fe}_{1,6}\text{Se}_{2}\), respectively \[15\]. It is easily found that the \(T_S\) corresponding to the beginning of the sharp increase in resistivity is 10–20 K higher than the \(T_S\) determined by susceptibility. Based on the observation by neutron scattering \[15\], we can infer that the resistivity starts to sharply increase due to the structural transition, and the kink temperature can be defined as the structural transition temperature. Therefore, we can observe the structural and antiferromagnetic transition from the resistivity and magnetic susceptibility, respectively. It should be pointed out that the \(T_S\) observed here in A = K and Cs is different from that reported by Shermadini et al. \[14\] and by Bao et al. \[15\]. It could be due to a different doping level although their \(T_c\) does not change so much. The black arrow in fig. 3 points out a transition at 332 K in magnetic susceptibility for the crystal \(\text{Tl}_0,5\text{KO}_3\text{Fe}_{2−y}\text{Se}_2\). Such behavior cannot be observed in the crystals \(\text{A}_0,8\text{Fe}_{2−y}\text{Se}_2\) \((A=\text{K, Rb, Cs})\). Such tiny transition may be due to small amount of \(\text{Tl}_0\text{Fe}_{2−y}\text{Se}_2\) because a similar transition has been observed in \(\text{Tl}_0\text{Fe}_{2−y}\text{Se}_2\) with different \(T_N\) \[12,13\].

In order to carefully determine \(T_S\), the resistivity and the corresponding derivative (\(d\rho/dT\)) as well as the comparison with the magnetic susceptibility is plotted in fig. 4(a) from 400 K to 600 K for the crystal \(\text{Rb}_0,8\text{Fe}_{2−y}\text{Se}_2\). A clear kink in resistivity is observed at 540 K. \(d\rho/dT\) shows two dips. One can easily find that the beginning of the high-\(T\) dip in \(d\rho/dT\) corresponds to the kink in resistivity. This temperature is defined as \(T_S\). \(T_S\) inferred from the susceptibility is 6 K less than \(T_S\). It indicates that \(T_S\) manifests another phase transition instead of the antiferromagnetic transition observed in susceptibility. This transition should be the structural transition due to the ordering of Fe vacancies because it has been found that the structural transition occurs just before the magnetic transition \[15\]. \(T_S\) is determined in the same way for \(\text{AEFe}_{2−y}\text{Se}_2\) with \(A=\text{K}_0,8, \text{Cs}_0,8, \text{Tl}_0,5\text{KO}_3, \text{and Tl}_0,4\text{Rb}_0,4, \) respectively, as shown in fig. 4(b) and fig. 4(c). The obtained \(T_S\) is also listed in table 1. One can find that all \(T_S\) are slightly higher than \(T_N\) in table 1, indicating the higher transition temperature for the ordering of Fe vacancies than that of magnetic transition. Therefore, the rapid increase in resistivity should be ascribed to the Fe vacancy ordering, and consequently the very large resistivity in the normal state in the intercalated iron selenides originates from the existence of a large amount of Fe vacancies and their ordering. One can note that the \(d\rho/dT\) shows two dips for all the \(\text{AEFe}_{2−y}\text{Se}_2\) crystals except for the \(\text{Tl}_0,4\text{Rb}_0,4\text{Fe}_{2−y}\text{Se}_2\). The dip actually manifests the change of resistivity. Therefore, the second dip can be related to the occurrence of the antiferromagnetism.

One puzzle in the intercalated iron selenide single crystals is how to enter into the superconducting state from
Fig. 4: (Color online) (a) Comparison of the high-temperature resistivity, its derivative and magnetic susceptibility for the crystal Rb$_8$Fe$_2-y$Se$_2$. $T_S$ inferred from the resistivity data and $T_N$ inferred from magnetic susceptibility are shown. (b) and (c): the high-temperature resistivity and its derivative for single crystals AFe$_2-y$Se$_2$: $A = $ K$_{0.8}$ and Cs$_{0.8}$ (b); Tl$_{0.5}$K$_{0.3}$ and Tl$_{0.4}$Rb$_{0.4}$ (c). $T_S$ inferred from the resistivity is shown.

an antiferromagnetic state with ordering Fe magnetic moment of 3.3$\mu_B$ [15] and from the high-temperature semiconductor-like behavior with very high magnitude of resistivity. One may note that resistivity increases rapidly below the structural transition temperature. This suggests that the ordering of the Fe vacancy is responsible for the semiconductor-like behavior and the large magnitude of resistivity above $T_h$ump. The resistivity rapidly increases from 21.5 m$\Omega$ cm to 94.3 m$\Omega$ cm with decreasing temperature from $T_S$ to $T_h$ump, for the crystal K$_{0.8}$Fe$_{2-y}$Se$_2$. However, the antiferromagnetic spin-density-wave transition in iron pnictides has been thought to be related to the reconstruction of Fermi surface (RFS). Such RFS can induce a more metallic resistivity (like in BaFe$_2$As$_2$ and LnOFeAs systems). One possible origin of the metallic resistivity below $T_h$ump can be the joint result of the ordering of the Fe vacancies and the occurrence of antiferromagnetism. All of these mysteries require further experimental and theoretical study.

The above results indicate that the superconductivity in A$_x$Fe$_{2-y}$Se$_2$ happens in an antiferromagnetic ordering state with very high transition temperature $T_N$. In order to understand the coexistence of superconductivity and antiferromagnetic order with very high $T_N$, we measured the resistivity and susceptibility in the non-superconducting crystal KFe$_{2-y}$Se$_2$ (the data are not shown here). Although this sample is not superconducting and shows a semiconducting behavior in the whole temperature range, resistivity and magnetic susceptibility display a similar behavior at high temperatures as those of the superconducting samples. An antiferromagnetic transition with $T_N = 527$ K is observed in susceptibility. Surprisingly, the $T_N$ is lower than that in the superconducting K$_{0.8}$Fe$_{2-y}$Se$_2$ crystal. Resistivity shows a transition at 540 K due to iron vacancy ordering. Both $T_N$ and $T_S$ are higher in the superconducting sample K$_{0.8}$Fe$_{2-y}$Se$_2$ than in the non-superconducting sample. This implies that the coexistence of antiferromagnetic ordering and superconductivity is not simply competing. In fact, there appears a static magnetic phase which microscopically coexists with superconductivity in FeSe$_{1-x}$ under pressure above 0.8 GPa [21]. Furthermore, both superconducting transition temperature $T_c$ and the magnetic order parameter simultaneously increase with increasing pressure above 0.8 GPa in FeSe$_{1-x}$ [21,22], which suggests that higher $T_c$ under high pressure has close relationship with the magnetic order. $\mu$SR experiments have indicated that superconducting state is microscopically coexisting with a strong magnetic phase in Cs$_{0.8}$(FeSe$_{0.98}$)$_2$ [14]. Neutron scattering experiments also found that the superconducting K$_{0.8}$Fe$_{1.6}$As$_2$ had a long-range AFM order with Fe magnetic moment of 3.3$\mu_B$ [15]. $\mu$SR, neutron scattering and our high temperature resistivity and magnetization suggest a microscopical coexistence of superconductivity and AFM in these intercalated iron selenide superconductors. However, one needs to clarify how superconductivity occurs in such antiferromagnetic ordered state.

In summary, we first report the magnetic susceptibility and resistivity from 5 K to 600 K for the crystals AFe$_{2-y}$Se$_2$ ($A = $ K$_{0.8}$, Rb$_{0.8}$, Cs$_{0.8}$, Tl$_{0.5}$K$_{0.3}$ and Tl$_{0.4}$Rb$_{0.4}$). The structural and antiferromagnetic transition temperatures are systematically determined by resistivity and susceptibility for all the superconducting crystals, indicative of the coexistence of antiferromagnetism and superconductivity in these intercalated iron selenides. A sharp increase in resistivity starts at $T_S$ slightly higher than $T_N$. Such increase in resistivity could arise from the Fe vacancy ordering. The higher $T_N$ and $T_S$ in the superconducting crystal relative to non-superconducting crystal suggests that antiferromagnetic magnetism and superconductivity are not simply competing to each other. Occurrence of superconductivity in an antiferromagnetic ordered state with so high $T_N$ and the large magnetic moment of Fe up to 3.3$\mu_B$ may suggest new physics in this type of unconventional superconductor.

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XHC would like to thank W. BAO for useful discussion. This work is supported by the National Natural Science Foundation of China (973 Program No. 2011CB00101

27008-p4
and Grant No. 51021091), the Ministry of Science and Technology of China, and Chinese Academy of Sciences.

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