Contrasting effects of magnetic ions on the superconductivity in Tl$_{0.4}$K$_{0.4}$Fe$_{2−y−x}$M$_x$Se$_2$ ($M = \text{Mn and Ni}$)

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Abstract. The transport and magnetic properties together with the superconductivity of Tl$_{0.4}$K$_{0.4}$Fe$_{2−y−x}$M$_x$Se$_2$ ($M = \text{Mn and Ni}$) single crystals are studied. On the transport side, both Mn doping and Ni doping lead to a decrease of charge carrier density. However, contrasting effects on superconductivity are found, i.e. substitution of Fe by Ni results in a drastic depression of the onset superconducting transition temperature ($T_{\text{onset}}^c$), while the $T_{\text{onset}}^c$ value remains nearly unchanged in Mn-doped samples. A remarkable ferromagnetic interaction is found in Ni-doped samples but is absent in Mn-doped samples. The present results suggest that the magnetic pair-breaking effect alone cannot explain the different behavior of depression of superconductivity in Mn-doped and Ni-doped samples. The occurrence of ferromagnetic interaction is responsible for the rapid decrease of $T_{\text{onset}}^c$ in Ni-doped samples.
1. Introduction

$A_xFe_{2-y}Se_2$ ($A = K, Rb, Cs$ and $Tl$) superconductors have been under extensive study since their recent discovery [1–6]. The high transition temperature, the proximity to a Mott insulator and the distinct clearly Fermi surface shape from that of iron–arsenic superconductors make them interesting systems for investigating key issues such as the superconducting pairing symmetry, the interplay between magnetism and superconductivity and the role of impurities and inhomogeneity.

In $A_xFe_{2-y}Se_2$ compounds, one may tune the interplay of superconductivity and magnetism by changing the Fe-vacancy order. When $y \geq 0.5$, the $A_xFe_{2-y}Se_2$ compounds are an antiferromagnetic (AFM) Mott-like insulator [6, 7]. With increasing Fe content, metal–insulator transition takes place at a certain critical point $y_c$. The superconductivity in $A_xFe_{2-y}Se_2$ has developed from the AFM Mott insulator with a rather high Néel temperature, which is in sharp contrast to that in iron–arsenic superconductors where the parent compounds are bad metals [8–10]. Furthermore, angle-resolved photoemission spectroscopy measurements show electron Fermi surface pockets around the $M$ points, and show no hole-like pockets but very weak electron-like pockets near the zone center $\Gamma$ [11–13]. This is also in contrast to iron pnictide superconductors, where both hole and electron pockets are experimentally observed [14–16]. These findings seem to indicate that the sign change and $s_\pm$-wave pairing are not fundamental factors of iron-based superconductors. It is therefore of great interest to find out whether the $A_xFe_{2-y}Se_2$ superconductors represent a new type of high-temperature superconductors (e.g. similar to high-$T_c$ cuprates) or are similar to iron pnictides.

In a superconductor, the study of the effects of magnetic impurities on the superconducting transition temperature and the electromagnetic properties is of great importance because the magnetic moment of the impurity may couple to the conduction electrons and locally break the time-reversal symmetry. In high-$T_c$ cuprates, a small number of magnetic impurities can strongly break the Cooper pairs and reduce the transition temperature. However, in the $K_{0.8}Fe_{2-y}Se_2$ system, we have found that the introduction of Mn does not depress the $T^\text{onset}_c$ value, which is in sharp contrast to the rapid decrease of $T^\text{onset}_c$ in other transition-metal-doped samples [17]. It is important to investigate the effect of magnetic ions on the transport and magnetic properties of $A_xFe_{2-y}Se_2$ ($A = Rb, Cs$ and $Tl$) systems and compare this with that in the $K_{0.8}Fe_{2-y}Se_2$ system. In this work, we report on the Fe-site substitution effects on the superconductivity and electromagnetic properties of the $Tl_{0.4}K_{0.4}Fe_{2-y}Se_2$ superconductor.
2. Experiment

Single crystals of Tl\(_{0.4}\)K\(_{0.4}\)Fe\(_{2−y−x}\)\(M_x\)Se\(_2\) (\(M = \) Mn and Ni) were grown using the self-flux method. The growth procedures are similar to those described previously [17]. First, the starting materials FeSe, Fe\(_{2−x}\)Mn\(_x\)Se\(_2\) and Fe\(_{2−x}\)Ni\(_x\)Se\(_2\) were prepared using a high-purity powder of iron, manganese, nickel and selenium with Fe(Mn, Ni) : Se = 1 : 1 at 650 °C for 12 h. Then, Tl\(_2\)Se granules, K pieces, Fe, FeSe, Fe\(_{2−x}\)Mn\(_x\)Se\(_2\) and Fe\(_{2−x}\)Ni\(_x\)Se\(_2\) powder were put in a small quartz tube with nominal composition Tl\(_{0.4}\)K\(_{0.4}\)Fe\(_{2−y−x}\)\(M_x\)Se\(_2\) for each sample. The small quartz tube was sealed under high vacuum and then put in a bigger quartz tube followed by evacuation. Then the outer tube was sealed. The mixture was heated up to 950 °C and kept for 4 h. Then the furnace was cooled down to 600 °C with a cooling rate of 3 °C/h before the furnace was shut down. The obtained crystals were characterized by powder x-ray diffraction (XRD) and single-crystal XRD with Cu K\(_{α}\) radiation at room temperature. The actual composition of the crystal was determined by using energy dispersive x-ray spectrometry (EDX) carried out on an FEI-Sirion 200 field emission scanning electron microanalyzer. For each sample, five different areas were selected in the EDX measurements and the average was determined as the actual composition. The dc resistivity was measured using a standard four-probe method with a constant current of 1 mA. In the resistivity measurement, the samples were first cut into a rectangle shape with dimensions of about 4 × 2 × 0.3 mm\(^3\). It should be mentioned that the samples are not very stable under air. For example, the color of the sample changes from white shining into dark if the sample is put under air for several hours. In order to ensure reliability of the measurement, the Au wires are connected to the sample surface within half an hour by using silver paste. The thermoelectric power (TEP) was measured using a differential technique where a temperature gradient of 1 K is created across the sample. The temperature was controlled automatically within a precision of 0.01 K by using a Lakeshore 340 temperature controller. The copper metal was used as the reference material for the TEP measurement. Magnetic properties were investigated using a superconducting quantum interference device magnetometer with magnetic field parallel to the \(ab\)-plane. The typical mass of the sample for magnetic measurement was 0.005 g. Electron spin resonance (ESR) measurements were carried out at 9.40 GHz using a Bruker EMXplus 10112 spectrometer equipped with a continuous He gas-flow cryostat in the temperature range of 2–300 K by sweeping magnetic field parallel to the \(ab\)-plane.

3. Results

In order to determine the crystal lattice structure of the as-grown single crystals, we chose several pieces of crystals from each composition and ground them into fine powder, which is then measured by powder XRD. Figure 1(a) gives the powder XRD patterns of Tl\(_{0.4}\)K\(_{0.4}\)Fe\(_{2−y−x}\)\(M_x\)Se\(_2\) (\(M = \) Mn and Ni) samples. It is clear that all the diffraction peaks can be indexed with a ThCr\(_2\)Si\(_2\)-type structure (space group: \(I4/mmm\)) [18], revealing the formation of single-phase products for both the parent sample and the doped samples. By using the General Structure Analysis System (GSAS) program, we made a general fit to the XRD data of each sample and determined the lattice constants. The obtained lattice parameters for the Tl\(_{0.397}\)K\(_{0.411}\)Fe\(_{1.709}\)Se\(_2\) parent sample are \(a = 3.878\) Å and \(c = 13.915\) Å, which are similar to those in previous works [6]. The doping dependence of the lattice constants calculated from the XRD data for Mn-doped and Ni-doped samples is plotted in figure 1(b). Both Mn doping...
and Ni doping lead to a shrinkage of the $a$-axis lattice constant and an elongation of the $c$-axis lattice parameter. The monotonic variation of both the $a$-axis and the $c$-axis lattice constants with increasing Mn- or Ni-doping content suggests that the Mn and Ni atoms are substantially doped into the crystal lattice of the Tl$_{0.4}$K$_{0.4}$Fe$_{2-y-x}$M$_x$Se$_2$ system. In order to check the orientation of the single-crystal samples, we carried out single-crystal XRD measurements and the representative XRD pattern is shown in figure 1(a) (the curve at the bottom). Only the (00$l$) diffraction peaks with even $l$ are observed, confirming that the crystallographic $c$-axis is perpendicular to the shining surface. For all the diffraction peaks, the full-width at half-maximum is less than 0.1°, indicating the high quality of the single-crystal samples.

The real compositions of the as-grown single crystals are determined by EDX analysis. Table 1 presents a comparison between the nominal and the real compositions of the Tl$_{0.4}$K$_{0.4}$Fe$_{2-y-x}$M$_x$Se$_2$ ($M = \text{Mn and Ni}$) samples. For the parent sample, the detected Fe content in a unit cell is 1.709, indicating the existence of Fe vacancy. A noteworthy fact is that although both Mn and Ni dopants can substantially go into the Tl$_{0.4}$K$_{0.4}$Fe$_{2-y}$Se$_2$ crystal lattice, the real Mn content is significantly lower than the nominal concentration. For example, the real Mn content is only 0.039 in the sample with a nominal Mn concentration of 0.1. On the other hand, the real Ni content is nearly the same as the nominal concentration when $x \leq 0.1$. For $x > 0.1$, the real Ni content is slightly lower than the nominal content. These results suggest that in the Tl$_{0.4}$K$_{0.4}$Fe$_{2-y}$Se$_2$ system, Mn atoms have smaller solubility compared to Ni. The

**Figure 1.** (a) Powder XRD patterns for the Tl$_{0.4}$K$_{0.4}$Fe$_{2-y-x}$M$_x$Se$_2$ ($M = \text{Mn and Ni}$) samples. The curve at the bottom is a typical single-crystal XRD pattern. (b) The variation of lattice constants with increasing Mn- and Ni-doping content.
results are different from those in the K$_{0.8}$Fe$_{2-y}$Se$_2$ system [14], where Mn atoms have a much higher solubility compared to other transition-metal dopants, such as Cr, Co and Zn. Since we have grown a number of samples and the results are reproducible, we suggest that the solubility of transition metals in the two above-mentioned systems is quite different.

Figures 2(a) and (b) show the temperature dependence of in-plane resistivity for the Tl$_{0.4}$K$_{0.4}$Fe$_{2-y-x}$M$_x$Se$_2$ and Tl$_{0.4}$K$_{0.4}$Fe$_{2-y-x}$Ni$_x$Se$_2$ samples, respectively. The temperature dependence of in-plane resistivity for the Tl$_{0.397}$K$_{0.411}$Fe$_{1.709}$Se$_2$ parent compound exhibits semiconductor-like behavior at high temperature, while typical metallic-like conductor behavior is observed below $T_h \approx 88$ K. A ‘hump’-like shape is formed around $T_h \approx 88$ K, which is similar to that found in the K$_{0.8}$Fe$_{2-y}$Se$_2$ superconductor. From figure 2(a), we see that the normal-state resistivity of the Tl$_{0.4}$K$_{0.4}$Fe$_{2-y-x}$M$_x$Se$_2$ samples increases slightly with increasing M-doping level. For example, $\rho_{ab}(300)$ K is about 0.94 $\Omega$ cm in the $x = 0.063$ sample, which is six times as high as that in the parent sample, $\rho_{ab}(300)$ K $\sim 0.16$ $\Omega$ cm. The slight increase of resistivity is reasonable since the introduction of Mn dopants inevitably induces disorder scattering, which would hinder the motion of electrons. It is interesting that the onset of the superconducting transition temperature, $T_{\text{onset}}$, remains nearly constant in the $x \leq 0.039$ samples. For the Tl$_{0.4}$K$_{0.4}$Fe$_{2-y-x}$Ni$_x$Se$_2$ samples, the normal-state resistivity also increases with increasing Ni-doping level. For example, $\rho_{ab}(300)$ K is about 1.9 $\Omega$ cm in the $x = 0.162$ sample, which is 12 times as high as that in the parent sample, $\rho_{ab}(300)$ K $\sim 0.16$ $\Omega$ cm. A striking phenomenon is that the introduction of Ni dopants leads to a rapid decrease of the superconducting transition temperature, which is completely different from the result in the Mn-doped case. In order to compare the difference quantitatively, we plot in figure 2(c) the doping dependence of the $T_{\text{onset}}$ for the Tl$_{0.4}$K$_{0.4}$Fe$_{2-y-x}$M$_x$Se$_2$ ($M =$ Mn and Ni) samples. It can be seen that Mn doping leads to a slight increase of $T_{\text{onset}}$ value when $x \leq 0.039$. In contrast, the introduction of Ni drastically depresses the superconductivity. The present result is similar to our previous finding in the transition-metal-doped K$_{0.8}$Fe$_{2-y}$Se$_2$ system, where substitution of Fe by

Table 1. The comparison between the nominal and real compositions of Tl$_{0.4}$K$_{0.4}$Fe$_{2-y-x}$M$_x$Se$_2$ ($M =$ Mn and Ni) samples.

| Nominal composition | Real composition from EDXS |
|---------------------|---------------------------|
| Tl$_{0.4}$K$_{0.4}$Fe$_{2y}$Se$_2$ | Tl$_{0.397\pm0.004}$K$_{0.411\pm0.006}$Fe$_{1.709\pm0.008}$Se$_2$ |
| Tl$_{0.4}$K$_{0.4}$Fe$_{1.99}$Mn$_{0.01}$Se$_2$ | Tl$_{0.401\pm0.004}$K$_{0.413\pm0.006}$Fe$_{1.701\pm0.008}$Mn$_{0.007\pm0.002}$Se$_2$ |
| Tl$_{0.4}$K$_{0.4}$Fe$_{1.98}$Mn$_{0.02}$Se$_2$ | Tl$_{0.395\pm0.005}$K$_{0.407\pm0.006}$Fe$_{1.693\pm0.007}$Mn$_{0.013\pm0.002}$Se$_2$ |
| Tl$_{0.4}$K$_{0.4}$Fe$_{1.97}$Mn$_{0.03}$Se$_2$ | Tl$_{0.397\pm0.004}$K$_{0.411\pm0.006}$Fe$_{1.688\pm0.005}$Mn$_{0.019\pm0.003}$Se$_2$ |
| Tl$_{0.4}$K$_{0.4}$Fe$_{1.95}$Mn$_{0.05}$Se$_2$ | Tl$_{0.393\pm0.005}$K$_{0.403\pm0.006}$Fe$_{1.681\pm0.005}$Mn$_{0.026\pm0.003}$Se$_2$ |
| Tl$_{0.4}$K$_{0.4}$Fe$_{1.9}$Mn$_{0.1}$Se$_2$ | Tl$_{0.400\pm0.006}$K$_{0.412\pm0.007}$Fe$_{1.680\pm0.005}$Mn$_{0.039\pm0.003}$Se$_2$ |
| Tl$_{0.4}$K$_{0.4}$Fe$_{1.8}$Mn$_{0.2}$Se$_2$ | Tl$_{0.391\pm0.006}$K$_{0.402\pm0.008}$Fe$_{1.668\pm0.007}$Mn$_{0.063\pm0.005}$Se$_2$ |
| Tl$_{0.4}$K$_{0.4}$Fe$_{1.99}$Ni$_{0.01}$Se$_2$ | Tl$_{0.398\pm0.006}$K$_{0.399\pm0.006}$Fe$_{1.701\pm0.004}$Ni$_{0.010\pm0.001}$Se$_2$ |
| Tl$_{0.4}$K$_{0.4}$Fe$_{1.98}$Ni$_{0.02}$Se$_2$ | Tl$_{0.399\pm0.006}$K$_{0.405\pm0.006}$Fe$_{1.696\pm0.007}$Ni$_{0.019\pm0.002}$Se$_2$ |
| Tl$_{0.4}$K$_{0.4}$Fe$_{1.97}$Ni$_{0.03}$Se$_2$ | Tl$_{0.393\pm0.006}$K$_{0.403\pm0.006}$Fe$_{1.691\pm0.005}$Ni$_{0.030\pm0.002}$Se$_2$ |
| Tl$_{0.4}$K$_{0.4}$Fe$_{1.95}$Ni$_{0.05}$Se$_2$ | Tl$_{0.385\pm0.006}$K$_{0.389\pm0.007}$Fe$_{1.702\pm0.006}$Ni$_{0.051\pm0.003}$Se$_2$ |
| Tl$_{0.4}$K$_{0.4}$Fe$_{1.9}$Ni$_{0.1}$Se$_2$ | Tl$_{0.397\pm0.006}$K$_{0.400\pm0.007}$Fe$_{1.707\pm0.006}$Ni$_{0.092\pm0.004}$Se$_2$ |
| Tl$_{0.4}$K$_{0.4}$Fe$_{1.8}$Ni$_{0.2}$Se$_2$ | Tl$_{0.393\pm0.005}$K$_{0.401\pm0.006}$Fe$_{1.587\pm0.006}$Ni$_{0.162\pm0.006}$Se$_2$ |
Mn leads to a slight increase of the $T_{\text{onset}}$ value when $x \lesssim 0.067$, while the superconductivity is drastically depressed by a very small amount of Cr, Co and Zn doping [17].

In the $A_x\text{Fe}_{2-y}\text{Se}_2$ systems, the FeSe layers are the conducting layers where the motion of charge carriers takes place. The introduction of transition-metal dopants in the FeSe layers would induce random scattering effects on the motion of charge carriers, leading to an increase of resistivity. In figure 2(d) we present a comparison of the plots of $\rho_{\text{ab}}(300 \text{ K})$ versus $x$ for the Mn-doped and Ni-doped samples. At a certain doping content ($x$), it is found that the $\rho_{\text{ab}}(300 \text{ K})$ value for the Mn-doped samples is comparable with that for the Ni-doped samples, indicating that the effects of charge carrier localization induced by Mn and Ni dopants are similar. We also present a comparison of the plots of the residual resistivity ($\rho_0$) as a function of $x$ for the Mn-doped and Ni-doped samples. It is found that the $\rho_0-x$ relation for the Mn-doped and Ni-doped samples is comparable, indicating that the contribution of impurity scattering to the motion of charge carriers in both series of samples is similar.

In order to determine the effect of Mn and Ni dopants on the effective charge carrier density in the FeSe conducting layers, we carry out a TEP measurement on the $\text{T}_{0.4}\text{K}_{0.4}\text{Fe}_{2-y-x}\text{M}_x\text{Se}_2$ samples.

**Figure 2.** (a, b) The temperature dependence of resistivity for (a) $\text{T}_{0.4}\text{K}_{0.4}\text{Fe}_{2-y-x}\text{M}_x\text{Se}_2$ samples and (b) $\text{T}_{0.4}\text{K}_{0.4}\text{Fe}_{2-y-x}\text{Ni}_x\text{Se}_2$ samples. (c) Plot of $T_{\text{c}}$ versus $x$ for the $\text{T}_{0.4}\text{K}_{0.4}\text{Fe}_{2-y-x}M_x\text{Se}_2$ ($M = \text{Mn and Ni}$) samples. (d) Plot of the residual resistivity versus $x$. 

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Figure 3. Temperature dependence of TEP for the $\text{Tl}_{0.4}\text{K}_{0.4}\text{Fe}_{2−y−x}\text{M}_x\text{Se}_2 (M = \text{Mn and Ni})$ samples.

($M = \text{Mn and Ni}$) samples. The results are shown in figure 3. In the entire temperature region, the TEP ($S$) value is negative, suggesting that the electrons dominate the electrical conduction. For the $\text{Tl}_{0.397}\text{K}_{0.411}\text{Fe}_{1.709}\text{Se}_2$ parent sample, the nearly linear behavior of the $S$–$T$ curve in the $T_c < T < 130$ K region is consistent with that in a previous paper for the $\text{K}_x\text{Fe}_{2−y}\text{Se}_2$ superconductor [19]. At higher temperature, the $S$ value shows a minimum at about 150 K. In the entire temperature region, the $S$–$T$ relation does not exhibit a monotonic change, which may be due to the multi-band nature of Fe-based superconductors. Similar $S(T)$ curves have also been found in $\text{BaFe}_{2−x}\text{Co}_x\text{As}_2$, $\text{CaFe}_{2−x}\text{Co}_x\text{As}_2$, $\text{SmFeAsO}_{0.85}$ and $\text{LaFeAsO}_{1−y}\text{F}_y$ [20–23]. For all $\text{Tl}_{0.4}\text{K}_{0.4}\text{Fe}_{2−y−x}\text{M}_x\text{Se}_2 (M = \text{Mn and Ni})$ samples, the high-temperature part of the $S(T)$ dependence has several common features: $S$ is negative, has a positive slope and changes almost linearly with decreasing temperature, while at low temperature the $S(T)$ curves develop a broad peak in magnitude at about 150 K. The TEP can be defined in terms of the electrical potential ($\Psi$) and chemical potential ($\mu$) by using the formula

$$-S = \frac{1}{ne} \frac{d\mu}{dT} + \frac{1}{n} \frac{d\Psi}{dT}, \tag{1}$$

where $e$ is the charge of the electron and $n$ the charge carrier density. Thus $S$ is strongly dependent on the charge carrier concentration of the sample. From figure 3 it is seen that the $|S|$ value exhibits a slight increase with increasing Mn and Ni doping content, indicating a decrease of charge carrier concentration caused by Mn and Ni dopants. Since the introduction of transition-metal impurities would induce disorder and scattering effects, the charge carriers near the dopants are localized. Thus the decrease in charge carrier concentration is reasonable. However, we note that both Mn doping and Ni doping have a similar impact on the change in charge carrier density of the $\text{Tl}_{0.4}\text{K}_{0.4}\text{Fe}_{2−y}\text{Se}_2$ system, suggesting that the localization of
Figure 4. The temperature dependence of magnetic susceptibility measured under the ZFC process of the Tl$_{0.4}$K$_{0.4}$Fe$_{2-y-x}$M$_x$Se$_2$ ($M = $ Mn and Ni) samples. The insets in (a) and (b) present the comparisons of the $\chi$–$T$ curves measured under the ZFC process and the FC process for the Tl$_{0.4}$K$_{0.4}$Fe$_{2-y}$Se$_2$ parent sample and the Ni-doped sample with $x = 0.019$, respectively.

electrons cannot explain the different response of superconductivity to Mn dopants and Ni dopants in this system.

Figure 4 shows the temperature dependence of magnetic susceptibility measured under the zero-field cooling (ZFC) process of the Tl$_{0.4}$K$_{0.4}$Fe$_{2-y-x}$M$_x$Se$_2$ ($M = $ Mn and Ni) samples. The applied magnetic field is 100 Oe with magnetic field parallel to the $ab$-plane. In figures 4(a) and (b) the variation of the superconducting transition temperature and the shielding volume fraction at different doping contents is shown. From figure 4(a) it can be seen that the $T_c^{onset}$ value does not decrease in Mn-doped samples, while the shielding volume fraction decreases rapidly with increasing Mn-doping content. For the Ni-doped samples, the $T_c^{onset}$ value determined from magnetic susceptibility is slightly lower than that determined by resistivity measurement. In order to determine the Meissner effect of the samples, we present a comparison of the magnetic susceptibility as measured under the ZFC process and the field cooling (FC) process for the Tl$_{0.4}$K$_{0.4}$Fe$_{2-y}$Se$_2$ parent sample, as shown in the inset of figure 4(a). It is found that the diamagnetic signal measured under the FC process is much smaller than that measured under the ZFC process, indicating that the superconducting volume fraction in
this system is much less than the shielding volume fraction. In the inset of figure 4(b), we also present a comparison of the magnetic susceptibility as measured under the ZFC process and the FC process for the Ni-doped sample with \( x = 0.019 \). The result is similar to that for the \( \text{Tl}_{0.4}\text{K}_{0.4}\text{Fe}_{2-y}\text{Se}_2 \) parent sample. These results suggest the existence of microscopic phase separation in the \( \text{Tl}_{0.4}\text{K}_{0.4}\text{Fe}_{2-y-x}M_x\text{Se}_2 \) \( (M = \text{Mn and Ni}) \) samples, consistent with previous reports [6]. Figures 4(c) and (d) give the normal-state magnetic susceptibility for the Mn-doped samples and Ni-doped samples, respectively. The magnetic susceptibility slightly decreases with decreasing temperature and exhibits a transition at about 120 K. The decrease of magnetic susceptibility with decreasing temperature is consistent with previous reports on \( \text{K}_{x}\text{Fe}_{2-x/2}\text{Se}_2 \), \( \text{A}_{0.8}\text{Fe}_{2-y}\text{Se}_2 \) \( (A = \text{K, Rb, Cs, Tl}/\text{K and Tl}/\text{Rb}) \) and \( \text{Tl}_{0.53}\text{K}_{0.47}\text{Fe}_{1.64}\text{Se}_2 \) samples [6, 24, 25], where the coexistence of superconductivity and antiferromagnetism has been demonstrated from magnetization study. The transition at about 120 K is similar to that found in \( \text{K}_{x}\text{Fe}_{2-x/2}\text{Se}_2 \) [24], which is due to the \( \text{Pmna} + 14/m \) to \( 14/m \) phase transition. Fang et al [6] have found that the temperature of the transition strongly depends on the \( \text{Fe} \) content. For example, the transition temperature is about 365 K in \( \text{TlFe}_{1.3}\text{Se}_2 \), while it decreases to 265 K when the \( \text{Fe} \) content reaches 1.47. The transition temperature eventually decreases to 123 K in \( \text{Tl}_{0.53}\text{K}_{0.47}\text{Fe}_{1.64}\text{Se}_2 \). These results seem to indicate that the transition temperature decreases with increasing \( \text{Fe} \) content. In the present work, the transition temperature is 120 K in the \( \text{Tl}_{0.397}\text{K}_{0.411}\text{Fe}_{1.709}\text{Se}_2 \) parent sample, which is consistent with the results of Fang et al [6]. It is also found that the transition temperature only exhibits a slight change with increasing \( \text{Mn-} \) and \( \text{Ni-} \) doping content. This is because of the small change in the \( \text{Fe} \)-site-occupying content in all samples (the total \( \text{Fe} + M \) content varies from 1.706 to 1.799). In the \( \text{Tl}_{0.4}\text{K}_{0.4}\text{Fe}_{2-y-x}M_x\text{Se}_2 \) \( (M = \text{Mn and Ni}) \) samples, it is found that a decrease of magnetization and a transition at about 120 K are present in all \( \text{Mn-doped} \) and \( \text{Ni-doped} \) samples, indicating that both \( \text{Mn} \) dopants and \( \text{Ni} \) dopants do not severely destroy the antiferromagnetism and phase transition in the \( \text{Tl}_{0.4}\text{K}_{0.4}\text{Fe}_{2}\text{Se}_2 \) system.

The magnetic susceptibility measurement is a macroscopic probe where the measured susceptibility data are the average (or sum) over a large number of magnetic moments. It is very powerful, but the shortcoming of magnetic susceptibility is that it cannot provide the magnetic state microscopically (or locally). In a phase separation system or inhomogeneous system, a microscopic probe on the local magnetic state is usually very important. In order to investigate in detail the magnetic states of the \( \text{Tl}_{0.4}\text{K}_{0.4}\text{Fe}_{2-y-x}M_x\text{Se}_2 \) \( (M = \text{Mn and Ni}) \) samples, we make ESR measurements on several representative samples between 1.9 and 300 K, and the results are shown in figure 5. The ESR spectra of the \( \text{Tl}_{0.397}\text{K}_{0.411}\text{Fe}_{1.709}\text{Se}_2 \) parent sample exhibit a dip-like signal in the low-field region, which is due to the magnetic shielding below the lower critical field \( H_{cl} \approx 80 \text{ Oe} \). The dip-like behavior disappears when the temperature is higher than 30 K, consistent with the disappearance of superconductivity. In the high-temperature region, it is found that the ESR spectra show no evidence of resonance absorption in the entire temperature range. From the theory of ESR experiment, the absence of resonance absorption may be due to two reasons: one is that the material contains no unpaired electrons and the other is that the material shows strong itinerant conducting behavior. In the \( \text{Tl}_{0.397}\text{K}_{0.411}\text{Fe}_{1.709}\text{Se}_2 \) sample, \( \text{Fe}^{2+} \) is magnetic ion which has \( e_0^2t_{2g}^2 \) spin configuration. In this configuration, there are four unpaired electrons that can contribute to ESR absorption. More importantly, in the Fe-based superconducting systems, there are several works in the literature on the ESR study of the local magnetic state where ESR signal can be detected [26–30]. In the so-called 122 systems, our previous study on the \( \text{BaFe}_{2-x}\text{Co}_x\text{As}_2 \) and \( \text{K}_{0.8}\text{Fe}_{2-y}\text{Se}_2 \) systems suggests that the ESR signal
Figure 5. Electron-spin-resonance spectra at different temperatures for (a) Tl$_{0.397}$K$_{0.411}$Fe$_{1.709}$Se$_2$, (b) Tl$_{0.400}$K$_{0.412}$Fe$_{1.680}$Mn$_{0.039}$Se$_2$ and (c) Tl$_{0.397}$K$_{0.400}$Fe$_{1.707}$Ni$_{0.092}$Se$_2$. The magnetic field is parallel to the ab-plane of the samples. The blue curves in (a) and (b) indicate the curves in the superconducting range. The red and green curves denote the position where the resonance occurs. (d) Electron-spin-resonance spectra for Tl$_{0.397}$K$_{0.400}$Fe$_{1.707}$Ni$_{0.092}$Se$_2$ sample with magnetic field parallel to the c-axis of the sample. The insets give the relative intensity of the ESR signal for the Mn-doped and Ni-doped samples.

is weak, indicating moderate itinerancy of the conducting behavior [17, 29]. For these reasons, we conclude that the Tl$_{0.397}$K$_{0.411}$Fe$_{1.709}$Se$_2$ sample exhibits much stronger itinerancy, especially when compared to the BaFe$_{2-x}$Co$_x$As$_2$ and K$_{0.8}$Fe$_{2-x}$Se$_2$ systems.

For the Mn-doped sample ($x = 0.039$), the ESR spectra below 30 K also show dip-like behavior, consistent with the occurrence of superconductivity. The ESR spectra above $T_c$ exhibit very weak resonant signal near $\mu_0 H = 3330$ Oe (marked with the red line). Taking into account the fact that the frequency of the microwave radiation in our ESR instrument is $\nu = 9.4$ GHz, it can be concluded that the detected weak resonant signal in the Mn-doped sample is a paramagnetic signal. This paramagnetic signal is due to two possible reasons: that it originates from the unpaired electrons of the Mn dopants (for example, Mn$^{2+}$ ions have...
e^{2/3} \chi \text{ spin configuration where all five 3d electrons are unpaired electrons) or that introduction of Mn dopants leads to the localization of electrons in the Fe(Mn)Se conducting layer. In the inset of figure 5(b) we plot the temperature dependence of relative intensity (I/I_{100 K}) of the ESR signal for the Mn-doped sample. It is found that the relative intensity increases with decreasing temperature in the 100 K < T < 300 K region. Strikingly, the relative intensity shows a significant decrease below ~100 K. The decrease in ESR intensity indicates that below this temperature, the number of unpaired spins contributing to the ESR decreases. Since ESR can also be called ‘electron paramagnetic resonance’, the decrease in the number of unpaired spins means that a certain number of paramagnetic ions is involved in some kind of magnetic interaction below ~100 K. This fact confirms that the detected ESR signal comes from the Tl_{0.4}K_{0.4}Fe_{2−x}Mn_xSe_2 samples, but not from the un-reacted Mn impurity. The sudden decrease in ESR signal below ~100 K has also been found previously in BaFe_{2−x}Co_xAs_2 and K_{0.8}Fe_{2−x}Se_2 systems, which is possibly due to the enhancement of AFM magnetic fluctuation [17, 29].

Figures 5(c) and (d) display the ESR spectra for the Ni-doped sample (x = 0.092) with magnetic field H parallel to the ab-plane and the c-axis, respectively. It is found that the dip-like behavior does not present even when the temperature is down to 2 K, consistent with the complete depression of superconductivity. In the case of H // ab, it is found that the position of the resonance magnetic field (\mu_0 H_{res}) is located below 3330 Oe, suggesting the existence of ferromagnetic interaction in Ni-doped samples. Furthermore, the resonance field shifts to lower magnetic field with decreasing temperature (marked by the green curve), indicating that the ferromagnetic interaction is enhanced with decreasing temperature. In the inset of figure 5(c) we plot the temperature dependence of relative intensity (I/I_{120 K}) of the ESR signal. The intensity shows an abrupt decrease below ~120 K, due to the enhancement of AFM magnetic interaction, which overwhelms the presence of FM signal. For the H // c case, the resonance magnetic field is located below 3330 Oe (marked by the green curve), indicating the existence of ferromagnetic interaction. However, the intensity of ESR resonance is much weaker compared to that in the H // ab case.

4. Discussion

In conventional element superconductors and alloy superconductors, the Bardeen, Cooper and Schrieffer theory has proposed an s-wave superconducting pairing symmetry, which is common in ‘low-temperature superconductors’. However, in the so-called ‘high-temperature superconductors’, such as the cuprates, the pairing symmetry is anisotropic d-wave. The electron–phonon interaction that mediates the bounding state of Cooper pairs in conventional superconductors is invalid in cuprate high-temperature superconductors. In high-Tc cuprate superconductors, the introduction of dopants in the CuO_2 conducting planes generally leads to drastic destruction of the superconductivity as well as significant adverse impact on the transport properties and other physical properties. For example, the substitution of Cu by transition-metal impurities leads to strong pair-breaking effects and the localization of charge carriers in the CuO_2 plane. However, in the A_xFe_{2−y}Se_2 (A = K, Rb, Cs and Tl) superconductors, the situation seems to be different. The present results suggest that Mn doping and Ni doping in the Tl_{0.4}K_{0.4}Fe_{2−x}Se_2 lead to entirely different effects on both the superconductivity and magnetic states. In the Mn-doped sample, the superconducting transition temperature remains nearly constant at T_{c onset} ~ 30 K when x \leq 0.039. On the other hand, T_{c onset} decreases monotonically.
with increasing doping content in the Ni-doped case. Although the magnetic susceptibility data indicate that both Mn dopants and Ni dopants do not suppress the AFM order in the Tl$_{0.4}$K$_{0.4}$Fe$_{2-\gamma}$Se$_2$ system, ESR measurements probe explicit ferromagnetic interaction in Ni-doped samples, which is absent in Mn-doped samples. These results indicate that although both the Mn ions and the Ni ions are transition-metal ions, they introduce contrasting effects on the superconductivity and magnetic states in the Tl$_{0.4}$K$_{0.4}$Fe$_{2-\gamma}$Se$_2$ system.

In order to set up the superconducting theory, a magnetic mechanism has been proposed for high-temperature superconductivity in which an electron magnetically polarizes its environment, resulting in an attractive pairing interaction for oppositely polarized spins [31–35]. In a magnetic mechanism, magnetic ions do not disrupt the pairing interaction, which can qualitatively explain why magnetic ions, such as Co, Ni, etc, have a weaker influence on the superconductivity compared to the non-magnetic Zn dopant in high-$T_c$ cuprates [34–36]. In the A$_{0.8}$Fe$_{2-\gamma}$Se$_2$ (A = K, Rb, Cs and Tl) system, the coexistence of the superconductivity and the magnetic order with an extraordinary high Néel temperature as well as the presence of the long-range AFM ordering has been confirmed by means of neutron diffraction and other experiments. In this work, the results of the temperature dependence of magnetic susceptibility are consistent with the scenario of the coexistence of superconductivity and antiferromagnetism. In both the Mn-doped and the Ni-doped samples, the introduction of dopants does not break the AFM interaction. In the Mn-doped samples, besides the coexistence of superconductivity and AFM order, ESR measurements probe paramagnetic signal in a wide range of temperatures, suggesting that both the paramagnetism and antiferromagnetism can coexist with superconductivity. The ESR resonance occurs at lower external magnetic field compared to that in Mn-doped samples, suggesting the occurrence of ferromagnetic interaction in Ni-doped samples [37–39]. It is well known that the occurrence of ferromagnetic interaction is inimical to the superconductivity. Thus the rapid suppression of superconductivity in Ni-doped samples might be due to the occurrence of ferromagnetic interaction.

If the FM interaction is established at high temperature, it is possible that the FM interaction can persist down to very low temperature. However, from figure 5 we note that the intensity of the resonance signal decreases below $\sim$100 K and the ESR signal is not detectable below $\sim$80 K. We will briefly discuss the reason. In a phase-separated sample with magnetic exchange interaction, the spin Hamiltonian can be written as [37]

$$H_s = H_z + H_{ex} + H_{anis} = \mu_0 B_0 [g_1 S_1 + g_2 S_2] - J S_1 S_2 + H_{anis},$$  \hspace{1cm} (2)

where $B_0 = \mu_0 H$ is the applied magnetic field and $\mu_B$ is the Bohr magneton, the term $JS_1S_2$ is the exchange interaction between the spin operators $S_1$ and $S_2$ and $H_{anis}$ contains dipolar and other anisotropic interactions. $H_{ex} = -JS_1S_2$ is ferromagnetic when $J > 0$ and AFM when $J < 0$. Owing to the existence of magnetic exchange interaction, the electron’s Landé $g$-factor is smaller than $g_e = 2.0023$ (the Landé $g$-factor of a free electron) in the presence of FM interaction. On the other hand, $g$ is larger than 2.003 in the environment of AFM interaction. Thus if there exists FM interaction, the magnetic position where the ESR resonance occurs is below $\mu_0 H = 3330$ Oe. And the resonance field is higher than $\mu_0 H = 3330$ Oe due to the existence of AFM interaction. It should be mentioned that in an X-band ESR instrument, we cannot detect any ESR signal if the electrons are under the environment of AFM interaction. In Ni-doped Tl$_{0.4}$K$_{0.4}$Fe$_{2-\gamma}$Se$_2$ samples, ESR results suggest the occurrence of FM interaction. The weak FM interaction could be attributed to the local magnetic interaction between Ni$^{2+}$ ions.
and adjacent Ni$^{2+}$ ions (or Fe$^{2+}$ ions). In this sense, small regions containing FM interaction can coexist with regions of AFM interaction. The term $H_\text{ex}$ in the spin Hamiltonian is then the sum of the contributions from both the FM interaction and the AFM interaction. At high temperature, we can detect very weak ESR signal when the electrons are in the regions containing FM interaction. When the temperature is decreased, the AFM magnetic interaction is strongly enhanced below $\sim 100$ K [17, 29]. The term $H_\text{ex}$ mainly comes from the contribution of AFM interaction. In this respect, one cannot detect any ESR signal even though the FM interaction exists in the sample. The existence of FM interaction below $\sim 80$ K can be further confirmed by neutron scattering experiments [40].

5. Conclusion

To summarize, we have studied the effects of magnetic ion doping on the superconductivity in Tl$_{0.4}$K$_{0.4}$Fe$_{2-\gamma}$M$_{\gamma}$Se$_2$ ($M = $ Mn and Ni) systems. In Ni-doped samples, the introduction of Ni dopants induces significant ferromagnetic interaction, resulting in a drastic depression of superconductivity. In contrast, Mn doping induces no ferromagnetic interaction. The present results support that the exchange field of the ferromagnetic interaction breaks the Cooper pairs, which is the reason for the rapid depression of superconductivity in the Ni-doped system.

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