Effects of annealing, acid and alcoholic beverages on Fe$_{1+y}$Te$_{0.6}$Se$_{0.4}$

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Abstract
We have systematically investigated and compared different methods to induce superconductivity in the iron chalcogenide Fe$_{1+y}$Te$_{0.6}$Se$_{0.4}$, including annealing in a vacuum, N$_2$, O$_2$ and I$_2$ atmospheres and immersing samples into acid and alcoholic beverages. Vacuum and N$_2$ annealing are proved to be ineffective in inducing superconductivity in a Fe$_{1+y}$Te$_{0.6}$Se$_{0.4}$ single crystal. Annealing in O$_2$ and I$_2$ and immersion in acid and alcoholic beverages can induce superconductivity by oxidizing the excess Fe in the sample. Superconductivity in O$_2$ annealed samples is of a bulk nature, while I$_2$, acid and alcoholic beverages can only induce superconductivity near the surface. By comparing the different effects of O$_2$, I$_2$, acid and alcoholic beverages we propose a scenario to explain how the superconductivity is induced in the non-superconducting as-grown Fe$_{1+y}$Te$_{0.6}$Se$_{0.4}$.

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

1. Introduction
The recent discovery of superconductivity at 26 K in an iron oxypnictide, LaFeAs(O, F) [1], has stimulated great interest among condensed-matter physicists. A tremendous amount of work has been carried out, leading to the emergence of novel iron-based superconductor families with different crystal structures: 1111 (LaFeAs(O, F)) [1], 122 ((Ba, K)Fe$_2$As$_2$) [2], 111 (LiFeAs) [3] and 11 (Fe(Te, Se)) [4]. Among these, FeTe$_{1−x}$Se$_x$ has received special attention due to its simple crystal structure, comprising only Fe(Te, Se) layers. Superconductivity and magnetism of this system are not only dependent on the doping level but are also sensitive to Fe non-stoichiometry, which originates from the partial occupation of excess Fe at the interstitial site in the Te/Se layer [5, 6]. For the undoped parent compound Fe$_{1+y}$Te, the commensurate antiferromagnetic order can be tuned by the excess Fe to an incommensurate magnetic structure [5]. In Se-doped FeTe samples, excess Fe was found to suppress superconductivity and cause the magnetic correlations [6]. In the other end member, Fe$_{1+y}$Se, superconductivity is reported to reside just in a very narrow concentration region of excess Fe [7]. To probe the intrinsic properties of FeTe$_{1−x}$Se$_x$ without the influence of excess Fe, some previous works have been performed to remove the effect of excess Fe by annealing it in different conditions. Superconductivity was found to be induced by annealing in a vacuum [8, 9], air [10], oxygen [11, 12], nitrogen [13], I$_2$ vapour [14] and even by immersing into nitric acid HNO$_3$ [13]. Recently superconductivity was also reported to be induced in FeTe$_{0.8}$Se$_{0.2}$ by immersing it into alcoholic beverages [15, 16]. The interpretations for these treatments for inducing superconductivity are still controversial, including the improvement of homogeneity [8], oxygen intercalation [11] and deintercalation of excess Fe [10, 13, 14]. Although superconductivity can be successfully induced, some annealed samples show a very broad transition width [11, 13, 14, 16], which implies an inhomogeneous superconductivity. In order to address these issues, and try to understand how the superconductivity is induced in Fe$_{1+y}$Te$_{0.6}$Se$_{0.4}$, we have systematically investigated different methods to induce superconductivity by annealing in a vacuum, N$_2$, O$_2$ and I$_2$ atmospheres, and immersing the samples into acid and alcoholic beverages. By comparing the results, we give a possible scenario to explain how the superconductivity is induced in the non-superconducting as-grown Fe$_{1+y}$Te$_{0.6}$Se$_{0.4}$. 

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2. Experimental methods

Single crystals with nominal compositions FeTe$_{0.6}$Se$_{0.4}$ and FeTe$_{0.8}$S$_{0.2}$ were prepared from high purity Fe (99.99%), Te (99.999%), Se (99.999%) and S (99.9999%) grains [8]. More than 10 g of stoichiometric quantities was loaded into a small quartz tube with $d_1 \sim 10$ mm and the tube evacuated and sealed. Then we sealed this tube into a second evacuated quartz tube with $d_2 \sim 20$ mm. The whole assembly was heated up to 1070°C and kept for 36 h, followed by slow cooling down to 710°C at a rate of 6°C h$^{-1}$. After that, the temperature was cooled down to room temperature by shutting down the furnace. The as-grown single crystal with typical dimensions of $5.0 \times 5.0 \times 1.0$ mm$^3$ for FeTe$_{0.6}$Se$_{0.4}$ and $2.0 \times 2.0 \times 0.1$ mm$^3$ for FeTe$_{0.8}$S$_{0.2}$ can be easily cleaved perpendicular to the c axis. For vacuum annealing, the sample was loaded into a quartz tube, which was carefully baked and examined to ensure that no appreciable amount of gas was emitted under the same conditions as the sample annealing. The quartz tube was carefully evacuated by a diffusion pump before sealing the sample. For annealing with $I_2$, the sample was loaded into a quartz tube with $I_2$ chips (99.9%). For annealing in O$_2$ and N$_2$ atmospheres, after evacuating, we filled controlled amounts of O$_2$ and N$_2$ gas before sealing the quartz tube. During these processes, a diaphragm-type manometer with an accuracy of 10$^{-3}$ Torr was used for real-time monitoring of the pressure in the system to prevent gas leakage and to check the amount of gas in the tube. Then the samples were annealed at 400°C for more than a day, followed by quenching in water. For O$_2$ annealing, we tried annealing the sample under 0.1%, 1% and 1 atmosphere (atm) of O$_2$ gas. Fe$_{1+y}Te_{0.6}$Se$_{0.4}$ samples annealed both under 0.1% and 1% atm of O$_2$ show a superconducting transition temperature, $T_c$, higher than 14 K, and the former exhibits larger $J_c$. By contrast, the sample annealed in 1 atm O$_2$ was totally damaged, which indicates that the sample itself was oxidized during annealing in too much O$_2$. Other pieces of as-grown samples were put into glass bottles (10 ml) filled with 20% hydrochloric acid HCl, beer (Asahi Breweries Ltd), Japanese sake (Hakutsuru Sake Brewing, Co. Ltd), shochu (Iwagawa Jozo Co. Ltd) or whisky (Suntory Holdings Ltd). The samples immersed in alcoholic beverages (beer, red wine, Japanese sake, shochu, whisky), 20% HCl, were kept at 70°C for 40 h. The sample immersed into 20% HCl was kept at room temperature for 100 h, because we found heating the sample up to 70°C with acid damaged the sample quickly. Magnetization measurements on the as-grown and post-treated samples were performed using a commercial superconducting quantum interference device magnetometer (MPMS-XL5, Quantum Design). Magneto-optical (MO) images were obtained by using the local field dependent Faraday effect in the in-plane magnetized garnet indicator film employing a differential method [17, 18].

3. Results and discussion

Figure 1(a) shows the temperature dependence of zero-field-cooled (ZFC) and field-cooled (FC) magnetization at 5 Oe for the as-grown, vacuum, N$_2$, 0.1% atm O$_2$, and $I_2$ atmosphere annealed Fe$_{1+y}Te_{0.6}$Se$_{0.4}$. Because of the low $T_c$ and weak diamagnetic signal, ZFC and FC curves of the as-grown, vacuum and N$_2$ annealed samples are almost merged together as pointed out by the arrow. (b) Fe$_{1+y}Te_{0.6}$Se$_{0.4}$ immersed into alcoholic beverages (beer, red wine, Japanese sake, shochu, whisky), 20% HCl, and FeTe$_{0.8}$S$_{0.2}$ immersed into beer, together with the result of O$_2$ annealing for comparison.
samples immersed into alcoholic beverages, acid as well as of superconductivity, magnetic hysteresis loops (MHLs) of when the non-superconducting region is covered by a superconducting, the diamagnetic signal becomes significant Fe and the diamagnetic signal is even smaller than that in beer at 70°C. In this case, the transition width is also very broad, similar to that observed in high quality Ba(Fe1−xCo)x2As2 single crystal [20–22], it is the largest among those reported in Fe(Se, Te) [8, 23–28]. This fact demonstrates the high quality of our O2 annealed sample. To further confirm the homogeneous current flow within the sample, we took MO images of 0.1% atm O2 immersed into alcoholic beverages, acid and FeTe0.85Se0.4 immersed into beer. The inset shows a MO image in the remanent state taken at 6 K in 0.1% atm O2 annealed Fe1−yTe0.66Se0.4. The lower inset shows the magnetic induction profile along the dashed line in the MO image.

From the MHLs, we can obtain the critical current density, $J_c$, by using the Bean model [19]:

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

(1)

where $\Delta M$ is $M_{down} - M_{up}$, $M_{up}$ and $M_{down}$ are the magnetization when sweeping fields up and down, respectively, $a$ and $b$ are sample widths ($a < b$). Magnetic field dependence of $J_c$ at 2 K is summarized in figure 3. $J_c$ of the O2 annealed sample reaches a value greater than 5 × 10^5 A cm$^{-2}$ at zero field. It is robust under applied field, keeping a value larger than 1 × 10^5 A cm$^{-2}$ even at 50 kOe. Although the value of $J_c$ is still lower than that of Ba(Fe1−xCo)x2As2 single crystal [20–22], it is the largest among those reported in Fe(Se, Te) [8, 23–28]. This fact demonstrates the high quality of our O2 annealed sample. To further confirm the homogeneous current flow within the sample, we took MO images of 0.1% atm O2 annealed crystal in the remanent state. In the inset of figure 3, a typical MO image taken at 6 K after cycling the field up to 800 Oe along the c axis is shown. The MO image manifests a typical roof-top pattern, similar to that observed in high quality Ba(Fe1−xCo)x2As2 single crystals [20, 29, 30], indicating a nearly uniform current flow in the crystal. The uniformity of $J_c$ is much better than that reported in [8]. The profile of the magnetic induction along the dashed line in the MO image is also shown in the inset of figure 3. $J_c$ can be roughly estimated by $J_c \sim \Delta B/t$, where $\Delta B$ is the trapped field and $t$ is the thickness of the sample. With $\Delta B \sim 1076$ G and $t = 50 \mu$m, $J_c$ is estimated as $2.2 \times 10^5$ A cm$^{-2}$ at 6 K, consistent with estimation from the Bean model. The large $J_c$ estimated from MHLs and the MO shown in figure 2(a). Although an obvious superconducting hysteresis loop can be seen, it is too weak to persist up to applied fields larger than 20 kOe. The absolute value of magnetization is also very small compared with that of O2 annealed Fe1−yTe0.66Se0.4 crystals, as shown in figure 2(b).

Figure 2. (a) Magnetic hysteresis loops (MHLs) of Fe1−yTe0.66Se0.4 immersed into alcoholic beverages, acid, and annealed in I2 atmosphere and FeTe0.85Se0.4 immersed into beer measured at 2 K. (b) MHLs of samples immersed into alcoholic beverages, acid and annealed in an I2 atmosphere plotted together with the 0.1% atm O2 annealed sample for comparison.

Figure 3. Field dependence of $J_c$ at 2 K for Fe1−yTe0.66Se0.4 annealed in I2, 0.1% atm O2, immersed into alcoholic beverages, acid and FeTe0.85Se0.4 immersed into beer. The inset shows a MO image in the remanent state taken at 6 K in 0.1% atm O2 annealed Fe1−yTe0.66Se0.4.
image cannot be sustained only by superconductivity near the surface. Thus, the superconductivity induced by O₂ annealing must be a bulk property of the sample. In \( \text{Fe}_{1+y}\text{Te}_{0.6}\text{Se}_{0.4} \) single crystal immersed in alcoholic beverages or acid as well as annealing with I₂, \( J_c \) at 2 K under zero field is smaller than \( 1 \times 10^4 \text{ A cm}^{-2} \). In addition, \( J_c \) decreases very quickly with increasing field, and becomes smaller than \( 1 \times 10^3 \text{ A cm}^{-2} \) at fields above 20 kOe. For \( \text{FeTe}_{0.8}\text{S}_{0.2} \), the value of the zero field \( J_c \) is smaller than 500 A cm\(^{-2} \) and easily suppressed by the modest applied field, which decreases to less than 100 A cm\(^{-2} \) at fields about 10 kOe. The much smaller value of \( J_c \) compared with that in the O₂ annealed sample shows that the superconductivity comes from the surface.

To directly prove that the superconductivity induced by I₂, acid and alcoholic beverages is only near the surface, we cut the four edges of the sample, polished the double surfaces (more than half of the sample was removed after polishing), and then compared the superconducting property of the whole sample and the inner part. In figures 4(a) and (b), the results on samples annealed in 1% atm O₂ and immersed into beer are compared. In the case of the O₂ annealed sample, \( T_c \) of the inner part is almost the same as that in the whole sample, and the diamagnetic signal as well as \( J_c \) do not decrease but become a little larger than the whole sample. It should be noted that the 1% atm O₂ annealed sample shows smaller \( J_c \) than that annealed under 0.1% atm O₂, although \( T_c \) is similar. The decrease in \( J_c \) may be caused by the fact that the sample itself was partially oxidized by the excess O₂, especially on the surface, which changes colour after annealing, as reported before [10]. After removing the over-oxidized surface, the diamagnetic signal and \( J_c \) are increased. By contrast, in the sample immersed in beer, both the diamagnetic signal and the \( J_c \) of the inner part are decreased to about 10% of the whole sample. The significant degradation in superconducting properties after removing the surface directly proves that the observed superconductivity mainly comes from the surface.

Compiling the obtained results, we propose a scenario to explain how the superconductivity is induced by different methods. Vacuum and N₂ annealing cannot induce superconductivity, which indicates that homogeneity is not the key factor for inducing superconductivity. The previously reported vacuum annealing and N₂ annealing induced superconductivity may be caused by the leakage of O₂, since we found that only trace amount of O₂ can successfully enhance superconductivity. Furthermore, all oxidizing agents, O₂, I₂, acid and alcoholic beverages can induce superconductivity, possibly by removing the excess Fe in the sample rather than the O₂ itself being doped into the crystal. Among these, only O₂ can easily intercalate between the layers of the single crystal, and deintercalates the excess Fe from the inner part of the sample because of its small size, inducing bulk superconductivity in \( \text{Fe}_{1+y}\text{Te}_{1-x}\text{S}_x \). On the other hand, I₂, acid and the alcoholic beverages can just induce superconductivity near the surface because their relatively larger size prevents them from intercalating between the layers of the crystal. Thus, the rate of excess Fe deintercalation is much slower than the O₂ annealing, and can induce superconductivity only near the surface of the crystal.

Very recently, the alcoholic beverage effect was also reported in \( \text{Fe}_{1+y}\text{Te}_{0.8}\text{S}_{0.2} \) polycrystal [31]. O₂ annealing and alcoholic beverages have been reported to be effective in \( \text{Fe}_{1+y}\text{Te}_{1-x}\text{S}_x \) single crystals [15, 32]. While for O₂ annealed \( \text{Fe}_{1+y}\text{Te}_{1-x}\text{S}_x \) single crystals, superconductivity can be suppressed by the following vacuum annealing, which is quite different from the case of O₂ annealed \( \text{Fe}_{1+y}\text{Te}_{1-x}\text{S}_x \), in which the superconductivity is stable under vacuum annealing (data not shown). This suggests that the oxygen is doped into \( \text{Fe}_{1+y}\text{Te}_{1-x}\text{S}_x \) rather than deintercalating the excess Fe. However, although superconductivity is successfully induced in \( \text{Fe}_{1+y}\text{Te}_{1-x}\text{S}_x \), there is still no proof for bulk superconductivity like large \( J_c \) or an obvious jump of specific heat at \( T_c \). More efforts along these lines are necessary to clarify the origin of different effects between \( \text{Fe}_{1+y}\text{Te}_{1-x}\text{S}_x \) and \( \text{Fe}_{1+y}\text{Te}_{1-x}\text{S}_x \) single crystals.

4. Conclusion

In conclusion, we have found that vacuum and N₂ annealing cannot enhance superconductivity in \( \text{Fe}_{1+y}\text{Te}_{0.8}\text{S}_{0.2} \) single crystal. O₂ and I₂ annealing, acid and alcoholic beverages can
induce superconductivity by oxidizing the excess Fe in the sample. The large value of $J_c \sim 5 \times 10^5$ A cm$^{-2}$ obtained from MHLs and the MO image shows that bulk superconductivity can be induced by O$_2$ annealing. The self-field $J_c$ at 2 K of the samples annealed in an I$_2$ atmosphere or immersed in acid or alcoholic beverages are smaller than 1 x 10$^4$ A cm$^{-2}$, and suppressed by the modest magnetic field. Furthermore, the diamagnetic signal and $J_c$ of the inner part of these samples are much smaller than those obtained from the whole sample. These results indicate that the I$_2$ atmosphere, acid and alcoholic beverages can only induce superconductivity near the surface.

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