

Moisture-induced superconductivity in $\text{FeTe}_{0.8}\text{S}_{0.2}$

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Moisture-induced superconductivity was observed in $\text{FeTe}_{0.8}\text{S}_{0.2}$. With exposing the sample to the air, the zero-resistivity temperature and the superconducting volume fraction were enhanced up to 7.2 K and 48.5%, respectively, while the as-grown sample showed only filamentary superconductivity. We concluded that the causes of the evolution of superconductivity were water-related ions and/or molecules because only the sample kept in water at room temperature for several days showed superconductivity. The speed of evolution of superconductivity was strongly enhanced by immersing the sample into the hot water.

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I. INTRODUCTION

Iron chalcogenides attract researchers as the simplest iron-based superconductors.^{1,2} The tetragonal FeSe superconductor shows dramatic pressure effect on transition temperature T_c ; the onset temperature T_c^{onset} increases from 13 to 37 K at 4–6 GPa.^{3–6} Crystal structural analysis and NMR studies under high pressure indicated that the enhancement of T_c was related to the change in the crystal structure or the magnetic states.^{4,5,7} Correlation between superconductivity and magnetism is likely to be important to understand the mechanism of superconductivity in the iron chalcogenides. In fact, tetragonal FeTe, which has a structure analogous to superconducting FeSe, undergoes antiferromagnetic ordering at ~ 70 K and does not show superconductivity. The magnetic ordering is suppressed by S or Se substitution, and superconductivity appears.^{8–11} However, hydrostatic pressure did not induce superconductivity in FeTe.^{12,13} To clarify the reason why only the Te-site substitution can induce superconductivity in FeTe, we focus on S-substituted FeTe.

An optimum way to synthesize the high-quality superconducting sample of $\text{FeTe}_{1-x}\text{S}_x$ has not been established yet, probably due to a solubility limit of S for the Te site. The superconducting properties of $\text{FeTe}_{1-x}\text{S}_x$ depend on the sample preparation method.⁸ The $\text{FeTe}_{0.8}\text{S}_{0.2}$ sample synthesized by the melting method showed a sharp superconducting transition at $T_c^{\text{onset}}=10.5$ K; however, the obtained sample contained impurity phases. On the other hand, the $\text{FeTe}_{0.8}\text{S}_{0.2}$ sample synthesized using the solid-state reaction method was almost the single phase; however the solid-state-reacted sample showed a broad transition in temperature dependence of resistivity, and diamagnetism corresponding to superconductivity was not observed. The cause of filamentary superconductivity in the solid-state-reacted sample would be an insufficiency of the shrinkage of lattice, in other words, an insufficiency of S concentration. Here we report moisture-induced superconductivity in $\text{FeTe}_{0.8}\text{S}_{0.2}$ synthesized by the solid-state reaction.

II. EXPERIMENTAL DETAILS

The polycrystalline samples of $\text{FeTe}_{0.8}\text{S}_{0.2}$ were prepared using the solid-state reaction method as described in Ref. 8.

At first, we synthesized the TeS precursor by reacting the Te (99.9 %) and S (99 %) powders to produce a homogeneous reaction. The Te and S powders were sealed into an evacuated quartz tube, heated at 500 °C for 10 h, and furnace cooled. Then the powders of Fe (99.9 %), Te (99.9 %), and TeS were sealed into an evacuated quartz tube with a nominal composition of $\text{FeTe}_{0.8}\text{S}_{0.2}$ and heated at 600 °C for 15 h. After furnace cooling, the products were ground, palletized, sealed into the evacuated quartz tube, and heated again at 600 °C for 15 h. Temperature dependence of resistivity was measured down to 2 K using the four-terminal method. Temperature dependence of susceptibility after both zero-field cooling and field cooling was measured using a superconducting quantum interference device magnetometer down to 2 K under a magnetic field of 10 Oe. Powder x-ray diffraction patterns were collected using the Cu $K\alpha$ radiation. The room temperature of the laboratory was kept at 20–25 °C.

III. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of resistivity

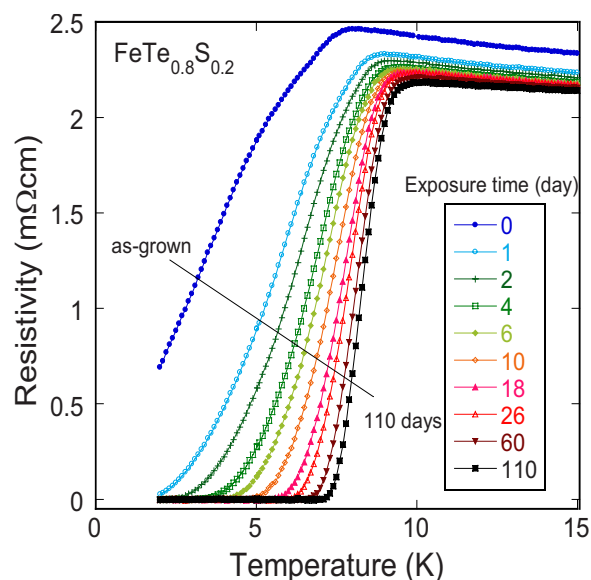


FIG. 1. (Color online) Temperature dependence of resistivity for the $\text{FeTe}_{0.8}\text{S}_{0.2}$ sample kept in the air for several days.

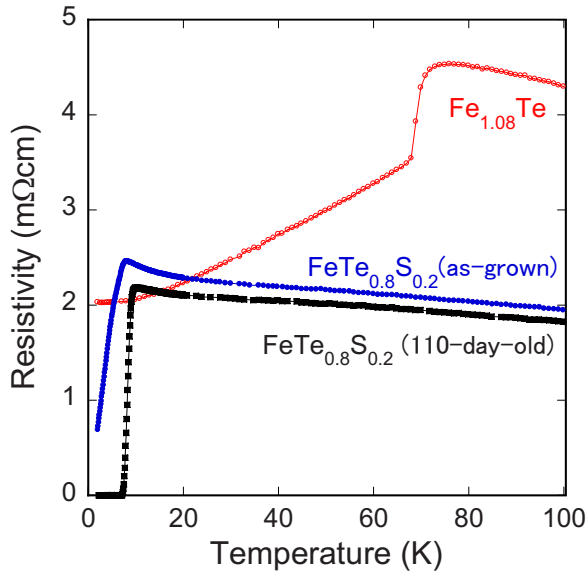


FIG. 2. (Color online) Temperature dependence of resistivity for as-grown $\text{FeTe}_{0.8}\text{S}_{0.2}$, 110-day-old $\text{FeTe}_{0.8}\text{S}_{0.2}$ and $\text{Fe}_{1.08}\text{Te}$. The anomaly observed in $\text{Fe}_{1.08}\text{Te}$ around 70 K was not observed for both as-grown $\text{FeTe}_{0.8}\text{S}_{0.2}$ and 110-day-old $\text{FeTe}_{0.8}\text{S}_{0.2}$, indicating that the magnetic ordering was suppressed by the S substitution.

for $\text{FeTe}_{0.8}\text{S}_{0.2}$ with several air-exposure time from 0 to 110 days. For the as-grown sample, zero resistivity is not observed while an onset of the superconducting transition is observed at 8.0 K. The diamagnetic signal was not observed in the susceptibility measurement, indicating the absence of bulk superconductivity. Surprisingly, after exposing the sample to the air for 2 days, zero resistivity appears around $T_c^{\text{zero}} = 2$ K. With increasing air-exposure time, both the T_c^{onset} and T_c^{zero} increased up to 10.2 K and 7.2 K, respectively. The superconducting transition becomes sharper with increasing air-exposure time. Figure 2 shows the temperature dependence of resistivity for as-grown $\text{FeTe}_{0.8}\text{S}_{0.2}$, 110-day-old

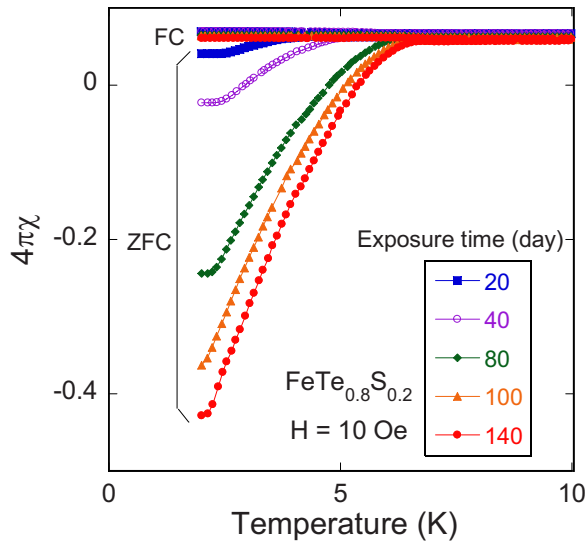


FIG. 3. (Color online) Temperature dependence of magnetic susceptibility for the $\text{FeTe}_{0.8}\text{S}_{0.2}$ sample kept in the air for several days.

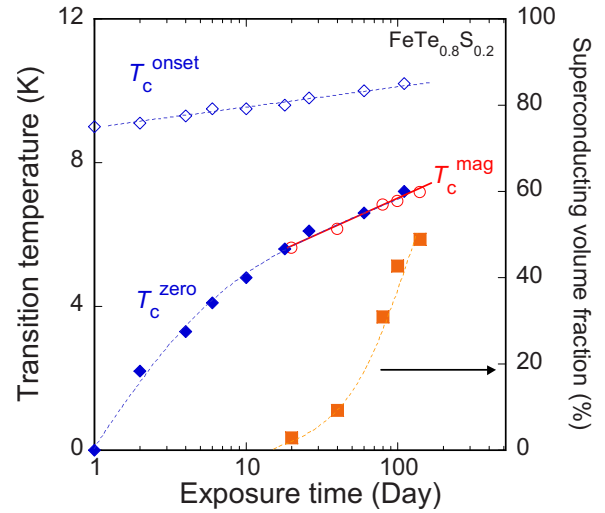


FIG. 4. (Color online) Air-exposure time dependence of the T_c^{onset} , T_c^{zero} , T_c^{mag} , and the superconducting volume fraction. The horizontal axis is logarithmic.

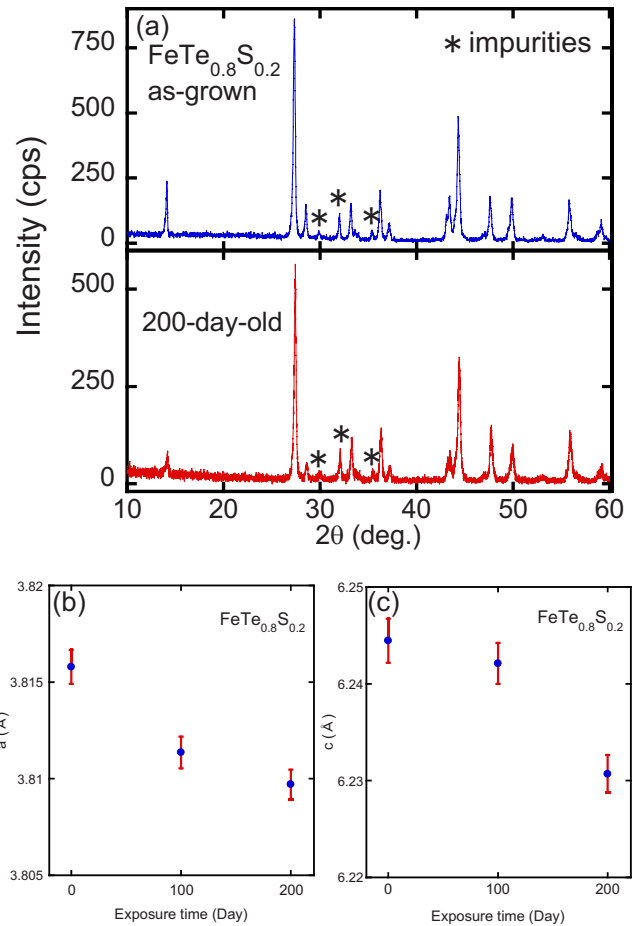


FIG. 5. (Color online) (a) Powder x-ray diffraction patterns collected just after the synthesis and after 200 days. All peaks of the tetragonal $\text{FeTe}_{0.8}\text{S}_{0.2}$ phase are indexed using the $P4/nmm$ space group. The asterisks indicate the impurity phases. The calculated lattice constants a and c are plotted in (b) and (c) as a function of air-exposure time, respectively.

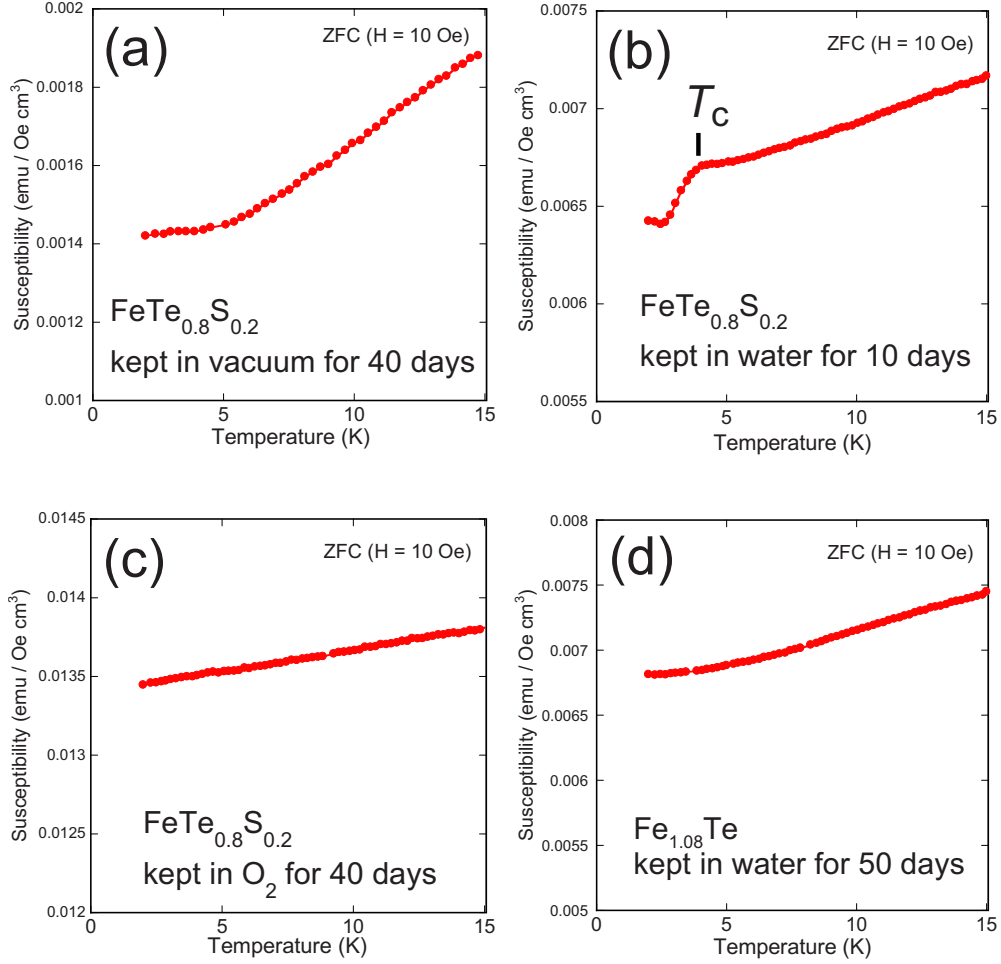


FIG. 6. (Color online) Temperature dependence of magnetic susceptibility for (a) $\text{FeTe}_{0.8}\text{S}_{0.2}$ kept in vacuum, (b) $\text{FeTe}_{0.8}\text{S}_{0.2}$ kept in water, (c) $\text{FeTe}_{0.8}\text{S}_{0.2}$ kept in O_2 gas, and (d) $\text{Fe}_{1.08}\text{Te}$ kept in water. The superconducting transition was observed only in (b).

$\text{FeTe}_{0.8}\text{S}_{0.2}$ and $\text{Fe}_{1.08}\text{Te}$. For $\text{Fe}_{1.08}\text{Te}$, we can find an anomaly corresponding to the structural and magnetic transition around 70 K. The anomaly seems to be suppressed completely for as-grown $\text{FeTe}_{0.8}\text{S}_{0.2}$; however, bulk superconductivity is not observed. After 110 days, the sharp superconducting transition appears. The normal-state resistivity of 110-day-old $\text{FeTe}_{0.8}\text{S}_{0.2}$ is clearly lower than that as grown, implying the change in the carrier density by the air exposure.

Figure 3 shows the temperature dependence of magnetic susceptibility for $\text{FeTe}_{0.8}\text{S}_{0.2}$ with several air-exposure time from 20 to 140 days. Although we did not observe the superconducting transition for the as-grown sample, the diamagnetic signal corresponding to superconductivity appeared for 20-day-old $\text{FeTe}_{0.8}\text{S}_{0.2}$. With increasing air-exposure time, the T_c increases and the diamagnetic signal is enhanced. The T_c estimated from susceptibility (T_c^{mag}) is plotted in Fig. 4 as a function of air-exposure time with the T_c^{onset} and T_c^{zero} determined from the resistivity measurements. The T_c^{mag} almost corresponds to T_c^{zero} and reaches 7.2 K after 140 days. The superconducting volume fraction was calculated from a difference between the value of the normal state and 2 K, and plotted in Fig. 4 as a function of air-exposure time. The superconducting volume fraction is dramatically enhanced

up to 48.5%, indicating that the bulk superconductivity is induced by the air exposure while as-grown $\text{FeTe}_{0.8}\text{S}_{0.2}$ shows only filamentary superconductivity.

To clarify the origin of the dramatic change in the superconducting properties induced by the air exposure, we car-

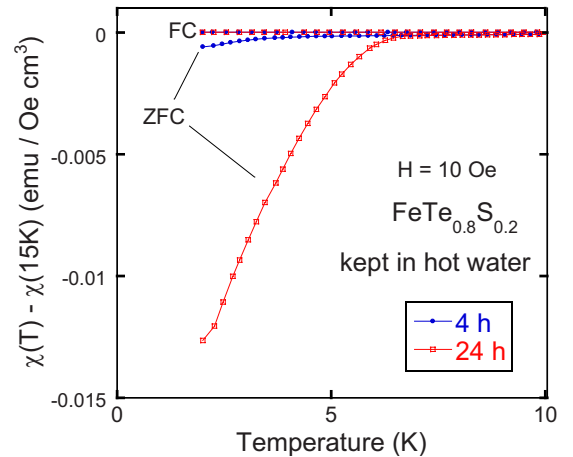


FIG. 7. (Color online) Temperature dependence of normalized susceptibility for the samples kept in the hot water for 4 h and 24 h, respectively.

ried out powder x-ray diffraction for $\text{FeTe}_{0.8}\text{S}_{0.2}$ just after the synthesis and after 100 and 200 days. Figure 5(a) shows the x-ray diffraction patterns for as-grown and 200-day-old $\text{FeTe}_{0.8}\text{S}_{0.2}$. The peaks were indexed using the $P4/nmm$ space group. Lattice constants were calculated to be $a = 3.8158(9)$ and $c = 6.2445(23)$ Å for as-grown $\text{FeTe}_{0.8}\text{S}_{0.2}$, $a = 3.8114(8)$ and $c = 6.2421(21)$ Å for 100-day-old $\text{FeTe}_{0.8}\text{S}_{0.2}$, and $a = 3.8097(8)$ and $c = 6.2307(20)$ Å for 200-day-old $\text{FeTe}_{0.8}\text{S}_{0.2}$, respectively. The calculated lattice constants a and c are plotted in Figs. 5(b) and 5(c) as a function of air-exposure time. The lattice constants slightly decrease with the air exposure for 200 days. The shrinkage of lattice should be related to the dramatic change in the superconducting properties induced by air exposure.

To investigate the factor that induced superconductivity, we measured temperature dependence of susceptibility for the samples kept in several conditions. The as-grown $\text{FeTe}_{0.8}\text{S}_{0.2}$ samples were kept in vacuum (<0.5 Pa), ion-exchanged water, O_2 gas, and N_2 gas for several days at room temperature. Figures 6(a)–6(c) show the typical temperature dependence of susceptibility for the samples kept in vacuum for 40 days, water for 10 days, and O_2 gas for 40 days, respectively. The superconducting transition is observed only for the sample kept in water, although the samples kept in both vacuum and O_2 gas do not show the superconducting transition. Also the sample kept in N_2 gas for 40 days does not show the superconducting transition. Therefore, we concluded that the moisture in the air induced the dramatic change in the superconducting properties. We also investigated the magnetic properties of $\text{Fe}_{1.08}\text{Te}$ kept in the water for 50 days as shown in Fig. 6(d). There is no sign of superconductivity. In fact, moisture-induced superconductivity is unique for $\text{FeTe}_{1-x}\text{S}_x$ among the iron chalcogenides.

Recently, water-induced superconductivity was reported also in SrFe_2As_2 , which is one of the parent phases of the iron-based superconductors.¹⁴ The authors suggested that superconductivity was induced when the lattice was compressed by exposing the sample to H_2O -related species. Moisture-induced superconductivity in $\text{FeTe}_{0.8}\text{S}_{0.2}$ might be induced as in SrFe_2As_2 . In the case of the water-intercalated superconductor $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$, superconductivity appears when the c axis is expanded by the partial substitution of Na^+ ion by H_3O^+ ion.¹⁵ On the basis of the shrinkage of lattice in the air-exposed $\text{FeTe}_{0.8}\text{S}_{0.2}$, the H_3O^+ ion would not be the origin of moisture-induced superconductivity.

In this respect, one of the candidate elements to explain moisture-induced superconductivity in $\text{FeTe}_{0.8}\text{S}_{0.2}$ is the H^+ ion because the ionic radius is very small. Similar situation was reported in the Li^+ -intercalated $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ superconductor. Superconductivity is induced by the Li^+ intercalation without any change in the lattice constants.¹⁶ The H^+ -ion intercalation into the interlayer of $\text{FeTe}_{0.8}\text{S}_{0.2}$ would not change the lattice constants largely. If the H^+ was intercalated, the electron carriers should be generated in the Fe layer. The decrease in resistivity for the air-exposed $\text{FeTe}_{0.8}\text{S}_{0.2}$ as shown in Fig. 2 would be originated in the

increase in the electron carrier density. It might completely suppress the magnetism that had barely survived in as-grown $\text{FeTe}_{0.8}\text{S}_{0.2}$. Another candidate is the OH^- ion. If the OH^- ion were intercalated to the interlayer site, it would compress the lattice because there is the excess Fe at the interlayer site.

The O^{2-} ion is also a candidate to explain this phenomenon because the solution of oxygen in the water should not be neglected. Furthermore, O^{2-} has a valence same with S^{2-} and Te^{2-} , and its ionic radius is the smallest among them. The shrinkage of lattice might be due to the partial substitution of O for the Te/S site. However, the sample kept in O_2 gas for 40 days did not show superconductivity. If the origin of moisture-induced superconductivity in $\text{FeTe}_{0.8}\text{S}_{0.2}$ were the O^{2-} ion, the water should play an important role to induce superconductivity as a catalyst at room temperature. In any case, the microscopic investigation sensitive to a local structure such as extended x-ray absorption fine structure is needed to determine the element that induces superconductivity.

If any chemical intercalation or substitution would occur in the moisture, the speed of the reaction should depend on the surrounding temperature. In this respect, we investigated the temperature dependence of susceptibility for the samples kept in the hot water (ion-exchanged water) with a temperature of $\sim 70^\circ\text{C}$. Figure 7 shows the temperature dependence of normalized susceptibility for the two samples kept in the hot water for 4 and 24 h. Although the sample kept in the cold water (at room temperature) for a few days shows no sign of superconductivity, the superconducting transition is observed for the sample kept in the hot water for only 4 h. Furthermore, with increasing immersion time, both T_c and the superconducting volume fraction are enhanced up to 6.8 K and 15.6%, respectively. This suggests that the phenomena that we reported here are much sensitive to the surrounding temperature.

IV. CONCLUSION

We reported moisture-induced superconductivity in $\text{FeTe}_{0.8}\text{S}_{0.2}$ synthesized by the solid-state reaction method. With increasing air-exposure time, the T_c and superconducting volume fraction were enhanced up to 7.2 K and 48.5%, respectively, while the as-grown sample showed only filamentary superconductivity. The shrinkage of lattice was observed by the air exposure. We concluded that the origin of the dramatic change in superconductivity was moisture in the air because only the sample kept in water at room temperature showed superconductivity. The speed of evolution of superconductivity was strongly enhanced by immersing the sample into the hot water, indicating the sensitivity of moisture-induced superconductivity to the surrounding temperature.

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