Composition and annealing effects on superconductivity in sintered and arc-melted Fe$_{1+\varepsilon}$Te$_{0.5}$Se$_{0.5}$

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Abstract. We present the results of x-ray diffraction, electrical resistivity, and ac magnetic susceptibility measurements on specimens of the “11”-structure superconductor Fe$_{1+\varepsilon}$Te$_{0.5}$Se$_{0.5}$ (0 ≤ $\varepsilon$ ≤ 0.15). Samples were initially either sintered in sealed quartz tubes or melted in a zirconium-gettered arc furnace. Sintered samples were fired two to three times at temperatures of 425°C, 600°C, or 675°C, while arc-melted samples were studied both as-melted and after annealing at 650°C. X-ray diffraction data show a predominant PbO-type tetragonal phase, with a secondary hexagonal NiAs-type phase; for sintered specimens annealed at 600°C, the secondary phase decreases as $\varepsilon$ increases over the range 0 ≤ $\varepsilon$ ≤ 0.10, with the composition Fe$_{1.10}$Te$_{0.5}$Se$_{0.5}$ exhibiting x-ray phase purity. A higher annealing temperature of 675°C provided such tetragonal phase purity at the composition Fe$_{1.05}$Te$_{0.5}$Se$_{0.5}$. The resistive superconducting transition temperature $T_c$ was nearly independent of the iron concentration 1+$\varepsilon$, suggesting a single superconducting phase, while the magnetic screening fraction varied greatly with concentration and conditions, peaking at $\varepsilon = 0.07$, indicating that the amount of superconducting phase is strongly dependent on conditions. We propose that the behaviour can also be viewed in terms of an electron-doped, chalcogen-deficient stoichiometry.

1. Introduction

After the discovery of superconductivity in the simplest iron-based superconducting “11” structure, FeSe with $T_c \approx 8$ K [1], intense research on this and similar materials revealed a wealth of discoveries: the increase of $T_c$ in single-layer films to 65 K [2]; extremely large increases of $T_c$ with pressure [3]; and, recently, the substitution of other chalcogens for Se, namely S and Te [4,5], with an increase of the bulk $T_c$ of from 8 K in FeSe to 14 K in FeTe$_{0.5}$Se$_{0.5}$. Bulk FeTe is antiferromagnetic; the isostructural (no anion doping) Te-for-Se substitution results is the spectrum of behaviour from antiferromagnet to superconductor, presumably by shifts in electronic structure; a thorough review of electronic structure, transport, tunnelling, pressure dependence, and nuclear magnetic resonance recently appeared [6]. Detailed chalcogen substitutions in the Fe(Te,Se) system have revealed, for example, that an optimal $T_c$ occurs for Fe(Te,Se) near the midway composition Fe$_{0.5}$Te$_{0.5}$Se$_{0.5}$.

Early studies of antiferromagnetic FeTe [7] indicate that the “FeTe” structure is actually two structures, with a PbO-type tetragonal phase stable for iron-rich stoichiometries near Fe$_{1.1}$Te while an NiAs hexagonal structure is more stable near or just below Fe$_{1.0}$Te; annealing-temperature and quenching conditions also played a role in the composition dependence of the phases. More recent studies of the Fe(Te,Se) system [4,5] show a similar complex behaviour: some studies have concluded that such “excess” Fe can promote the purity of the tetragonal phase, while hindering bulk superconductivity [8]; others that oxygen annealing may help [9]. The recent studies suggest that phase evolution is most sensitive to the temperature of anneals and to other details affecting the
diffusion of ions, but all suggest a complex interplay of phase purity, stability, and superconductivity. In many superconducting systems, a nearby instability plays an important role.

In this study, we examined the dependence of the structural and superconducting properties of the “11”-structure materials as a function of iron composition, for a series of specimens of composition $\text{Fe}_{1+\varepsilon}\text{Te}_{0.50}\text{Se}_{0.50}$, $0 \leq \varepsilon \leq 0.15$. We also examine the route by which this achieved, including sintering in sealed quartz ampoules, annealing at higher temperatures, arc-melting, and arc-melting with post-annealing. We find that while the resistive $T_c \approx 14$ K varies only weakly across these compositions, indicating no appreciable electronic or doping changes in the superconducting phase, we do find strong variations in the magnetic superconducting screening fraction; thus, the amount of superconductivity varies noticeably, with volume fractions greater than 50% observed only for very particular conditions.

2. Experimental
For sintered samples, high-purity Fe (99.9%), Te (99.999%), and FeSe (99.9%) (Alfa-Aesar) in stoichiometric ratios were weighed and thoroughly ground in an argon-atmosphere glove box using an agate mortar and pestle, and then pressed into pellets. First, a “survey” series of $\text{Fe}_{1+\varepsilon}\text{Te}_{0.50}\text{Se}_{0.50}$ with $\varepsilon = 0.00, 0.05, 0.10, 0.15$ were sealed in quartz ampoules and fired at 425°C (below the melting point of Te) for 24 hours to react the tellurium, then fired again at 600°C for 24 hours. The samples were reground, pressed, and fired again at 600°C for another 24 hours. A portion of these specimens (labelled “A” below) were then reground, pressed, and annealed again, at 675°C. After structural and superconducting analyses, it was determined that the best structural and superconducting properties occurs in the range $\varepsilon = 0.05-0.10$; thus, a second detailed series of specimens was synthesized for $\varepsilon = 0.06, 0.07, 0.08, 0.09$. The final specimens were dense polycrystalline specimens, approximately 90% of their x-ray density.

Arc-melted samples were synthesized from the same high-purity starting materials. For this technique, often a small percentage of the volatile Te is lost, evaporated onto the arc chamber interior. By weighing the sample before and after the melt, the amount lost, attributed to the most volatile component, tellurium (or, in previous studies, sulphur), could be determined. With extensive experience synthesizing FeTe and Fe(Se,S) compounds this way, a reproducible technique was developed: first, the starting materials were layered onto the copper hearth in the same order as their melting points: Te powder on the bottom, FeSe powder next, and Fe powder on top. Then the arc flame was only brought near (~ 2 mm) but not touching, melting the Te gently and dissolving the FeSe and Fe in it. The ingot was turned and melted indirectly again, and then turned twice more, heated directly each time. The final ingots were shiny metallic with very high density, essentially 100% of their x-ray density. The tellurium loss was always about 2.0±0.5% using these techniques. Thus adjusted starting compositions of $\text{Fe}_{1+\varepsilon}\text{Te}_{0.54}\text{Se}_{0.50}$ (2% excess Te) were used, resulting in nearly $\text{Fe}_{1+\varepsilon}\text{Te}_{0.50}\text{Se}_{0.50}$ final compositions. Specimens with $\varepsilon = 0.01, 0.08, 0.10$ were prepared by arc-melting and studied.

X-ray measurements were performed on a Philips XPERT diffractometer using Cu K$_\alpha$ radiation. Four-wire resistivity data and ac susceptibility (17 Hz, milligauss) data were obtained on ~1x1x4 mm$^3$ specimens using either a Stanford Research Systems SIM921 ac resistance bridge or a Linear Research LR-400 ac resistance/mutual inductance bridge, calibrated with an identically-sized lead (Pb) standard.

3. Results
Typical x-ray diffraction data for the sintered samples are shown in Fig. 1. All specimens show the dominant tetragonal Pb-O structure phase with a nearly constant tetragonal c-axis lattice constant $c = 0.6010\pm0.0008$ nm, and an a-axis lattice constant that increases from $a = 0.3785\pm0.0005$ nm to $a = 0.3803\pm0.0005$ nm as the Fe concentration in excess of unity, $\varepsilon$, increases from 0.00 to 0.10, in agreement with previous studies of $\varepsilon = 0.02$ [4] and 0.10 [5] samples. The peak just below 20 = 32° is the dominant (101) reflection of the hexagonal NiAs impurity phase. As is evident, for samples with $\varepsilon = 0.00-0.10$ and final firings at 600°C, the impurity phase is largest at $\varepsilon = 0.00$, and tends to decrease with increasing Fe concentration; the $\varepsilon = 0.10$ samples appears to be phase-pure. The $\varepsilon = 0.05$ sample that was re-annealed at 675°C shows that the NiAs impurity can also be eliminated with annealing.

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Figure 1. X-ray intensity as a function of angle $2\theta$ in a $0-2\theta$ scan for sintered Fe$_{1+\varepsilon}$Te$_{0.50}$Se$_{0.50}$ powders.

Figure 2 shows resistivity data as a function of temperature for the sintered samples. In the inset, arc-melted data shows the behaviour typical at high temperatures for all samples; as observed previously [4], beginning at room temperature, the resistivity of Fe$_{1+\varepsilon}$Te$_{0.50}$Se$_{0.50}$ slightly increases with decreasing temperature down to about 125–150 K, then decreases until the transition onset $T_c \approx 14$ K. Perhaps coincidentally, the antiferromagnetic transition in the parent alloy FeTe occurs at 130 K. For each curve, the temperatures at which the resistance reaches 90%, 50%, and 10% of the extrapolated normal state values were determined; the 10%–90% range defines the transition width $\Delta T_c$. These values are shown in Fig. 3. The most striking observation from the resistivity data is that $T_c$ does not vary appreciably. This is most likely an indication that the iron concentration is not directly changing the carrier density or other gross electronic properties of the superconducting phase; whatever that phase is, and however much of it is present, the resistive superconductivity measurements short the sample at essentially the same temperature for all $\varepsilon$. For the 675°C-annealed specimens (labelled “A”), even though their tetragonal phase purity was greater, it is obvious that annealing has broadened the superconducting transition, possibly due to non-optimal annealed chalcogen site occupancy.

Figure 2. Electrical resistivity $R$ as a function of temperature $T$ over the range 5–20 K for Fe$_{1+\varepsilon}$Te$_{0.50}$Se$_{0.50}$ ($\varepsilon=0.00$–0.15) sintered samples. $T_c$ remains relatively constant. Inset: $R$ vs. $T$ for $T = 0$–300 K for an arc-melted sample; such behaviour was typical of almost all sintered and arc-melted samples.
Figure 3. Temperatures at 90%, 50%, and 10% of the resistive superconducting transitions for sintered specimens of Fe$_{1+\varepsilon}$Te$_{0.50}$Se$_{0.50}$ annealed at 600°C (open symbols) or 675°C (solid symbols, A).

Quite different insight into the story of the “11” materials is provided by the ac magnetic susceptibility data shown in Fig. 4, as a function of temperature near the transition. While the resistivity showed little variation, large changes in the magnetic screening signal are evident. Perhaps similar to the resistivity, the magnetic onset temperature predominantly remains near 14 K; however, the screening fraction varies with Fe concentration and annealing temperature. The screening fraction at $T = 4.2$ K is shown in Fig. 5, for the first survey series (every $\Delta\varepsilon = 0.05$) in the left panel, and the second series, focusing on the central region with $\Delta\varepsilon = 0.01$, in the right. Evidently, for these synthesis conditions, a very large volume fraction is obtained for $\varepsilon = 0.07$.

Figure 4. Magnetic susceptibility data vs. temperature for sintered Fe$_{1+\varepsilon}$Te$_{0.50}$Se$_{0.50}$ ($0 \leq \varepsilon \leq 0.15$).

Figure 5. Superconducting screening fraction for a first ($\Delta\varepsilon = 0.05$) and a second ($\Delta\varepsilon = 0.01$) series of sintered Fe$_{1+\varepsilon}$Te$_{0.50}$Se$_{0.50}$ samples.
For the arc-melted samples, x-ray data are shown in Fig. 6, resistivity data in Fig. 7, and ac magnetic susceptibility data in Fig. 8. Compared to the sintered data, the rapid-quench conditions shift the apparent Fe ε-dependence significantly. However, the sharpest, large magnetic superconducting transition to date was observed with this method (Fig. 8); the diamagnetic drop represents an ~65% screening volume fraction. The nominal ε ~ 0.01 sample also exhibits a large, positive normal-state susceptibility, attributable to a small ferromagnetic (Fe) impurity. Note that evaporation in arc-melted samples results in somewhat uncertain concentrations (as discussed above, the quoted compositions assume all loss was Te). The lattice constants for the nominal ε ~ 0.01 arc-melted sample are \( a = 0.3800\pm0.0005 \) nm and \( c = 0.602\pm0.001 \) nm, similar to the \( \varepsilon = 0.07 \) sintered sample. We point out that that the rapid quench, in addition to promoting some impurity phases, results in some disorder, typically chalcogen vacancies, similar to behaviour in rapid-cooled oxygen-deficient copper oxides.

**Figure 6.** X-ray intensity as a function of angle 2θ in θ-2θ scans for various arc-melted \( \text{Fe}_{1+\varepsilon}\text{Te}_{0.50}\text{Se}_{0.50} \).

**Figure 7.** Electrical resistivity as a function of temperature \( T \) over the range 5–35 K for arc-melted \( \text{Fe}_{1+\varepsilon}\text{Te}_{0.50}\text{Se}_{0.50} \).

**Figure 8.** Magnetic susceptibility data as a function of temperature for arc-melted \( \text{Fe}_{1+\varepsilon}\text{Te}_{0.50}\text{Se}_{0.50} \).
4. Discussion and Summary

The data for sintered samples indicate that the best superconducting volume fractions occur for samples near \( \varepsilon = 0.07 \), and that the \( a \)-axis lattice constant increases with increasing Fe concentration. We find that for our conditions, stabilizing the purest, tetragonal PbO-structure phase does not coincide with the best superconducting fraction; instead, superconductivity may best occur with some defect, or other instability, nearby. We have, following the literature, written these stoichiometries as \( \text{Fe}_{1+\varepsilon}\text{Te}_{0.50}\text{Se}_{0.50} \); indeed, even the earliest literature \cite{Shunk1974} suggests the similar FeTe ‘‘11’’ structure actually has stoichiometry \( \sim \text{Fe}_{1.1}\text{Te} \), also previously written \( \text{Fe}_{9}\text{Te}_{8} \), suggesting a line compound. We suggest that all these results are consistent with a picture of chalcogen vacancies, and could be written \( \text{Fe}_{1.00}(\text{Te}_{0.50}\text{Se}_{0.50})_{1-\varepsilon} \), where we have used \( (1+\varepsilon)^{-1} \approx 1-\varepsilon \). A chalcogen vacancy is, effectively, an electron donor (each anion would have accommodated two extra electrons; each vacancy thus dopes two electrons). Similar oxygen vacancy doping is common in the electron-doped copper oxides \cite{Markert1996}, where interstitial oxygen also sometimes plays a role. The increase in the \( a \)-axis lattice constant is in accord with this view, as each doped electron expands the planes, relieving bond tension; this is the primary difference between \( T \)-phase (hole) and \( T' \)-phase (electron) \( 2\text{-}1\text{-}4 \) copper oxides. Such doping behaviour contributes to the bond corrugation effects in Fe(Te,Se) reviewed previously \cite{Mizuguchi2010}. The superconducting properties in the arc-melted samples, at shifted \( \varepsilon \) compared to the sintered samples, likely indicate that the anion vacancy concentration increases with rapid quenching, or perhaps that quenching promotes both iron and chalcogen vacancies.

In summary, we have synthesized nominal \( \text{Fe}_{1+\varepsilon}\text{Te}_{0.50}\text{Se}_{0.50} \) \( (0.00 \leq \varepsilon \leq 0.15) \) samples by sintering and by arc-melting, and have found that low normal-state resistivity \( (< 1 \text{ m}\Omega\text{-cm}) \) and high superconducting volume fraction specimens with \( T_c \approx 14 \text{ K} \) can be obtained with both methods. Optimal behaviour was found around \( \varepsilon \approx 0.07 \) for the sintered samples, as well as for the arc-melted sample with lattice constants most similar to those of the \( \varepsilon \approx 0.07 \) sintered sample. Viewed instead as a possible chalcogen-deficient structure, our data suggests that the larger superconducting volume fractions are associated with larger \( a \)-axis lattice-constant structures, which could occur when a chalcogen vacancy acts as an electron donor. We observe no supercell reflections in our x-ray data; further work may determine whether ordered vacancy structures occur or can be synthesized, and neutron diffraction experiments are encouraged that could determine chalcogen site occupancy.

Acknowledgments

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5. References

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