Oxygen-annealing effects on superconductivity in polycrystalline Fe$_{1+x}$Te$_{1-y}$Se$_y$

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Abstract
Superconductivity in anti-PbO-type iron chalcogenides Fe$_{1+x}$Te$_{1-y}$Se$_y$ ($x=0$, $0.1$, $y=0.1$–0.4) depends on the amount ($x$) of interstitial iron atoms located between the FeTe$_{1-y}$Se$_y$ layers. Non-superconducting samples of nominal Fe$_{1.1}$Te$_{1-y}$Se$_y$ convert to superconductors with critical temperatures up to 14 K after annealing at 300 °C in an oxygen atmosphere. The process is irreversible upon subsequent hydrogen annealing. Magnetic measurements are consistent with the formation of iron oxides, suggesting that oxygen annealing preferably extracts interstitial iron from Fe$_{1+x}$Te$_{1-y}$Se$_y$, which interferes with superconductivity.

Keywords: iron based superconductors, selenide, chemical modification

(Some figures may appear in colour only in the online journal)

1. Introduction

Superconducting iron chalcogenides Fe$Ch$ ($Ch$ = Se, Te) attract considerable interest, because their simple anti-PbO-type crystal structures make them perfect candidates for studying unconventional superconductivity [1, 2], and because recent reports indicate critical temperatures ($T_c$) up to 100 K in single-layer FeSe films [3–5].

Fe$Ch$ compounds consist of stacked layers of edge-sharing Fe$Ch_{4/4}$ tetrahedra with up to 25% iron located in the van der Waals gap [6]. These interstitial iron atoms in Fe$_{1+x}$Ch interfere with superconductivity by their magnetic moments and/or their unfavourable contributions to the Fermi surface. Virtually stoichiometric FeSe [7, 8] has critical temperatures of 8–10 K [9], which increases to 36 K under pressure [10] and up to 45 K by intercalation of innocent electron transferring species [11–13]. Stoichiometric FeTe is unknown, while Fe$_{1+x}$Te ($x \approx 0.14$) is magnetic and non-superconducting. The critical temperatures of solid-solution FeTe$_{1-y}$Se$_y$ raises to 14 K at $y \approx 0.5$, depending on the amount of interstitial iron [14–18]. Thus, understanding and controlling the excess iron in Fe$Ch$ superconductors is fundamentally important also with respect to possible applications in superconducting wires.

Different post-preparation manipulations revealed significant influences on the superconducting properties of FeTe$_{1-y}$Se$_y$. These treatments include exposure to HNO$_3$ [19], I$_2$ [20], O$_2$ [21], Te [22], and S [23] at ambient conditions or annealing at higher temperatures, as well as under N$_2$ [20] or vacuum [24]. Especially, annealing Fe$_{1+x}$Te$_{1-y}$Se$_y$ single crystals in an oxygen atmosphere improved the superconducting properties significantly. As-prepared samples are superconducting only for $y=0.5$, whereas after O$_2$ annealing, already compounds with $y=0.1$ are superconducting [21]. Since then, the mechanism of O$_2$ annealing has been debated. Several assumptions, including a homogenization effect, the substitution of O for Ch, the intercalation of oxygen, or the removal of interstitial Fe, were considered reasonable, whereby the latter is discussed preferentially [21, 25]. Recently the removal of excess iron from a Fe$_{1+x}$Te$_{0.6}$Se$_{0.4}$ single crystal was monitored by STM measurements [26]. However, it remains unclear what happens with that iron and if the process is solely the removal of interstitial iron while the layer iron is unaffected. Maybe it is more complex and...
possibly reversible under reductive conditions in a hydrogen atmosphere.

Here we study polycrystalline samples of Fe_{1+y}Te_{1−y}Se_y (x = 0, 0.1, y = 0.1–0.4), with different amounts of nominal interstitial iron, concerning the influences of oxygen and hydrogen annealing on the superconducting properties. In order to exclude effects due to heating we also performed control experiments under an Ar-atmosphere. If the extraction of interstitial Fe atoms is essential, the emergence of iron oxide as an impurity phase can be expected in polycrystalline samples, and the process should be irreversible under reductive conditions.

2. Methods

2.1. Synthesis

Fe_{1+y}Te_{1−y}Se_y (x = 0–0.1, y = 0.1–0.4) was synthesized by using stoichiometric amounts of the elements. These samples will be referred to as ‘as-prepared’ in the following. Fe_{1.0}Te_{0.9}Se_y (y = 0.1–0.4) samples (0.7 g) were synthesized in alumina crucibles inside sealed silica ampoules by heating to 1050 °C for 24 h, cooled to 350 °C for 10 h, and then cooled to room temperature (step 1). Four samples were combined and annealed at 800 °C for 10 h, followed by 10 h at 350 °C before cooling to room temperature (step 2). Fe_{1.1}Te_{1−y}Se_y (y = 0.1–0.4) was synthesized in one step according to step 1 but on a larger scale (2.0 g). Oxygen annealing was performed by heating samples to 300 °C for 2 h in alumina crucibles inside sealed Duran® glass ampoules under an oxygen atmosphere (‘O2-annealed’ samples). For hydrogen annealing, O2-treated samples in alumina crucibles inside a Duran® tube connected to a bubble counter were heated to 200 °C for 2 h under a continuous flow of hydrogen (‘H2-annealed’ samples). Control experiments were performed with as-prepared samples under an Ar atmosphere at 300 °C for 2 h.

2.2. Powder x-ray diffraction (XRD)

Powder x-ray diffraction (XRD) patterns were recorded on a STOE Stadi P (MoKα radiation, Ge (111) primary monochromator, λ = 70.93 pm, silicon as external standard, rotating capillary 0.3 mm outer diameter). Rietveld refinements were performed with the TOPAS 4.1 program package [27]. To generate the reflection profiles, the fundamental parameters approach was used. The preferred orientation of the crystallites was described with fourth-order spherical harmonics.

2.3. Energy dispersive x-ray spectroscopy (EDX)

Scanning electron microscopy of polycrystalline samples was performed on a Carl Zeiss EVO-MA 10 microscope with SE and BSE detectors, which was controlled by the SmartSEM [28] software. The microscope was equipped with a Bruker Nano EDX detector (X-Flash detector 410-M) for EDX investigations using the QUANTAX 200 [29] software to collect and evaluate the spectra. Elements contained in the sample holder and adhesive carbon tabs were disregarded.

2.4. Magnetic measurements

A commercial Quantum Design MPMS XL5 SQUID magnetometer was used at temperatures between 1.8–300 K. The polycrystalline sample was ground and poured into a gelatine capsule, which was fixed in a plastic straw. The magnetic measurements were performed with the MPMS MultiVu software. Ac-susceptibility measurements were performed on a fully automatic self-built ac-susceptometer with a Janis shut-950 two-stage closed-cycle Cryostate with 4He exchange gas (Janis Research Company, Wilmington, USA) and a dual-channel temperature controller (model 332 by LakeShore, Westerville, USA) at temperatures between 3.5–300 K.

2.5. Conductivity measurements

The electrical measurements were also performed with the self-built susceptometer. A Keithley Source-Meter 2400 (Cleveland, USA) was available as the current source. The differential voltage drop between signal-high and signal-low was recorded with a Keithley 2182 Nano-Voltmeter and used to calculate the sample resistance in one direction according to Ohm’s law and the specific resistance according to the van der Pauw approximation. For the measurements cold-pressed (5 kN) pellets of respective samples (diameter, 4.0 mm; thickness, 0.4–0.9 mm) were produced. Applying the four-probe method, the pellet was contacted with four equidistant probes using silver-conducting paint. All preparations were performed under an inert atmosphere in a glovebox.

3. Results and discussion

As-prepared, O2-annealed and H2-annealed polycrystalline FeTe_{1−y}Se_y and Fe_{1.1}Te_{1−y}Se_y samples were characterized by powder XRD and Rietveld refinements (figure 1). An impurity of FeTe_2 (≤12%) occurs in all FeTe_{1−y}Se_y samples, except in as-prepared Fe_{1.1}Te_{1−y}Se_y. Comparing as-prepared

Figure 1. XRD patterns of Fe_{1+y}Te_{0.9}Se_y as-prepared, O2-annealed, and H2-annealed.
with O2- and H2-annealed samples reveals minor changing XRD intensity ratios along with an increase (FeTe1−ySey) or evolution (Fe1.1Te1−ySey, y = 0.1, 0.2) of FeTe2 (asterisks, figure 1). Crystallographic details are given in table SI1.

The lattice parameters a decrease slightly by 0.4% with increasing Se content, while c decrease more strongly by 2.7%, as expected, due to the smaller radius of Se compared to Te. After annealing, only small changes not exceeding 0.1% were found (figure 2).

Small changes of interstitial iron amounts are unreliably detectable by XRD because of very weak scattering of the only ≈10% Fe2 occupied 2c site (figure SI1). It is furthermore likely that the oxygen treatment proceeds from the surface, leading to inhomogeneous particles [16]. However, the structural data from the Rietveld refinements agree with those obtained by single-crystal methods (d(Fe1-Se) ≈ 240 pm; d(Fe1-Te) ≈ 260 pm; chalcogen heights: hSe ≈ 150 pm; hTe ≈ 170 pm) [30].

The compositions were determined by careful EDX analysis. Iron contents in table 1 are relative to the sums of Te and Se. All ratios Te: Se agree well with the nominal composition and are constrained to 1. The iron contents of the O2-annealed samples are slightly reduced, while selenium and tellurium contents are unaffected. Most significant is the large amount of 20–30% oxygen in all phases after O2 annealing. This indicates oxide species at the surfaces of the particles. If these species are at least partially iron oxides, the iron content inside the O2-annealed particles is even lower than given in table 1, because EDX cannot discriminate iron in the surface oxide and in Fe1+xTe1−xSey. Hence, the quantity of actually extracted Fe upon O2 annealing might be higher than detected by EDX.

Forcing the reaction in a continuous oxygen flow for 2 h at 300 °C instead of static O2 pressure in sealed ampoules partly decomposes FeTe1−ySey to impurity phases, among them FeTe2 and iron oxides discernible in powder XRD. This agrees with the recent results by Sun et al, who over-annealed single crystals of Fe1+xTe0.6Se0.4 at 400 °C [26].

### Table 1. Sample compositions from EDX analysis.

| Nominal   | as-prepared      | O2-annealed      |
|-----------|------------------|------------------|
| Fe1.00Te0.90Se0.10 | Fe1.00Te0.90Se0.10(O0.00) | Fe1.00Te0.90Se0.10(O0.24) |
| Fe1.00Te0.80Se0.20 | Fe1.00Te0.80Se1.00(O1.00) | Fe1.00Te0.80Se0.00(O0.00) |
| Fe1.00Te0.90Se0.10 | Fe1.00Te0.90Se0.10(O0.00) | Fe1.00Te0.90Se0.10(O0.00) |
| Fe1.00Te0.80Se0.20 | Fe1.00Te0.80Se1.00(O1.00) | Fe1.00Te0.80Se0.00(O0.00) |
| Fe1.00Te0.90Se0.10 | Fe1.00Te0.90Se0.10(O0.00) | Fe1.00Te0.90Se0.10(O0.00) |
| Fe1.00Te0.80Se0.20 | Fe1.00Te0.80Se1.00(O1.00) | Fe1.00Te0.80Se0.00(O0.00) |
| Fe1.00Te0.90Se0.10 | Fe1.00Te0.90Se0.10(O0.00) | Fe1.00Te0.90Se0.10(O0.00) |

Figure 2. Lattice parameters of Fe1+xTe1−xSey (x = 0, 0.1, y = 0.1–0.4).

Figure 3. A.c magnetic susceptibilities of (a) FeTe1−ySey after O2 and H2 annealing (inset: as-prepared, and Ar-annealed); (b) Fe1.1Te1−ySey as-prepared and after O2 annealing.
As-prepared O\textsubscript{2}-, H\textsubscript{2}- and Ar-annealed samples of Fe\textsubscript{Te\textsubscript{1−y}Se\textsubscript{y}} are superconducting with \(T\textsubscript{c}\) up to 14 K, according to ac-susceptibility data shown in figure 3(a). In contrast, as-prepared Fe\textsubscript{1.1}Te\textsubscript{1−y}Se\textsubscript{y} samples are not superconducting and convert to superconductors only after O\textsubscript{2} annealing (figure 3(b)). Oxygen treatments significantly shift the superconducting transitions to lower selenium concentrations. As-prepared FeTe\textsubscript{0.9}Se\textsubscript{0.1} is not superconducting until O\textsubscript{2} annealing induces a \(T\textsubscript{c}\) of 12 K.

Electrical transport data are in line with these findings. The resistivity of as-prepared, O\textsubscript{2}-annealed and H\textsubscript{2}-post-annealed FeTe\textsubscript{0.8}Se\textsubscript{0.2} drops to zero at 14 K (figure 4). On the contrary, Fe\textsubscript{1.1}Te\textsubscript{0.8}Se\textsubscript{0.2} is only superconducting after O\textsubscript{2} treatment (insert in figure 4). The oxygen treatment strongly affects the high-field dc magnetization. The magnetic moment (\(\mu/\mu\text{B}\)) of as-prepared superconducting FeTe\textsubscript{0.8}Se\textsubscript{0.2} is weak and increases linearly, while a clear S-shaped ferromagnetic background occurs after O\textsubscript{2} annealing (insert in figure 5). This effect is even stronger at 1.8 K, where we find the superposition of a ferromagnetic hysteresis with the magnetization of a type II superconductor (figure 5). The magnetization at 1.8 K at highest external field remains very weak (\(\leq 0.05 \mu\text{B}\)), which means that the ferromagnetism is not a bulk property but caused by a magnetic impurity phase.

From our data we estimate that already 0.5% Fe\textsubscript{2}O\textsubscript{4} (\(T\textsubscript{c}=858\text{ K}, \mu=4.1 \mu\text{B}\)) or 0.8% Fe\textsubscript{2}O\textsubscript{3} (\(T\textsubscript{c}=948\text{ K}, \mu=2.5 \mu\text{B}\)) would produce these magnetizations [31]. Such tiny amounts are certainly undetectable by XRD, which strongly supports the idea that O\textsubscript{2} annealing extracts iron from the Fe\textsubscript{1.1}Te\textsubscript{0.8}Se\textsubscript{0.2} compounds and forms iron oxides that probably reside at the surface of the particles.

H\textsubscript{2} annealing affects the magnetic measurements only slightly. H\textsubscript{2} could partly reduce formed Fe\textsubscript{2}O\textsubscript{4} or Fe\textsubscript{2}O\textsubscript{3} to ferromagnetic Fe and H\textsubscript{2}O. Hence, the magnetic component might change from iron oxide to Fe upon H\textsubscript{2} annealing, resulting in slightly differing values of the magnetic measurements of O\textsubscript{2}- compared to H\textsubscript{2}-annealed samples as a consequence of the different magnetic moments of iron oxide and Fe, respectively. The emerging ferromagnetic contribution is furthermore clearly visible in magnetic susceptibility measurements measured under zero-field cooled (zfc) and field-cooled (fc) conditions, depicted in figure 6. After annealing the curves are significantly shifted to positive susceptibilities.

4. Conclusion

By combining all findings we conclude that oxygen treatment at 300 °C improves the superconducting properties of polycrystalline Fe\textsubscript{1.1}Te\textsubscript{1−y}Se\textsubscript{y} through irreversible oxidative de-intercalation of interstitial iron atoms. Traces of magnetic iron oxides are formed. The heterogeneous reaction begins at the surface and probably causes inhomogeneous particles accompanied by FeTe\textsubscript{2} impurity formation. Thus the
anti-PbO-type phase obviously rather degrades if iron is extracted from the layers of Fe(Te_{1−y}Se_y)_{4/4} tetrahedra, in contrast to the formation of iron-deficient layers in K_{1−x}Fe_{2−y}Se_{2} [32, 33] or in Na_{1−x}Fe_{2−y}As_{2} by sodium de-intercalation of NaFeAs at comparable mild reaction conditions [34].

Supporting information

Interstitial iron content of Fe_{1+x}Te_{1−y}Se_y from Rietveld refinements; Refined structural parameters, exemplarily for FeTe_{0.9}Se_{0.1}.

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