Superconductivity and magnetism in Rb$_2$Fe$_{2-y}$Se$_2$: Impact of thermal treatment on mesoscopic phase separation

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An extended study of the superconducting and normal-state properties of various as-grown and post-annealed Rb$_2$Fe$_{2-y}$Se$_2$ single crystals is presented. Magnetization experiments evidence that annealing of Rb$_2$Fe$_{2-y}$Se$_2$ at 413 K, well below the onset of phase separation $T_p \simeq 489$ K, neither changes the magnetic nor the superconducting properties of the crystals. In addition, annealing at 563 K, well above $T_p$, suppresses the superconducting transition temperature $T_c$ and leads to an increase of the antiferromagnetic susceptibility accompanied by the creation of ferromagnetic impurity phases, which are developing with annealing time. However, annealing at $T = 488$ K $\simeq T_p$ increases $T_c$ up to 33.3 K, sharpens the superconducting transition, increases the lower critical field, and strengthens the screening efficiency of the applied magnetic field. Resistivity measurements of the as-grown and optimally annealed samples reveal an increase of the upper critical field along both crystallographic directions as well as its anisotropy.Muon spin rotation and scanning transmission electron microscopy experiments suggest the coexistence of two phases below $T_p$: a magnetic majority phase of Rb$_2$Fe$_y$Se$_4$ and a nonmagnetic minority phase of Rb$_{3-x}$Fe$_x$Se$_2$. Both microscopic techniques indicate that annealing the specimens just at $T_p$ does not affect the volume fraction of the two phases, although the magnetic field distribution in the samples changes substantially. This suggests that the microstructure of the sample, caused by mesoscopic phase separation, is modified by annealing just at $T_p$, leading to an improvement of the superconducting properties of Rb$_2$Fe$_{2-y}$Se$_2$ and an enhancement of $T_c$.

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I. INTRODUCTION

Iron-chalcogenide superconductors are usually related to the selenium-deficient compound FeSe$_{1-x}$, having a transition temperature $T_c \simeq 8$ K. Higher $T_c$’s can be accessed by applying hydrostatic pressure $p$, by inducing chemical pressure, or by intercalating alkali atoms between the Fe$_2$Se$_2$ layers, yielding $A_x$Fe$_{2-y}$Se$_2$ ($A = $ K, Rb, Cs). Aside from superconductivity, many iron chalcogenides feature coexisting magnetic order, where subtle modifications of the crystal structure lead to drastic changes in superconducting and magnetic properties. This is the case for the compound Rb$_x$Fe$_{2-y}$Se$_2$, which is superconducting below $T_c \simeq 33$ K and antiferromagnetic below the Néel temperature $T_N$ as high as 500 to 540 K. In addition to these superconducting and magnetic orders, iron-vacancy ordering accompanied by a structural distortion at the temperature $T_a$ as well as phase separation in magnetic and nonmagnetic domains at the temperature $T_p$ are observed.

Although it was shown by various groups that $A_x$Fe$_{2-y}$Se$_2$ exhibits bulk superconductivity$^{12-14}$ muon spin rotation ($\mu$SR) experiments reported that only a minor volume fraction of $\sim 10\%$ of the sample is superconducting, whereas $\sim 90\%$ of the volume is antiferromagnetic. From neutron experiments, the minority phase was identified to have the $I\bar{4}/mmm$ space group with a small in-plane lattice constant $a$ and a large out-of-plane lattice constant $c$. It was discussed whether $A_x$Fe$_{2-y}$Se$_2$ should be treated as a filamentary or granular superconductor. Besides, mesoscopic phase separation in Rb$_x$Fe$_{2-y}$Se$_2$ was reported to prevail down to the nanoscale. Microscopic techniques probing the stoichiometry of these distinct phases yield in average the composition Rb$_3$Fe$_4$Se$_5$ for the antiferromagnetic vacancy-ordered majority phase (245-phase) and the composition Rb$_{1-x}$Fe$_2$Se$_2$ for the superconducting Rb-deficient minority phase (122-phase). Thus, the studied material may be treated as follows: the minority 122-phase is superconducting and is embedded in an antiferromagnetic matrix of the vacancy-ordered 245-phase.

Interestingly, it was observed that some post-annealed iron-chalcogenide samples may become superconducting despite their insulating as-grown behavior. It was discussed that a possible change in the vacancy ordering and the related phase separation might be related to the observed changes in the electronic properties. Obviously, by carefully tuning the conditions of annealing, one may gain direct control of the phase separation in $A_x$Fe$_{2-y}$Se$_2$ and by that of the superconducting and magnetic properties. In order to examine this scenario and to investigate the influence of vacancy ordering and phase separation on superconductivity and magnetism, we performed an extended study of thermally treated Rb$_x$Fe$_{2-y}$Se$_2$ single crystals.

II. EXPERIMENTAL DETAILS

A set of Rb$_x$Fe$_{2-y}$Se$_2$ single crystals with nominal composition Rb$_{0.85}$Fe$_{1.09}$Se$_2$ was grown by the Bridgman method, similarly as described in Refs. 7 and 30. Here, a mixture of high-purity Fe, Se, and Rb (at least 99.99%; Alfa Aesar)
were chosen to post anneal the as-grown Rb\textsubscript{2}Fe\textsubscript{2−\textit{y}}Se\textsubscript{2} (see text). The three annealing temperatures 413, 488, and 563 K were chosen to post anneal the as-grown Rb\textsubscript{2}Fe\textsubscript{2−\textit{y}}Se\textsubscript{2} crystals for the subsequent experiments.

was sealed in an evacuated quartz ampoule. This ampoule, protected by a surrounding evacuated quartz tube, was heated to 1030 °C for 2 h. The melt was cooled first with −6 °C/h to 750 °C and finally to room temperature at a fast rate of −200 °C/h. After synthesis, the ampoule was transferred to a glove box and opened there to protect the crystals from degradation in air.

In order to study the thermal evolution of the mesoscopic phase separation, an as-grown Rb\textsubscript{2}Fe\textsubscript{2−\textit{y}}Se\textsubscript{2} single crystal was initially characterized by differential scanning calorimetry (DSC). With DSC, the differential amount of heat \(\Delta Q\) required to increase the sample temperature \(T\) by \(\Delta T\) with respect to a reference is recorded.\textsuperscript{31} Measurements were performed with a Netzsch DSC 204F1 system, by heating up from 290 to 670 K with a constant heating rate of 20 K/min. Both sample and reference were always maintained at the same temperature throughout the experiment. In Fig. 1, the measured \(\Delta Q\) in the temperature range between 400 and 600 K for the as-grown single crystal is presented. The three peaks at the temperatures \(T_p, T_N,\) and \(T_s\) are related to three distinct onset temperatures of this system: (i) \(T_p \simeq 540\) K corresponds to the onset temperature of iron-vacancy ordering, at which the unit cell transforms from the high-temperature 14/\textit{mmm} structure into a low-temperature superstructure 14/\textit{m}. (ii) \(T_N \simeq 517\) K is the Néel temperature, and (iii) \(T_s \simeq 489\) K corresponds to the onset temperature of phase separation between coexisting 14/\textit{mmm} and 14/\textit{m} phases.\textsuperscript{16}

The mesoscopic phase separation of as-grown Rb\textsubscript{2}Fe\textsubscript{2−\textit{y}}Se\textsubscript{2} is visualized with scanning transmission electron microscopy (STEM) at room temperature using a Titan 80-300 Cubed instrument operating at 300 keV. The specimens for STEM investigations were carefully prepared by a focused ion beam (FIB) to avoid degradation on air exposition. The STEM images taken with the electron beam perpendicular to the tetragonal \textit{c} axis are shown in Fig. 2. The brightness of the STEM images allows us to distinguish the actual composition of the sample. According to the results of energy dispersive x-ray spectroscopy (EDXS), the composition of the darker regions was found to correspond to Rb\textsubscript{0.5}Fe\textsubscript{2}Se\textsubscript{2}, whereas in the brighter regions, the composition is Fe- and Rb-deficient Rb\textsubscript{0.5}Fe\textsubscript{1.6}Se\textsubscript{2}.

Although the transition temperatures \(T_N\) and \(T_s\) both correspond to thermodynamic ordering phenomena in this system, the onset of phase separation \(T_p\) is of different origin. It can be presumed that thermal history of this material crucially influences the phase separation in the sample. This rises the question as to whether it might be possible to tune the phase separation in Rb\textsubscript{2}Fe\textsubscript{2−\textit{y}}Se\textsubscript{2} by proper thermal treatment, and by that to control the superconducting and magnetic properties. In order to study the influence of post annealing on the properties of Rb\textsubscript{2}Fe\textsubscript{2−\textit{y}}Se\textsubscript{2} single crystals, a set of samples was annealed with an Elite Thermal Systems Ltd. single-zone high-temperature furnace at three annealing temperatures characteristic for the studied samples (see Fig. 1): (i) \(T \simeq 413\) K...
(well below $T_p$), (ii) $T \simeq 488$ K (just at $T_p$), and (iii) $T \simeq 563$ K (well above $T_p$). For this purpose, the samples were loaded in a furnace, which was heated from room temperature with a fast rate of $\sim 10$ K/min. Having reached the desired annealing temperature $T_{\text{ann}}$, the temperature was kept constant for a time $t_{\text{ann}}$, after which the samples were removed from the hot furnace and were rapidly cooled back to room temperature.

As-grown and annealed samples were systematically studied by various experimental methods. The superconducting and normal-state magnetization was studied with a Quantum Design Magnetic Property Measurement System (MPMS) XL with a differential superconducting quantum interference device (SQUID) equipped with a reciprocating sample option (RSO). In order to prevent these samples from degradation in air, all investigated crystals were vacuum sealed in quartz ampoules of 5 mm diameter and approximately 10 cm length. The platelike crystals were oriented with their crystallographic $c$ axis along the ampoule axis and were fixed between two quartz cylinders of approximately 5 cm length. The diameter of the crystals was adapted to the inner diameter of the quartz tube. Such sample mounting provides a homogeneous surrounding of the examined crystal and produces only a minor background signal during the measurements. Resistivity measurements with electrical current flowing in the $ab$ plane were performed with a Quantum Design Physical Property Measurement System (PPMS). The Rb$_2$Fe$_4$Se$_2$ single crystal was cleaved along the $ab$ plane in argon atmosphere inside a glove box and contacted on the cleaved surface by the four-probe technique with gold wires ($50 \mu$m diameter) and silver epoxy. The as-grown sample was sealed directly after the measurements and annealings, the samples were kept inside the sealed ampoules. The as-grown specimens (see Table II), whereas for the sample A563[36 h] $\sim 5\%–6\%$ is found in comparison to A488[36 h] and A563[36 h] exhibit a clearly narrower transition to the superconducting state with a higher $T_c$. In contrast, sample A563[36 h] behaves in the opposite way, showing a drastically lower $T_c$. The transition width $\Delta T_c$ was defined as the inverse of the maximal slope of the normalized magnetization $M/M(0)$ as a function of $T$:

$$\Delta T_c = \left( \frac{1}{M(0)} \max \left[ \frac{dM}{dT} \right] \right)^{-1}.$$  

The estimated values for $T_c$ and $\Delta T_c$ for all the samples studied are listed in Table II. In order to better specify the change for a measured property $P$ with annealing time $t_{\text{ann}}$, we introduce the following quantity:

$$\delta_{t_{\text{ann}}} (P) = \frac{P(t_{\text{ann}}) - P(0 \text{ h})}{P(0 \text{ h})}.$$  

With this formula, a clear increase of $T_c$ by $\sim 5\%–6\%$ is found for the samples A488[36 h] and A563[36 h] in comparison to the as-grown specimens (see Table II), whereas $T_c$ decreases for sample A563[36 h] by $\sim 27.3\%$ and remains almost constant for sample A413[36 h]. The relative transition width $\Delta T_c/T_c$ of the samples A413[36 h] and A563[36 h] changes only slightly with annealing, whereas for the samples A488[36 h] and A563[36 h],

### Table I. List of all as-grown and annealed Rb$_2$Fe$_4$Se$_2$ single-crystal samples investigated by various experimental techniques in this work.

| Sample     | $T_{\text{ann}}$ | $t_{\text{ann}}$ | Experiment           |
|------------|------------------|------------------|----------------------|
| A413[0 h] | 413 K            | 0 h              | Magnetometry         |
| A413[3 h] | 413 K            | 3 h              | Magnetometry         |
| A413[36 h]| 413 K            | 36 h             | Magnetometry         |
| A488[0 h] | 488 K            | 0 h              | Magnetometry         |
| A488[3 h] | 488 K            | 3 h              | Magnetometry         |
| A488[36 h]| 488 K            | 36 h             | Magnetometry         |
| A563[0 h] | 563 K            | 0 h              | Magnetometry         |
| A563[3 h] | 563 K            | 3 h              | Magnetometry         |
| A563[36 h]| 563 K            | 36 h             | Magnetometry         |
| A563[36 h]| 488 K            | 0 h              | Magnetometry         |
| A563[36 h]| 488 K            | 3 h              | Magnetometry         |
| A563[36 h]| 488 K            | 36 h             | Magnetometry         |
| B488[0 h] | 488 K            | 0 h              | Transport            |
| B488[3 h] | 488 K            | 3 h              | Transport            |
| C488[0 h] | 488 K            | 0 h              | $\mu$SR             |
| C488[60 h]| 488 K            | 60 h             | $\mu$SR             |
| D488[0 h] | 488 K            | 0 h              | STEM                 |
| D488[3 h] | 488 K            | 3 h              | STEM                 |
| A488[0 h] | 488 K            | 0 h              | Magnetometry         |
| A563[0 h] | 563 K            | 0 h              | Magnetometry         |

III. RESULTS

In Fig. 3, the zero-field-cooled (ZFC) magnetization, measured in a magnetic field $\mu_0 H = 0.3$ mT applied along the $c$ axis for the samples A413[36 h], A488[36 h], A563[36 h], and $A_{\text{488}}^\ast T_{\text{ann}}$ (see Table I) with $T_{\text{ann}} = 0$, 3, and 36 h are shown. The magnetization $M$ was normalized to the individual linear extrapolated value of $M(0)$. This allows us to directly compare the curves of the various crystals to each other despite their different masses and shapes. In a first step, the properties of the pristine as-grown samples (i.e., for $t_{\text{ann}} = 0$ h) were investigated [see Fig. 3(a)]. After these measurements, the samples were annealed at $T_{\text{ann}}$ for 3 h and were remeasured afterwards [see Fig. 3(b)], then again annealed at $T_{\text{ann}}$ for another 33 h (leading to a total annealing time of $t_{\text{ann}} = 36$ h), and finally remeasured [see Fig. 3(c)]. During all the measurements and annealings, the samples were kept inside the sealed ampoules. The as-grown samples A413[0 h], A488[0 h], and A563[0 h] show very similar behavior, exhibiting superconducting diamagnetism with a rather broad transition width. Only the sample A488[0 h] exhibits a slightly higher $T_c$ and a narrower transition width. The insets to Fig. 3 present a closeup of the onset of diamagnetism. Importantly, the transition temperature $T_c$ clearly changes for most of the samples after annealing for $t_{\text{ann}} = 3$ h and for $t_{\text{ann}} = 36$ h. Only $T_c$ for the sample A413[36 h] is essentially independent of $t_{\text{ann}}$. Note that both samples A488[36 h] and A563[36 h] exhibit a clearly narrower transition to the superconducting state with a higher $T_c$. In contrast, sample A563[36 h] behaves in the opposite way, showing a drastically lower $T_c$. The transition width $\Delta T_c$ was defined as the inverse of the maximal slope of the normalized magnetization $M/M(0)$ as a function of $T$:

$$\Delta T_c = \left( \frac{1}{M(0)} \max \left[ \frac{dM}{dT} \right] \right)^{-1}.$$  

The estimated values for $T_c$ and $\Delta T_c$ for all the samples studied are listed in Table II. In order to better specify the change for a measured property $P$ with annealing time $t_{\text{ann}}$, we introduce the following quantity:

$$\delta_{t_{\text{ann}}} (P) = \frac{P(t_{\text{ann}}) - P(0 \text{ h})}{P(0 \text{ h})}.$$  

With this formula, a clear increase of $T_c$ by $\sim 5\%–6\%$ is found for the samples A488[36 h] and A563[36 h] in comparison to the as-grown specimens (see Table II), whereas $T_c$ decreases for sample A563[36 h] by $\sim 27.3\%$ and remains almost constant for sample A413[36 h]. The relative transition width $\Delta T_c/T_c$ of the samples A413[36 h] and A563[36 h] changes only slightly with annealing, whereas for the samples A488[36 h] and A563[36 h].
FIG. 3. (Color online) Normalized ZFC magnetization $M(T)/M(0)$ for the Rb$_2$Fe$_{2-y}$Se$_2$ single crystals $A_{413}[t_{\text{ann}}]$, $A_{488}[t_{\text{ann}}]$, $A_{563}[t_{\text{ann}}]$, and $A_4^{*}[t_{\text{ann}}]$ in a magnetic field $\mu_0 H = 0.3$ mT applied along the $c$ axis. The panels present the data for the as-grown samples with $t_{\text{ann}} = 0$ h (a), annealed samples for $t_{\text{ann}} = 3$ h (b), and for $t_{\text{ann}} = 36$ h (c). The respective insets show closeups of the onset of diamagnetism.

**TABLE II.** Evolution of the transition temperature $T_c$ and transition width $\Delta T_c$ [see Eq. (1)] of the samples $A_{413}[t_{\text{ann}}]$, $A_{488}[t_{\text{ann}}]$, $A_{563}[t_{\text{ann}}]$, and $A_4^{*}[t_{\text{ann}}]$ with annealing time $t_{\text{ann}}$. The changes with annealing $\delta_{\text{ann}}(T_c)$ and $\delta_{\text{ann}}(\Delta T_c)$ were calculated applying Eq. (2).

| Sample       | $T_c$ (K) | $\delta_{\text{ann}}(T_c)$ | $\Delta T_c$ (K) | $\delta_{\text{ann}}(\Delta T_c)$ | $\Delta T_c/T_c$ |
|--------------|-----------|----------------------------|------------------|-----------------------------------|------------------|
| $A_{413}[0 \text{ h}]$ | 30.1(1)   | 14(1)                      |                 | 47(2)%                            |                   |
| $A_{413}[3 \text{ h}]$ | 30.1(1)   | ±0.0%                      | 14(1)           | ±0%                               | 47(2)%           |
| $A_{413}[36 \text{ h}]$ | 29.5(1)   | −2.0%                      | 16(1)           | +14%                              | 54(2)%           |
| $A_{488}[0 \text{ h}]$ | 30.0(1)   | 16(1)                      |                 |                                   | 53(3)%           |
| $A_{488}[3 \text{ h}]$ | 31.7(1)   | +5.7%                      | 9.5(5)          | −41%                              | 30(1)%           |
| $A_{488}[36 \text{ h}]$ | 31.8(1)   | +6.0%                      | 7.0(4)          | −56%                              | 22(1)%           |
| $A_{563}[0 \text{ h}]$ | 30.0(1)   | 17(1)                      |                 |                                   | 57(3)%           |
| $A_{563}[3 \text{ h}]$ | 28.0(1)   | −6.7%                      | 15(1)           | −12%                              | 54(3)%           |
| $A_{563}[36 \text{ h}]$ | 21.8(1)   | −27.3%                     | 10(1)           | −41%                              | 46(4)%           |
| $A_4^{*}[0 \text{ h}]$ | 31.6(1)   | 13(1)                      |                 |                                   | 41(2)%           |
| $A_4^{*}[3 \text{ h}]$ | 33.1(1)   | +4.7%                      | 2.2(2)          | −83%                              | 6.6(3)%           |
| $A_4^{*}[36 \text{ h}]$ | 33.3(1)   | +5.4%                      | 2.1(2)          | −84%                              | 6.3(3)%           |

**FIG. 4.** (Color online) Zero-field-cooled (ZFC) magnetization curves for the Rb$_2$Fe$_{2-y}$Se$_2$ single crystals $A_{413}[t_{\text{ann}}]$, $A_{488}[t_{\text{ann}}]$, $A_{563}[t_{\text{ann}}]$, and $A_4^{*}[t_{\text{ann}}]$ measured at 2.0 K as a function of $H_{\text{int}}$ along the $c$ axis. The corresponding $t_{\text{ann}}$ of the different panels are $t_{\text{ann}} = 0$ h (a), $t_{\text{ann}} = 3$ h (b), and $t_{\text{ann}} = 36$ h (c).

A clear improvement is seen. Note that the transition for $A_4^{*}[t_{\text{ann}}]$ becomes almost ideally sharp with long annealing.

Field-dependent magnetization measurements were performed to further investigate the superconducting properties of the samples $A_{413}[t_{\text{ann}}]$, $A_{488}[t_{\text{ann}}]$, $A_{563}[t_{\text{ann}}]$, and $A_4^{*}[t_{\text{ann}}]$. In Fig. 4, the corresponding ZFC magnetization curves measured at $T = 2.0$ K with variable $t_{\text{ann}}$ are presented. The internal magnetic field $H_{\text{int}}$ was calculated by correcting the applied magnetic field $H$ for the demagnetization of the samples

$$H_{\text{int}} = H - DM,$$

where $D$ is the demagnetization factor. The dimensions of the crystals used in this experiment were $\sim 2 \times 2 \times 0.5$ mm$^3$, yielding $D \approx 0.8$ for the measurements with $H$ applied along the $c$ axis being the shortest dimension. Hence, it was possible to determine the magnetization $M$ as a function of $H_{\text{int}}$. In Fig. 4(a), the $M(H_{\text{int}})$ data for $t_{\text{ann}} = 0$ h are presented. All samples show rather poor superconducting properties. Although $M(H_{\text{int}}) \approx -H_{\text{int}}$ for low magnetic fields (almost ideal diamagnetism), the $M(H_{\text{int}})$ curves strongly deviate from this linear behavior for fields exceeding 1–2 mT, indicating a rather small out-of-plane lower critical field $H_{c1}^{\parallel}$. By means of
the relation between \( H_{c1}^{\text{le}} \) and the in-plane magnetic penetration depth \( \lambda_{ab} \),

\[
\mu_0 H_{c1}^{\text{le}} = \frac{\Phi_0}{4\pi \lambda_{ab}^2} \left( \ln \kappa_{ab} + \frac{1}{2} \right),
\]

it was argued that a very small \( \mu_0 H_{c1} \approx 0.3 \text{ mT} \) is consistent with a large \( \lambda \approx 1-2 \mu\text{m}. \) However, this behavior is drastically changed with annealing as seen in Figs. 4(b) and 4(c). Although the measurements for sample \( A_{413}[t_{\text{ann}}] \) reveal no obvious change with increasing \( t_{\text{ann}} \), the samples \( A_{488}[t_{\text{ann}}] \) and \( A_{563}[t_{\text{ann}}] \) show both a considerably higher diamagnetic response at higher \( t_{\text{ann}} \), indicating an improved screening of the applied magnetic field. By defining \( H_{c1} \) as the magnetic field where the curves deviate from ideal diamagnetism, the best sample \( A_{563}[t_{\text{ann}}] \) yields a considerably larger \( \mu_0 H_{c1} \approx 10 \text{ mT} \) compared to the estimate \( \lesssim 1 \text{ mT} \) for the as-grown samples. Such a large value of 10 mT is consistent with \( \lambda \approx 270 \text{ nm} \), assuming a realistic Ginzburg-Landau parameter \( \kappa_{ab} \approx 100 \) in Eq. (4). For a quantitative comparison of the superconducting properties of the different samples, the superconducting susceptibility \( \chi_{sc}(\mu_0 H_{\text{int}}) \) was estimated using the relation

\[
\chi_{sc}(\mu_0 H_{\text{int}}) = \frac{M(\mu_0 H_{\text{int}})}{H_{\text{int}}}. \tag{5}
\]

In Table III, \( \chi_{sc}(1 \text{ mT}) \) and \( \chi_{sc}(10 \text{ mT}) \) are listed. Comparing \( \chi_{sc}(\mu_0 H_{\text{int}}) \) for the sample \( A_{413}[t_{\text{ann}}] \) with increasing \( t_{\text{ann}} \), no improvement of the diamagnetic response was found with annealing. However, for all other samples \( A_{488}[t_{\text{ann}}] \), \( A_{563}[t_{\text{ann}}] \), and \( A_{563}[t_{\text{ann}}] \), both \( \chi_{sc}(1 \text{ mT}) \) and \( \chi_{sc}(10 \text{ mT}) \) increase substantially with increasing \( t_{\text{ann}} \). Whereas the improvement of screening in 10 mT indicates an increase of critical current density, the changes observed in very low magnetic fields are rather related to an increase of \( H_{c1} \) connected with a decrease of \( \lambda \). This suggests that the changes induced by annealing directly influence the density and the mobility of the charge carriers in the superconducting phase.

Aside from magnetization, also resistivity experiments are expected to exhibit pronounced changes with annealing. Resistivity studies may provide independent and complementary information to the magnetization experiments. Whereas magnetization measurements probe the global macroscopic properties of a sample, its resistivity is sensitive to microscopic currents flowing through this mesoscopic phase-separated material. Figure 5 shows the in-plane resistivity \( \rho \) for the \( \text{Rb}_x\text{Fe}_{2-y}\text{Se}_2 \) single crystal, measured in zero magnetic field by cooling from 300 to 5 K. The measurements were performed on the as-grown sample (B488[0 h]) and were repeated after annealing in 488 K for 3 h (B488[3 h]) using the same contacts. A clear reduction of \( \rho \) in the normal state was found together with an increase of \( T_c \) from 31.5 K in the pristine sample to 33.1 K for the annealed sample (see Table IV), in very good agreement with the increase observed by magnetization (see Table II). The hump in \( \rho(T) \) between 100 and 150 K for the as-grown sample (B488[0 h]) seen in Fig. 5 was earlier interpreted as a possible metal-insulator transition.\(^{28}\) Such a transition would be likely related to the mesoscopic phase separation present in \( \text{Rb}_x\text{Fe}_{2-y}\text{Se}_2 \). In this picture, the minority phase is connected with percolative paths along which electrical current may flow.\(^{17}\) Interestingly, this hump is strongly decreased with annealing at 488 K for 3 h, indicating that normal-state electric conductivity is enhanced in the annealed sample.

In Figs. 6(a)–6(d), the resistivity measurements at low temperatures performed on the pristine and annealed \( \text{Rb}_x\text{Fe}_{2-y}\text{Se}_2 \) single crystal \( B_{488}[t_{\text{ann}}] \) for various magnetic fields applied along the \( c \) axis and in the \( ab \) plane are presented. The transition temperature \( T_c \) is reduced with increasing \( H \) for all configurations. In order to quantify this phase transition, the upper critical field \( H_{c2} \) is determined by following field and temperature at which 50% of the normal-state resistivity is suppressed [dashed lines in Figs. 6(a)–6(d)]. Figure 6(e) shows the estimated upper critical field along the \( c \) axis \( [H_{c2}^{sc}(T)] \) and in the \( ab \) plane \( [H_{c2}^{ab}(T)] \) for the as-grown and annealed samples. An increase of \( T_c \) with annealing is observed in the whole temperature-field phase diagram. The slopes \( -\mu_0 dH_{c2}^{\alpha}/dT \) (\( \alpha = c,ab \)) of the phase

![FIG. 5. (Color online) In-plane resistivity \( \rho \) of the \( \text{Rb}_x\text{Fe}_{2-y}\text{Se}_2 \) samples B488[0 h] and B488[3 h]. The pronounced hump in the normal-state resistivity of the as-grown sample B488[0 h] decreases dramatically after annealing and the superconducting \( T_c \) increases from 31.5 to 33.1 K.](image-url)
TABLE IV. Evolution of $T_c$, $-dH^c_{c2}/dT$, and $-dH^{ab}_{c2}/dT$ with annealing time $t_{ann}$ for fields applied parallel to the $c$ axis and to the $ab$ plane for samples $Rb\text{Fe}_{2-y}Se_2$ single crystals with $y=0.0$ and $y=3/8$ respectively. $T_c$ increases by 1.6 K as a result of annealing. The solid lines are guides to the linear part of the $H_{c2}(T)$ curves, used in the WHH approximation [Eq. (6)].

| Sample | $T_c$ (K) | $\delta t_{ann}$ | $-\mu_0 dH^c_{c2}/dT$ (T/K) | $-\mu_0 dH^{ab}_{c2}/dT$ (T/K) |
|--------|-----------|------------------|-----------------------------|-----------------------------|
| $Rb\text{Fe}_{2-y}Se_2$ | $T_c$ | $\delta t_{ann}$ | $-\mu_0 dH^c_{c2}/dT$ (T/K) | $-\mu_0 dH^{ab}_{c2}/dT$ (T/K) |
| $Rb\text{Fe}_{2-y}Se_2$ | 31.54(5) | $+4.9\%$ | 1.58(3) | 4.6(1) |
| $Rb\text{Fe}_{2-y}Se_2$ | 33.07(5) | $+6.0\%$ | 1.59(2) | 5.8(1) |

where $-dH^c_{c2}/dT$ is defined as the maximal slope of the $H_{c2}(T)$ curve for fields applied parallel to the $c$ axis, and $-dH^{ab}_{c2}/dT$ is used to determine the upper critical field $H_{c2}(T)$ curve in the vicinity of $T_c$. Here, we considered the linear part of the curve well below but not too far from $T_c$. The solid lines are guides to the linear part of the $H_{c2}(T)$ curves, used in the WHH approximation [Eq. (6)].

\[
H_{c2}(0) = -0.69 T_c \frac{dH_{c2}}{dT},
\]

where $-dH^c_{c2}/dT$ is defined as the maximal slope of the $H_{c2}(T)$ curve in the vicinity of $T_c$. Here, we considered the linear part of the curve well below but not too far from $T_c$, emphasized in Fig. 6(e), which yields a more reliable estimate for the upper critical field of superconductors with an upturn curvature close to $T_c$. Interestingly, the upper critical field anisotropy

\[
\gamma_H = \frac{H_{c2}^c}{H_{c2}^{ab}}
\]

increases with annealing by 24.1% (see Table V). This suggests that thermally treated iron-chalcogenide superconductors with improved macroscopic physical properties are more anisotropic.

Aside from investigating the properties in the superconducting state, it is also important to monitor the changes in normal-state properties of the $Rb\text{Fe}_{2-y}Se_2$ single crystals as a result of post annealing. In Fig. 7, we present the magnetic moment $m$ measured in 1 T and in 3 T for $A_{413}[I_{ann}]$, $A_{488}[I_{ann}]$, $A_{563}[I_{ann}]$, and $A_{413}[I_{ann}]$, with $t_{ann} = 0, 3, 6$ h, and $T_c$ increases by 1.6 K as a result of annealing. The solid lines are guides to the linear part of the $H_{c2}(T)$ curves, used in the WHH approximation [Eq. (6)].

**FIG. 6.** (Color online) Resistivity of the samples $Rb\text{Fe}_{2-y}Se_2$ for magnetic fields of 0 and 9 T, varied by 0.5-T steps, for fields in the $ab$ plane and along the $c$ axis. The measurements were performed for the as-grown sample $Rb\text{Fe}_{2-y}Se_2$ [panels (a) and (b)] and for the annealed sample $Rb\text{Fe}_{2-y}Se_2$ [panels (c) and (d)], with $H$ applied along the $c$ axis and in the $ab$ plane. The dashed lines denote 50% of the extrapolated normal-state resistivity, which was used as a criterion to determine $H_{c2}(T)$, shown in panel (e). The transition temperature $T_c$ increases by 1.6 K as a result of annealing. The solid lines are guides to the linear part of the $H_{c2}(T)$ curves, used in the WHH approximation [Eq. (6)].

**FIG. 7.** (Color online) Measured magnetic moment $m(10^6 \mu_0 \text{m}^2)$ for pristine and annealed $Rb\text{Fe}_{2-y}Se_2$ single crystals in the temperature range between 50 and 370 K for magnetic fields of 1 T (a) and 3 T (b), applied along the $c$ axis.
TABLE V. Evolution of $H^\parallel_{c2}(0)$, $H^\perp_{c2}(0)$, and $\gamma_H$ with annealing time $t_{ann}$ for samples B488[0 h] and B488[3 h]. The changes with annealing $\delta_t[H^\parallel_{c2}(0)]$, $\delta_t[H^\perp_{c2}(0)]$, and $\delta_t(\gamma_H)$ were calculated applying Eq. (2).

| Sample     | $\mu_0 H^\parallel_{c2}(0)$ (T) | $\delta_t[H^\parallel_{c2}(0)]$ | $\mu_0 H^\perp_{c2}(0)$ (T) | $\delta_t[H^\perp_{c2}(0)]$ | $\gamma_H$ | $\delta_t(\gamma_H)$ |
|------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|-------------|-----------------------|
| B488[0 h]  | 34.6(7)                         | +5.5%                           | 101(3)                          | +31.7%                         | 2.9(2)      | +24.1%                |
| B488[3 h]  | 36.5(5)                         |                                 | 133(3)                          |                                 | 3.6(2)      |                       |

36 h. The magnetic moment in the normal state, recorded between 50 and 370 K, systematically increases with $t_{ann}$ for all investigated samples. In the normal state, the major component of the magnetic moment is stemming from the antiferromagnetic phase. However, some small ferromagnetic contribution is present in all Rb$_x$Fe$_{2-y}$Se$_2$ crystals, most likely due to a ferromagnetic impurity phase. From the measurements presented in Fig. 7 we determined the antiferromagnetic susceptibility $\chi_{AFM}(T)$ according to

$$\chi_{AFM}(T) = \frac{1}{M} \frac{m(\mu_0 H) - m(\mu_0 H')}{H - H'},$$

where $M$ denotes the sample mass. Here, $\mu_0 H$ and $\mu_0 H'$ are 1 and 3 T, respectively. The ferromagnetic contribution to the magnetization is assumed to be constant in field and is derived accordingly:

$$M_{FM}(T) = \frac{m(\mu_0 H)}{M} - \chi_{AFM}(T)H.$$

The antiferromagnetic susceptibility for all the as-grown samples and those annealed for 3 h and for 36 h are shown in Fig. 8(a). The ferromagnetic component of the magnetization $M_{FM}(T)$ is shown in Fig. 8(b). Sample A413 [$t_{ann}$] remains unaffected by annealing, as already observed in the ZFC magnetization experiments performed in the superconducting state as discussed above. However, for the samples A488 [$t_{ann}$], A563 [$t_{ann}$], and A413 [$t_{ann}$], the high-field susceptibility $\chi_{AFM}(T)$ increases substantially with increasing $t_{ann}$. In Table VI, we list the observed values for $\chi_{AFM}(50 \, K)$ for all samples and $t_{ann}$. Obviously, the change in $\chi_{AFM}(50 \, K)$ is most pronounced for the sample A488 [$t_{ann}$], annealed at 563 K. In addition, the ferromagnetic component $M_{FM}(T)$ is almost unchanged for sample A413 [$t_{ann}$], but increases for the samples A488 [$t_{ann}$], A563 [$t_{ann}$], and A413 [$t_{ann}$] with increasing $t_{ann}$. Again, the change in $M_{FM}(50 \, K)$ is maximal for sample A563 [$t_{ann}$].

The effect of annealing on the magnetic and superconducting properties of Rb$_x$Fe$_{2-y}$Se$_2$ single crystals was further investigated by means of transverse-field (TF) and zero-field (ZF) $\mu$SR experiments. The $\mu$SR measurements are based on the observation of the time evolution of the muon spin polarization. (For a detailed description of the $\mu$SR technique, see e.g. Ref. 36.) For these experiments, two mosaics of samples were prepared: (i) C488[0 h], consisting of three as-grown Rb$_x$Fe$_{2-y}$Se$_2$ single crystals, and (ii) C488[60 h], consisting of three Rb$_x$Fe$_{2-y}$Se$_2$ single crystals simultaneously annealed in 488 K for 60 h. Previous $\mu$SR experiments revealed that Rb$_x$Fe$_{2-y}$Se$_2$ consists of a magnetic ($\sim 90\%$) and a nonmagnetic superconducting ($\sim 10\%$) phase. In order to investigate the superconducting properties, a field of 70 mT was applied transverse to the initial muon spin polarization and parallel to the crystallographic c axis. In this TF configuration, the muons probe the local magnetic field distribution $P(B)$ of the vortex lattice formed in the superconducting areas. Simultaneously, the signal stemming from the magnetic regions of the sample is suppressed since the

FIG. 8. (Color online) (a) Antiferromagnetic susceptibility $\chi_{AFM}(T)$ in the normal state of pristine and annealed Rb$_x$Fe$_{2-y}$Se$_2$ single crystals determined from the data shown in Fig. 7 using Eq. (8). For clarity, the curves representing the four different annealing sets are vertically shifted to each other. Whereas no change of $\chi_{AFM}(T)$ is found by annealing for sample A413 [$t_{ann}$], for all other samples, $\chi_{AFM}(T)$ increases with increasing $t_{ann}$. (b) Ferromagnetic component $M_{FM}(T)$, being constant for sample A413 [$t_{ann}$] as a function of $t_{ann}$. For all other samples, $M_{FM}(50 \, K)$ increases substantially with increasing $t_{ann}$. 

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superposition of the strong internal field and the weak external field leads to a fast depolarization and to a loss of asymmetry.

Consistent with the above presented macroscopic magnetization and resistivity results, also the intrinsic superconducting properties are significantly improved after annealing. The line shape of the local magnetic field distribution \( P(B) \) of \( C_{488}[60 \text{ h}] \) shown in Fig. 9(a) is more asymmetric compared to that of \( C_{488}[0 \text{ h}] \), indicating the presence of a more homogeneous and more regular vortex lattice in the superconducting regions. Note that the sharp peak of \( P(B) \) at 70 mT is stemming from the signal of background muons, the spins of which rotate simply in the applied magnetic field. A more detailed analysis of the as obtained \( P(B) \) yields that the shielding of the magnetic field for \( C_{488}[60 \text{ h}] \) is substantially larger due to a reduction of the first moment \( \langle B \rangle \) of \( P(B) \) by \( \sim 5\% \). This is surprising since the microscopic in-plane magnetic penetration depth \( \delta_{ab}(0) \approx 258(2) \text{ nm} \), as well as the total asymmetry of the superconducting part, remain essentially unchanged after 60 h annealing [see Fig. 9(b)].

These results imply that the volume fraction of the magnetic and the nonmagnetic phases is unaffected by annealing, in contradiction to the conclusions of a neutron diffraction study, reporting a reduction of the minority phase after annealing of \( \text{Rb}_x\text{Fe}_{2-y}\text{Se}_2 \) single crystals for 100 h at 488 K.16 This discrepancy might arise from the difference in \( T_p \) of the samples studied here (489 K) and in Ref. 16 (475 K).

Importantly, the normal-state relaxation rate \( \sigma \) of the \( \mu \)SR time spectra derived from the data at 40 K (well above \( T_c \)) increases drastically with \( t_{\text{ann}} \) [see Figs. 9(b) and 9(c)]. Whereas for the as-grown sample \( C_{488}[0 \text{ h}] \) \( \sigma = 0.141(33) \mu \text{s}^{-1} \), the relaxation rate of the 60-h annealed sample \( C_{488}[60 \text{ h}] \) is considerably larger \( [\sigma = 3.03(43) \mu \text{s}^{-1}] \). This indicates a substantially increased field inhomogeneity in the nonmagnetic part of the sample. Since the volume fraction is unchanged during annealing, this suggests that the microstructure of the sample caused by mesoscopic phase separation is modified by annealing at 488 K, in such a way that the individual size of the nonmagnetic regions is reduced and their number is increased, but their total volume remains unaffected.

In order to examine our samples for the internal magnetic field distribution when no magnetic field is applied, low-temperature ZF \( \mu \)SR experiments were performed on the same \( \text{Rb}_x\text{Fe}_{2-y}\text{Se}_2 \) single crystals. Consistent with the results of the TF experiments, the total volume of the nonmagnetic regions was found to be \( \sim 10\% \) of the total sample volume only. In the ZF data, a clear oscillating signal may be found in all samples for very short time scales as shown in Fig. 10. An analysis of the time evolution of this signal revealed that two internal magnetic fields \( B_{\text{int.1}} \approx 1 \text{T} \) and \( B_{\text{int.2}} \approx 3 \text{T} \) are present in the samples. In analogy to the evolution of the magnetic volume fraction, \( B_{\text{int.1}} \) and \( B_{\text{int.2}} \) are not affected by annealing at 488 K. They are directly proportional to the iron moment in the antiferromagnetic phase. Moreover, annealing again does not affect the ratio \( B_{\text{int.1}}/B_{\text{int.2}} \). Hence, no changes in the internal magnetic fields were observed by \( \mu \)SR after annealing the as-grown \( \text{Rb}_x\text{Fe}_{2-y}\text{Se}_2 \) single crystals, even though the macroscopic superconducting properties were substantially improved (see Figs. 3 and 4).

In order to visualize microscopic changes in the phase separation of our \( \text{Rb}_x\text{Fe}_{2-y}\text{Se}_2 \) single crystals with annealing, additional STEM images were taken on as-grown and annealed samples \( D_{488}[0 \text{ h}] \) and \( D_{488}[3 \text{ h}] \) (see Fig. 11). The microstructure caused by mesoscopic phase separation in the annealed sample \( D_{488}[3 \text{ h}] \), shown in Fig. 11(b), is modified compared to the one of the as-grown sample \( D_{488}[0 \text{ h}] \), shown in Fig. 11(a). Whereas a few inclusions of the minority phases only are observed at the surface of \( D_{488}[0 \text{ h}] \), sample \( D_{488}[3 \text{ h}] \) reveals plenty of such inclusions in the same area. However, the inclusions of the minority phase of sample \( D_{488}[3 \text{ h}] \) are in general smaller in size than the ones of the as-grown sample \( D_{488}[0 \text{ h}] \), in agreement with the results of the above \( \mu \)SR experiments.

### IV. DISCUSSION

The superconducting and normal-state properties of mesoscopically phase-separated \( \text{Rb}_x\text{Fe}_{2-y}\text{Se}_2 \), where nonmagnetic regions exist in a magnetic surrounding, are strikingly similar to those expected for granular superconductors. From early work on granular superconductors it is known that

| Sample      | \( x_{\text{AFM}}(50 \text{ K}) \) \( \times 10^{-8} \text{ m}^2/\text{kg} \) | \( \delta_{\text{int}}[x_{\text{AFM}}(50 \text{ K})] \) | \( M_{\text{FM}}(50 \text{ K}) \) \( \times 10^{-3} \text{ Am}^2/\text{kg} \) | \( \delta_{\text{int}}[M_{\text{FM}}(50 \text{ K})] \) |
|-------------|---------------------------------|-----------------|-----------------|-----------------|
| \( A_{413}[0 \text{ h}] \) | 2.020(1)                        | \(-0.7\%\)      | 2.79(1)         | \(-1.4\%\)     |
| \( A_{413}[3 \text{ h}] \) | 2.060(1)                        | \(-1.2\%\)      | 2.75(1)         | \(+0.0\%\)     |
| \( A_{413}[6 \text{ h}] \) | 2.044(1)                        | \(-1.2\%\)      | 2.79(1)         | \(+0.0\%\)     |
| \( A_{488}[0 \text{ h}] \) | 1.808(1)                        | \(-9.4\%\)      | 2.77(1)         | \(+0.4\%\)     |
| \( A_{488}[3 \text{ h}] \) | 1.883(1)                        | \(+4.1\%\)      | 5.91(1)         | \(+11.3\%\)    |
| \( A_{488}[6 \text{ h}] \) | 1.953(1)                        | \(+8.0\%\)      | 10.73(1)        | \(+28.7\%\)    |
| \( A_{563}[0 \text{ h}] \) | 2.400(1)                        | \(-9.4\%\)      | 6.91(1)         | \(+15.0\%\)    |
| \( A_{563}[3 \text{ h}] \) | 2.598(1)                        | \(+8.3\%\)      | 17.25(1)        | \(+31.7\%\)    |
| \( A_{563}[6 \text{ h}] \) | 2.778(1)                        | \(+15.8\%\)     | 28.78(1)        | \(+31.7\%\)    |
| \( A_{488}[0 \text{ h}] \) | 1.796(1)                        | \(-9.4\%\)      | 2.67(1)         | \(+28.5\%\)    |
| \( A_{488}[3 \text{ h}] \) | 1.883(1)                        | \(+4.8\%\)      | 3.43(1)         | \(+496\%\)     |
| \( A_{488}[6 \text{ h}] \) | 1.947(1)                        | \(+8.4\%\)      | 15.92(1)        | \(+496\%\)     |
the macroscopic properties of such materials studied by various techniques may vary substantially, depending on the particular grain-size distribution and their coupling by Josephson links.37–39 Importantly, granular superconductors may easily appear as bulk superconducting, however, their critical fields ($H_{c1}$ and $H_{c2}$) differ substantially from those of related nongranular superconductors. Such a scenario may also hold for mesoscopically phase-separated Rb$_2$Fe$_{2-y}$Se$_2$ since various experimental techniques provide quite different values for $\lambda$. For Rb$_2$Fe$_{2-y}$Se$_2$, recent $\mu$SR studies yielded $\lambda_{\text{int}}(0) \approx 250$–260 nm,15,40 in agreement with $\lambda_{\text{int}}(0) \approx 290$ nm obtained for K$_x$Fe$_{2-y}$Se$_2$ by means of high-field nuclear magnetic resonance (NMR) experiments.41 These values are considerably smaller than those usually obtained by macroscopic techniques [$\lambda_{\text{int}}(0) \approx 1.6$–2.2 $\mu$m].$^{12,42,43}$ In a mesoscopically phase-separated superconductor, macroscopic experiments yield an effective magnetic penetration depth, which is a measure of the length scale over which the magnetic field penetrates the sample. On the other hand, $\mu$SR is a microscopic probe of the vortex state and is only sensitive to the superconducting fraction of the sample. Therefore, $\mu$SR measures a value of the magnetic penetration depth which is closer to the intrinsic value than the values usually obtained by macroscopic techniques. Since so far no single-phase superconducting $A_1$Fe$_{2-y}$Se$_2$ sample could be synthesized, it should not be excluded that granularity might be an important ingredient for the appearance of superconductivity in this system.

As strongly suggested by the presented magnetization and resistivity data, pronounced changes of the physical properties of Rb$_2$Fe$_{2-y}$Se$_2$ are caused by tuning the annealing conditions. Whereas annealing at 413 K, well below $T_p$, does not lead to any significant change in magnetic and transport properties, annealing just at $T_p$, the onset of phase separation, favors the enhancement of superconductivity. Accordingly, $T_c$ increases, the transition sharpens, the normal-state resistivity decreases, and $H_{c2}$ increases. However, after annealing at 563 K, well above $T_p$, all superconducting properties get drastically sup-

![FIG. 9. (Color online) Results of the TF $\mu$SR investigation of as-grown and 60-h annealed Rb$_2$Fe$_{2-y}$Se$_2$ single crystals, C$_{asg}$[0 h] and C$_{asg}$[60 h], in a magnetic field of 70 mT applied along the c axis. (a) $P(B)$ for both samples at 5 K. The line shape for C$_{asg}$[60 h] is more asymmetric compared to that for the as-grown sample C$_{asg}$[0 h]. (b) and (c) $\mu$SR time spectra at 40 K for sample C$_{asg}$[0 h] and C$_{asg}$[60 h]. The thin solid line is a fit to the data assuming a single relaxation rate $\sigma$. The thick solid line is the envelope of the oscillating function. The data for the annealed sample C$_{asg}$[60 h] exhibit a significantly faster damping.]

![FIG. 10. (Color online) Results of the ZF $\mu$SR investigation of as-grown and 60-h annealed Rb$_2$Fe$_{2-y}$Se$_2$ single crystals, C$_{asg}$[0 h] and C$_{asg}$[60 h]. All data were modeled assuming two internal magnetic fields $B_{int,1} \approx 1$ T and $B_{int,2} \approx 3$ T.]

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pressed. In addition, the antiferromagnetic susceptibility and the ferromagnetic saturation magnetization of the investigated samples systematically increase. This may be related to the change in iron valency as observed in annealed K$_{0.8}$Fe$_{1.6}$Se$_{2.44}$ or with an increase of Fe-based impurity phases.

A recent neutron diffraction study of the Rb$_x$Fe$_{2-y}$Se$_2$ system reports a pronounced reduction of the minority 122-phase when the samples were annealed at 488 K for 100 h.\textsuperscript{16} However, the present $\mu$SR experiments yield clear evidence that the volume fraction of the two phases remains unchanged by annealing, while the field inhomogeneity in the nonmagnetic parts of the sample increases substantially. This implies that the microstructure caused by mesoscopic phase separation in the sample is modified by annealing just at $T_p$ in such a way that the size of nonmagnetic regions is reduced, and the number of regions is increased, but their total volume remains unaffected. Since the $\mu$SR results clearly demonstrate that the total volume of the minority phase is constant, even after 60 h of annealing, this rearrangement of the coexisting phases leads to the conclusion that changes of the coupling between these regions must be related to the improvement of superconductive properties. Whereas 488 K was chosen to match the onset of phase separation $T_p \approx 489$ K in the single crystals studied here, the samples used in the neutron diffraction study had a significantly lower $T_p \approx 475$ K.\textsuperscript{16} Therefore, the observed reduction of the minority phase found by the neutron study might be due to a partial degradation of the minority phase as a result of 100-h annealing at temperatures exceeding $T_p$. That this scenario appears to be reasonable is further supported by the data presented in Fig. 12, where a series of magnetization measurements are shown for a Rb$_x$Fe$_{2-y}$Se$_2$ single crystal of a similar batch as the one used above. Here, always the same temperature dependence of the ZFC magnetization measurement in a magnetic field of $\mu_0 H = 0.3$ mT along the $c$ axis was performed after each subsequent annealing of the sealed single crystal in a quartz ampoule.

Note that $T_c$ of the as-grown sample is easily shifted to higher values by an annealing at 488 K for some hours. However, after the subsequent annealings during which the temperature was modestly increased up to 563 K, superconductivity is strongly suppressed, as seen by the decrease of $T_c$ and the broadening of the transition. During the final annealing, again the optimal annealing temperature of 488 K was chosen, this

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure11.png}
\caption{(Color online) STEM images of as-grown and annealed Rb$_x$Fe$_{2-y}$Se$_2$ single crystals D$_{asg}$[0 h] and D$_{asg}$[3 h]. The microstructure caused by mesoscopic phase separation in the annealed sample D$_{asg}$[3 h], shown in panel (b), is modified compared to the one of the as-grown sample D$_{asg}$[0 h], shown in panel (a).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure12.png}
\caption{(Color online) Series of temperature-dependent ZFC magnetization measurements on a Rb$_x$Fe$_{2-y}$Se$_2$ single crystal in 0.3 mT. The curves obtained after the various post annealings of the sample are labeled by the respective number.}
\end{figure}
time for a very long annealing time up to 72 h. However, superconductivity did not fully recover. Obviously, the short annealings at temperatures exceeding $T_p$ formed additional magnetic phases, which can not be reversed anymore, even by choosing a very long annealing time.

All changes of superconducting and magnetic properties caused by annealing are evidently related to changes in the microstructure of the sample caused by mesoscopic phase separation in Rb$_2$Fe$_{2−x}$Se$_2$. The difference of the superconducting properties between the as-grown and annealed single crystals is likely explained by assuming that inhomogeneities (in particular, phase boundaries and/or stripes) are necessary to enhance superconductivity.\(^{45-49}\) In the present case, the existing boundaries between the magnetic majority regions and nonmagnetic minority regions may play the role of such inhomogeneities. In the current case, reviewing the changes observed of the superconducting and normal-state properties with annealing, it is likely that the intergrain coupling between magnetic and nonmagnetic domains is crucial. Annealing of Rb$_2$Fe$_{2−x}$Se$_2$ single crystals just at $T_p$ favors the mesoscopic phase separation in such a way that domain boundaries are further developed, improving all superconducting properties. However, if the samples are annealed at higher temperature, the superconducting phase degrades and by that it is more difficult to build up a percolative network favorable for superconductivity. In total, \(\sim\)10\% of the sample remains superconducting in a magnetic field of 70 mT, whereas its macroscopic properties strongly depend on the optimal coupling between the superconducting regions, being strongly field and temperature dependent. This scenario appears similar to that of a granular superconductor in which the macroscopic physics is directly connected to the microscopic Josephson coupling between the individual grains. In addition, all changes in the phase separation may be related to changes in crystal structure and lattice parameters.\(^{10}\) Thus, internal pressure on the superconducting and nonsuperconducting domains may be likely involved in the appearance of superconductivity. Besides, also metallic nanoclusters were reported to show enhanced superconducting properties.\(^{30}\)

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**V. CONCLUSIONS**

Extended magnetization and resistivity measurements of Rb$_2$Fe$_{2−x}$Se$_2$ single crystals revealed that post annealing at a temperature well below the onset temperature of phase separation $T_p$ neither changes the magnetic nor the superconducting properties of the crystals. Annealing at a temperature above $T_p$ reduces the value of $T_c$ drastically and suppresses antiferromagnetic order. However, annealing at 488 K just at $T_p$ leads to a substantial increase of $T_c$ and sharpens the transition to the superconducting state. These results suggest that the superconducting properties of mesoscopically phase-separated Rb$_2$Fe$_{2−x}$Se$_2$ can be tuned by the annealing temperature. In addition, $\mu$SR and STEM investigations indicate that nonmagnetic regions of the sample rearrange with annealing at 488 K in such a way that their individual size is reduced and the number of regions is increased, but their total volume remains unaffected. At temperatures exceeding $T_p$, where the majority $F_4/m$ phase prevails, ferromagnetism is enhanced with annealing time, but is presumably detrimental to the formation of the superconducting phase. In conclusion, by annealing single crystals of Rb$_2$Fe$_{2−x}$Se$_2$, the microstructure of the crystals arising from mesoscopic phase separation is changed, leading to an improvement of the superconducting properties and an enhancement of $T_c$.

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