Experimental report

16/11/2016

Proposal: 5-11-414 **Council:** 4/2015

Title: Crystal structure details of a two-phase Fe1+y(Te1-xSex) x=0.4 singlecrystal as a function of a heat treatment

Research area: Physics

This proposal is a continuation of 5-15-606

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Samples: Fe1+y(Te1-xSex) x=0.4 single crystal

Instrument	Requested days	Allocated days	From	To
D23	0	0		
D9	0	0		
D10	8	6	10/11/2015	16/11/2015

Abstract:

This proposal is a continuation of the recently performed proposal 5-15-606 (4 days on D10). With this continuation experiment we suggest to study an inhomogeneous superconducting Fe1+y(Te1-xSex) x=0.4 single crystals that contains large inclusions of Fe3Se2.1Te1.8. Their size enabled us in nthe previous experiment to determine the crystal structure of both the matrix and the secondary phase. In the current experiment we suggest to study the influence of a heat-treatment (up to 800 K). We anticipate that at elevated temperatures the inhomogeneous sample becomes homogeneous again. The study should be able to resolve conflicting claims in the literature concerning the phase purity and question which phase hosts the superconductivity.

The iron chalcogenide $Fe_{1+y}(Te_{1-x}Se_x)$ is from the crystal structure point of view arguably one of the simplest Fe-based superconductors [1]. The x = 1.0 system exhibits antiferromagnetic phase transition temperature T_N = 65 K and at T_C = 8K superconducting phase transition, which, however, seems not to be a bulk property. Bulk superconductivity exists (with the superconducting volume fraction is larger than 75 %) for x>0.29 [2]. However, the mechanism of superconductivity remains still unclear. The superconducting FeSexTe1-x samples are often not perfect single crystals showing presence of secondary phases. The content and morphology of present secondary phases depends strongly on the heat treatment of crystals, more specifically on the cooling rate. This in turn is directly related to their superconducting properties. It seems that foreign phases that appear as macroscopic (up to 0.25 mm) inclusions in the matrix are a mandatory ingredient for the observation of bulk superconductivity [3].

This striking observation prompted us to determine the crystal structure of both the inclusions and the matrix and to follow the changes in their structure as a function of the increasing temperature.

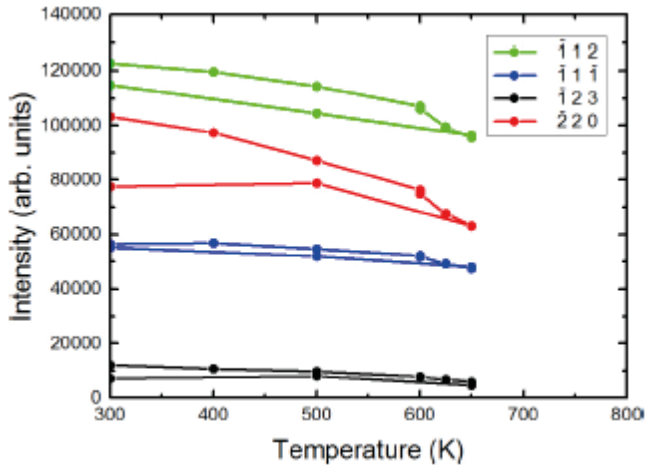

Fig. 1: Temperature dependence of representative Bragg reflections belonging to the matrix of FeTe0.6Se0.4.

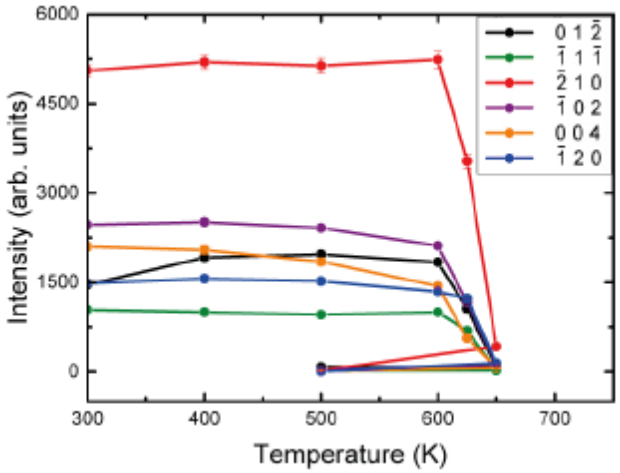

Fig. 2: Temperature dependence of some representative Bragg reflections belonging to one of the largest inclusions. Note an abrupt decrease of their intensities.

Inclusions appear to have composition close to $Fe_3Se_{2.1}Te_{1.8}$ and order in an NiAs type crystal structure with the space group P63/mmc. The matrix apper to have anticipated tetragonal P4/nmm crystal structure with a slight Fe deficiency and moderately alternated ratio between Fe and Te.

The integrated intensity of the reflections originating from matrix and one sufficiently large inclusion were followed as a function of temperature from 300 K up to 650 K and are shown in Fig. 1. During the increase of temperature the intensity of all recorded reflections gradually decrease. This is expected due to increase of Debye-Waller factors. However, the decrease seems to be stronger than expected and shows further time-dependent decrease as a function of the annealing time at constant temperature. On cooling to 300 K, the intensities are not recovered indicating a structural change during the heating cycle. This change is not equal for all reflections. In this respect, the 220 reflection is apparently affected most.

The intensity of the inclusions reflections remains almost constant until 600 K. At 625 K the intensity quickly decreases by approximately one third. A second measurement at this temperature two hours later showed an even smaller signal indicating again a time dependence of the change. Further heating to 650 K, completely suppresses the inclusions signal. Upon cooling they do not reappear again. However, an

extensive search at room temperature showed that reflections belonging the secondary phase occur at different orientations. However, within error bars no alternation of the crystal structure is detected (for both – the matrix and for the secondary phase).

The surface morphology has been checked after the experiment with help of an optical microscope and showed basically no major changes. More than 20 % of the sample consists of the secondary phase, partially in grains of 0.1 mm diameter. A major melting or softening of the material would have been visible. A subsequent measurement of the macroscopic properties, especially of bulk superconductivity is still under way (forestalled by the radioactivity of the sample). Our interim conclusion is that the morphology, in particular the interface region between the matrix and inclusions play an important role in the superconducting mechanism in this highly interesting system.
This work is partially included in PhD Thesis of S. Hartwig (HZB 2016).

References

[1] Hsu, F. C. et al. Proc. Nat Acad. Sci. USA **105**, 14262_14264 (2008).
[2] T.J. Liu et al., Nature Materials **9**, 716 (2010)
[3] K. Prokes et al., J. Cryst. Growth **432**, 95 (2015)