Inhomogeneities and superconductivity in poly-phase Fe-Se-Te systems

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ABSTRACT

The impact of synthesis conditions, post-preparation heating procedure, aging and influence of pressure on the superconducting properties of $FeSe_{0.4}Te_{0.6}$ crystals is reported. Two $FeSe_{0.4}Te_{0.6}$ single crystals were used in the study, prepared from stoichiometric melt but cooled down with very different cooling rates, and investigated using magnetic bulk and electrical-resistivity methods. The fast-cooled crystal contains large inclusions of $Fe_3Se_{2.1}Te_{1.8}$ and exhibits bulk superconductivity in its as-prepared state, while the other is homogeneous and shows only traces of superconductivity. AC susceptibility measurements under hydrostatic pressure show that the superconducting transition temperature of the inhomogeneous crystal increases from 12.3 K at ambient pressure to T_{sc} = 17.9 K at 9 kbar. On the other hand, neither pressure nor mechanically-induced stress is sufficient to induce superconductivity in the homogeneous crystal. However, an additional heat treatment at 673 K followed by fast cooling down and/or long-term aging at ambient conditions leads to the appearance of bulk superconductivity also in the latter sample. This sample remains homogeneous on a scale down to few μm but shows an additional magnetic phase transition around 130 K suggesting that it must be inhomogeneous. For comparison also $Fe_3Se_{2.1}Te_{1.8}$ polycrystals have been prepared and their magnetic properties have been studied. It appears that this phase is not superconducting by itself. It is concluded that nano-scale inhomogeneities that appear in the $FeSe_xTe_{1-x}$ system due to a spinodal decomposition in the solid state are necessary for bulk superconductivity, possibly due to minor changes in the crystal structure and microstructure. Macroscopic inclusions quenched by fast cooling from high temperatures lead obviously to strain and hence variations in the lattice constants, an effect that is further supported by application of pressure/stress.

1. Introduction

Superconductivity in an Fe-based compound was thought impossible for a long time owing to the magnetic properties of Fe that seemed to contradict the superconducting properties. However, since the surprising discovery of superconductivity in La $(O_{1-x}F_x)$FeAs (example of the (1111) type of compounds) a large variety of superconducting materials has been found [1,2]. Besides the (122)-compounds, like AFe_2As_2, A = Ca, Sr, Ba and the (111)-compounds like LiFeAs, the investigation of $FeSe_xTe_{1-x}$ plays a special role since this basic (11)-type iron superconductor is considered to be structurally the simplest example of this class of materials [3–6].

$FeSe_xTe_{1-x}$ compounds adopt a crystal structure with space group $P4/nmm$ (No. 129) and cell parameters $a \approx 3.8$ Å and $c \approx 6.1$ Å [7,8].

Except for the stoichiometric FeTe, traces of filamentary superconductivity can be found for all x-values [8] (for x = 1 with T_{sc} = 8 K). Bulk superconductivity can only be obtained for $x \geq 0.29$ [9]. The highest transition temperature can be reached for $x \approx 0.4$ with $T_c \approx 14$ K. Although different reports differ in values of the superconducting transition temperature, T_{sc} is always reported to be strongly dependent on pressure [10–12].

Many reports also show that the superconducting properties are very sensitive to the iron content that can be either deficient or in excess, depending on the details of preparation conditions [8,13]. Equally, different preparation conditions and post-preparation heat treatment leads to a presence/absence of additional secondary phases [14–16]. Most of the studies report a presence of traces of secondary, magnetically ordered non-superconducting iron-containing phases that are generally

ignored in the interpretation of the observed sample properties [17–20]. In the present paper, it is shown that the impact of various secondary phases must be taken into account to interpret and understand the properties of the Fe-Se-Te system. In particular, it is shown that these foreign phases are important for the observation of superconductivity. However, neither the sometimes observed $Fe_3Se_{2.1}Te_{1.8}$-inclusions [7] nor the in some publications mentioned Fe_7Se_8, which are crystallographically similar and differ only in ordered vacancies, are superconducting themselves. Therefore, it is important to explain the interplay between these compounds and the superconductivity in $FeSe_xTe_{1-x}$ compounds which will stimulate new approaches in this field [19].

So far, no concise explanation exists why these secondary phases not only do not destroy the superconductivity but apparently enhance existing superconductivity. Equally unclear remains the relation between the superconductivity and nano-scale homogeneity in this system and aging effects.

To address these questions, two different types of $FeSe_{0.4}Te_{0.6}$ single crystals have been grown by applying different cooling procedures to study the relation between the secondary phases and the superconductivity in this system. One sample shows bulk superconducting properties but contains macroscopic inclusions of a secondary phase (this crystal is denoted as inhomogeneous, or SC), while the second crystal is homogenous and not superconducting (denoted as NSC). In a previous publication we studied carefully differences of the amount of excess iron in both samples and were able to exclude this feature to be a reason for the different qualitative behavior [7]. In the current study, we analyze the differences of both samples using X-ray diffraction (XRD) and susceptibility measurements under pressure and strain. Additionally, a sample with the same composition as the experimentally observed inclusions was prepared and investigated as well. It is shown that the freshly prepared homogeneous sample does not exhibit superconductivity under pressure and even after application of stress. The amount of the superconducting volume fraction is of the order of ∼1% (this crystal is denoted as three years aged NSC). However, after ∼3 years aging at ambient conditions, the same crystal exhibits a significantly increased superconducting volume fraction of about 7%. An even larger superconducting volume fraction of about 20% can be achieved after a heat treatment followed by a fast cooling (this crystal is denoted as HT-NSC). The presence of magnetically ordered secondary phase in this system has been indicated by magnetic measurements as well. However, energy dispersive X-ray (EDX) spectroscopy shows that the system remains homogeneous on μm scale. It is concluded that the phase separation must occur on a nm scale and that it is a complicated function of the sample-preparation history.

2. Sample preparation

The two single crystals used in the present investigation are the same as studied previously. Both crystals have been grown by a modified Bridgman-method using metallic iron (99.7%), tellurium (99.999%) and selenium (Se shots, 99.999%) from a stoichiometric melt. The same preparation protocol except for cooling has been used for both crystals. The crystal that appears to be superconducting but multiphase has been cooled at a rate of 2 K/min. The sample that is homogeneous on a μm scale and free of macroscopic secondary phases and shows no bulk superconductivity has been cooled down ten times slower. The amount of interstitial iron between 3.6% and 4.0% suggests that both crystals should be in principle in a superconducting state at low temperatures [13,21]. Further preparation details and characterization of the crystals are given in a previous publication [7].

In order to check whether the homogeneous crystal becomes eventually superconducting after the heat treatment, the already characterized and measured NSC crystal has been enclosed into an evacuated quartz tube and annealed it at 673 K for 100 h according to procedure described by Noji et al. [22], followed by cooling at a rate of about

2 K/min. After this some of the magnetic bulk, electrical transport measurements have been repeated and electron microscopy has been performed. Also the originally NSC crystal has been investigated after ∼3 years aging at ambient conditions without exposing it to elevated temperatures.

As $Fe_3Se_{2.1}Te_{1.8}$ appears to be the main secondary phase found in the SC crystal, a sample with identical nominal composition has been prepared and measured as well. For the synthesis of this sample, the constituent pure elements were sealed in appropriate stoichiometry in a quartz ampule and heated to 800 °C. The melt stayed at this temperature for seven days, before it was cooled down to room temperature within one hour. The resulting sample was polycrystalline, single-phase and was pulverized for further studies.

3. Experimental techniques

Analyses by scanning electron microscopy (SEM) were performed on freshly cleaved and polished single crystals, since the material surface quality deteriorates significantly with time upon exposure to air. A Zeiss UltraPlus electron microscope with combined electron backscatter diffraction (EBSD) and EDX measurement system (Oxford Instruments AZtec, using NordlysNano EBSD and 80 mm² XMax X-ray detectors) has been used. The acceleration voltage applied was 15 kV.

X-ray powder patterns have been obtained by use of a Bruker D8 (Cu Kα) powder diffractometer on a rotating powder sample at room temperature and have been analyzed with the Jana2006-program [23].

Magnetic property measurements have been performed on a Quantum Designs 7T MPMS DC vibrating sample magnetometer (VSM) with oven option in the temperature range 2–600 K in a magnetic field up to 7 T at zero-field-cooled (zfc) and field-cooled (fc) conditions. For high temperature measurements the powder sample was glued within ZIRCAR-cement. The combination two data sets causes a minor gap in the magnetization data.

Additionally, the AC susceptibility has been measured using a self-made pick-up coil system. This first order gradiometer is particularly suited for the usage of large and heavy pressure cells. The low-temperature measurements have been performed down to 1.6 K in a standard orange cryostat.

For pressure measurements a copper-beryllium clamped-type pressure cell was used. The sample was embedded in spindle oil as a pressure-transmitting-medium. The pressure has been determined at room temperature via resistivity measurements of a manganin sensor. The pressure drop at the lowest temperature is well known and amounts to 2 kbar. Additionally, some measurements under applied stress by bending the samples were performed.

Although the influence of the various parts of the pressure cell for the AC susceptibility measurements is not negligible, the detection of bulk superconductivity is straightforward. Filamentary superconductivity in the pure $FeSe_{0.4}Te_{0.6}$ has been detected earlier by resistivity measurements, but it's volume presence is too small to be visible in the AC susceptibility experiments [7].

The electrical resistivity has been measured by a standard four-point ac method using a 14T Quantum Design Physical Property measurement system (PPMS) in fields up to 14 T applied perpendicular to the *c* axis. Current of up to 2 mA have been applied perpendicular to the *c* axis.

4. Results

4.1. Influence of macroscopic inclusions

As noted above, previous measurements revealed that the inhomogeneous fast-cooled sample shows bulk superconductivity (see Figs. 1 and 2 in Ref. [7] and the inset of Fig. 9) [14]. The superconducting volume fraction is (despite a significant amount of secondary phases) close to 100%. On the other hand, the homogeneous crystal surpris-