Electrotransport and magnetic measurements on bulk FeSe superconductors

T Karwoth¹, K Furutani¹,², M R Koblischka¹,², X L Zeng¹, A Wiederhold¹, M Muralidhar², M Murakami², and U Hartmann¹

¹ Experimental Physics, Saarland University, Campus C 6 3, 66123 Saarbrücken, Germany
² Superconducting Materials Laboratory, Department of Materials Science and Engineering, Shibaura Institute of Technology, Tokyo 135-8548, Japan
E-mail: m.koblischka@mx.uni-saarland.de

Abstract. The superconducting properties of bulk, polycrystalline FeSe samples were characterized through magnetic and electric transport measurements. In order to improve the superconducting properties, the sintering temperature was varied up to 900 °C and to improve the grain connectivity, silver was added (0 to 7 wt.-%). Electric properties of the samples were investigated by the four point probe method (R-T measurements and V-I characteristics). Generally, the sample with 4 wt.-% Ag-addition showed the highest critical transition temperature among all the samples fabricated with the same preparation parameters. The critical currents were obtained from V-I measurements in various applied magnetic fields up to 6 T. Via Arrhenius plots, the pinning potential U₀ was determined for all samples studied. The magnetic properties (M-T and M-H) of the samples were measured using an extraction magnetometer in a Quantum Design PPMS with applied magnetic fields up to 7 T. The scaling of the normalized volume pinning force versus the reduced field indicated a peak position at ~0.2 for the Ag-added sample, which points to a pinning at the grain boundaries.

1. Introduction
The polycrystalline, bulk FeSe superconductor (¹¹’-compound) is considered as candidate for several types of applications like superconducting supermagnets despite the low superconducting transition temperature, T_c [1, 2]. FeSe offers a simple preparation route, is free of rare-earth elements and shows many similarities to the cuprate high-temperature superconductors like high critical fields, and no flux jumps as in the case of MgB₂. The transport and flux pinning properties of this compound, however, have yet to be explored in detail as only some reports concerning the electric transport and flux pinning of the ¹¹-system can be found in the literature [3–6]. Furthermore, to improve the sample resistivity and the mechanical strength of the otherwise porous granular material, Ag was added to the samples. This was done in the literature already for conventional superconductors like Nb₃Sn [7] and MgB₂ [8, 9] and for YBa₂Cu₃Oₓ, where Ag was found to be located at the grain boundaries, thus improving the connectivity between the grains [10–13]. Recently, it was found that in FeSe some Ag enters into the crystal structure itself [14,15], leading to an improvement of the superconducting transition temperature, T_c. This clearly demonstrates that more detailed investigations of the superconducting properties of the FeSe-Ag-system are required. Therefore, we investigate in the present contribution a series of FeSe samples with Ag content ranging up to 7 wt.-% by means
Figure 1. (a) Resistance vs. temperature in the range $3 \text{ K} < T < 300 \text{ K}$, zero applied field. (b) presents the normalized superconducting transitions of the Ag-containing samples; the inset shows the superconducting transitions in detail. The red lines indicate the determination of $T_c$.

of electric transport and magnetization measurements. Using the scaling approach of the flux pinning forces, we determine the acting flux pinning mechanism.

2. Experimental procedures

| Sample | addition | $T_c$ [K] | $\Delta T_c$ [K] | $R$ (300 K) [$\Omega$] | RRR | grain connectivity [%] | $U_0/k_B$ (1 T) [K] |
|--------|----------|-----------|-----------------|-----------------|------|-----------------------|-------------------|
| 1      | pure     | 8.35      | 2.35            | 0.03224         | 2.16 | 3.9                   | 51.2              |
| 2      | 4 wt.-%  | 9.42      | 0.98            | 0.00930         | 4.49 | 6.52                  | 171.2             |
| 3      | 5 wt.-%  | 9.28      | 1.18            | 0.00926         | 3.33 | 7.3                   | 62.1              |
| 4      | 6 wt.-%  | 9.36      | 1.12            | 0.00718         | 2.41 | 11.3                  | 99.3              |
| 5      | 7 wt.-%  | 9.18      | 0.94            | 0.00335         | 2.44 | 23.8                  | 45.6              |

The FeSe material was produced using commercial powders of Fe (99.9% purity), and Se (99.5% purity). Firstly, the powders were mixed in a nominal ratio Fe:Se = 1:1 in a glove box and thoroughly ground using an agate mortar and loaded into a ceramic vial under high-purity argon atmosphere inside the glove box. The ball milling was performed in a glove box for 6 h. The as-milled powder mixture was then pressed into pellets of 5 mm in diameter and 2 mm thickness using an uniaxial pressure of 100 MPa, and sealed into an evacuated quartz tube and heated at 600 °C for 24 h. In a second step, after furnace cooling, the product was opened in the glove box. Then, the sintered pellets were once more thoroughly ground and mixed, and again ballmilled similar to the first step. The samples were sealed in quartz tubes and sintered at two different temperatures for 24 h, and finally, the temperature was lowered to room temperature at a cooling rate of 230 °C/h. Pure FeSe samples were prepared at 900 °C and 950 °C, while samples with Ag-addition received a treatment at a lower reaction temperature at 825 °C. The constituent phases of the samples were identified with a high-resolution automated X-ray powder
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Figure 2. Resistance vs. temperature in applied magnetic fields ($H \perp$ sample surface) for all Ag-containing FeSe-samples.

diffraction (RINT2200), using Cu-K$^\alpha$ radiation generated at 50 kV and 300 mA. A detailed description of the microstructure of the samples is given elsewhere [6, 16]. We notice a slight shift of the 001 reflection in our samples with increasing Ag-content, similar to the observation in Ref. [4], which may indicate that Ag is incorporated in the FeSe lattice.

3. Results and discussion

For the transport measurements, long bars with dimensions $1 \times 2 \times 5$ mm$^3$, resulting in a distance of 3 mm between the voltage contacts, were cut from the bulk samples using a diamond saw. Thin copper wires of 100$\mu$m in diameter were used as leads for low resistance contacts placed onto the samples by means of silver paste. The electric measurements were performed in an Oxford Instruments 10/12 T Teslatron cryostat in the temperature range 2 K $-$ 300 K. The resistance was measured in four-probe configuration with a dc current of 2.5 mA applied perpendicular to the magnetic field direction. Field steps of 0.5 T (low fields) and 1 T (high fields) were used for the $R(T)$ measurements. The magnetic field sweep rate was 0.7 T/min, and temperature steps of 0.25 K were applied. The measurements were controlled by a MatLab program operating a stabilized current source (Keithley 2400) and a voltmeter (Keithley 2100 multimeter) [17].

Magnetic measurements were performed in a QD PPMS system with $\pm 7$ T applied field (perpendicular to the sample surface. For these measurements, cubic samples with dimensions $1 \times 1 \times 0.5$ mm$^3$ were cut from the bulks. Table 1 summarizes all the properties of the samples
investigated here.

Figure 1 (a) presents the resistance measurements on the Ag-containing samples in the temperature range $3 \text{ K} < T < 300 \text{ K}$. The change of resistance due to the Ag-addition is obvious from the graph. While the room temperature resistance for samples with 4 wt.-% and 5 wt.-% Ag-addition is similar, the further Ag-addition clearly reduced the resistance measured.

Figure 1 (b) gives a detailed view of the superconducting transitions of all Ag-containing samples. The main panel presents a comparison of the superconducting transitions normalized by the resistance value at 14 K (just above the superconducting transition). All data nearly fall on a common line except the data of the sample with 7 % Ag-addition at around 8 K, whereas the the sample with 4 wt.-% Ag-addition reveals the highest $T_c$ of all samples measured. The inset to (b) shows the non-normalized superconducting transitions. The superconducting transition temperatures, $T_c$, were determined as indicated in the inset to (b). The transition widths, $\Delta T$, were determined using a 10%-90% criterion. From these measurements, we determine the residual resistance ratio ($\text{RRR} = R(T = 300 \text{ K})/R(T = 14 \text{ K})$). The RRR is increased at the sample with 4 wt.-% Ag-addition, and then decreases again with increasing amount of Ag content. This behavior is similar to that seen in [4], except that in our case, the 4 wt.-% Ag sample was found to be the optimum in our sample series. Another important measure is the grain connectivity. The geometrical connectivity can be estimated using an approach describing different MgB$_2$ samples [18]. The connectivity $\kappa$ is calculated using

$$\kappa = \frac{\Delta \rho_g}{\Delta \rho},$$

Figure 3. Resistance derivative, $dR/dT$, versus temperature for all Ag-containing samples.
Figure 4. Arrhenius plots of all Ag-containing samples including the fitting to determine the pinning potential, $U_0$.

Figure 5. TAFF pinning potential, $U_0$, as function of the applied field in a double-log representation. The lines are indicating the change in field dependence above an applied field of 3 T.
Figure 6. Magnetization loops for the sample with 4 wt.-% Ag-addition at various temperatures. The shape of the loops reveal the polycrystalline character of the sample. (b) shows the irreversibility line of the sample with 4 wt.-% Ag-addition.

while $\Delta \rho_g$ can be assumed to be 0.472 m$\Omega$cm for randomly oriented three dimensional FeSe samples [19,20] and $\Delta \rho = \rho(300 \text{ K}) - \rho(14 \text{ K})$. All these data are summarized in Table 1.

Figure 2 presents the resistance data in applied magnetic fields ($H \perp$ sample surface) for all Ag-containing samples. The superconducting transitions broaden on applying magnetic fields. Also here, the 4 wt.-% Ag sample shows the sharpest superconducting transitions. In Fig. 3, we present $dR/dT$-plots of the data. In all cases, we obtain a peak at the superconducting transition. No further steps in the derivative $dR/dT$ at around 65 – 85 K were observed in the present samples, whereas the pure sample does show this step [19]. This indicates that the Ag-addition is suppressing the structural transition.

The resistance data can be converted into Arrhenius-plots by plotting the logarithm of the electric resistivity against the inverse temperature, which is shown in Fig. 4. From the slopes of the linear parts, the thermally activated flux-flow (TAFF) pinning potential can be calculated [21]. The results of this procedure are summarized in Fig. 5, where the obtained pinning potentials, $U_0$, in the TAFF regime are presented as a function of the applied field, $\mu_0 H$. Here, it is remarkable that the sample with 4 wt.-% Ag-addition shows the highest pinning potential of all samples measured. All values of $U_0$ taken at 1 T applied field are listed in Table 1 to enable a comparison with the data of Ref. [4]. It should be noted here that our data show the same overall behavior as reported in [4], but are somewhat smaller indicating that the preparation temperature/time can still be further optimized. The values of $U/k_B$, where $k_B$ is the Boltzmann constant, are obtained from the slopes of the $\ln \rho$ versus $1/T$ dependences at the different applied fields. The activation energy $U_0$ shows a weak field dependence at low fields, changing in a stronger one at $B \approx 3$ T. Both branches can be described by a power law behavior, $U \sim B^{-\beta}$, with $\beta \approx 0.5$ at low fields, and $\beta \approx 1.8$ at high fields. An explanation for the parabolic-like shape of the curves may be the presence of strong grain boundary pinning [22].

We now turn to the magnetic measurements. In Fig. 6 (a), $M(H)$-loops are given for the sample with 4 wt.-% Ag at temperatures between 2 K and 5 K. The field sweep rate was 0.35 T/min. All curves exhibit an asymmetric shape being a sign of granular behavior. There are no flux jumps observed, even at the lowest temperature. The critical current densities were
Figure 7. Pinning force scaling for the sample with 4 wt.-% Ag-addition, compared to the pure samples and other data of the literature. The red line is a fit to all data.

calculated using the extended Bean approach. The irreversibility fields, \( H_{\text{irr}} \), were determined using a criterion of 100 A/cm\(^2\) from double-log plots \([23]\). The dependence of \( H_{\text{irr}} \) on temperature is illustrated in Fig. 6 (b). A remarkable result is further that the hysteresis loops do not change much when measuring with a field sweep rate of 0.7 T/min. This indicates that dynamic relaxation is only small for bulk FeSe. Figure 7 presents the results of the pinning force scaling \( (F_p/F_{p,\text{max}} \text{ vs. } h = H_a/H_{\text{irr}} \text{ [24]}) \) on the 4 wt.-% Ag-added FeSe sample. The pure FeSe samples exhibited a good scaling and a peak at \( h_0 \sim 0.4 \) \([6, 25]\). In contrast to this, the Ag-added samples are found to show a peak at \( h_0 \sim 0.2 \) considering all measured data (red line). This is similar to the pure FeSe sample prepared at 950 °C \([6]\). It should be noted that the data at 2 K and 3 K differ from the ones measured at 4 K and 5 K in the region just above \( h_0 \), which is a sign of different contributions to the flux pinning: At higher \( T \), the grain boundary pinning is dominant, whereas at low \( T \), the pinning at point defects inside the FeSe grains plays a more important role. In case the FeSe grains are well coupled, one has to consider a current flow through the entire sample perimeter. This current flow is then affected by percolation as well as the anisotropy due to the non-textured FeSe grains. In this case, the approach of Eisterer \([26]\) for MgB\(_2\) samples is to be considered for our samples. The consequence is then that all peak positions are appearing at lower \( h \) as in the standard approach. Other impurity phases which were seen in the X-ray data \([6,16]\) are forming separate grains or are located at the grain boundaries, so no effect on the flux pinning is expected. Finally, from the comparison with data presented in Ref. \([25]\), we can deduce that the Ag-added FeSe samples exhibit an improved flux pinning at the grain boundaries, which gets even more pronounced at temperatures close to \( T_c \). Here, it is important to point out that the present polycrystalline FeSe samples were prepared using a classical sintering technique at relatively low reaction temperatures. This is in contrast to previous work, where the samples were subjected to much higher temperatures (1050 °C) to partially melt the material. In this case, it is much more likely that Ag enters the FeSe crystal structure as compared to the sintering process. Nevertheless, our data were found to coincide reasonably well with other data in the literature. The change of resistivity due to the Ag-addition in our samples is obvious, and the sample with the best superconducting properties
was found to be the sample with 4 wt.-% Ag-addition.

4. Conclusions
We have performed resistivity measurements and magnetic measurements on Ag-containing polycrystalline, bulk FeSe samples. The resistance data clearly reveal the improvement of grain connectivity due to the Ag-addition. Our data were found to coincide reasonably well with other data in the literature, even though the preparation route (sintering at lower reaction temperatures) was different. The magnetization loops exhibit an asymmetric shape which indicates granularity. The irreversibility fields determined do not vary much with temperature. The pinning force scaling demonstrates a peak position, $h_0 \sim 0.2$, indicating dominant pinning provided by point defects (low $T$) and grain boundaries (high $T$).

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