Superconductivity in oxygen-annealed FeTe$_{1-x}$S$_x$ single crystal

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We investigated the S-doping-driven phase transition from antiferromagnetic to superconducting in FeTe$_{1-x}$S$_x$ single crystals. The partial substitution of Te by S suppresses antiferromagnetism in Fe-square lattice. Superconductivity is induced by oxygen annealing for only FeTe$_{1-x}$S$_x$ in which the long-range magnetic ordering is suppressed. To realize superconductivity in FeTe$_{1-x}$S$_x$, both S concentration enough to suppress antiferromagnetism and oxygen annealing are required. Anisotropy of superconductivity in oxygen-annealed FeTe$_{0.886}$S$_{0.114}$ was estimated to be 1.17.


I. INTRODUCTION

FeTe$_{1-x}$S$_x$ is one of the Fe-chalcogenide superconductors with transition temperature $T_c$~10 K. Although the parent phase FeTe exhibits antiferromagnetic ordering below 70 K, a partial substitution of Te by S suppresses the magnetic ordering and induces superconductivity. The FeTe$_{1-x}$S$_x$ superconductor is one of the potential compounds for applications due to its simple composition and comparably low toxicity among the Fe-based superconductors. However, the synthesis of FeTe$_{1-x}$S$_x$ that shows bulk superconductivity is difficult due to the low solubility limit of S for the Te site caused by a large difference in the ionic radius between S and Te. First we reported the discovery of superconductivity in FeTe$_{1-x}$S$_x$ synthesized by the melting method but the sample was containing impurities and the superconducting volume fraction was less than 20%. Hu et al. reported superconductivity in the FeTe$_{1-x}$S$_x$ single crystals grown using the self-flux method. Although those single crystals showed superconductivity, the superconducting volume fraction was less than 10% and the anomaly corresponding to the antiferromagnetic transition was also observed in the superconducting FeTe$_{1-x}$S$_x$ single crystals. This indicates that the S concentration of these crystals was insufficient to suppress the magnetism completely. Furthermore, Zhang et al. reported an enhancement of $T_c$ with an application of pressure for an inhomogeneous FeTe$_{1-x}$S$_x$ sample, while a homogenous single crystal exhibited a decrease in $T_c$ under pressure. To clarify the intrinsic properties of FeTe$_{1-x}$S$_x$ superconductor under both ambient and high pressure, growth of high-quality FeTe$_{1-x}$S$_x$ single crystal is required.

Recently, we reported that the post treatments induced bulk superconductivity in FeTe$_0.886$S$_{0.114}$. Polycrystalline FeTe$_0.886$S$_{0.114}$ does not show bulk superconductivity just after synthesis using the solid-state reaction method. However, superconductivity is induced by exposing the sample to the air. Heating the sample in water, ethanol and alcoholic drinks also induce superconductivity. Furthermore, it was found that the better way to quickly induce superconductivity in FeTe$_0.886$S$_{0.114}$ is oxygen annealing at 200 °C. The basic crystal structure of FeTe$_{1-x}$S$_x$ with the space group of $P4/nmm$ does not change with those post treatments but the slight shrinkage of lattice is observed. To clarify a cause of the evolution of superconductivity by those post treatments, systematic studies using high-quality single crystals are required. We investigated the oxygen annealing effect on physical and structural properties of FeTe$_{1-x}$S$_x$ single crystals with several S concentrations. Here we discuss the roles of S and oxygen for inducing superconductivity in FeTe$_{1-x}$S$_x$.

II. EXPERIMENTAL DETAILS

Single crystals of FeTe$_{1-x}$S$_x$ were synthesized using a self-flux method. Fe powder (99.9%), S grains (99% up) and Te grains (99.99%) with several nominal compositions ($x$ = 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4, and 0.5) were placed in an alumina crucible and sealed into an evacuated quartz tube. The samples were heated at 1050 °C for 20 h and cooled down to 650 °C with a rate of ~4 °C/h. The obtained single crystals were sealed into a quartz tube filled with atmospheric pressure of oxygen gas, and heated at 200 °C for 2 h. The actual composition of the crystal was determined using electron probe micro analyzer. The value was estimated using an average of four measurements. Detailed information of crystal characterization is summarized in Ref. 4. The lattice constant $c$ for the obtained crystals was estimated by $x$-ray diffraction using the $2\theta$-$\theta$ method with Cu $K\alpha$ radiation. Temperature dependence of in-plane resistivity from 300 to 2 K was measured using a four-terminal method. To discuss anisotropy of superconductivity, temperature dependence of resistivity was measured under magnetic fields up to 7 T both parallel and perpendicular to the $c$ axis of the crystal. Temperature dependence of magnetic susceptibility

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from 15 to 2 K was measured using a superconducting quantum interference device magnetometer with an applied field of 10 Oe.

III. RESULTS AND DISCUSSION

Figure 1 is an optical-microscope image of typical oxygen-annealed FeTe$_{0.886}$S$_{0.114}$ single crystals. The surface of the oxygen-annealed crystal is still shining as well as before annealing. The four terminals for the resistivity measurement were attached on the as-annealed surface.

Figures 2(a) and 2(b) show the temperature dependence of resistivity for as-grown and oxygen-annealed FeTe$_{1-x}$S$_x$, respectively. The anomaly corresponding to the magnetic transition, observed in FeTe around 70 K, is suppressed with increasing S concentration. The magnetic transition temperatures for oxygen-annealed FeTe$_{0.97}$S$_{0.03}$ and FeTe$_{0.952}$S$_{0.048}$ are almost the same as those before annealing, respectively, which indicates that oxygen annealing does not affect the magnetic transition temperature. In fact, these samples did not show zero resistivity even after oxygen annealing, suggesting that oxygen annealing cannot suppress long-range ordering.

Although the magnetic transition seems to be suppressed by the S substitution for $x=0.064$ and 0.114, zero resistivity is not observed for as-grown crystals as shown in Fig. 2(a). By annealing those as-grown crystals in oxygen, superconducting transition is induced as shown in Fig. 2(b). Figure 3 is an enlargement of temperature dependence of resistivity below 30 K. Zero resistivity temperature is estimated to be $T_c^{zero}=7.0$ K for both $x=0.064$ and 0.114. Interestingly, the superconducting transition temperature for $x=0.064$ and 0.114 are almost the same, in spite of the difference in S concentration. This implies that $T_c$ in this system is essentially independent of the S concentration. The $T_c$ of Fe-based superconductor is much sensitive to the local crystal structure; the anion height from the Fe-square lattice is one of the key factors that determine the $T_c$. Recently, for FeTe$_{1-x}$Se$_x$, it was found that Te and Se were located at the other anion height; the difference in anion height between Te and Se was determined to be 0.24 Å. The $T_c$ of FeTe$_{1-x}$Se$_x$ would be determined by the local anion height, and does not show significant dependence on Te/Se concentration. Furthermore, the valence of S, Se, and Te is the same value of −2; S or Se substitution for Te does not change the total carrier density. In this respect, the anion height of S or Te would determine the local $T_c$. Therefore, $T_c$ of FeTe$_{1-x}$S$_x$ would not be sensitive to S concentration. Figure 4 shows the temperature dependence of magnetic susceptibility for the
oxygen-annealed FeTe$_{1-x}$S$_x$ crystals. Diamagnetic signal corresponding to superconducting transition is observed below 7.5 K only for $x$=0.064 and 0.114. The $T_c$ estimated from magnetic susceptibility is almost the same as $T_{c\text{ zero}}$ in Fig. 3.

Figures 5(a) and 5(b) shows the temperature dependence of in-plane resistivity for oxygen-annealed FeTe$_{0.886}$S$_{0.114}$ under the magnetic fields up to 7 T perpendicular and parallel to $c$ axis, respectively. The suppression of superconductivity by magnetic field of $H_{ab}$ is more remarkable than that under $H_{ab}$ due to two-dimensional superconducting nature. To estimate an upper critical field $\mu_0H_{c2}$, $T_{c\text{ onset}}$ was determined using 90% of resistivity above $T_c$. The estimated $T_{c\text{ onset}}$ and applied field are plotted in Fig. 5(c). Using the Werthamer–Helfand–Hohenberg (WHH) theory, which gives $\mu_0H_{c2}(0)=-0.69T_c(d\mu_0H_{c2}/dT)|_{T_c}$, the upper critical fields $\mu_0H_{c2}(0)$ and $\mu_0H_{c2}(0)$ are estimated to be 55 T and 47 T, respectively. Anisotropy at 0 K, $H_{c2}(0)/H_{c2}(0)$, is estimated to be $\sim$1.17. Small anisotropy is consistent with the previous reports on transport properties of FeTe$_{1-x}$Se$_x$ and FeTe$_{1-x}$S$_x$.5,14,15

To discuss the change in crystal structure, lattice constant was determined using x-ray diffraction. The obtained x-ray profile showed only (00l) reflections as observed in the as-grown crystals.4 Lattice constant $c$ for both as-grown and oxygen-annealed FeTe$_{1-x}$S$_x$ crystal is plotted in Fig. 6 as a function of $x$. The lattice constant linearly decreases with increasing S concentration. For all oxygen-annealed crystals, the shrinkage of lattice is observed, as observed in the polycrystalline samples.9 Although the lattice constant is compressed for $x$=0.03 and 0.048 as well, the magnetic transition temperature does not change by oxygen annealing. For $x \geq 0.064$, superconductivity appears with the shrinkage of lattice by oxygen annealing. The $c$ axes of $x$=0.064 and 0.114 after oxygen annealing are almost the same value. The same $T_c$ observed in $x$=0.064 and 0.114, discussed above, would be related to the similarity of $c$ axis length. The binding of oxygen in FeTe$_{1-x}$S$_x$ would be weak, because superconductivity in FeTe$_{1-x}$S$_x$ induced by oxygen annealing is reversible; superconductivity is suppressed when the superconducting FeTe$_{1-x}$S$_x$ is annealed in vacuum. Then, reannealing in oxygen reproduces superconductivity in FeTe$_{1-x}$S$_x$. On the basis of these facts, we think that the oxygen is not substituted for the Te site and would be intercalated into the interlayer site. The evolution of superconductivity by oxygen annealing might be related to a suppression of magnetic moment of excess Fe, which exists at the interlayer site and destroys superconductivity.16–19 To clarify the intrinsic role of oxygen in FeTe$_{1-x}$S$_x$, studies sensitive to local structure are required.

Figure 7 is a phase diagram of oxygen-annealed FeTe$_{1-x}$S$_x$ single crystals grown using the self-flux method. Due to the low solubility limit of S for the Te site, we did not obtain the crystals with $x>0.12$ using this growth method. The antiferromagnetic phase is suppressed, and superconducting phase appears, with increasing S concentration. However, oxygen annealing is required to induce superconductivity for FeTe$_{1-x}$S$_x$ in which the log-range magnetic ordering is suppressed. In fact, both two factors are required for the appearance of superconductivity in FeTe$_{1-x}$S$_x$. One factor is S substitution for Te, which suppresses the long-range antiferromagnetic ordering of Fe-square lattice. The other factor is oxygen, which would suppress the local moment of excess Fe that interferes with superconductivity.

IV. CONCLUSION

We synthesized FeTe$_{1-x}$S$_x$ single crystals using the self-flux method. By oxygen annealing, lattice constant $c$ for all crystals was decreased. Oxygen annealing induced superconductivity in FeTe$_{1-x}$S$_x$ crystals, only when the antiferromagnetic transition had been suppressed by S substitution.

FIG. 5. (Color online) (a) Temperature dependence of in-plane resistivity for FeTe$_{0.886}$S$_{0.114}$ under magnetic fields up to 7 T perpendicular to $c$ axis. (b) Temperature dependence of in-plane resistivity for FeTe$_{0.886}$S$_{0.114}$ under magnetic fields up to 7 T parallel to $c$ axis. (c) Temperature dependence of upper critical field $\mu_0H_{c2}$.

FIG. 6. (Color online) S concentration dependence of lattice constant $c$ for both as-grown and oxygen-annealed FeTe$_{1-x}$S$_x$ crystal.
Anisotropy of superconductivity in oxygen-annealed FeTe$_{1-x}$S$_x$ was estimated to be 1.17. The phase diagram of oxygen-annealed FeTe$_{1-x}$S$_x$ single crystal was established. To realize superconductivity in FeTe$_{1-x}$S$_x$, both S substitution enough to suppress the antiferromagnetism and oxygen annealing are required.

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