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Abstract – Oxygen annealing dramatically improved the superconducting properties of solid-state-reacted FeTe$_{0.8}$S$_{0.2}$, which showed only a broad onset of superconducting transition just after the synthesis. The zero resistivity appeared and the transition temperature $T_c$ reached 8.5 K by the oxygen annealing at 200 $^\circ$C. The shielding volume fraction was also enhanced from 0 to almost 100%. The lattice constants were compressed by the oxygen annealing, indicating that the evolution of bulk superconductivity in FeTe$_{0.8}$S$_{0.2}$ was correlated to the shrinkage of the lattice.

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Introduction. – Since the discovery of superconductivity at a transition temperature $T_c = 26$ K in LaFeAsO$_{1-x}$F$_x$, several types of Fe-based superconductors, essentially composed of 2-dimensional Fe-square lattices, have been discovered [1–6]. Anti-PbO-type FeSe is the simplest Fe-based superconductor [4], and shows comparably high-$T_c$ of 37 K under high pressure [7–10]. In contrast, FeTe is an antiferromagnet with an ordering temperature of 70 K, while it has a structure quite similar to superconducting FeSe. The substitution of S or Se for the Te site suppresses the antiferromagnetic ordering and achieves superconductivity [11–14]. The FeTe$_{1-x}$Se$_x$ superconductors have provided several information useful for understanding the mechanism of Fe-based superconductivity, because the large single crystals could be grown easily. In contrast, the synthesis of the high-quality FeTe$_{1-x}$S$_x$ sample is difficult, due to the solubility limit of S for the Te site [14,15].

The superconducting properties of FeTe$_{1-x}$S$_x$ depend on the synthesis method. FeTe$_{0.8}$S$_{0.2}$ synthesized by a melting method showed superconductivity at $T_c^{\text{zero}} = 7.8$ K, but it contained impurity phases and its superconducting volume fraction was only 20%. The nearly single-phase sample of FeTe$_{0.8}$S$_{0.2}$ is obtained by using the solid-state reaction method. However, the sample shows only filamentary superconductivity and zero resistivity is not observed, due to an insufficiency of S concentration. To elucidate the intrinsic properties of the FeTe$_{1-x}$S$_x$ superconductor, achieving bulk superconductivity in the single-phase sample is strongly required. Recently, we reported moisture-induced superconductivity in FeTe$_{0.8}$S$_{0.2}$ which was synthesized by the solid-state reaction method and showed only filamentary superconductivity just after the synthesis [16]. Only the sample immersed into the water at room temperature for several days showed an evolution of superconductivity. Furthermore, the sample immersed into the hot water showed superconductivity with a superconducting volume fraction above 15% in only 1 day, indicating that the speed of evolution of superconductivity was strongly enhanced by heating. In this respect, we investigated the effect of annealing at several temperatures in oxygen gas for as-grown FeTe$_{0.8}$S$_{0.2}$, and found that the FeTe$_{0.8}$S$_{0.2}$ sample annealed at 200 $^\circ$C showed bulk superconductivity with a sharp superconducting transition.

Experimental methods. – The polycrystalline samples of FeTe$_{0.8}$S$_{0.2}$ were prepared using the solid-state reaction method as described in refs. [13] and [16]. The obtained samples were quickly sealed into the quartz tubes filled with oxygen gas of atmospheric pressure, and annealed at 100, 200, 300 and 400 $^\circ$C for 2 hours, respectively. The samples were characterized by X-ray diffraction using a Cu-$K_{\alpha}$ radiation. Temperature dependence of resistivity was measured using a four-terminals method from 300 to 2 K. Temperature dependence of

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magnetic susceptibility was measured using a SQUID magnetometer in a zero-field–cooling (ZFC) mode with an applied magnetic field of 10 Oe. Here we define the sample name as the annealed temperature; for example, \( T_a = 100 \) °C is the FeTe\(_{0.8}S\(_{0.2}\) sample annealed at 100 °C for 2 hours.

**Results and discussion.** – Figure 1 shows the temperature dependence of magnetic susceptibility normalized at 15 K for oxygen-annealed FeTe\(_{0.8}S\(_{0.2}\). For the as-grown sample, no sign of superconductivity is observed. With annealing the sample at 100 °C, the superconducting transition appears around 7 K. The sharp superconducting transition at 9.0 K is observed for \( T_a = 200 \) °C, and the shielding volume fraction reaches almost 100%. Both \( T_c \) and shielding volume fraction decreases for \( T_a = 300 \) °C. Furthermore, superconductivity is not observed for \( T_a = 400 \) °C, indicating that the annealing above 300 °C degrades superconductivity.

Figure 2(a) shows the temperature dependence of resistivity below 15 K for the as-grown sample and \( T_a = 100, 200 \) and 300 °C. The as-grown sample shows only an onset of the superconducting transition around 5 K. By annealing at 100 °C, the superconducting transition becomes sharper and the zero-resistivity state appears at 4.3 K. For \( T_a = 200 \) °C, a sharp superconducting transition with \( T_{\text{onset}} = 10.7 \) K and \( T_{\text{zero}} = 8.5 \) K is observed. With annealing at higher temperature of 300 °C, the \( T_c \) is suppressed, corresponding to the result in the magnetic susceptibility measurements. The temperature dependence of resistivity from 300 to 2 K for all samples is shown in fig. 2(b). For \( T_a = 100 \) °C, the temperature dependence of resistivity shows an increase with decreasing temperature above \( T_c \). In contrast, the temperature dependence of resistivity for \( T_a = 200 \) °C exhibits a broad hump around 60 K and a decrease with cooling above \( T_c \). The behavior is quite similar to that of the optimally doped FeTe\(_{1-x}Se_x\), indicating that the oxygen annealing optimizes superconductivity for FeTe\(_{0.8}S\(_{0.2}\). The annealing at both 300 and 400 °C increases the resistivity. It would be due to a decomposition of the PbO structure and an increase of impurity phases such as FeTe\(_2\) or hexagonal phases.

To investigate the superconducting properties of inside of the annealed samples, the surface of the samples were ground down after the first resistivity measurement. After trimming the sample to less than 1/5 of the pellet, the new terminals were fabricated, and the resistivity was
measured again with the same condition. Figure 3 shows the temperature dependence of normalized resistivity for the as-annealed and the trimmed sample with \( T_a = 100 \) and 200 °C. For both samples, no difference in resistive transition is observed between the surface and the inside, indicating a homogeneity of the oxygen-annealed sample.

Figure 4(a) shows the temperature dependence of resistivity for \( T_a = 200 \) °C under the magnetic field up to 7 T with an increment of 1 T. Both the upper critical field \( \mu_0 H_{c2} \) and irreversible field \( \mu_0 H_{irr} \) are plotted in fig. 4(b) as a function of temperature. Due to the high critical fields, the changes of the onset temperature under magnetic fields were not obvious. Therefore, the \( T_{onset} \) was defined by a cross-point of two lines described in the inset of fig. 4(a). As described in fig. 4(b), \( \mu_0 H_{c2} (0) \) and \( \mu_0 H_{irr} (0) \) are estimated to be \( \sim 100 \) T and \( \sim 60 \) T by the linear extrapolation. By using the WHH theory [17], \( \mu_0 H_{c2} (0) \) was calculated to be \( \sim 70 \) T. These values are almost the same as the previous report on the FeTe\(_{0.8}S\(_{0.2}\) synthesized by the melting method [14]. Oxygen-annealed FeTe\(_{0.8}S\(_{0.2}\) is one of the candidate materials for application, due to its high \( \mu_0 H_{c2} \) and the homogeneity of the annealed sample.

To clarify the origin of the evolution of bulk superconductivity, the X-ray diffraction measurements were performed for the oxygen-annealed samples. The X-ray profiles for the as-grown sample and \( T_a = 100, 200, 300 \) and 400 °C are shown in fig. 5(a). The asterisks indicate the peaks of impurity phases FeTe\(_2\) and hexagonal Fe\(_1\)−S. For \( T_a = 300 \) and 400 °C, the peaks of the impurity phase FeTe\(_2\) are enhanced. The typical diffraction peaks of (101) and (002) are shown in fig. 5(b). The peaks shift to higher angles for \( T_a = 100, 200 \) and 300 °C compared to the as-grown sample, indicating that the oxygen annealing compresses the lattice. With annealing at 400 °C, the peaks shift to lower angles and the peaks of the impurity phases grow up. The calculated lattice constants \( a \) and \( c \) were plotted in figs. 5(c) and (d), respectively, as a function of annealing temperature. For comparison, we also plot the lattice constants of FeTe\(_{0.8}S\(_{0.2}\) synthesized by the melting method, which showed superconductivity with the superconducting volume fraction of \( \sim 20\% \) [14]. The lattice constants are clearly compressed for \( T_a = 100, 200 \) and 300 °C compared to the as-grown sample. In particular, the \( a \)-axis of the oxygen-annealed samples are smaller than that of FeTe\(_{0.8}S\(_{0.2}\) synthesized by the melting method. These results suggest that bulk superconductivity of FeTe\(_{1−x}\)S\(_x\) can be induced when the lattice is optimally compressed. To elucidate the accurate site of oxygen introduced by the oxygen annealing, the detailed evolution of superconductivity by oxygen annealing in FeTe\(_{0.8}S\(_{0.2}\)
structural analysis and/or the measurements sensitive to the local structure should be performed.

To investigate the effects of the annealing in several atmospheres other than oxygen, the as-grown samples were sealed into the evacuated quartz tube and tubes filled with nitrogen and argon gas, respectively, and annealed at 200°C for 2 hours. Figure 6(a) shows the temperature dependence of magnetic susceptibility normalized at 15 K for those samples. Superconductivity is not observed for the samples annealed in vacuum, nitrogen and argon. We also investigated the oxygen-annealing effect for polycrystalline FeTe, which shows the antiferromagnetic/structural transition around 70 K. Figure 6(b) shows the temperature dependence of magnetic susceptibility for FeTe and FeTe$_{0.8}$S$_{0.2}$ both annealed in oxygen at 200°C for 2 hours. There is no sign of superconductivity for oxygen-annealed FeTe. Although oxygen-incorporation–induced superconductivity was recently reported in FeTe films [18,19], superconductivity was not observed for the bulk FeTe sample annealed in oxygen. The difference between the thin film and the bulk sample of FeTe is the presence/absence of strain stress induced by substrate. In fact, the optimally strain-stressed FeTe film shows superconductivity without O, S or Se substitutions for the Te site [20]. The oxygen annealing would be effective to overcome the insufficiency of the strain stress and achieve superconductivity in the FeTe thin film. On the basis of these results, the oxygen annealing would also overcome the insufficiency of the S concentration in FeTe$_{1-x}$S$_x$ and achieve superconductivity.

We have investigated a reversibility of superconductivity in FeTe$_{0.8}$S$_{0.2}$ by the oxygen and vacuum annealing. At first, the as-grown sample was annealed in oxygen at
solid-state–reacted FeTe$_{0.8}$S$_{0.2}$, which shows only filamentary superconductivity just after the synthesis. The zero resistivity appears and $T_{\text{zero}}$ reaches 8.5 K by the oxygen annealing at 200 °C. The shielding volume fraction is also enhanced from 0 to almost 100%. High upper critical field of 70 T was estimated for oxygen-annealed FeTe$_{0.8}$S$_{0.2}$. Because of the high critical field and the homogeneity of the annealed sample, oxygen-annealed FeTe$_{0.8}$S$_{0.2}$ is one of the candidate materials for application. The lattice constants are compressed by the oxygen annealing, indicating that the evolution of bulk superconductivity is correlated to the shrinkage of the lattice. Superconductivity induced by the oxygen annealing is suppressed with annealing in vacuum, and reproduced by the reannealing in oxygen.

Fig. 7: (Colour on-line) (a) Temperature dependence of magnetic susceptibility for the oxygen-annealed sample is indicated by filled blue circles. Green squares indicate the data measured after annealing in vacuum for 24 hours after the optimal oxygen-annealing process. (b) Green squares are the data same as those plotted in (a). Filled red diamonds indicate the data collected after reannealing in oxygen for 2 hours.

200 °C for 2 hours. The sharp superconducting transition with the shielding volume fraction of almost 100% was observed as plotted by filled blue circles in fig. 7(a). Next, the sample was placed in a vacuum furnace evacuated using a rotary pump and annealed at 200 °C for 24 hours. As shown in fig. 7(a), the shielding volume fraction decreased down to 25% by the vacuum annealing. This suggests that the oxygen inserted into FeTe$_{0.8}$S$_{0.2}$ is removable. To investigate the reversibility, the sample was annealed again in oxygen at 200 °C for 2 hours. The sharp superconducting transition was reproduced by the oxygen reannealing as shown in fig. 7(b). Superconductivity of FeTe$_{0.8}$S$_{0.2}$ can be alive in oxygen but dies in vacuum, which seems like a breath of the superconductor.

**Conclusion.** – In conclusion, the oxygen annealing dramatically improves the superconducting properties for solid-state–reacted FeTe$_{0.8}$S$_{0.2}$, which shows only filamentary superconductivity just after the synthesis. The zero resistivity appears and $T_{\text{zero}}$ reaches 8.5 K by the oxygen annealing at 200 °C. The shielding volume fraction is also enhanced from 0 to almost 100%. High upper critical field of 70 T was estimated for oxygen-annealed FeTe$_{0.8}$S$_{0.2}$. Because of the high critical field and the homogeneity of the annealed sample, oxygen-annealed FeTe$_{0.8}$S$_{0.2}$ is one of the candidate materials for application. The lattice constants are compressed by the oxygen annealing, indicating that the evolution of bulk superconductivity is correlated to the shrinkage of the lattice. Superconductivity induced by the oxygen annealing is suppressed with annealing in vacuum, and reproduced by the reannealing in oxygen.

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