Inconsistent pressure effect on superconducting transition temperature and volume in Fe$_{1+y}$Te$_{1-x}$Se$_x$ single crystals

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Abstract. The role of Se in determining the superconductivity of Fe$_{1+y}$Te$_{1-x}$Se$_x$ is still unclear. In this paper, we examine the chemical effect generated by Se substitution by applying external pressure on Fe$_{1+y}$Te$_{1-x}$Se$_x$ single crystals. With increasing pressure, the superconducting volume increases; however, the onset temperature of the superconducting diamagnetic signal, $T_{c mag}$, does not change monotonically. The inconsistent pressure effect on superconducting volume and $T_{c mag}$ is in agreement with Se substitution, which suggests that the chemical pressure effect dominates the superconductivity. Our results also imply that the superconducting and magnetic phases coexist in the form of phase separation.

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1. Introduction

During the past 2 years, a great deal of effort has been devoted to studying the interplay between superconductivity and magnetism in iron-based superconductors [1–10]. For iron pnictides, the parent compounds exhibit commensurate static magnetic order. Doping with carriers or applying pressure suppresses magnetism and favors superconductivity, which implies competition between superconductivity and static magnetism [1–4]. However, the general trend in iron pnictides does not seem to be applicable to another family of iron-based superconductors, the iron chalcogenides FeSe(Te) [5, 6], despite the fact that they have almost the same planar sublattices [7]. Although density functional studies showed that FeSe(Te) has the SDW ground state, the ARPES investigation on FeTe shows that its magnetism arises from a different interaction than in the iron pnictides [8, 9]. For FeSe, the superconducting transition temperature \( T_c \) was dramatically increased from 8–9 to 34–37 K when applying high pressure around 7–9 GPa [6, 10–14]. With further increase in the pressure, \( T_c \) decreases and its structure transforms to a hexagonal phase [6, 10, 11]. The increase in \( T_c \) is accompanied by an increase in spin fluctuation, but no static magnetism was observed in the whole pressure range [6, 15]. FeTe, in contrast, is non-superconducting but displays incommensurate or commensurate antiferromagnetic order, depending on the content of excess Fe [16, 17]. Application of pressure suppresses the magnetic transition [18]; however, no superconductivity has been detected, which might be due to the collapse of the lattice or the appearance of other high-pressure phases [18, 19]. With the substitution of Se on the Te sites, e.g. Fe\(_{1+y}\)Te\(_{1-x}\)Se\(_x\), a trace of superconductivity first develops for \( x = 0.1 \) and bulk superconductivity is seen for compositions near \( x = 0.5 \), accompanied by the suppression of long-range magnetic order [20, 21]. For \( 0.1 < x < 0.5 \), superconductivity is found to coexist with (short-range) incommensurate antiferromagnetism [20, 22].

On going from FeTe to FeSe, the lattice parameter decreases monotonically [17, 21]. Accordingly, the substitution of Se for Te could be viewed as exerting positive chemical pressure on the system. On the other hand, the local atomic structure study reveals that the valence charge distribution in Fe–Se bonds is different from that in Fe–Te bonds [23]. Moreover, in addition to the variation in Se content, superconductivity in Fe\(_{1+y}\)Te\(_{1-x}\)Se\(_x\) is also modulated by excess Fe [21, 24], which complicates the role of Se in determining superconductivity. To understand the chemical pressure effect on superconductivity in Fe\(_{1+y}\)Te\(_{1-x}\)Se\(_x\), it is necessary to examine it with external pressure, although it fails to drive superconductivity in FeTe [18]. To our knowledge, there is still no clear evidence that pressure favors superconductivity by suppressing magnetism in Fe\(_{1+y}\)Te\(_{1-x}\)Se\(_x\).

In this paper, the superconductivity in Fe\(_{1+y}\)Te\(_{1-x}\)Se\(_x\) is investigated in four single crystals, with \( y \) increasing from 0.01 to 0.05 and \( x \) around 0.19–0.26. The pressure effect on superconductivity was examined in two samples with \( y = 0.01 \) and 0.03, respectively. With increasing pressure we show that the onset temperature of the superconducting diamagnetic signal, \( T_c^{\text{mag}} \), does not change monotonically for both samples; however, the superconducting volume increases notably. The pressure effect is found to be analogous to increasing Se content, and it can be understood in a scenario of phase separation with the coexistence of superconducting and magnetic areas in real space.
Table 1. Chemical compositions of Fe$_{1+y}$Te$_{0.8}$Se$_{0.2}$ single crystals.

| Nominal composition | Real composition | Label of sample |
|---------------------|------------------|-----------------|
| Fe$_{1.0}$Te$_{0.8}$Se$_{0.2}$ | Fe$_{1.01}$Te$_{0.73}$Se$_{0.26}$ | SC1             |
| Fe$_{1.02}$Te$_{0.8}$Se$_{0.2}$ | Fe$_{1.03}$Te$_{0.76}$Se$_{0.21}$ | SC2             |
| Fe$_{1.04}$Te$_{0.8}$Se$_{0.2}$ | Fe$_{1.04}$Te$_{0.81}$Se$_{0.19}$ | SC3             |
| Fe$_{1.08}$Te$_{0.8}$Se$_{0.2}$ | Fe$_{1.05}$Te$_{0.79}$Se$_{0.21}$ | SC4             |

2. Experimental

Single crystals with nominal composition Fe$_{1+y}$Te$_{0.8}$Se$_{0.2}$ ($y = 0, 0.02, 0.04, 0.08$) were prepared from high-purity powders of iron (99.9%), tellurium (99.9%) and selenium (99.9%). The mixed powders were ground thoroughly and sealed in an evacuated quartz tube. The tube was heated up to 950 °C for 24 h and slowly cooled to 500 °C at a rate of 2 °C h$^{-1}$ before the furnace was shut down. The obtained crystals can easily be cleaved with typical dimensions of 3 mm × 3 mm × 0.5 mm. The phase purity and structure of the crystals were examined by x-ray diffraction (XRD) with Cu-K$_\alpha$ radiation at room temperature. The homogeneity and chemical compositions of the samples were confirmed using an energy-dispersive x-ray spectrometer (EDX). The nominal and measured compositions of the samples used in this study are summarized in table 1. In accordance with the variation in Fe content in nominal compositions, the real composition of excess Fe increases gradually from SC1 to SC4.

The resistivity was measured using a standard four-probe method from 4 to 300 K in a quantum design physical properties measurement system (PPMS). The temperature dependence of magnetization was measured using a superconducting quantum interference device (SQUID) magnetometer in a zero-field cooling sequence with the magnetic field parallel to the c-axis. To eliminate the remnant field in SQUID, the magnet was reset before every sequence. The remnant field is lower than 2 Oe. The application of pressure was performed in an Easylab Mcell 10 Pressure cell.

3. Results and discussions

Figure 1 shows single-crystal XRD patterns for SC1, SC2, SC3 and SC4. Only (00 l) diffraction peaks appear, indicating that the c-axis is perpendicular to the cleavage surface for all samples. To examine the purity of the prepared crystals, we further performed powder XRD measurements for each composition by grinding partial crystals into powders. All the peaks can be well indexed using the P4/nmm space group and no impurity phase is observed; see a typical powder pattern for SC1 included in figure 1. The calculated lattice constants for SC1 are $c = 6.172(3)$ Å, $a = 3.826(7)$ Å, close to those reported for single crystals of similar composition [21, 22].

The temperature dependence of in-plane resistivity $\rho_{ab}$ for single crystals from SC1 to SC4 is shown in figure 2. All samples are superconducting with the onset transition temperature $T_{c}^{onset}$ near 14 K. Although the resistivity measurements show that all samples are superconducting, only SC1 with less Fe and more Se content displays a bulk diamagnetic signal, as shown in figure 3. From SC2 to SC4, where the Se content is almost constant near 0.2, the decrease...
Figure 1. Powder x-ray diffraction pattern for SC1 and single-crystal XRD patterns for SC1, SC2, SC3 and SC4.

Figure 2. In-plane resistivity $\rho_{ab}$ as a function of temperature for single crystals from SC1 to SC4.

of $T_c^{onset}$ in resistivity and superconducting volume fraction with increasing excess Fe is in agreement with the results reported by another group [24].

In $\text{Fe}_{1+y}\text{Te}_{1-x}\text{Se}_x$, as mentioned above, the superconductivity is not only tuned by the excess Fe but also dependent on the Se content. Since Se has the same valence and smaller ionic radius in comparison with Te, the substitution of Se for Te first generates positive chemical pressure and then modulates the micro-structure. If chemical pressure plays an important role in determining superconductivity, applying external pressure should have a similar effect. For this point, we further examined the pressure effect on superconductivity for SC1 and SC2.

Figure 4 shows the temperature dependence of dc susceptibility under different pressures for SC1 and SC2. For SC1, the onset temperature of superconducting diamagnetic signal, $T_c^{mag}$,
Figure 3. Magnetic susceptibility as a function of temperature $\chi(T)$ measured under a magnetic field of 100 Oe (applied along the $c$-axis) at ambient pressure.

Figure 4. Magnetic susceptibility as a function of temperature with $H = 100$ Oe under different pressures for SC1 and SC2. The inset shows $T_c^{\text{mag}}$ as a function of pressure for SC1, SC2 and FeSe. The data of FeSe are from [28].

increases from 8.8 K up to 10.9 K with increasing pressure to 5 kbar, and then decreases to 10.2 K as the pressure is further increased to 10 kbar. For SC2, applying a pressure of 5 kbar has no evident influence on $T_c^{\text{mag}}$, and 10 kbar leads to the decrease of $T_c^{\text{mag}}$ down to 9 K. Clearly,
the pressure effect on $T_{\text{mag}}$ has no consistent variation. However, for both samples there is a significant increase in superconducting volume fraction with increasing pressure.

Normally, we should conjecture that the pressure favoring/disfavoring superconductivity is always concomitant with the enhancement/weakening of both $T_c$ and superconducting volume fraction. Clearly, the pressure effect on Fe$_{1+y}$Te$_{1-x}$Se$_x$ seems to be different. Recently, by performing muon-spin rotation and neutron diffraction measurements, Khasanov et al developed a phase diagram for Fe$_{1+\alpha}$Te$_{1-\gamma}$Se$_\gamma$ [20]. We can clearly see that, with increasing Se content from 0.1 to 0.5, $T_c$ changes slightly whereas the superconducting volume increases notably. Therefore, a similar effect generated by the applied pressure suggests that the chemical effect generated by Se substitution for Te plays an important role in determining the superconductivity of Fe$_{1+y}$Te$_{1-x}$Se$_x$.

For compositions between 0.1 and 0.5, it is believed that superconductivity coexists with short-range magnetic order either in atomic scale or in nanoscale with electronic phase separation characteristics [20, 25]. In a homogeneous system, the applied pressure suppressing magnetism and favoring superconductivity should lead to the enhancement of both $T_c$ and superconducting volume. Therefore, although we cannot exclude the possibility of the coexistence of two order parameters on the atomic scale, the inconsistent pressure effect on $T_c$ and superconducting volume suggests that FeTe(Se) might be intrinsically inhomogeneous and display mixed-phase properties, similar to the case of manganese oxides [26]. In manganese oxides, the antiferromagnetic insulator (AFI) coexists with ferromagnetic metal (FM) with optimal charge carrier concentration. With the application of magnetic field or pressure, the FM phase grows in volume at the expense of the AFI phase [26]. A similar picture should also work for FeTe(Se), where the system is phase segregated into magnetic domains and superconducting areas with optimal $T_c$ in real space.

Recent neutron diffraction measurements on FeTe(Se) showed that a small change in composition does not change $T_c$ but considerably changes the position of the incommensurate peaks [27]. This implies that the pressure effects on the superconducting and magnetic phases are different. The applied pressure may have a more intensive effect on the magnetic areas, by suppressing the magnetism and inducing superconductivity there. In contrast, the pressure effect on the superconducting areas might be weak as optimal $T_c$ is already present in those places. The decrease in $T_c$ on further increasing the pressure to 10 kbar might be due to changes in micro-structure, being analogous to the case of FeSe (see the inset of figure 4) [28]. In FeSe, $T_c$ is found to decrease with increasing pressure in the range from 1 to 1.5 GPa, followed by a significant increase in $T_c$ on further increasing the pressure [28, 29].

4. Conclusion

In conclusion, the pressure effect on the superconductivity of SC1 and SC2 has been investigated. It is found that the pressure effect is analogous to the chemical pressure effect generated by Se substitution. The inconsistent changes in $T_{\text{mag}}$ and superconducting volume with pressure are examined in a scenario of phase separation with superconducting and magnetic areas coexisting in real space. It is suggested that the applied pressure suppresses magnetism in the magnetic areas and drives superconducting in those areas; however, it does not contribute any positive effect to the superconducting areas.
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