Influence of substitution, nonstoichiometry and annealing-conditions on superconductivity and normal conductivity of Fe$_{1+\delta}$(Te$_{1-x}$X$_x$) (X=Se, S)

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Abstract. Thermal evolution of resistivity, $\rho(T,x)$, of as-prepared samples of Fe$_{1+\delta}$Te$_{1-x}$S$_x$ ($\delta \approx 0$, $x \leq 0.2$ = solubility limit) demonstrate a granular log-in-$T$ character within $T_s < T < 300K$, a Kondo-like resistive contribution within $T_c < T < T_s$ and granular superconductivity at low temperature ($T_c =$ structural transition point of Fe$_{1+\delta}$Te, $T_s =$superconducting transition point). We attribute the log-in-$T$ character as well as the nonbulk superconducting features of as-prepared samples to their granular superconductor nature. Annealing in oxygen removes Kondo-like contribution, annihilates pair-breaking centres and establishes bulk superconductivity but, in contrast, the high-temperature granular log-in-$T$ character is hardly influenced. This analysis was successfully extended to the isomorphous Fe$_{1+\delta}$Te$_{1-x}$Se$_x$ as well as to other types of post-synthesis sample-treatment (e.g. annealing in different gas ambient or soaking in particular liquids).

1. Introduction

Extensive studies on the normal and superconducting phase diagrams of Fe$_{1+\delta}$(Te$_{1-x}$X$_x$) (X=Se, S) [see e.g. Refs.[1, 2] and references therein] established that (i) Fe$_{1+\delta}$Te is an antiferromagnetic nonsuperconducting metal, (ii) Fe$_{1+\delta}$Se is a nonmagnetic superconductor and (iii) for Fe$_{1+\delta}$(Te$_{1-x}$X$_x$) ($0.05 < x <$solubility limit), an increase in $x$ leads to a quench of magnetism, a surge of superconductivity and an enhancement of normal-state conductivity. Two additional factors are also influential in shaping the phase diagram of Fe$_{1+\delta}$(Te$_{1-x}$X$_x$): sample nonstoichiometry [3, 4, 5, 6, 7] and sample treatment whether annealing in suitable gas or vapor (such as O, Te, Se, S, and I) or soaking in liquid (such as beverage or nitric acid) [1, 2].

Among these various treatment processes, annealing in oxygen is quite remarkable: While it has weak (negative, poisonous) influence on Fe$_{1+\delta}$Te (Fe$_{1+\delta}$Se [Ref.[3]]), it enhances tremendously both the superconductivity and low-$T$ normal-state conductivity of Fe$_{1+\delta}$(Te$_{1-x}$X$_x$) $x > 0.05$ [8, 9, 10, 11]. The mechanism behind this O-annealing-induced influence is controversial but there is a general inclination towards attributing it to the following process: diffused oxygen “removes” interstitial Fe which manifests $\sim 2.5 \mu_B$ [4, 6, 12, 13, 14, 15, 5, 7]. However, $^{57}$Fe Mössbauer studies on Fe$_{1+\delta}$(Te$_{1-x}$X$_x$) revealed only one asymmetric doublet indicative of nonmagnetic Fe$^{2+}$-like site and, moreover, their spectra before and after annealing...
are almost identical [16, 3, 17, 18, 19, 20]. Within the Mössbauer frequency window, this excludes all types of interstitial Fe states and, as well, any pair-breaking Fe moment; as such the influence of O-annealing cannot be due to a "removal" of such inexistent Fe species. Nevertheless, experiments did reveal a magnetic pair-breaking agent which is removed by optimized annealing or soaking and, as a consequence, superconductivity is established, normal-state conductivity is enhanced and localization effects [4, 21, 22] are removed. It is worth adding that the process of loading and unloading oxygen and its influence on, say, the superconducting properties is reversible [8].

This work proposes that, for Fe\(_{1+\delta}(Te_{1-x}X_x)_{1-y}\), \(\delta \approx 0\), some compensating defect such as chalcogen vacancies (instead of additional interstitial Fe species) are created and that they are nonuniformly distributed within nano-sized stoichiometric metallic/superconducting granules; these granules are separated from each other by nonstoichiometric, less conducting and nonsuperconducting batches. This constitutes a granular metallic/superconducting system. According to this scenario, normal-state conductivity of Fe\(_{1+\delta}(Te_{1-x}X_x)_{1-y}\) should exhibit a granular log-in-\(T\) character while its superconducting properties would be tuned by Josephson coupling of the superconducting granules [23, 24]. Furthermore, we attribute the observed magnetic moments to a trapping of odd electronic spins into the vacancies (reminiscent of paramagnetic color-centres); these paramagnetic scattering centers are considered to give rise to Kondo-like contribution within the normal-state phase and to Abrikosov-Gorkov pair-breaking effects within the superconducting phase. Optimized annealing (soaking) in favorable ambient causes a removal of these vacancies leading to a disappearance of Kondo-type localization effects, enhancement of normal-state conductivity, removal of magnetic pair-breaking centres and establishment of bulk superconductivity.

With the objective of demonstrating the validity of these arguments, we studied the normal and superconducting properties of various as-prepared and oxygen-annealed Fe\(_{1+\delta}Te_{1-x}S_x\) samples. We show that while both as-prepared and O-annealed samples exhibit a similar characteristic log-in-\(T\) granular character at higher temperatures, their low-\(T\)\(< T_S\) conductivities are distinctly different. We show that these same features are valid for isomorphous Fe\(_{1+\delta}Te_{1-x}Se_x\) system.

2. Experimental
The procedures used for samples preparation, heat-treatment, as well as structural, resistivity and magnetization characterizations are given in the supplementary materials. Also given in the supplementary materials are the X-ray diffractograms of the studied as-prepared and O-annealed samples.

3. Results and analysis
Figure 1 shows \(\rho(T, x)\) curves of as-prepared and O-annealed Fe\(_{1+\delta}Te_{1-x}S_x\) \((x=0, 0.05, 0.1, 0.15, 0.2)\). These are similar to the reported data of, e.g., Refs [8, 25, 26, 27, 28, 29]. Three main temperature ranges can be identified. Below, the evolution of \(\rho(T, x)\) within each regime will be analyzed and discussed in terms of the scenario of granularity. We also discuss how granular normal conductivity and superconductivity are being influenced by O-annealing.

3.1. \(T_s \prec T < 300 K\) regime
Figure 1 indicates that, within \(T_s \prec T < 300K\), \(\frac{\partial \rho}{\partial T} < 0\) for all \(x\) as well as for both as-prepared and O-annealed samples. This evolution is not due to intrinsic semiconducting feature [30]; rather it is taken as a manifestation of granularity wherein metallic/superconducting granules are embedded within a less conducting nonsuperconducting matrix [23, 24]. As mentioned above the distribution of conductance is taken to be stemming from nonuniform distribution.
Figure 1. $\rho(T,x)$ curves of as-prepared (blue squares) and annealed (green triangles) Fe$_{1+\delta}$Te$_{1-x}$S$_x$ samples. (a-d) $\rho(T,x)$ curves. Solid red lines are fit to Eq.(1); (f-j) normalized $\rho(T,x)/\rho(300K,x)$ curves showing the similarity of curves within the $T_s < T < 300K$ regime. The semilog normalized differences are shown as crosses within inset of (g-j): Solid red lines are fit to Eq.(2).

Figure 2. (a-c) Parameters obtained from the fit of Eq.(1) to $\rho(T,x)$ curves of as-prepared (blue squares) and O-annealed (green triangles) Fe$_{1+\delta}$Te$_{1-x}$S$_x$ samples: (a) $g(x)$; (b) $\rho_o(x)$; (c) $T_{cb}(x)$. (d-f) Parameters of the fit of Eq.(2) to normalized differences of the insets of Fig.1. (d) $T_K(x)$; (e) $|F|\rho_oK$; (f) $\rho_oK(x)$ which, in contrast to that of panel (b), is the sum of all non-Kondo-type contributions that are different among the two normalized curves. Dashed lines are guides to the eye.

of nonstoichiometry [31] and defects. The thermal evolution of the resistivity within this range follows the characteristic granular log-in-$T$ behavior [24]:

$$\rho(T) = \frac{\rho_o}{1 - \frac{1}{\eta g} \ln\left(\frac{300K}{T_s}\right)}$$

(1)
Figure 3. Normalized semilog plots of $\rho(T,x)/\rho(300K,x)$ curves of as-prepared (squares) and annealed (triangle) $Fe_{1+\delta}Te_{1-x}Se_x$ samples as reported in Ref. [6]. Solid red lines are fit to Eq.(1): the obtained parameters and their evolutions are similar to those of Fig.2(a-c). The normalized low-$T$ semi-log plots of differences are shown as crosses in Figs.(d...h.2). Solid red lines are fit to Eq.(2): the parameters of the fits are shown in (i) $F,\rho_o,K$ and (j) $\rho_o,K$. $T_K$ increases with $x$.

wherein $g$ is a tunneling conductance, $T_{cb}$ is a measure of the effective Coulomb blocking temperature which can be determined from the measured $\rho(T)$ curves and $\rho_0$ is the resistivity at $T_{cb}$. Applying this granular scenario to the high-$T$ resistivity of FeSe [32, 33], we identified its $T_{cb}$ to be 580 K while 350 K is a point of crossover from a log-in-$T$ behavior into a homogeneously disordered granular metallic state. Since we were unsuccessful in experimentally determining $T_{cb}$ of $Fe_{1+\delta}Te_{1-x}S_x$ during our present work, then setting $T_{cb}(x)=350K$ amounts to assigning $T_{cb}(x)$ to some possible value and as such ensures a minimum number of parameters when fitting Eq.1 to $\rho(T,x)$ curves of Fig.1. The obtained fit parameters are shown in Fig.2.

The evolution of both $g(x)$ and $\rho_0(x)$ reflects a weak dependence on $x$ as well as a similarity between the high-$T$ curves of as-prepared and annealed samples: exception is $Fe_{1+\delta}Te$ samples [compare the pair of curves in Fig.1(a) and Fig.1(f)] wherein there is a slight O-anneal-induced change in $g$ and $\rho_0$ but no drastic change in $T_s$ or magnetic contribution to resistivity. It is concluded that granular log-in-$T$ behavior in $Fe_{1+\delta}Te_{1-x}S_x$ is manifested for all $x$ as well as for both the as-prepared and O-annealed samples (below, similar conclusions are valid for $Fe_{1+\delta}Te_{1-x}Se_x$).

3.2. $T_c < T < T_s$ regime

On approaching $T^*_c$, $\rho(T,x)$ of all samples start to deviate downwards away from the granular log-in-$T$ behavior; the extent of deviation depends on $x$ and the annealing conditions. For both as-prepared and annealed $Fe_{1+\delta}Te$, $\rho(T,x=0)$ drops sharply at $T_s$ [1, 2]. Well below $T_s$, $\rho(T < T_s,x=0)$ is mostly governed by magnon scattering process which, at lower temperatures, is dominated by a quadratic-in-$T$ behavior. In contrast, for sulfur doped samples, $\rho(T,x)$ evolves differently: First, there is no sharp drop in $\rho(T,x)$ that can be identified as an onset of structural transformation (most evident at $x<0.05$) [31]. However, one observes a change of slope in the as-prepared $\rho(T,x)$ curves around 60~100K (around $T_s$ of $Fe_{1+\delta}Te$). Most remarkably, a coherent peak is manifested in $\rho(T,x)$ curves of annealed samples such that below that peak a metallic, $\partial \rho/\partial T > 0$, character is established. These features suggest an increase in conductance $g$ and this, in turn, is attributed to some short-ranged, on nano-sized level, structural modification (reminiscent
of the case of Fe$_{1+x}$Te) which is hard to detect by conventional structural techniques.

The most important difference among $\rho(T_c < T < T_s, x)$ curves of as-prepared and annealed samples is the additional resistive contribution shown in insets of Figs.2(g-j): This contribution is evaluated as the difference $\Delta \rho_K = \left( \frac{\rho_{\text{asp}}(T,x)}{\rho_{\text{asp}}(300K,x)} - \frac{\rho_{\text{ann}}(T,x)}{\rho_{\text{ann}}(300K,x)} \right)$: these exclude any possible errors in estimating sample geometrical dimensions. Based on insets of Figs.2(g-j), $\Delta \rho_K$ is analyzed in terms of

$$\Delta \rho_K = \rho_{o,K} \left( 1 + F \ln(\frac{T_K}{T}) \right)$$

(2)

where $F$ and $T_K$ are parameters of the contribution which is assumed to be Kondo-type rather than quantum-correction-type (such as Anderson-type or Altshuler-Aronov-type) since the latter is expected to be manifested at much lower temperatures than this range (extending to an upper limit of $\sim 70K$). As can be noticed from insets of Figs.1(g-j) and the fit parameters in Figs.2(d-f), both $F\rho_{o,K}$ and $T_K$ as well as the temperature range increase with $x$: further sulfur incorporation leads to an increase in the concentration of magnetic scatterer (the above-mentioned color-centre-type paramagnetic moments). Annealing in oxygen eliminates these centres and, as a consequence, removes $\Delta \rho_K$ contribution.

3.3. 2 $K<T<T_c$ regime

Figure 1 indicates that, with the exception of Fe$_{1+x}$Te, all studied as-prepared samples exhibit an onset of superconductivity at $T_{\text{onset}}^c \simeq 8-9$ K indicative of granular superconductivity with no long-range coherence. This $T_{\text{onset}}^c$ event becomes more sharper and well defined when $x$ is increased: $x \rightarrow 0.2$, $T_{\text{c,asp}}^c \rightarrow 6.8$ K and $T_{\text{c,ann}}^c \rightarrow 9.1$ K. On O-annealing, long-range coherence, and as such bulk SC, is established with $T_{\text{c,ann}}^c \approx 9.1$K, $T_{\text{c,Se}}^c \approx 8$K. The similarity and difference among the onset and zero-resistivity points are typical of granular superconductivity.

4. Discussion and Summary

Let us recall our starting assumption that all as-prepared Fe$_{1+x}$Te$_{1-x}$S$_x$, $x > 0.05$, samples are granular superconductors wherein substitution of Te by S leads to a creation of additional nonuniformly-distributed defects which strongly influence both the superconductivity and normal-state conductivity and, furthermore, that a reduction or a removal of these defects, by heat treatment or soaking in favorable ambient, enhances both superconductivity and normal-state conductivity. Based on this unified and consistent scenario, we explained various effects within both the normal and superconducting phases. Furthermore, this same scenario enables one to construct a generalized $x-T$ phase diagram of Fe$_{1+x}$Te$_{1-x}$S$_x$, not shown here, that clarifies how each state (namely antiferromagnetism, granularity with log-in-T, Kondo-like localization or superconductivity) evolves with concentration and annealing conditions. Indeed, such evolution can be seen in the various earlier reported diagrams [8, 10, 27, 26, 34] which indicate, just as mentioned above, that doping of sulfur destroys the magnetic and structural transition, introduces an additional low-T Kondo-like contribution and induces granular superconductivity; similarly, O-annealing maintains high-T granularity, establishes bulk SC and suppresses any low-T anomalous resistive contribution.

It is interesting to extend this granular scenario to analyze the extensively studied normal and superconducting phase diagram of isomorphous Fe$_{1+x}$Te$_{1-x}$Se$_x$ which manifest similar structural, magnetic and superconducting properties [6, 11, 13, 35, 36, 37, 38]. Similarities of superconductivity and normal conductivities are best illustrated in Fig.3 which shows $\rho(T, x)$ curves of as-prepared and O-annealed Fe$_{1+x}$Te$_{1-x}$Se$_x$ samples as reported by Sun et al. [6] As evident, $\rho(T, x)$ curves of as-prepared samples reveal the log-in-T granularity, Kondo-type contribution and granular superconductivity. In contrast, $\rho(T, x)$ of O-annealed samples exhibit the induced enhancement of both the superconductivity and normal-state conductivity.
We verified that these granular features are manifested in most reported data on Fe$_{1+y}$(Te$_{1-x}$X$_x$) (X = Se, S; see e.g. [4, 5, 6, 7, 12, 13, 14, 15]). We also verified that these features are manifested in polycrystalline [1, 2] as well as monocrystalline [see e.g. Refs. [4, 6, 12, 26, 39]] samples of these Fe$_{1+y}$(Te$_{1-x}$X$_x$) systems.

In summary, we showed that the model of (defective) granular superconductor is an adequate unifying scenario for explaining the normal-state and superconducting properties of Fe$_{1+y}$(Te$_{1-x}$X$_x$) systems. This is particularly valid for the followings: the log-in-$T$ granular character of both as-prepared and treated samples, the Kondo-like behavior and weak superconductivity of as-prepared samples, as well as the metallic character below a coherent peak and bulk superconductivity of treated samples. It would be an interesting continuation of this work to investigate how applied pressure or intercalation of cations such as potassium would influence the granular character of both the superconducting and normal-state properties of these Fe$_{1+y}$(Te$_{1-x}$X$_x$) (X = Te, Se) systems.

Acknowledgments

We acknowledge partial financial support from CNPq and CAPES.

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