Topical Review

Review of annealing effects and superconductivity in Fe$_{1+y}$Te$_{1-x}$Se$_x$ superconductors

Yue Sun$^{1,2,3,4}$, Zhixiang Shi$^{1,4}$ and Tsuyoshi Tamegai$^3$

$^1$School of Physics and Key Laboratory of MEMS of the Ministry of Education, Southeast University, Nanjing 211189, People’s Republic of China
$^2$Department of Physics and Mathematics, Aoyama Gakuin University, Sagamihara 252-5258, Japan
$^3$Department of Applied Physics, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan

E-mail: sunyue@phys.aoyama.ac.jp and zxshi@seu.edu.cn

Received 20 September 2018, revised 5 May 2019
Accepted for publication 1 July 2019
Published 22 August 2019

Abstract

Among iron-based superconductors, Fe$_{1+y}$Te$_{1-x}$Se$_x$ is unique in its structural simplicity, consisting of only FeTe/Se layers, which is favorable for probing the mechanism of superconductivity. Recently, a topological surface superconductivity as well as Majorana fermions has been observed, which makes Fe$_{1+y}$Te$_{1-x}$Se$_x$ the first high-temperature topological superconductor. Thus, Fe$_{1+y}$Te$_{1-x}$Se$_x$ is unique for the study of both high temperature and topological superconductivities. Since the large size single crystal of Fe$_{1+y}$Te$_{1-x}$Se$_x$ can be easily grown, much research has been performed. However, a large number of the reported results are controversial, or differ between groups, including those related to basic properties such as resistivity, susceptibility, the Hall effect, gap structure, phase diagram, etc. These controversies are believed to stem from the sample-dependent Fe nonstoichiometries, which originate from the partial occupation of the second Fe site (the excess Fe site, expressed as $y$ in the formula of Fe$_{1+y}$Te$_{1-x}$Se$_x$) in the Te/Se layer. The excess Fe with valence near Fe$^{4+}$ will provide electron doping into the system. Meanwhile, excess Fe is also strongly magnetic, which provides local moments that interact with the adjacent Fe layers. The magnetic moment from the excess Fe will act as a paring breaker and also localize the charge carriers. Thus, the existence of the excess Fe complicates the study of Fe$_{1+y}$Te$_{1-x}$Se$_x$ from the superconducting to normal state properties. Removing excess Fe is essential in order to probe the intrinsic properties and mechanism of superconductivity, as well as for the applications of Fe$_{1+y}$Te$_{1-x}$Se$_x$ compounds. In this topical review, we present an overview of the reported annealing methods, and conclude the effective approaches to remove the excess Fe in Fe$_{1+y}$Te$_{1-x}$Se$_x$. Furthermore, we discuss the mechanism of annealing based on the evolutions of structure, composition, and morphology. We also review the annealing effects on the normal state and superconducting properties, including the magnetism, transport properties, band structure, $T_c$, phase diagram, upper critical field, anisotropy, critical current density, gap structure, and superconducting pairing. This review presents not only the optimal way to prepare crystals without excess Fe, but also the intrinsic properties of Fe$_{1+y}$Te$_{1-x}$Se$_x$ without the influence of excess Fe.

Keywords: iron chalcogenides, Fe$_{1+y}$Te$_{1-x}$Se$_x$, annealing effect, superconductivity, excess Fe

(Some figures may appear in colour only in the online journal)

---

4 Authors to whom any correspondence should be addressed.
1. Introduction

As a member of the iron-based superconductors (IBSs), iron chalcogenide FeSe was first reported to be a superconductor in 2008 by Hsu et al. [1]. Although the initial superconducting transition temperature, $T_c$, of FeSe was only $\sim 9$ K, it was increased up to 14 K with an appropriate Te substitution [2], and to 37 K under high pressure [3]. Furthermore, by intercalating spacer layers between adjacent FeSe layers, $T_c$ has been enhanced to over 40 K for example Li$_x$(NH$_3$)$_2$(NH)$_2$FeSe$_2$ [4], Li$_{1-y}$Fe$_y$(OH)Fe$_{1-y}$Se [5], and Na(C$_2$H$_8$N$_2$)$_2$Fe$_2$Se$_2$ [6]. Moreover, gate-induced carrier doping using the electric double layer was reported to increase the $T_c$ of FeSe flakes to 48 K [7]. More interestingly, angle-resolved photoemission spectroscopy (ARPES) revealed an unexpectedly large superconducting gap $\sim$19 meV in a monolayer FeSe, suggesting a $T_c$ as high as 65 K [8], and a sign of $T_c$ even above 100 K was also reported [9]. Thus, $T_c$ of iron chalcogenides can be easily tuned by doping, pressure, intercalating, or even reducing the dimensionality, which is fascinating for the study of superconductivity (SC).

Among iron chalcogenides, Fe$_{1+y}$Te$_{1-x}$Se$_x$ is unique in its structural simplicity, composing of only iron–chalcogenide layers, which is favorable for exploring the mechanism of SC. Band structure calculation [10] and ARPES [11] results show that the Fermi surface of FeTe$_{1-x}$Se$_x$ is characterized by hole bands around the $\Gamma$ point and electron bands around the $M$ point, which is similar to iron pnictides. Moreover, the competition between magnetism and SC, similar to iron pnictides, is also observed in iron chalcogenides [12]. The parent compound Fe$_{1+y}$Te is not superconducting, but exhibits a spin–density wave (SDW) ground state. With Se doping, SC emerges and $T_c$ goes up to 14 K accompanied by the suppression of SDW. Iron chalcogenides also manifest some differences compared with iron pnictides. In particular, Fe$_{1+y}$Te$_{1-x}$Se$_x$ exhibits a bi-collinear antiferromagnetic ordering and it can be either commensurate or incommensurate depending on the Fe content [13, 14], which is different from the common collinear commensurate antiferromagnetic ordering observed in iron pnictides.

In the band structure, an extremely small Fermi energy is observed in Fe$_{1+y}$Te$_{1-x}$Se$_x$ by ARPES measurements, which indicates that it is in the crossover regime from Bardeen–Cooper–Schrieffer (BCS) to Bose–Einstein condensation (BEC) [15]. Recently, a topological surface SC [16, 17] as well as Majorana fermions have been observed [18, 19], which makes Fe$_{1+y}$Te$_{1-x}$Se$_x$ the first high-temperature topological superconductor. These features make Fe$_{1+y}$Te$_{1-x}$Se$_x$ one of the most attractive compounds in the study of condensed matter physics. Furthermore, its high upper critical magnetic field ($\sim$50 Tesla) and the lower toxicity compared with iron pnictides suggest that Fe$_{1+y}$Te$_{1-x}$Se$_x$ is also favorable for applications. To date, tapes with transport $J_c$ over $10^7$ A cm$^{-2}$ under a self-field and over $10^5$ A cm$^{-2}$ under 30 T at 4.2 K have been fabricated [20].

Although significant efforts have been focused on both fundamental and application studies of Fe$_{1+y}$Te$_{1-x}$Se$_x$, there remains controversy over some fundamental properties. For resistivity, both metallic and nonmetallic behaviors have been reported, and the absolute value just above $T_c$ has a spread from 200 to 1500 $\rho$ cm [2, 21–26]. For the Hall coefficient, conflicting low-temperature behaviors have been observed in crystals with nominally the same amount of Se [23–25]. The reported critical current density, $J_c$, measured at the same condition (such as 5 K, zero field), ranges from $10^7$ A cm$^{-2}$ to over $10^5$ A cm$^{-2}$ in the optimally-doped crystals [21, 27–29]. In the phase diagram, although Liu et al reported that bulk SC resides only in the region where the Se level is higher than 29% [12], it was observed in the Se doping level between 10 and 50% by Noji et al [30]. For the gap structure, two ARPES measurements suggest that the isotropic superconducting gap [16, 31], while an anisotropic gap structure was suggested by another ARPES report [32] and angle-resolved specific heat measurement [33].

These controversies are believed to come from the sample-dependent Fe nonstoichiometries, which originate from the partial occupation of the second Fe site (excess Fe site, expressed as $y$ in the formula of Fe$_{1+y}$Te$_{1-x}$Se$_x$) in the Te/Se layer [13, 34]. The excess Fe with valence near Fe$^+$ will provide electron doping into the 11 system. The excess Fe is also strongly magnetic, which provides local moments that interact with the adjacent Fe layers [35]. The magnetic moment from excess Fe will act as a pair breaker and also localize the charge carriers [23, 25]. In the study of the topological SC of Fe$_{1+y}$Te$_{1-x}$Se$_x$, the excess Fe obscures the surface state in the ARPES measurements [36]. The excess Fe will also lift up the gap-bottom of the tunneling spectrum in STM measurements, and contributes a robust zero-energy bound state, which disturbs the observation of possible Majorana fermions [37]. Thus, the existence of excess Fe complicates the study of Fe$_{1+y}$Te$_{1-x}$Se$_x$ from the normal state to its superconducting properties, as well as the fundamental and applied research.

Unfortunately, the excess Fe is almost unavoidable in the currently used growth technique employing slow cooling. To explore the intrinsic properties of Fe$_{1+y}$Te$_{1-x}$Se$_x$, many groups have tried different methods to remove the excess Fe, including annealing in various atmospheres, deintercalating by immersing crystals in liquids, and electro-chemical methods. Some methods are effective in totally removing the excess Fe, and induce bulk SC, while others only partially reduce the excess Fe or are even invalid. Hence, the reported properties of the annealed (including the deintercalated and electro-chemical treated) crystals from different groups vary considerably.

In this review, we first summarize all reported annealing methods, and propose the most effective approaches to remove the excess Fe in Fe$_{1+y}$Te$_{1-x}$Se$_x$ (section 2.1-2.2). We next discuss the mechanism of annealing based on the evolutions of structure, composition, and morphology with annealing (section 2.3-2.4). Then, we systematically review the annealing effects based on the evolution of physical properties before and after annealing. In section 3, we discuss the annealing effect on the normal state properties, including the magnetism, transport properties, and the band structure. In section 4, we discuss the annealing effects on the superconducting properties, including the $T_c$, phase diagram, upper
critical field, anisotropy, critical current density, the gap structure, and superconductor pairing. Finally, we conclude the review with a summary and perspective in section 5.

2. Experiments

2.1. Crystal growth

An FeTe$_1$–$_x$Se$_x$ (x = 0 ~ 0.4) single crystal can be successfully grown using standard melting techniques, including the self-flux method with slow cooling [38] (in some papers this is called the Bridgman method) and optical zone-melting [39]. The self-flux method is much easier and frequently used. Single crystals grown by melting methods usually unavoidably contain excess Fe, residing in the interstitial sites of the Te/Se layer, which may be preferable in stabilizing the crystal structure during the growth of single crystals [39]. In this paper, we use y in the Fe$_{1+y}$Te$_{1-x}$Se$_x$ to represent the amount of excess Fe. In detail, high purity Fe (99.99%), Te (99.999%), Se (99.999%) grains with stoichiometric compositions of FeTe$_{1-x}$Se$_x$ (more than 10 g) were loaded into a small quartz tube with $d_1$ ~ 10 mm φ, evacuated, and sealed. The small tube was then sealed into a second evacuated quartz tube with $d_2$ ~ 20 mm since the first (small) tube often cracks during the cooling process. The whole assembly was heated to 1070°C and kept at this temperature for 36 h, followed by a slow cooling to 710°C at a rate slower than ~6°C/h. After that, the assembly was cooled down to room temperature by shutting down the furnace. Large size single crystals reaching centimeter-scale with a mirror-like surface (corresponding to the ab-plane) as shown in figure 1(a) can be obtained. The excess Fe is indicated by the orange ball in the crystal structure in figure 1(b), the amount of which depends on the growth condition, and was reported to be as large as ~15% [13, 40].

2.2. Annealing in various atmospheres and liquids

The first attempt to anneal Fe$_{1+y}$Te$_{1-x}$Se$_x$ was made by Taen et al [21]. They found that bulk SC with $T_c$ ~ 14 K can be induced by vacuum annealing the non-superconducting Fe$_{1+y}$Te$_{0.61}$Se$_{0.39}$ at 400°C for more than ten days. After that, vacuum annealing was also applied to remove the excess Fe in Fe$_{1+y}$Te$_{1-x}$Se$_x$ single crystals with x ranging from 0 to 0.5 [22, 43]. Then, N$_2$ annealing was also reported to be effective to remove excess Fe [44]. However, it was later confirmed that vacuum and N$_2$ annealing have no effect on the excess Fe, and the reported ‘vacuum’ annealing effect has been proven to be from the effect of a residual small amount of O$_2$ [38], which will be discussed later. Due to the effect of O$_2$, crystals annealed in the air condition [26] also show the improvement of SC. Therefore, we have to be very careful about the vacuum level during the study of the annealing effect, as well as searching for the optimal annealing condition.

For the O$_2$ annealing, as-grown single crystals were cut and cleaved into thin slices with dimensions of about 2.0 × 1.0 × 0.05 mm$^3$, then weighed and loaded into a quartz tube with $d$ ~ 10 mm. The quartz tube was carefully baked and tested so as not to emit any gas under the same conditions as the sample annealing. The quartz tube was carefully evacuated by a diffusion pump, and the pressure was detected by a diaphragm-type manometer with an accuracy greater than 1 mTorr. After fully removing the gas, we filled the quartz tube with Ar/O$_2$(1%) mixed gas and sealed it to the length of 100 mm. During the sealing process, the manometer monitored the pressure in the system in real-time to prevent gas leakage and control the O$_2$ pressure in the quartz tube. The annealing system is shown schematically in figure 2. Because of the fixed volume, the amount of O$_2$ filled into the quartz tube can be evaluated by the pressure. Then the crystals were annealed at selected temperatures (ranging from 200°C to 400°C) for different periods of time, followed by water quenching. We also confirmed that almost all the O$_2$ in the quartz tube was consumed by the crystal by breaking the quartz tube in a larger quartz tube while monitoring its pressure. Furthermore, the weight increase in the crystal after annealing is equal to the mass of O$_2$ filled into the quartz tube. Our careful experiments described above guarantee that the O$_2$ was totally absorbed by the crystal [40].

The O$_2$ annealing effect is demonstrated in figure 3, which shows the temperature dependence of zero-field-cooled (ZFC) and field-cooled (FC) magnetization at 5 Oe for a Fe$_{1+y}$Te$_{0.61}$Se$_{0.39}$ single crystalannealed with increasing the amount of O$_2$. The as-grown crystal usually shows no SC or a very weak diamagnetic signal below ~3 K. After annealing, SC emerges and $T_c$ is gradually enhanced by increasing the cumulative amount of O$_2$. $T_c$ reaches the maximum value of over 14 K when the molar ratio of oxygen to the nominal Fe
reaches $\sim1.5\%$ ($T_c$ is defined as the separating temperature for the FC and ZFC curves). However, annealing with too much O$_2$ will damage the crystal (the inset of figure 4 shows the crystals annealed in a pure O$_2$ flow for two days). Redundant O$_2$ reacts with the crystal, and finally completely oxidizes the whole sample as indicated by the power XRD pattern of the over-annealed crystal in the main panel of figure 4, which shows no SC.

Next we study the effect of annealing temperature and time. In this experiment, the crystals were annealed with the optimal amount of O$_2$ (the ratio of oxygen to the nominal Fe is 1.5%) at different temperatures with increasing time. It should be noted that the total amount of O$_2$ reacted with the crystal is larger than 1.5%, since we fix the amount of O$_2$ in all the annealing processes. A typical result of annealing at $200^\circ$C is shown in figure 5(a). With an increasing annealing time, $T_c$ gradually shifts to higher temperatures together with the sharpening of the transition width and the increase of diamagnetic signal. The maximum $T_c$ is $\sim14.3$ K similar to that annealed at 400°C (see figure 3). Figure 5(b) shows the evolution of $T_c$ with time annealed in O$_2$ at temperatures of $200^\circ$C, $250^\circ$C, $300^\circ$C, and $400^\circ$C. $T_c$ is enhanced more quickly to the maximum value when the crystal is annealed at higher temperatures. Particularly, $T_c$ reaches the optimal values only after 5 min annealing at $400^\circ$C. We also tested annealing the crystal at higher temperatures, such as $500^\circ$C. In this case, the crystal was damaged, and SC was not induced.

The annealing atmospheres are not restricted to the gas at room temperature and ambient pressure. Elements with vapor pressure larger than the vacuum level of the annealing system can be used to supply the annealing atmosphere. Elements such as Te, Se, S, P, As, I, and Sb have been confirmed to provide effective atmospheres to remove excess Fe [47–53]. In our experiments, the same system presented in figure 2 was used to vacuum seal the crystals. In contrast to the O$_2$
annealing, the required amounts of elements (Te, Se, S, P, As, I, or Sb) were weighed and vacuum sealed together with the single crystal. Then they were annealed at selected temperatures, such as 400 °C for 20 h, followed by water quenching. Owing to the high vapor pressure of iodine at room temperature, it would be vaporized during the evacuation. Therefore, the bottom part of the quartz tube containing the iodine and crystals was immersed in a mixture of ice and salt at 4 Oe for Fe$_{1+y}$Te$_{0.6}$Se$_{0.4}$ single crystals annealed at 400 °C. [47] © [2013] The Physical Society of Japan.

Figure 6. (a) Temperature dependence of ZFC and FC magnetization at 5 Oe for Fe$_{1+y}$Te$_{0.6}$Se$_{0.4}$ single crystals annealed at 400 °C with an increasing amount of Te vapor (the molar ratio of Te to the sample ranges from 0.01 to 80) [47]. (b) $T_c$ as functions of molar ratio of Te to a Fe$_{1+y}$Te$_{0.6}$Se$_{0.4}$ single crystal annealed at 400 °C. [47] © [2013] The Physical Society of Japan.

The acid and alcoholic beverage effects were further improved to become a more controllable electrochemical reaction method performed by a standard three-electrode method [55, 56]. A Ag plate and a Pt mesh were used as the reference and counter electrodes, respectively, while an FeTe$_{1-x}$S$_x$ sample was used as the working electrode. The ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate was used as the electrolyte, and was kept at 80 °C during the electrochemical reactions. An increasing voltage at a rate of 0.15 V min$^{-1}$ up to a set value (typically 0.8 V) was applied between the reference and working electrodes and kept for a constant time. Schematics of the electrochemical reaction method are shown in figure 9(a) [57]. The removal of excess Fe was suggested based on the increase of $T_c$ (see figure 9(b)). The electrochemical reaction was also reported to accelerate by fabricating the crystal into a narrow bridge [57]. However, there is still no bulk evidence of the SC induced by the electrochemical reaction method.

2.3. Evolution of structure, composition, and morphology with annealing

Crystal structure change after removing the excess Fe was carefully studied by powder neutron diffraction measurements on crystal annealed by iodine [52]. The lattice constant $a$ was found to have increased after annealing (see figure 10(a)). The expansion of the $ab$ plane on reduction of the excess Fe reflects the attractive bonding involving the excess Fe within volume ~100%, similar to that annealed in the O$_2$ atmosphere.

The removal of excess Fe can be also realized by immersing the crystals into acids [38, 44], or even alcoholic beverages [38]. The alcoholic beverage effect on the excess Fe was first reported by Deguchi et al [54] on the polycrystalline FeTe$_1-S_x$, which was followed by a similar effect in FeTe$_{1-S_x}$ single crystals [38]. In these experiments, several pieces of as-grown single crystals were put into glass bottles (10 ml) filled with 20% hydrochloric acid HCl, beer (Asahi Breweries Ltd), red wine (Asahi Breweries Ltd), Japanese sake (Hakutsure Sake Brewing, Co. Ltd), shochu (Iwagawa Jozo Co. Ltd), or whisky (Suntory Holdings Ltd). The crystals immersed in the alcoholic beverages (beer, red wine, Japanese sake, shochu, and whisky) were kept at 70 °C for 40 h. The sample immersed into 20% HCl was kept at room temperature for 100 h, because heating up to 70 °C in acid rapidly damages the sample. SC could be induced in all these crystals. However, the transition width is very broad compared with the crystal annealed by O$_2$ (see figure 8(a)) [38]. The broad transitions are due to the fact that SC induced by acid and alcoholic beverages is only near the surface. After cutting off the four edges, and polishing the top and bottom surfaces of the samples immersed in acid and alcoholic beverages (more than half of the crystal was removed), both the $T_c$ and the diamagnetic signal are largely reduced (see the example of the crystal immersed in beer in figure 8(b)). For comparison, the inner part of the O$_2$ annealed crystal shows similar superconducting properties to the whole crystal (see figure 8(c)) [38].
the van der Waals layers. By contrast, the lattice constant remains almost unchanged after annealing (see figure 10(b)), which was further confirmed in Fe$_{1-x}$Te$_{1-y}$Se$_{x}$ with $x$ ranging from 0 to 0.43 (figure 10(c)). A graphical comparison of the annealing effect on the crystal structure is shown in figure 10(d). Similar structural change after annealing was also reported based on the XRD refinement [58].

The amount of excess Fe usually depends on the growth condition, which was reported to range from several percents to $\sim$15% depending on the group. Even in the same batch of crystals, the amount of excess Fe is not constant. It was reported that crystals with mirror-like surfaces usually contain more excess Fe than crystals with a textured surface. However, textured surfaces are associated with a slight misorientation of grains, due to strain effects that develop on cooling in the constrained cross section of the quartz tube [39]. To avoid the uncontrollable influence from the misorientation of grains, we prefer to use the well-orientated crystals with a mirror-like surface. In our as-grown single crystals, the amount of excess Fe is $\sim$14%, as analyzed by inductively-coupled plasma (ICP) atomic emission spectroscopy [40]. Here, we want to emphasize that the surface composition analyses techniques, such as energy dispersive x-ray spectroscopy (EDX) and using an electron probe microanalyzer (EPMA), usually underestimate the amount of excess Fe. This is due to the inhomogeneous distribution of excess Fe in the crystal, and the excess Fe seems more stably located in the bulk of the sample than the surface. The EDX analyses on the same as-grown crystals for ICP gave us a value of excess Fe of only about 1%–3%. A similar observation was also claimed by other groups [52, 60].

Accurate determination of the amount of excess Fe in the annealed crystal is even more difficult, although many reports have claimed that excess Fe was reduced after annealing. Even though excess Fe may be removed after annealing, it should still remain in the crystal, mostly near the surface, in some form of oxides (this topic will be discussed later). Thus, traditional compositional analysis methods like ICP, EDX, and EPMA can not reliably estimate the amount. In fact, our ICP analyses on the O$_2$-annealed crystal showed that the amount of excess Fe is not zero. To precisely determine the change in the amount of excess Fe, we employed scanning tunneling microscopy (STM) measurement, which has atomic resolution. The excess Fe occupies the interstitial site in the Te/Se layer, and a previous report proved that the cleaved Fe$_{1+y}$Te$_{1-x}$Se$_{y}$ single crystal possesses only the termination layer of Te/Se [61], which guarantees that the STM can directly observe the excess Fe in the Te/Se layer without the influence of the neighboring Fe layers. Figure 11(a) shows the STM image for the as-grown Fe$_{1+y}$Te$_{0.6}$Se$_{0.4}$ single crystal. There are several bright spots in the image, which represent the excess Fe according to the previous STM analysis [62]. After optimal annealing, the bright spots, i.e. the excess Fe, disappeared in the STM images as shown in figure 11(b) and the larger region in figure 11(c). STM observations were performed by two separate groups on different pieces of annealed crystals, and searched several different regions. Almost no bright spots can be found, which directly proves that the excess Fe was totally removed by annealing [19, 40].

Surface color change after annealing has been reported in several publications [26, 43]. To carefully observe the surface color change, we annealed the crystals with O$_2$ in a transparent furnace. The sample was quickly heated up to 400 °C at a rate of 130 °C min$^{-1}$ as shown in figure 12(f). During the annealing process, a charge-coupled device (CCD) camera was used to acquire the images of the sample surface. Typical
images of the crystal before and after being annealed for 90 s (∼200 °C), 130 s (∼300 °C), 160 s (∼370 °C), 200 s (∼400 °C) are shown in figures 12(a)–(e), respectively. Clearly, the crystal surface first changes color to brown, then turns to blue, which indicates that some compounds were formed on the surface during the annealing. We should point out here that the color change only happens on the sample surface. After cleaving the surface layers, the inner part of the crystal still retains the mirror-like surface similar to the as-grown single crystal. The surface color change was also observed in crystals annealed in other atmospheres such as Te, Se, and S. By contrast, the crystals annealed in the vacuum did not show a change in color, which confirms that the color change directly relates to the annealing effect.

In the O2-annealed single crystals, oxygen was reported to be detected by using electron energy loss spectroscopy (EELS) [63], and the EPMA [43]. Figure 13(a) shows a typical EELS spectrum with O–K, Te–M4,5, and Fe–L2,3 edges labeled. The peaks around 530 eV indicate the Fe 3d level hybridized with the oxygen 2p level. After subtracting the background, the O–K edge is shown in figure 13(b). For comparison, the fine structure of O–K edges of FeO and α–Fe2O3 in the same energy range are plotted in figure 13(c). The similar EELS spectra shown in figures 13(b) and (c) indicate the existence of the FeO and/or α–Fe2O3 in the annealed surface layers [63]. Figure 14 shows the EPMA results of the crystal annealed in a poor vacuum (it is actually the O2 annealing, based on our description before). The oxygen was found only on the surface layers of the annealed crystal, and the surface layers contain only the elements of Fe and O. Oxygen was not detected in the inner part of the annealed crystals after peeling off their surfaces, which proves that it was not doped into the crystals [43].

The reduction of excess Fe in the inner part of the crystal, and the formation of the FeO surface layers, indicate that the excess Fe reacts with O2 and moves to the surface of the crystal. However, it is well known that the detection of oxygen is relatively difficult for the EPMA and EELS measurements. To confirm this point, we chose the crystals annealed in an As atmosphere [53], which is an exotic and easily detectable heavy element to Fe1+yTe1−xTe1−xSex. Careful ICP and EDX measurement of the composition of the inner and surface layers confirmed that Fe reacts with As on the surface of the crystal and the reaction itself acts as a driving force to drag out the excess Fe.
For crystals annealed in other atmospheres, the formation of surface layers was also observed. Figures 15(b)–(d) show SEM images for the surface of the Fe$_{1+y}$Te$_{0.6}$Se$_{0.4}$ single crystals annealed in S, Se, or Te atmospheres [64]. Clearly, the mirror-like surface of the as-grown crystal turns polycrystal-like. EDX measurement shows that the polycrystal-like surface for the sample annealed in S/Se contains only Fe and S/Se, with a molar ratio of roughly 1:1, while the molar ratio is roughly 1:2 in the sample annealed in Te. X-ray diffraction (XRD) measurements show that the surface layers are most probably FeS, Fe$_7$Se$_8$, and FeTe$_2$ for the crystals annealed in atmospheres of S, Se or Te, respectively. The formation of the FeM$_x$ (M represents the elements used for providing the annealing atmospheres, such as O, S, Se, Te, Sb, P, As) was also observed in many other studies [47–49, 53, 64, 65].

2.4. Mechanism of annealing

In the following, we study the spatial evolution of the annealing effect by monitoring the evolution of SC in the crystal using the magneto-optical (MO) images. In this experiment, a thin crystal with a perfect mirror-like surface, without cracks or damages, is used. Figures 16(a) and (b) show the MO images of shielding of the 5 Oe field after zero-field cooling at 10 K for the crystal annealed at 400 °C in the O$_2$ atmosphere for 1 and 3 min, respectively. When the sample is annealed for 1 min, only the edge shows a Meissner state, while the central part still remains non-superconducting. When the annealing time is increased to 3 min, all parts of the sample become the Meissner state. This indicates that the SC mainly evolves from the edges of the crystal to the center [40].

Figure 11. STM images for (a) as-grown, and (b)–(c) O$_2$-annealed Fe$_{1+y}$Te$_{0.6}$Se$_{0.4}$ single crystal. The bright spots in (a) correspond to the excess Fe, which disappear in the optimally-annealed crystal. Reproduced from [40]. CC BY 3.0.
The magnetic properties of Fe$_{1-y}$Te are unique in IBSs. As first reported by Bao et al. [13], the magnetic wave vector in Fe$_{1-y}$Te is in the $(\delta \pi, \delta \pi)$ direction (along the diagonal direction of the Fe–Fe square), which is different from the $(\pi, 0)$ along the $a$-axis direction in Fe–pristine and FeSe superconductors [figure 17] [14]. By contrast, the magnetic order is incommensurate in Fe$_{1+y}$Te with redundant excess Fe $(y \sim 0.141)$, decreases with reducing excess Fe, and becomes commensurate in a crystal with $y \sim 0.076$ [13]. Theoretical calculations find that the excess Fe with valence near Fe$^+$ is strongly magnetic, which provides local moments that interact with the plane Fe magnetism [35]. To give further detail, the excess Fe modifies the local moments’ exchange interactions via the multiorbital generalization of the long-range Ruderman–Kittel–Kasuya–Yosida interaction [67]. Neutron scattering measurement also shows that excess Fe in superconducting Fe$_{1+y}$Te$_{0.75}$Se$_{0.25}$ induces a magnetic Friedel-like oscillation and involves more than 50 neighboring Fe sites [68]. Those results manifest that the excess Fe does not act as a separated point-like defect, but has a global effect due to the strong magnetic nature. Thus, the excess Fe affects almost all the properties of Fe$_{1+y}$Te$_{1-x}$Se$_x$ from the normal state to superconducting state.

The muon–spin rotation measurements on Fe$_{1+y}$Te$_{0.75}$Se$_{0.25}$ with different amounts of excess Fe show that the magnetic transition temperature $T_N$ is gradually suppressed by reducing the excess Fe, and the $T_N$ is enhanced (figure 18) [34]. The influence of excess Fe and the annealing effect on the magnetism of Fe$_{1+y}$Te$_{1-x}$Se$_x$ with $0 \leq x \leq 0.43$ was systematically studied by the magnetic susceptibility measurements under the 1 T magnetic field [59]. Figures 19(a) and (b) show the normalized magnetic susceptibilities for the as-grown and annealed Fe$_{1+y}$Te$_{1-x}$Se$_x$ ($0 \leq x \leq 0.43$) single crystals, respectively. The as-grown Fe$_{1+y}$Te shows a sharp transition at $\sim 58$ K, which is due to the antiferromagnetic (AFM) transition. With Se doping, the AFM transition temperature $T_N$ is gradually suppressed to lower temperatures, and becomes much broader at $x = 0.09$. 

**Figure 12.** Bright view of the surface colors for the crystals (a) before and after annealing for (b) 90 s ($\sim$ 200 °C), (c) 130 s ($\sim$ 300 °C), (d) 160 s ($\sim$ 370 °C), (e) 200 s ($\sim$ 400 °C), (f) is the temperature control sequence during annealing. Reproduced from [40]. CC BY 3.0.

3. Annealing effects on normal state properties

3.1. Annealing effects on magnetism

The magnetic properties of Fe$_{1+y}$Te$_{1-x}$Se$_x$ are unique in IBSs. As first reported by Bao et al. [13], the magnetic wave vector...
Afer that, the AFM transition disappears and is replaced by a very broad hump-like feature. Such a feature may originate from the spin glass state according to the neutron scattering results [69]. The hump-like feature survives up to $x = 0.33$, and is not observed for $x > 0.43$.

In the annealed crystal, the value of magnetic susceptibility does not show a systematic evolution and is irregular, which is caused by the magnetism from some Fe impurities. During the annealing, the excess Fe are removed from their original positions, and form some compounds like Fe$_2$O$_3$ or FeTe$_2$ based on the discussion above. Although those impurities are mainly formed in the surface layers, and removed by polishing, small parts may still remain inside the crystals and disturb the magnetic susceptibility value because of their strong magnetism. However, we can still obtain some important information from the data regardless of the irregularity in the absolute value. As shown clearly in figure 19(b), the value of $T_N$ for the pure FeTe is enhanced to $\sim 72$ K after removing the interstitial Fe. The AFM transition is only observed in crystals with $x = 0$ and 0.03. When the Se doping level is increased over 0.05, the AFM is totally suppressed. In comparison, the hump-like feature observed in the as-grown crystals is not observed after annealing. For $x > 0.03$, the annealed crystals only show the SC transition at low temperatures.

3.2. Annealing effects on transport properties

The magnetic moment from excess Fe will localize the charge carriers affecting the normal state transport properties, as first reported by Liu et al [23]. Benefitting from the controllable

Figure 13. (a) EELS spectrum of the O$_2$-annealed Fe$_{1+y}$Te$_{0.5}$Se$_{0.5}$ single crystals with O-K, Te-M$_{4,5}$, and Fe-L$_{2,3}$ edges labeled. (b) The background subtracted experimental data of the O–K edge are shown as the open symbols. The solid curve, obtained by smoothing the experimental data, shows three peaks (a)–(c) indicated by the arrows, respectively. The pre-peak (a) indicates the hybridization of the Fe 3d and O 2p states. (c) Fine structure of FeO and $\alpha$-Fe$_2$O$_3$. Reprinted with permission from [63]. Copyright 2012 by the American Physical Society.

Figure 14. (a) Optical microscope image of the annealed crystal. (b)–(e) Elemental mapping of Fe, O, Se, and Te for the same area as (a). The left-hand side of the area is peeled to remove the surface black layers, and the right-hand side is the as-annealed surface. On the as-annealed surface, almost no Se or Te is detected. Reprinted with permission from [43].

Figure 15. Scanning electron microscope (SEM) images for (a) as-grown, (b) S-annealed, (c) Se-annealed, and (d) Te-annealed Fe$_{1+y}$Te$_{0.6}$Se$_{0.4}$ single crystals. Insets are enlarged images. Reprinted from [64], Copyright (2014), with permission from Elsevier.
Figure 16. Meissner state magneto–optical (MO) images under 5 Oe at 10 K for Fe$_{1+y}$Te$_0.6$Se$_{0.4}$ annealed at 400 °C for (a) 1 and (b) 3 min. MO images in the remanent state at (c) 5 K, (d) 7 K, (e) 8 K, (f) 10 K, (g) 12 K, and (h) 14 K for the crystal annealed for 3 mins. This state is prepared by applying 400 Oe along the c-axis for 1 s and removing it after zero-field cooling. (i) Local magnetic induction profiles at temperatures from 5 K to 14 K taken along the dashed lines in (c). (j) Spatial distribution of $J_c/J_c^\text{max}$ at 10 K for the crystal annealed for 3 min. Reproduced from [40]. CC BY 3.0.
annealing technique reported above, we studied in detail the influence of excess Fe on transport properties by measuring the resistivity, Hall effect, and the magnetoresistance (MR) in three selected crystals: the as-grown, half-annealed, and fully-annealed [25]. Combined ICP and STM measurements confirmed that the amount of excess Fe in the as-grown, half-annealed, and fully-annealed crystals were roughly 14%, 6.5%, and 0, respectively. The $T_c$ of the three crystals obtained by susceptibility measurements was below 3 K, $\sim$7.5 K, and $\sim$14.3 K, respectively (see inset of figure 20). However, the resistivities of all three crystals showed transitions at $\sim$14 K due to the filamentary SC (figure 20).

Resistivities for all three crystals maintain a nearly constant value above 150 K. From 150 K down to the superconducting transition temperature, the as-grown sample shows a nonmetallic behavior ($d\rho/dT < 0$), which is caused by the charge carrier localization induces by the excess Fe. This nonmetallic behavior was suppressed by removing the excess Fe and a flattened resistive behavior above $T_c$ was found in the half-annealed crystal. When the excess Fe is totally removed as in the fully-annealed crystal, resistivity manifests a metallic behavior ($d\rho/dT > 0$).

Figure 17. Schematic in-plane spin structure of FeTe and SrFe$_2$As$_2$. The solid arrows and hollow arrows represent two sublattices of spins. The shaded area indicates the magnetic unit cell. Reprinted with permission from [14]. Copyright 2009 by the American Physical Society.

Figure 18. (a) Temperature dependence of the volume susceptibility $\chi_v$ of representative compositions ($y = 0.95$, 1.00, and 1.10 of single-crystal Fe$_{0.75}$Te$_{0.25}$Se$_2$). The onset of the superconducting transition $T_c$ onset and the midpoint corresponding to $\chi_v = -0.5$ are indicated. (b) Temperature dependence of the muon–spin polarization of the slow relaxing component ($P_{\text{slow}}$). The magnetic transition $T_N$ is determined from a fit to a Fermi-type function. Reprinted with permission from [34]. Copyright 2010 by the American Physical Society.

Figure 19. Magnetic susceptibilities measured at 1 T with $H\parallel c$ for Fe$_{1+y}$Te$_{1-x}$Se$_x$ ($0 \leq x \leq 0.43$) (a) before and (b) after O$_2$ annealing. Reproduced from [59]. CC BY 4.0.
Figure 20. Temperature dependence of the resistivities scaled by the values at 300 K for the as-grown, half-annealed and fully-annealed Fe$_{1+y}$Te$_{0.6}$Se$_{0.4}$ single crystals. The inset shows the temperature dependences of ZFC and FC magnetizations at 5 Oe for the three samples. Reprinted with permission from [25], Copyright (2014) by the American Physical Society.

Figures 21(b)–(d) show the Hall resistivity $\rho_{yx}$ at several temperatures for the as-grown, half-annealed, and fully-annealed Fe$_{1+y}$Te$_{0.6}$Se$_{0.4}$ single crystals, respectively. The $\rho_{yx}$ for the as-grown crystal follows a linear relationship with the applied field and has a positive slope, $d\rho_{yx}/dH > 0$. For the half-annealed crystal, $\rho_{yx}$ remains positive and linearly increases with magnetic field although the slopes are reduced. However, $\rho_{yx}$ for the fully-annealed crystal becomes negative when temperature decreases below 40 K, and an obvious nonlinear behavior can be witnessed. The nonlinear behavior and sign reversal observed in $\rho_{yx}$ proves the existence of the multiband effect. The Hall coefficients $R_H$ can be simply obtained from $R_H = \rho_{yx}/\mu_0 H$, and are shown in figure 21(a). For the nonlinear $\rho_{yx}$ at low temperatures in the fully-annealed crystal, $R_H$ was simply calculated from the linear part at small fields. $R_H$ is almost temperature-independent above 100 K, and keeps a constant value $\sim 1 \times 10^{-9}$ m$^3$/C for all three samples. When the temperature decreases below 100 K, an obvious divergence in $R_H$ is observed. In the as-grown crystal, $R_H$ gradually increases with decreasing temperature showing an obvious upturn at low temperatures. This upturn is almost suppressed in the half-annealed crystal, in which $R_H$ just slightly increases with decreasing temperature. In the fully-annealed crystal, $R_H$ remains nearly temperature-independent above 60 K, followed by a sudden decrease, and finally changes sign from positive to negative before approaching $T_C$. The sign reversal in the Hall coefficient is usually attributed to the multiband structure, indicating the dominance of the electron in the charge carriers before the occurrence of SC in Fe$_{1+y}$Te$_{0.6}$Se$_{0.4}$.

The dramatic change in the temperature dependence of resistivity and Hall coefficients after annealing were observed in all the Fe$_{1+y}$Te$_{1-x}$Se$_x$ single crystals with different Se doping levels, as shown in figure 22 [59].

In a multiband system, the MR is usually described by the following expression [70],

$$MR \equiv \frac{\Delta \rho(H)}{\rho(0)} \approx \frac{1}{2} \sum_{ij} \frac{\Sigma \omega_i \tau_j (\omega_i \tau_j - \omega_j \tau_i)^2}{(\Sigma \omega_i \tau_i)^2},$$

(1)

where $\sigma_i$ is the conductivity, $\tau_i$ is the relaxation time and $\omega_i$ is the cyclotron frequency, which has the opposite sign for the electron and hole bands. In this case, the $(\omega_i \tau_i - \omega_j \tau_j)^2$ term becomes larger because the $\omega_i \tau_i$ terms add up, which will result in a large positive MR. However, the MR of the as-grown crystal is just $\sim 0.03\%$ at 16 K under 9 T as shown in the inset of figure 23(a). This unexpected small MR can be also explained by the effect of the excess Fe. Neutron scattering measurements revealed that the excess Fe induces a magnetic Friedel-like oscillation at the $(\pi, 0)$ order and involves more than 50 neighboring Fe sites [68]. Spins from these Fe clusters will be weakly polarized under a magnetic field inducing a negative MR, which will cancel out the positive MR of the sample itself. In fact, previous reports on Fe$_{1+y}$Te$_{1-x}$Se$_x$ all show such small values of MR, and sometimes even a negative MR was observed [71, 72]. Such a small MR is increased to $\sim 0.14\%$ in the half-annealed crystal because parts of the excess Fe were removed. After completely removing the excess Fe, the MR of the fully-annealed Fe$_{1+y}$Te$_{0.6}$Se$_{0.4}$ reaches a value of larger than 17% at 16 K under 14 T.

More interestingly, the MR of the fully-annealed Fe$_{1+y}$Te$_{0.6}$Se$_{0.4}$ linearly increases with the applied field from the intermediate field (e.g. 2 T at 16 K) to the measurement limit of 14 T, whereas just a small parabolic bend remains at low fields. This is in sharp contrast to the semi-classical field dependence of MR, in which MR generally develops in proportion to $H^2$ over the entire field range. The linear dependence of MR on the field is more evident in the first-order derivative $dMR/dB$ as shown in figure 23(b). $dMR/dB$ is proportional to the magnetic field at low $H$, then saturated at high fields. The linear MR can be interpreted by considering a quantum limit where all the carriers occupy only the lowest Landau level (LL) [73, 74]. This situation usually happens when the field is very large and the difference between the zeroth and first LLs $\Delta_{LL}$ exceeds the Fermi energy $E_F$ and the thermal fluctuation $k_B T$. However, the linear MR was identified in a low field region in some materials hosting Dirac fermions with linear energy dispersion, such as graphene [75], topological insulators [76], Ag$_2$ (Te/Se) [77], $\alpha$-(BEDT–TTF)$_2$I$_3$ [78], some layered compounds with two-dimensional Fermi surface (like SrMnBi$_2$ [79, 80]), and iron-based Ba(Sr)Fe$_2$As$_2$ [81–83] and La(Pr)FeAsO [84, 85]. For the Dirac state, $\Delta_{LL}$ is described as $\Delta_{LL} = \pm \sqrt{2eB}$, leading to a much larger LL splitting compared with the parabolic band. Consequently, the quantum limit can be achieved in the low field region [73].

The characteristic field $B^*$, defined as the crossover field between the semiclassical regime and the quantum linear regime, is marked by the arrow in figure 23(b). The temperature dependence of $B^*$ is shown in figure 23(c), which is obviously violating the linear relation expected from...
conventional parabolic bands, and can be well fitted by \( B^* = (1/2e\hbar)(k_B T + E_F)^2 \) for the Dirac fermions as shown in figure 23(c) [76]. The good agreement of \( B^* \) with the above equation indicates the existence of Dirac fermions in \( \text{Fe}_{1+y} \text{Te}_{0.6} \text{Se}_{0.4} \). Recently, the Dirac cone band structure and the topological SC in \( \text{FeTe}_{1-x} \text{Se}_x \) were confirmed by the ARPES measurements [16, 17]. The report in [17] was performed on our fully-annealed single crystals. The fitting gives
Figure 23. (a) Magnetic field dependence of magnetoresistance \( MR = \frac{\rho(H) - \rho(0)}{\rho(0)} \) for the fully-annealed \( Fe_{1+y}Te_{0.6}Se_{0.4} \) single crystal at different temperatures. Inset is the MR for the as-grown and half-annealed crystals at 16 K. (b) The field derivative of the in-plane MR at different temperatures for the fully-annealed \( Fe_{1+y}Te_{0.6}Se_{0.4} \) single crystal. The solid lines denote the semiclassical regime and the quantum linear region, respectively. The characteristic field \( B^* \) is marked by the arrow. (c) Temperature dependence of the characteristic field \( B^* \) (red circles) and the effective MR mobility \( \mu_{MR} \) (blue squares). The red line is the fitting of \( B^* \) by \( B^* = \left( \frac{1}{2e} \frac{\hbar \gamma}{k_B T} \right) \left( k_B T + E_F \right) \). Reprinted with permission from [25], Copyright (2014) by the American Physical Society.

Figure 24. (a–c) ARPES spectra for three \( Fe_{1+y}Te_{1-x}Se_x \) samples in order of decreasing \( y \) (excess Fe) from left to right. The spectra are normalized using the intensity from high-order photons, and a constant background is removed. The spectra are sharpened by adding a small part of their second derivative to the original data. The green dashed line is the best fit to the data using a simple parabolic dispersion. (d–f) Spectral functions, calculated using the model and parameters described in the text, to describe the BCS–BEC crossover seen in the data in the top panels. (g) Schematic band structure and the effect of excess Fe on various bands. The red and blue curves correspond to the samples with a small and large amount of excess Fe, respectively. Reproduced from [86]. CC BY 4.0.
a large Fermi velocity $v_F \sim 1.1 \times 10^5$ ms$^{-1}$ and $E_F \sim 5.5$ meV, which are close to the previous reports for similar compounds BaFe$_2$As$_2$ ($v_F \sim 1.88 \times 10^5$ ms$^{-1}$, $E_F \sim 2.48$ meV) [82] and SrFe$_2$As$_2$ ($v_F \sim 3.11 \times 10^5$ ms$^{-1}$ and $E_F \sim 6.9$ meV) [83].

### 3.3. Annealing effects on band structure

The large difference in the Hall effects of the as-grown, half-annealed, and fully-annealed crystals indicates that the band structure should be also affected by the excess Fe, i.e. changing after annealing. Details on the band structure evolution with the decrease of excess Fe were observed by ARPES measurement (see figures 24(a)–(f) [86], and the schematics of the electronic structures in figure 24(g). With decreasing excess Fe, the electron-type band at the $M$-point, and the hole-type $\alpha_3$-band at the $\Gamma$-point move down, which is consistent with the Hall effect in figure 21(a). In contrast to the electron and $\alpha_2$-band, no significant shift in the hole $\alpha_1$ and $\alpha_3$ band was observed. More interestingly, the Fermi energy $E_F$, obtained from the $\alpha_2$ hole band decreases from 19 meV to 6 meV with decreasing excess Fe, while the SC gap $\Delta$ keeps $\sim$3 meV. Thus, $\Delta/E_F$ increases from $\sim$0.16 to $\sim$0.5 after decreasing excess Fe, which indicates that the BCS to BEC crossover [15] can be tubed by excess Fe.

### 4. Annealing effects on superconducting properties

#### 4.1. Annealing effects on $T_c$ and phase diagrams

The annealing effect on $T_c$ has already been systematically studied (see figures 3, 4, and 6). To check the bulk nature of the SC, we also performed specific heat measurements on both the as-grown and fully-annealed Fe$_{1+y}$Te$_{0.6}$Se$_{0.4}$ single crystal (figure 25) [40]. Obviously, no specific heat jump can be observed in the as-grown crystal, which proves that the superconducting transition observed in the resistivity measurement (see figure 20) comes from the filamentary SC. After annealing, a clear specific heat jump can be observed, indicating the bulk nature of the SC. The specific heat jump $\Delta C/T_c$ was obtained as $\sim$66.3 mJ mol$^{-1}$K$^{-2}$ with $T_c = 14.5$ K determined by entropy balance consideration. The normalized specific heat jump at $T_c$, $\Delta C/\gamma_c T_c$, is $\sim$3.0 by using the fitted Sommerfeld coefficient of $\gamma_c = 22$ mK$^{-2}$. The value is much larger than the BCS weak-coupling value of 1.43, indicating that SC in the fully-annealed Fe$_{1+y}$Te$_{0.6}$Se$_{0.4}$ is strongly coupled in nature. The specific heat evidence for the bulk SC were also reported in the annealed Fe$_{1+y}$Te$_{1-x}$Se$_x$ with $x > 0.05$ [30].

Phase diagrams of Fe$_{1+y}$Te$_{1-x}$Se$_x$ have been already reported by several groups [12, 22, 26, 69, 87]. However, these are all under debate. Even some of the basic information in those reported results is controversial, such as the region of bulk SC, the coexistence of AFM and SC, and the spin glass state. Two well-known phase diagrams are shown in figures 26(a) and (b) [12, 69]. In figure 26(a), bulk SC was observed only in the region of $x > 0.27$, and the coexistence of AFM and SC was reported. In the phase diagram of figure 26(b), the spin glass state was reported together with the SC. Based on the discussion above, these controversies come from the sample-dependent amount excess Fe. The phase diagram of Fe$_{1+y}$Te$_{1-x}$Se$_x$ was also revised after reducing excess Fe by annealing in a vacuum [30], air [26], and $O_2$ [87]. However, due to the remaining of excess Fe as well as the lack of bulk evidence for the SC, the phase diagrams are still not unified.

Based on the description in the experimental section, the excess Fe was confirmed to be totally removed in our crystal after careful annealing. Thus, we established doping-temperature $(x - T)$ phase diagrams (figures 26(c) and (d)) for both the as-grown and fully-annealed (without excess Fe, $y = 0$) Fe$_{1+y}$Te$_{1-x}$Se$_x$ based on the magnetic susceptibility (figure 19), resistivity (figure 22(a)), and Hall effect measurements (figure 22(b)) shown above [59]. For the as-grown crystals, in the doping region of $x < 0.12$, the AFM transition, $\sim$58 K in the non-doped Fe$_{1+y}$Te, is monotonically suppressed with increasing Se substitution. Accompanied by the suppression of AFM, SC emerges from $x = 0.05$, and coexists with the antiferromagnetic phase until $x < 0.13$. That SC, marked by the squares, is not bulk in nature and can be only observed in resistivity measurement. For $x \geq 0.12$, the AFM transition is absent and replaced by a spin glass state (observed by magnetic susceptibility measurements, and marked by the right triangles) similar to figure 26(b). The spin glass state may originate from the effect of excess Fe, which interacts with more than 50 neighboring Fe in the adjacent Fe layers, and induces the magnetic Friedel-like oscillation [68].

After removing the excess Fe by annealing, the phase diagram of Fe$_{1+y}$Te$_{1-x}$Se$_x$ is dramatically changed. As shown in figure 26(d), the AFM state is suppressed into a very narrow region of $x < 0.05$, and the spin glass state disappears. Immediately after the disappearance of the AFM state, bulk SC emerges, and is observed in the doping region of $x \geq 0.05$. The coexistence of AFM and SC states is absent in the annealed crystals. Thus, the previously reported
coexistence of AFM, the spin glass state with SC originates from the effect of excess Fe. Besides this, the characteristic temperature $T^\ast$ observed in the $R_H$ is plotted in figure 26 (orange arrows in figure 22(b)), which also resides in the doping region of $x \geq 0.05$, and gradually increases with increasing the Se doping. It suggests that the multiband effect in Fe$_{1+y}$Te$_{1-x}$Se$_x$ may be strongly related to the occurrence of SC. By contrast, the rapid suppression of the AFM state with a small amount of doping, and the absence of the coexistence of the AFM and SC states are all similar to the phase diagrams of LaFeAsO$_{1−x}$F$_x$ [88] and CeFeAsO$_{1−x}$F$_x$ [89]. The step-like behavior of the magnetism and SC in the small region of $0.03 < x < 0.05$ suggests that the SC in the Fe$_{1+y}$Te$_{1-x}$Se$_x$ system may be related to the suppression of static magnetic order rather than the increase of the effective charge carrier density by the doping or structural distortion.

### 4.2. Annealing effects on upper critical field and anisotropy

To study the effect of annealing on the upper critical field, the resistive transitions measured in the magnetic field up to 9 T for $H||c$ and $H||ab$ for both the as-grown and annealed Fe$_{1+y}$Te$_{0.6}$Se$_{0.4}$ single crystals were compared in figure 27. For both crystals, with an increasing field along the $c$-direction, the resistive transition shifts to lower temperatures accompanied by a slight increase in the transition width, while this broadening is almost negligible for $H||ab$.

Compared with the as-grown crystal, the resistive transition shift under the magnetic field becomes weaker in the annealed crystal. The upper critical fields $H_{c2}$ for $H||c$ and $H||ab$ defined by the 90% of resistive transition are plotted in figure 27(c). The anisotropy $\gamma$ defined as the ratio of $H_{c2}^{ab}/H_{c2}^c$ close to $T_\xi$ are shown in the inset of figure 27(c). Obviously, $\gamma$ for the as-grown crystal is $\sim$2.5–3, which is slightly larger than the value $\sim$1.5–2 for the annealed crystal.

To obtain more information about the $H_{c2}$ and $\gamma$ at low temperatures, we also measured the resistive transitions under a pulse magnetic field up to 50 T [90]. The $H_{c2}$ for the as-grown, half-annealed, and fully-annealed crystals are shown in figures 28(a)–(c), respectively. All three crystals show a large value of $H_{c2} \sim 45$–50 T at 2 K, which is not affected by the excess Fe. However, $\gamma$ is decreased with a reduction in the amount of excess Fe in a large temperature range (see figure 28(d)), which is similar to the results close to $T_\xi$ shown in the inset of figure 27(c). At a low temperature of $T/T_\xi \leq 0.3$, all three crystals manifest a small $\gamma \sim 1$.

The excess Fe was also reported to affect the anisotropy in the $ab$-plane [91]. Figure 29(a) shows that $\rho_a$ and $\rho_b$ are almost identical at temperatures above $T_{SG}$, while they become different in the AFM state. The difference between $\rho_a$ and $\rho_b$ decreases with a reduction in the excess Fe. Similar behavior was also observed in the Se-doped FeTe (see figure 29(b)). However, in Fe$_{1+y}$Te$_{1-x}$Se$_x$, $\rho_a > \rho_b$, which is opposite to that of $\rho_a < \rho_b$ observed in IBSs-122 samples [92].
Figure 27. The resistive transitions of (a)–(b) as-grown and (c)–(d) fully-annealed Fe$_{1+y}$Te$_{0.6}$Se$_{0.4}$ single crystals measured in the magnetic field up to 9 T for $H_{||c}$ and $H_{||ab}$. (e) Temperature dependence of upper critical fields for $H_{||c}$ and $H_{||ab}$. $H_{c2}$ is defined by the 90% of resistive transition. Inset shows the anisotropy $\gamma$ close to $T_c$ for the as-grown and fully-annealed crystals.
4.3. Annealing effects on critical current density

As discussed above, the excess Fe affects the SC of Fe$_{1+y}$Te$_{1-x}$Se$_x$. Hence, it will also affect the $J_c$ of the crystal. Earlier studies on crystals with different amounts of excess Fe reported quite different values of $J_c$ in the same condition (such as 5 K, zero field), ranging from $10^4$ A cm$^{-2}$ to over $10^5$ A cm$^{-2}$ [21, 27–29]. To systematically study the annealing effect on $J_c$, we also measured the magnetic hysteresis loops after the susceptibility in the experiment of annealing Fe$_{1+y}$Te$_{0.6}$Se$_{0.4}$ single crystals with an increasing amount of O$_2$ (the susceptibility results are shown in figure 3). $J_c$ can be calculated by using the extended Bean model [94]:

$$J_c = \frac{20}{a(1 - a/3b)} \frac{\Delta M}{V}, \quad (2)$$

where $\Delta M = M_{\text{up}} - M_{\text{down}}$ [emu cm$^{-3}$] and $M_{\text{up}}$ [emu cm$^{-3}$] and $M_{\text{down}}$ [emu cm$^{-3}$] are the magnetization when sweeping fields up and down, respectively, and $a$ [cm] and $b$ [cm] are sample widths ($a < b$). The self-field $J_c$ at 2 K versus the amount of O$_2$ are summarized in figure 30 together with the change in $T_c$. The $J_c$ is gradually enhanced together with the increase of $T_c$ by annealing with an increasing amount of O$_2$, and reaches values larger than $10^5$ A cm$^{-2}$.

Figure 31 shows the magnetic field dependences of $J_c$ for $H||c$ and $H||ab$ at different temperatures for the O$_2$-annealed Fe$_{1+y}$Te$_{1-x}$Se$_x$ ($x = 0.1, 0.2, 0.3$, and $0.4$) [95, 96]. For all the crystals, $J_c$ reaches a large value over $10^4$ A cm$^{-2}$ at 2 K (self-field) for both $H||c$ and $H||ab$. Crystals annealed in other atmospheres such as the Te, Se, S, P, Sb, As, and I all show similar values of $J_c$ [47–50, 53, 97]. The $J_c$ of Fe$_{1+y}$Te$_{1-x}$Se$_x$ is the highest among iron chalcogenides [98–101].

The above estimations of $J_c$ using the Bean model rely on the assumption that homogeneous currents flow within the sample. To examine this assumption, we took MO images on the annealed Fe$_{1+y}$Te$_{1-x}$Se$_x$ ($x = 0.1, 0.2, 0.3$, and $0.4$) single crystals in the remanent state, which was prepared by applying 800 Oe along the $c$-axis for 1 s and removing it after zero-field cooling. Typical MO images for the four crystals are shown in figures 32(a)–(d) [41]. All the MO images manifest typical roof-top patterns, indicating a nearly uniform current flow in the $ab$-plane of the crystals. Furthermore, the typical current discontinuity lines (the so-called d-line, which cannot be crossed by vortices, can be observed in all the crystals and marked by the dashed lines in figures 32(a)–(d)). By measuring the angles of the discontinuity line for our rectangular sample, the in-plane anisotropy of the current densities can be easily estimated. For all the crystals, the angle $\theta$ is $\sim$45°, indicating that the critical current density within the $ab$-plane is isotropic in the annealed Fe$_{1+y}$Te$_{1-x}$Se$_x$, consistent with the fourfold symmetry of the superconducting plane. Figure 32(e) shows profiles of the magnetic induction at different temperatures along the dotted line shown in figure 32(d) at different temperatures. When the temperature is raised up to 8 K, the magnetic field can completely penetrate the sample, and a clear roof-top pattern is observed. For comparison, we also show the remanent state

![Figure 28.](image-url)
MO image taken on the as-grown Fe$_{1+y}$Te$_{0.8}$Se$_{0.4}$ single crystal at 10 K (see figure 32(f)) [21]. The white dashed lines show the sample’s position. Almost no trapped field was observed except for some weak spots in the lower left corner, which indicates the extremely weak (only surface or filamentary) and inhomogeneous SC of the as-grown crystal.

4.4. Annealing effects on gap structure and superconducting pairing

The Fe$_{1+y}$Te$_{1-x}$Se$_x$ contains an s-wave-like, multi-gap structure, as already reported by the STM measurements [62]. However, the tunneling spectra were found to be sensitive to the excess Fe as reported by Yin et al. [37]. In the crystal free of excess Fe (figure 33(a)), the tunnelling spectrum exhibits a pair of sharp peaks at ±1.5 meV and a pair of side peaks at ±2.5 meV, together with a stateless region between the ±1.5 meV peaks (figure 33(b)). By contrast, in the crystal with excess Fe (figures 33(c) and (e)), the superconducting coherent peaks become weaker and the gap-bottom is lifted up in the spectrum taken away from the excess Fe, while the spectrum taken at the excess Fe shows a sharp peak precisely at the zero bias (figure 33(d)). In addition, it is also claimed that the magnitude of the superconducting gap seems to be unaffected by the excess Fe, and hence the excess Fe weakens only the superconducting phase coherence, and not the strength of the superconducting pairs. Although the nodeless gap structure of Fe$_{1+y}$Te$_{1-x}$Se$_x$ has been confirmed by many experiments, the isotropic [16, 31] or anisotropic gap [32, 33] structure are still under debate. The controversy around the gap structure may need to be clarified in the future by an angle-resolved technique on crystals with (as-grown) and without (annealed) excess Fe.

Recently, the gap structure of FeSe was also reported to be affected by the Fe nonstoichiometry [102–104]. However, the nonstoichiometry in FeSe was proved to be the Fe vacancy [65], which is different from the excess Fe in Fe$_{1+y}$Te$_{1-x}$Se$_x$ (usually $x \leq 0.5$).

5. Summary and perspective

In this topical review, we presented an overview of the reported annealing methods on Fe$_{1+y}$Te$_{1-x}$Se$_x$, and concluded that annealing in O$_2$, S, Se, Te, P, As, Sb, and I atmospheres at appropriate temperatures (200°C–400°C) can totally remove the excess Fe, and induce bulk SC. Immersing the crystals into acids or alcoholic beverages, and the electrochemical reaction method, can partially remove the excess Fe, mainly on the surface layers, which will introduce weak and inhomogeneous SC. Annealing in a vacuum and N$_2$ has no effect on the excess Fe. The annealing effect of F$_2$ (provided by CaF$_2$ and SmF$_3$) and H$_2$ are also reported, but need to be tested further. The annealing mechanism is that the excess Fe is attracted to the surface and reacts with the atmospheric elements, and forms the FeM$_x$ surface layers. The annealing effect mainly evolves from the edge of the crystal to the center. We systematically compared the normal state and superconducting properties of the crystals before (with excess Fe) and after annealing (without excess Fe). Almost all the studied properties including the crystal structure, magnetism, transport properties, band structure, $T_c$, phase diagram, upper critical field, anisotropy, critical current density, gap structure, and superconducting...
pairing are all affected by the excess Fe. Thus, we strongly suggest that future study on Fe$_{1+y}$Te$_{1-x}$Se$_x$ should pay attention to the Fe content of the used crystals.

The nonstoichiometric Fe seems to be a common issue for the IBSs-11 system. In FeSe and the S-doped compound, the nonstoichiometry was found to be a Fe vacancy rather than excess Fe. The annealing may be still helpful to prepare stoichiometric FeSe, which is preferred for probing its SC and nematicity. In the S-doped FeTe compounds, the excess Fe was also confirmed. Although there are some reports about the annealing effect and the improvement of SC similar to Fe$_{1+y}$Te$_{1-x}$Se$_x$ [38, 54, 105, 106], there is still no evidence for bulk SC and total removal of excess Fe, and the SC of Fe$_{1+y}$Te$_{1-x}$S$_x$ is still mainly on the surface. The effect of excess Fe seems to be stronger in the interstitial site of the Te/S layer than the Te/Se layer, which makes the annealing more difficult. Fe$_{1+y}$Te$_{1-x}$S$_x$ may be another interesting system similar to its sister compounds Fe$_{1+y}$Te$_{1-x}$Se$_x$ and FeSe. However, it has not been well studied due to the lack of high-quality single crystals. Appropriate annealing in the future to totally remove excess Fe may open the door to the full potential of Fe$_{1+y}$Te$_{1-x}$S$_x$. 

Figure 31. Magnetic field dependences of critical current densities for $H//c$ (upper panel) and $H//ab$ (lower panel) at different temperatures for the O$_2$-annealed (a)–(b) Fe$_{1+y}$Te$_{0.9}$Se$_{0.1}$, (c)–(d) Fe$_{1+y}$Te$_{0.8}$Se$_{0.2}$, (e)–(f) Fe$_{1+y}$Te$_{0.7}$Se$_{0.3}$, and (g)–(h) Fe$_{1+y}$Te$_{0.6}$Se$_{0.4}$. Reproduced from [41]. © IOP Publishing Ltd. All rights reserved.

Figure 32. MO images in the remanent state after applying 800 Oe along the c-axis in annealed (a) Fe$_{1+y}$Te$_{0.9}$Se$_{0.1}$, (b) Fe$_{1+y}$Te$_{0.8}$Se$_{0.2}$, (c) Fe$_{1+y}$Te$_{0.7}$Se$_{0.3}$, and (d) Fe$_{1+y}$Te$_{0.6}$Se$_{0.4}$ [41]. (e) Local magnetic induction profiles at temperatures from 5 to 14 K for Fe$_{1+y}$Te$_{0.6}$Se$_{0.4}$ taken along the dotted line in (d) [95]. (f) MO image in the remanent state of an as-grown sample at 10 K. The white dashed lines show the sample’s position. (f) Reprinted with permission from [21]. Copyright 2009 by the American Physical Society.
Acknowledgments

The authors would like to thank Y Tsuchiya, T Taen, T Yamada, S Pyon, W Zhou, X Li, J T Chen, A Sugimoto, T Ekino, T Nishizaki, Y Q Pan, and S Ooi for their help with experiments. They would also like to thank P Zhang, H Kitano, and T Machida for helpful discussions. The present work was partly supported by the Strategic Priority Research Program of Chinese Acsdemy of Science (XDB25000000), National Natural Science Foundation of China (11674054, 11611140101), and KAKENHI (19K14661, 17H01141) from JSPS.

Figure 33. (a) Topographic image of (Te, Se) ($T = 1.5$ K, $V = 1100$ mV, $I = 0.1$ nA). Inset image is the crystal structure of Fe(Te, Se) without excess Fe. (b) Comparison between STS and ARPES data. The upper panel shows STS taken on the (Te, Se) surface ($T = 1.4$ K, $V = -10$ mV, $I = 0.3$ nA). The lower panel shows symmetrized ARPES spectra. (c) Topographic image of (Te, Se) of the crystal with 0.5% excess Fe (bright spots). Inset image is the crystal structure of Fe(Te, Se) with excess Fe. (d) Spectra taken at and away from the excess Fe. All the data are acquired at 1.5 K. (e) Zoomed-in image showing one excess Fe. Reprinted by permission from Macmillan Publishers Ltd: Nature Research [37], Copyright (2015).

ORCID iDs

Yue Sun  https://orcid.org/0000-0002-5189-5460
Zhixiang Shi  https://orcid.org/0000-0003-3881-5152

References

[1] Hsu F C et al 2008 Proc. Nat. Acad. Sci. 105 14262
[2] Sales B C, Sefat A S, McGuire M A, Jin R Y, Mandrus D and Mozharivskyj Y 2009 Phys. Rev. B 79 094521
[3] Medvedev S et al 2009 Nat. Mater. 8 630
[44] Hu J, Wang G C, Qian B and Mao Z Q 2012 Supercond. Sci. Technol. 25 084011

[45] Friederichs G M, Wörsching M P B and Johrendt D 2015 Supercond. Sci. Technol. 28 094005

[46] Li X, Sun Y, Zhang Y, Zhou W, Yuan F and Shi Z 2015 Physica C 517 16

[47] Sun Y, Tsuchiya Y, Yamada T, Taen T, Pyon S, Shi Z X and Tamegai T 2013 J. Phys. Soc. Jpn. 82 093705

[48] Sun Y, Tsuchiya Y, Yamada T, Taen T, Pyon S, Shi Z X and Tamegai T 2013 J. Phys. Soc. Jpn. 82 115002

[49] Yamada T, Sun Y, Pyon S and Tamegai T 2016 J. Phys. Soc. Jpn. 85 024712

[50] Chen J, Sun Y, Yamada T, Pyon S and Tamegai T 2016 J. Phys. Soc. Jpn. 85 104714

[51] Koshika Y, Usui T, Adachi S, Watanabe T, Sakano K, Simayi S and Yoshizawa M 2013 J. Phys. Soc. Jpn. 82 023703

[52] Rodriguez E E, Stock C, Hsieh P Y, Butch N P, Paglione J and Green M A 2011 Chem. Sci. 2 1782

[53] Zhou W, Sun Y, Zhang S, Zhuang J, Yuan F, Li X, Shi Z, Yamada T, Tsuchiya Y and Tamegai T 2014 J. Phys. Soc. Jpn. 83 064704

[54] Deguchi K, Mizzugiya Y, Kawasaki Y, Ozaki T, Tsuda S, Yamagata T and Takanu Y 2011 Supercond. Sci. Technol. 24 055008

[55] Yamashita A et al 2014 Solid State Commun. 200 29

[56] Yamashita A et al 2015 J. Phys. Soc. Jpn. 84 034706

[57] Okada K, Takagi T, Kobayashi M, Ohnuma H, Noji T, Koike Y, ya Ayukawa S and Kitanow H 2018 Jpn. J. Appl. Phys. 57 040305

[58] Bendele M, Babkevich P, Katryan S, Gvasaliya S N, Pomjakushina E, Condor K, Roessli B, Boothroyd K T, Khasanov R and Keller H 2010 Phys. Rev. B 81 024536

[59] Sun Y,黃 T, Yamada T, Pyon S, Shinohara T, Shi Z and Tamegai T 2014 Phys. Rev. B 89 144512

[60] Dong C, Wang H, Li Z, Chen J, Yuan H Q and Fang M 2011 Phys. Rev. B 84 224506

[61] Phys. Rev. Lett. 109 237011

[62] Zeng B, Mu G, Luo H Q, Xiong T, Mazzin I L, Yang H, Shan L, Ren C, Dài P O and Wen H H 2010 Nat. Commun. 1 112

[63] Bendele M, Babkevich P, Katryan S, Gvasaliya S N, Pomjakushina E, Conder K, Roessli B, Boothroyd A T, Khasanov R and Keller H 2010 Phys. Rev. B 82 212504

[64] Zhang L, Singh D J and Du M H 2009 Phys. Rev. B 79 012506

[65] Zhang P Private communication

[66] Yin J X et al 2015 Nat. Phys. 11 543

[67] Sun Y, Taen T, Tsuchiya Y, Shi Z X and Tamegai T 2013 Supercond. Sci. Technol. 26 015015

[68] Wen J, Xu G, Gu G, Tranquada J M and Birgeneau R J 2011 Rep. Prog. Phys. 74 124503

[69] Sun Y, Tsuchiya Y, Taen T, Yamada T, Pyon S, Sugimoto A, Ekino T, Shi Z X and Tamegai T 2014 Sci. Rep. 4 4585

[70] Sun Y, Taen T, Yamada T, Tsuchiya Y, Pyon S and Tamegai T 2015 Supercond. Sci. Technol. 28 044002

[71] Fujitsu S, Matsuishi S and Hosono H 2012 Int. Mater. Rev. 57 311

[72] Komiya S, Hanawa M, Tsukada I and Maeda A 2013 J. Phys. Soc. Jpn. 82 064710

[73] [48] Maier T A, Kalinin S V, Sales B C and Pan M 2015 Phys. Rev. B 91 060513

[74] Sun Y, Tsuchiya Y, Pyon S, Tamegai T, Zhang C, Ozaki T and Li Q 2014 Supercond. Sci. Technol. 28 014015

[75] Ducattman S, Fernandes R M and Perkins N B 2014 Phys. Rev. B 90 165123

[76] Thampy V et al 2012 Phys. Rev. Lett. 108 100702

[77] Katayama N et al 2010 J. Phys. Soc. Jpn. 79 113702

[78] Eom M J, Na S W, Hoch C, Kremer R K and Kim J S 2012 Phys. Rev. B 85 024536

[79] Chang H H, Luo Y J, Wu C T, Hsu F C, Huang T W, Wu P M, Wu M K and Wang M J 2012 Supercond. Sci. Technol. 25 035004

[80] Hu J, Liu T J, Qian B and Mao Z Q 2013 Phys. Rev. B 88 014504

[81] Abríkosov A A 1998 Phys. Rev. B 58 2788–94

[82] Abríkosov A A 2000 Europhys. Lett. 49 789

[83] Novoselov K S, Geim A K, Morozov S V, Jiang D, Katsnelson M I, Grigorieva I V, Dubonos S V and Firsov A A 2005 Nature 438 197

[84] Taskin A A, Ren Z, Sasaki S, Segawa K and Ando Y 2011 Phys. Rev. Lett. 107 016801
[77] Xu R, Husmann A, Rosenbaum T F, Saboungi M L, Enderby J E and Littlewood P B 1997 Nature 390 57

[78] Katayama S, Kobayashi A and Suzumura Y 2007 J. Phys. Soc. Jpn. 75 054705

[79] Park J et al 2011 Phys. Rev. Lett. 107 126402

[80] Wang K, Graf D, Lei H, Tozer S W and Petrovic C 2011 Phys. Rev. B 84 220401

[81] Richard P et al 2010 Phys. Rev. Lett. 104 137001

[82] Park J et al 2011 Phys. Rev. Lett. 107 126402

[83] Huynh K K, Tanabe Y and Tanigaki K 2011 Phys. Rev. Lett. 106 217004

[84] Chong S V, Williams G V M, Kennedy J, Fang F, Tallon J L and Kadowaki K 2013 Europhys. Lett. 104 17002

[85] Pallecchi I, Bernardini F, Tropeano M, Palenzona A, Martinelli A, Ferdeghini C, Vignolo M, Massidda S and Putti M 2011 Phys. Rev. B 84 134524

[86] Bhoi D, Mandal P, Choudhury P, Pandya S and Ganesan V 2011 Appl. Phys. Lett. 98 172105

[87] Rinott, Chashka K B, Ribak A, Rienks E D L, Taleb-Ibrahimi A, Le Fevre P, Bertran F, Randeria M and Kanigel A 2017 Sci. Adv. 3 e1602372

[88] Kawasaki Y, Deguchi K, Demura S, Watanabe T, Okazaki H, Oraki T, Yamaguchi T, Takeya H and Takano Y 2012 Solid State Commun. 152 1135

[89] Luetkens H et al 2009 Nat. Mater. 8 305

[90] Zhao J et al 2008 Nat. Mater. 7 953

[91] Pan Y Q in preparation

[92] Liu L, Mikami T, Takahashi M, Ishida S, Kakeshita T, Okazaki K, Fujimori A and Uchida S 2015 Phys. Rev. B 91 134502

[93] Chu J H, Analytis J G, De Greve K, McMahon P L, Islam Z, Yamamoto Y and Fisher I R 2010 Science 329 824

[94] Sun Y, Taen T, Tsujiya Y, Ding Q, Pyon S, Shi Z X and Tamegai T 2013 Appl. Phys. Express 6 043101

[95] Hu R, Bozin E S, Warren J B and Petrovic C 2009 Phys. Rev. B 80 214514

[96] Lei H and Petrovic C 2011 Phys. Rev. B 83 184504

[97] Le Fevre P, Bertran F, Randeria M and Kanigel A 2017 Sci. Adv. 3 e1602372

[98] Bourgeois-Hope P, Chi S, Bonn D A, Liang R, Hardy W N, Wolf T, Meingast C, Doiron-Leyraud N and Taillefer L 2016 Phys. Rev. Lett. 117 097003

[99] Sun Y, Pyon S, Yamazaki T, Yoshizawa H and Yaguchi H 2018 J. Phys. Soc. Jpn. 87 054705

[100] Hu R, Bozin E S, Warren J B and Petrovic C 2009 Phys. Rev. B 80 214514

[101] Sun Y, Pyon S, Yang R, Qiu X, Feng J, Shi Z and Tamegai T 2019 J. Phys. Soc. Jpn. 88 034703

[102] Bourgeois-Hope P, Chi S, Bonn D A, Liang R, Hardy W N, Wolf T, Meingast C, Doiron-Leyraud N and Taillefer L 2016 Phys. Rev. Lett. 117 097003

[103] Sun Y, Park A, Pyon S, Tamegai T and Kitamura H 2017 Phys. Rev. B 96 140505

[104] Mizuguchi Y, Deguchi K, Tsuda S, Yamaguchi T and Tamegai T 2010 Europhys. Lett. 90 57002

[105] Yamamoto K, Yamazaki T, Yamanaka T, Ueta D, Yoshizawa H and Yaguchi H 2018 J. Phys. Soc. Jpn. 87 054705