Direct observation of microstructures on superconducting single crystals of K$_x$Fe$_{2-y}$Se$_2$

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Potassium-intercalated FeSe has been reported as a superconductor with a superconducting transition temperature ($T_c$) of 30–48 K. However, the relationship among the surface morphology, compositional ratio, and crystal structure has not yet been clarified. This report directly reveals the correspondence among these three characteristics in single crystals with a $T_c$ onset of around 44 K by using a microsampling technique. Island-like parts on the surface of the crystals clearly exhibit the K$_x$Fe$_y$Se$_2$ structure with perfect FeSe layers, which is formed in conjunction with the K$_x$Fe$_y$Se$_2$ phase. This results in the appearance of the $T_c$ onset at 44 K.

After the discovery of superconductivity in potassium-intercalated FeSe,$^{11}$ there has been tremendous progress in the study of related A$_x$Fe$_{2-y}$Se$_2$ (A = K, Rb, Cs, Ti/Rb, Ti/K) systems that exhibit relatively high superconducting (SC) transition temperatures $T_c$ of around 30 K.$^{2-7}$ Formed in isolation from the 30 K phase, a trace amount of a 44–48 K SC phase was also found in some samples$^{8,9}$ or under high pressure.$^{10,11}$ Alkali or alkaline-earth intercalation into FeSe via a liquid ammonia route has been reported to show superconductivity at $T_c$ of around 44–46 K.$^{12,13}$ Further, a high $T_c$ is also observed in ultrathin FeSe films.$^{14,15}$ These reports imply that superconductivity as high as 40–48 K is a potential property of the FeSe layer structure.

K$_x$Fe$_{2-y}$Se$_2$ is one of the most investigated materials among metal-intercalated FeSe SC families. Its crystal structure comprises a basic FeSe layer, which incorporates some Fe deficiency mainly due to charge neutrality conservation. Many studies have shown that intrinsic phase separations occur in the material, leading to the coexistence of an SC phase with the ThCr$_2$Si$_2$-type structure (122-phase) and an Fe-vacancy ordered insulating K$_3$Fe$_2$Se$_2$ phase with $\sqrt{5} \times \sqrt{5} \times 1$ superstructure (245-phase), as shown in Figs. 1(a)–1(d).$^{16-30}$

In-situ observations with scanning electron microscopy and transmission electron microscopy (TEM) at elevated temperatures have shed some light on a potential growth mechanism of the SC phase in single crystals.$^{31,32}$ Recently, we have discussed the mechanism underlying the production of the higher-$T_c$ ($\sim$44 K) phase in K$_x$Fe$_{2-y}$Se$_2$ single crystals by means of in situ high-temperature single-crystal X-ray diffraction together with an examination of the surface morphology.$^{33}$ The X-ray diffraction pattern showed a reversible 245–122-phase transition with a transition temperature around 275 °C. The superstructure spots in the hk0 section corresponding to the 245-phase disappeared above 280 °C, as shown in Figs. 1(e) and 1(f). It was concluded that the higher-$T_c$ phase was generated by concentrating Fe onto the 122-phase with a driving force from the formation of the 245-phase.$^{33}$

However, the X-ray diffraction and scanning electron microstructural composition analyses always average the two phases on the measured single crystals. In contrast, TEM observation is highly localized and sometimes relies on the adventitious findings of the target sample. It might not be appropriately related to the microscale sections of the single crystals. It is necessary to show evidently the correspondence between the crystal structure, compositional ratio, and surface morphology of the single crystals. In this study, we clearly demonstrated the direct observations by combining TEM measurements with the Hitachi microsampling technique. The appearance of superconductivity in the K–Fe–Se system is discussed on the basis of the measurements and results of previous X-ray diffraction studies.

Target single crystals of K–Fe–Se system were prepared using a technique similar to the one-step-method.$^{34}$ Powders of K$_x$Se, Fe, and Se grains were mixed with a nominal composition of K$_{0.3}$Fe$_2$Se$_2$ in an Ar atmosphere. The starting mixtures were placed in an alumina crucible, and were sealed in evacuated quartz tubes. The quartz tube was heated to 900 °C in 5 h, and the temperature was then held at 900 °C for 12 h, followed by cooling to room temperature at a rate of 7 °C/h. Sample preparation was performed in an Ar-filled glove box. The temperature dependence of electrical resistivity was measured down to 2.0 K, with a physical property measurement system (PPMS; Quantum Design) using a standard four-probe method with the constant current mode. The electrodes were attached in the ab-plane with silver.
The temperature dependence of magnetization was measured using a superconducting quantum interference device (SQUID) magnetometer (MPMS; Quantum Design) down to 2 K under a field of 10 Oe, and the field was applied parallel to the c-axis. Back scattered electron (BSE) and secondary electron (SE) images were observed using a scanning electron microscope (JEOL JSM-6010LA). The sample fabrication for TEM observation was carried out by using focused ion beam (FIB) apparatus (Hitachi NB5000) with the Hitachi microsampling technique. The electron diffraction patterns were observed using Hitachi HF-3300 with an acceleration voltage of 300 kV. The elemental distribution mapping of energy dispersive X-ray (EDX) analysis was carried out by using a scanning transmission electron microscope (STEM) with spherical aberration correction (Hitachi HD-2700). An air protection holder was used to protect the sample from exposure to air when being transferred from one apparatus to another.

Figure 2(a) shows the temperature dependence of resistivity for the obtained single crystals. The crystal shows an SC transition with the onset temperature of $T_c$ at 44 K and zero resistivity at around 33 K. The transition was suppressed by applying a magnetic field. Figure 2(b) is an enlarged image of the temperature dependence of magnetic susceptibility ($\chi$) in the zero-field-cooling mode. It shows the Meissner signal at $\sim$43 and $\sim$33 K compatible with the resistivity drop. The shielding volume fractions of $\sim$43 and $\sim$33 K phases were roughly estimated at 2 K to be $\sim$1 and $\sim$10%, respectively.

The BSE and SE images for the same position of the obtained single crystals are shown in Fig. 3. It can be clearly seen that the crystals are composed of two different contrasted regions with clear boundaries. The bright island-like contrasted regions in the BSE image correspond to more iron and less potassium contents compared to the other dark regions (out-of-island part).

These facts indicate that there are two crystal structures, two SC transitions, and two compositional ratios on the same sample single crystals. It is necessary to identify the correspondence among the $T_c$, surface morphology, compositional ratio, and crystal structure. To reveal this correspondence, it is crucial to perform electron diffraction measurement and high resolution elemental mapping on a specific position of the sample crystals. The specimens are prepared by the Hitachi microsampling technique using FIB, and the procedures are shown in Fig. 4. Figure 4(a) is a scanning ion microscope image of a surface on the as-obtained single crystals. Clear island-like morphology is observed in the image. A section including the island-like parts was initially covered with a protective layer of carbon by FIB assisted deposition. Then, a portion of the sample (microsample) was separated from the bulk sample and picked up by bonding with a tungsten (W) micromanipulator probe with W deposition [Fig. 4(b)]. These operations were carried out both in the cross sectional and $ab$-plane directions of the crystal structure. The microsamples with different crystal orientations were mounted onto an edge of a TEM carrier by W deposition, and the probe was cut off by FIB milling [Figs. 4(c) and 4(d)]. Finally, the microsamples were thinned down to 40–100 nm in both orientations after being attached to the TEM carrier.

Fig. 3. BSE and SE images of the obtained single crystals.
EDX elemental mapping images for the fabricated microsample in the $ab$- and cross-sectional planes of the obtained crystals are shown in Figs. 5(a)–5(c) and Figs. 5(d)–5(f), respectively. The distribution difference of K and Fe atoms are well resolved to island-like shape [Figs. 5(a) and 5(b)], as seen in the BSE images. The Fe-rich-K-less regions are arranged in stripe-like patterns in the cross-sectional plane, and they are not seen in about half of the images [Figs. 5(d) and 5(e)], indicating three-dimensional network of the island-like parts, as was observed in a stripe patterns in Ref. 31. In contrast, the Se atoms are homogeneously distributed over the entire observed area [Figs. 5(c) and 5(f)]. The highly convergent electron beams of STEM and the sample thickness effectively improve the spatial resolution of EDX measurements.33)

The electron diffraction patterns of the fabricated microsamples were measured with the electron-beam incidence normal to the $ab$-plane; these are shown in Figs. 6(a) and 6(b). The pattern indicated that the microsample basically has a 4-fold symmetry axis. All diffraction spots can be indexed by tetragonal unit cell, although the diffractions from the out-of-island parts always show superstructure spots around the Bragg spots of the basic structure, as shown in Fig. 6(b). This pattern is identical to the room temperature X-ray diffraction pattern shown in Fig. 1(e). Note that the diffractions from the island-like parts did not show signatures of a superstructure spot. Namely, the “islands” are composed solely of the 122-phase structure, as observed in the higher temperature region above 275 °C, whereas the “out-of-island” parts have the 245-phase structure.

The crystals showed highly diffused patterns except for the $hk0$ plane in the single crystal X-ray diffraction measurements. In the TEM measurements, stacking-fault-like features along its $c$-axis direction were also observed only on the island-like parts in the cross-sectional directions, as shown by horizontal striped lines (data not shown). The highly diffused patterns in the X-ray diffraction measurements may be attributed to a break in the long-range order along the $c$-axis caused by an unregulated stacking of layers during the growth of the single crystal. The 122-phase accumulates the elastic strain along the $c$-axis during the crystal growth process, reflecting a difference in the $c$-value with the 245-phase, as is expected from the X-ray diffraction measurements.33)

These facts indicate a direct correspondence among the surface morphology, compositional ratio, and the crystal structures. The island-like part of the single crystal has a crystal structure of the 122-phase with the compositional ratio of $K_{0.43}Fe_{2.02}Se_2$. Namely, it contains “perfect” FeSe-layers in its crystal structure. In contrast, the out-of-island parts correspond to the 245-phase with a slightly richer Fe content compared to the stoichiometry of $K_2Fe_4Se_5$. The excess Fe plays a role of carrier doping to the insulating 245-phase, suggesting that this may affect the conducting nature in the transport measurement and result in a finite resistivity at room temperature.

When the 245-phase is grown below 275 °C, the excessively accommodated Fe is expelled from the structure to create Fe-vacancy sites. The migrated excess Fe is concentrated onto small isolated island-like regions forming perfect FeSe layers. It is reasonable that the 122-phase with perfect FeSe layers shows higher $T_c$ onset of about 44 K in the electrical or magnetization measurements, when taking into account a potential SC transition of FeSe up to $48$ K. However, the $\sim 33$ K superconducting phase is not yet clarified in terms of which part corresponds to the $\sim 33$ K phase in the single crystals.

In summary, the relationship among surface morphology, compositional ratio, and crystal structure of the K–Fe–Se superconducting system was directly identified by using a microsampling technique. Island-like parts of the crystals clearly showed diffraction spots identical to those of the 122-phase structure. The out-of-island part has a crystal structure of the 245-phase with excess Fe compared to its stoichiometry. The appearance of a higher $T_c$ onset of 44 K is attributed to the formation of the 122-phase with perfect FeSe layers.
assisted by the growth of the 245-phase. Microsample electrical measurement with the same sample pick up system is also necessary to reveal the structural evidence surrounding the two \( T_c \) onsets.

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