Disorder-driven electronic localization and phase separation in superconducting \( \text{Fe}_{1+y}\text{Te}_{0.5}\text{Se}_{0.5} \) single crystals

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We have investigated the influence of Fe-excess on the electrical transport and magnetism of \( \text{Fe}_{1+y}\text{Te}_{0.5}\text{Se}_{0.5} (y=0.04 \text{ and } 0.09) \) single crystals. Both compositions exhibit resistively determined superconducting transitions \( (T_c) \) up to 56 K promoting an intense search for novel Fe-based superconductors with similar crystal structure. Within a few months, several new superconducting phases were discovered. Among them, tetragonal FeSe has the nominally simplest crystal structure. It has no charge reservoir layer separating the Fe₃Se₂ layers and, hence, is considered as parent compound to all the Fe-based pnictide and chalcogenide superconductors. The superconducting transition temperature \( (T_c) \) is found to be extremely sensitive to the Fe:Se ratio, and the highest \( T_c \sim 8.5 \text{ K} \) at ambient pressure is observed when the compound is closest to the stoichiometric composition. By substituting Te for Se, \( T_c \) is enhanced to \( \sim 15 \text{ K} \) for about 50% Te doping. The end member \( \text{Fe}_{1+y}\text{Te} \) is non-superconducting and exhibits an incommensurate antiferromagnetic (AFM) order, coupled to a structural distortion near 67 K. The incommensurability \( \delta \) in \( \text{Fe}_{1+y}\text{Te} \) can be easily tuned by the value of \( y \), and the AFM order becomes commensurate for the samples close to the stoichiometric composition (i.e., \( y \sim 0 \)).

In mixed \( \text{Fe}_{1+y}\text{Te}_{1-x}\text{Se}_x \), the magnetic order is found to survive as short-range correlations for the samples with \( 0.25 \leq x \leq 0.49 \) even in the superconducting state. More recently, pressure-induced static magnetic order is observed in superconducting FeSe. Density functional theory (DFT) calculations on the stoichiometric end members FeSe and FeTe indicate Fermi surface (FS) structures very similar to those in Fe-pnictides, where a spin-density-wave (SDW) ground state is obtained due to FS nesting. In contrast to the DFT predictions, recent neutron diffraction studies demonstrate a composition-tunable \( (\delta \pi, \delta \pi) \) AFM order, which propagates along the diagonal direction of the Fe-square lattice in the ab-plane. This is unlike Fe-pnictides, where the propagation vector of the SDW-type AFM order is along the \((\pi, 0)\) edge of the Fe-square lattice. In fact, a SDW gap was not observed in \( \text{Fe}_{1+y}\text{Te} \) and FS nesting is not considered as the origin of magnetic order. Alternatively, a fluctuating-local-moment scenario has been invoked in order to explain the unusual magnetic properties of \( \text{Fe}_{1+y}\text{Te} \).

At this point, it is worthwhile to mention that the phase diagram of the Fe chalcogenides is extremely complex. In the case of FeSe, non-superconducting phases such as \( \text{Fe}_3\text{Se}_4 \) and \( \text{Fe}_7\text{Se}_8 \), and hexagonal FeSe form in close proximity in the temperature-composition phase diagram. Hence, the tetragonal superconducting phase might contain these secondary phases in small quantities. Further, the synthesis procedure is prone to oxygen contamination and thus producing unwanted phases such as \( \text{Fe}_2\text{O}_3 \) and \( \text{Fe}_3\text{O}_4 \). All these phases are magnetic and detrimental to superconductivity. Another crucial issue in the case of FeSe superconductors is the role played by excess of Fe. It is exceedingly difficult to obtain perfectly stoichiometric Fe chalcogenides, and excess of Fe appears to be always present in synthesized compounds. The excess Fe ions randomly occupy interstitial sites (designated as Fe(2) sites) in the chalcogenide layer. DFT calculations focusing on \( \text{Fe}_{1+y}\text{Te} \) indicate that the excess of Fe occurs in the...
+1 valence state with each $\text{Fe}^{2+}$ donating approximately one carrier to the FeTe layer. Further, $\text{Fe}^{2+}$ is found to be strongly magnetic with a local moment of 2.4 $\mu_B$. These moments can be expected to couple with the magnetism of the FeTe sublattice resulting in a more complex magnetic order. It is predicted that, when FeTe is doped with Se, magnetism of interstitial Fe persists and results in a pair-breaking effect in the superconducting state. Indeed, recent experimental results clearly show suppression of superconductivity and localization effects induced by excess Fe.

Here we present resistivity, magnetization, linear and non-linear response of the ac-susceptibility of nominal Fe$_{1+y}$Te$_{0.55}$Se$_{0.45}$ single crystals for two different values of $y$. The results clearly demonstrate that Fe-excess causes a broadening of the superconducting transition, a phase separation in the superconducting state, and a localization of the charge-carrier in the normal state.

II. EXPERIMENTAL

The single crystals used for the present investigation were grown using a horizontal Bridgman setup. Appropriate quantities of iron (purity 99.9 %), selenium (99.999 %) and tellurium (99.999 %) were mixed in a quartz ampoule in powdered form, evacuated to $10^{-6}$ mbar, sealed and kept in a secondary quartz ampoule which is also evacuated and sealed. The ampoules were kept inside the Bridgman setup and the precursors were melted together at 950 °C. Homogenization was done for 48 h by rotation of the melt in alternating clockwise and anti-clockwise direction. After homogenization the furnace was translated at a rate of 9.2 mm/h so that a temperature gradient of 60 °C/cm swept through the ampoule. Finally, the ampoule was cooled to room temperature at a rate of 25 °C/h. Platelet-like single crystals of typical size of 5 mm × 4 mm with a thickness of 0.5–1 mm were obtained. The as-grown crystals can easily be cleaved along the $ab$-plane. Composition and elemental mapping along a certain direction was conducted by energy dispersive x-ray analysis (EDX). The EDX compositions of the single crystals corresponding to different starting composition are listed in Table I.

| $C_{Nom}$ | $C_{EDX}$ | c-const | label |
|-----------|-----------|---------|-------|
| Fe$_{1.25}$Te$_{0.55}$Se$_{0.5}$ | Fe$_{1.09}$Te$_{0.55}$Se$_{0.45}$ | 6.052(8) | S1 |
| Fe$_{1.05}$Te$_{0.55}$Se$_{0.5}$ | Fe$_{1.04}$Te$_{0.53}$Se$_{0.48}$ | 6.109(3) | S2 |

The Laue photographs in Figs. (a) and (b) indicate a good quality of the single crystals. The single-crystal x-ray diffraction (XRD) data taken using Cu $K_{\alpha}$ radiation show, Fig. (c), the harmonic peaks corresponding to the (00l) reflection and are comparable with those published by Yadav and Paulose. In addition, we have conducted powder XRD on our samples, the results of which are presented in Fig. (d). As is obvious from the comparison of Figs. (c) and (d) the single crystals can be much better characterized by powder XRD. This, however, requires crushing the single crystals and can, therefore, only be conducted once all other measurements are completed. As identified in the Fig. (d), sample S1 contains tiny peaks corresponding to small amounts of (≤ 1%, see below) Fe$_3$O$_4$ and Fe$_7$Se$_6$ phases. But these peaks are not detected in the XRD pattern of sample S2. (Sample S2 might also contain these secondary phases below the detection limit of our powder XRD). The structure refinement was performed by Rietveld method using the FULLPROF code. The samples have a tetragonal structure and belong to the $P4/nmm$ space group.
The lattice constants obtained from the refinement are \( a = 3.7982(1) \), \( c = 5.9990(4) \) Å for sample S1 and \( a = 3.7975(2) \), \( c = 6.0031(5) \) Å for sample S2. These parameters are close to those reported by Sales et al. \(^{31}\) for single crystals of similar composition. Transport and ac-susceptibility measurements were performed with a Quantum Design Physical Property Measurement System. Magnetization measurements were carried out by means of a SQUID magnetometer (Quantum Design). The measurements were conducted with current and field applied within the ab-plane.

III. RESULTS AND DISCUSSION

The influence of Fe excess on the electrical transport is immediately obvious in Fig. 2 where the normalized resistance as a function of temperature for the two samples is plotted. The room temperature resistivity of samples S1 and S2 is about 0.9 and 0.6 mΩcm, respectively. Both the samples show an onset of the superconducting transition at around \( T_c \sim 15 \) K, marked by the dotted vertical line in Fig. 2. However, the width of the superconducting transition increases from 1 K to 6 K as \( y \) increases from 0.04 to 0.09. Further, in the normal state, sample S2 displays a metallic behavior (\( d\rho/dT > 0 \)), whereas a \( \rho \propto \log\frac{1}{T} \) divergence was observed for S1 below a temperature \( T_a \sim 130 \) K. A similar divergence is also reported by Liu et al. for Fe\(_{1.11}\)Te\(_{0.64}\)Se\(_{0.36}\) below 50 K. They also found a kink in resistivity at 120 K. The authors associated this kink with the magnetic anomaly observed earlier in polycrystalline samples.\(^{11}\) On the other hand, Janaki et al.\(^{32}\) attributed a similar anomaly observed around 125 K in the magnetization measurement of their polycrystalline samples to the Verwey transition of a Fe\(_3\)O\(_4\) spurious phase within the grain boundaries. In the present case, however, a \(-\log T\) divergence in \( \rho(T) \) appears below \( T_a \), where an anomaly in the magnetization is observed (see Fig. 3). This suggests that the electrical transport is extremely sensitive to the disorder caused by unwanted secondary phases. We note that a similar \(-\log T\) divergence was observed in the case of cuprates\(^{32,34}\) and 1111 Fe arsenides.\(^{35}\) This is ascribed to the onset of insulating behavior via disorder driven electron localization when superconductivity is suppressed by an external magnetic field.

Now we turn to the results of dc-magnetization and the ac-susceptibility, performed with the goal of establishing some evidence for the existence of local moments. Figures (a) and (b) show the zero-field-cooled (ZFC) and field-cooled (FC) magnetization as a function of temperature measured in a field of 30 Oe, applied parallel to the ab-plane, showing an anomaly at \( T_a \sim 130 \) K and \( T_b \sim 15 \) K. (c) and (d) ZFC dc-susceptibility for \( T < 20 \) K. (e) and (f) ZFC and FC dc-susceptibility measured in a field of 1000 Oe, also displaying similar anomalies at \( T_a \). An irreversibility observed between the ZFC and FC susceptibilities is marked by \( T_{irr} \).

![FIG. 3:](image_url) (a) and (b) Zero-field-cooled (ZFC) and field-cooled (FC) magnetization as a function of temperature measured in a field of 30 Oe, applied parallel to the ab-plane, showing an anomaly at \( T_a \sim 130 \) K and \( T_b \sim 15 \) K. (c) and (d) ZFC dc-susceptibility for \( T < 20 \) K. (e) and (f) ZFC and FC dc-susceptibility measured in a field of 1000 Oe, also displaying similar anomalies at \( T_a \). An irreversibility observed between the ZFC and FC susceptibilities is marked by \( T_{irr} \).
to that of S1. However, the fraction of the volume that is screened by superconducting currents estimated from the dimensionless dc-susceptibility is slightly less for sample S2, see Figures 3 (c) and (d). The full screening value is \( 4\pi \chi = -1 \). The dc-susceptibilities measured in both FC and ZFC protocols with a field of 1 kOe are shown in Figs. 3 (e) and (f). Here, an irreversibility is clearly observed below \( T_{irr} \) of about 280 K for S1, and 260 K for S2 in the ZFC and FC susceptibility. In addition to the superconducting transition, we observe an anomaly for sample S2 provided that \( T_{irr} \) is not too close to \( T_c \)ivated by the anomaly at \( T_o \) is associated with the Verwey transition of FeS2.41 Alternatively, neutron diffraction studies on FeSe0.5Te0.5 reported by Horigane et al.\(^{37} \) showed that the width of the (200) peak changes below 125 K, suggesting a possible structural transition. In order to unambiguously decide whether the anomaly at \( T_o \) is associated with the Verwey transition of FeSe or whether it is an intrinsic property of the tetragonal Fe(SeTe), experiments which probe the sample properties on a more local scale are required. In an attempt to extract the effective moments, the dc-susceptibility \( \chi \) in the FC protocol is fit-

\[ \chi = \chi_0 + C/(T - \theta) \]

in the temperature range 180−300 K. Here, \( \chi_0 \) is the temperature-independent susceptibility arising from diamagnetic core, paramagnetic van Vleck contributions, diamagnetic Landau orbital and paramagnetic Pauli spin susceptibilities from conduction electrons.\(^{38,39} \) \( C \) stands for the Curie constant and \( \theta \) is the Weiss temperature. It is known that in Fe-containing samples, data analysis is often hampered by the contribution of a ferromagnetic impurity\(^{40}\) and the inverse susceptibility in the paramagnetic regime can thus be field dependent, see Fig. 4. Therefore, we utilized the Honda-Owen method\(^{41}\) to eliminate the impurity contribution with the assumption that the magnetization of the ferromagnetic impurity saturates below 1 T. In this method, the magnetic susceptibility \( \chi(0) = \mu_B^2/4\pi \) is plotted against 1/H for each temperature. A Curie-Weiss law can be fitted to the extrapolated values of the magnetic susceptibilities in the limit 1/H \( \to 0 \) (Fig. 4). From the fit, we obtain \( \chi_0 = 0.0019 \text{ emu/g Oe}, \) an effective moment of \( \mu_{eff} = 1.49 \mu_B \) and \( \theta = -50 \text{ K} \) for sample S1. A similar approach for sample S2 provided \( \chi_0 = 0.0017 \text{ emu/g Oe}, \mu_{eff} = 1.49 \mu_B \), but \( \theta = -88 \text{ K} \). A Curie-like behavior in Fe1+yTe1−xSex
ous superconductors including the high- 
been used for characterizing the inhomogeneities in vari-
(non-linear) ac-susceptibility technique has extensively 
useful because it only probes the non-linear magneti-
surement of higher-harmonic susceptibility is even more 
with the afore-mentioned techniques.

insight into the nature of the transition not available,
an additional tuning parameter, the method can provide 
results clearly demonstrate that the physical properties of 

has been reported by other research groups as well 
and is attributed to Fe excess with localized moments.

In order to further probe the superconducting state, 
we performed linear and non-linear ac-susceptibility mea-
measurements. As this method gives more extensive in-
formation in the zero-field limit compared to the de-
magnetization, and because frequency can be used as 
an additional tuning parameter, the method can provide 
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tetragonal Fe-chalcogenide are extremely sensitive to disorder and impurities. Also, more experimental and theoretical studies are necessary to understand the nature of the couplings between interstitial Fe and the Fe in the Fe-square lattice.

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