Superconductivity and electronic state of annealed single-crystals of FeSe$_{1-x}$Te$_x$ $(0.6 \leq x \leq 1)$ studied by specific heat

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Abstract. We have investigated the superconductivity and electronic state in FeSe$_{1-x}$Te$_x$ $(0.6 \leq x \leq 1)$ from the specific heat measurements, using annealed single-crystals of good quality. First, it has been found that annealed single-crystals of $x = 0.6 - 0.9$ exhibit bulk superconductivity with a clear specific-heat jump at the superconducting (SC) transition temperature, $T_c$. Both $2\Delta_0/k_BT_c$ [$\Delta_0$: the SC gap at 0 K] and $\Delta C/(\gamma_n-\gamma_0)T_c$ [$\Delta C$: the specific-heat jump at $T_c$, $\gamma_n$: the electronic specific-heat coefficient in the normal state, $\gamma_0$: the residual electronic specific-heat coefficient at 0 K in the SC state] are largest at $x = 0.7$ and are 4.29 and 2.38, respectively, indicating that the superconductivity is strong-coupling. Secondly, it has been found that the $\gamma_n$ value is much larger than that estimated from the band calculation and increases with increasing $x$ and suddenly decreases above $x = 0.9$ due to the antiferromagnetic ordering around $x = 1$. The large value of $\gamma_n$ is guessed to be due to the enhancement of the effective mass related to spin fluctuation and/or orbital fluctuation. Finally, it has been found that there remains a finite value of the electronic specific-heat coefficient at 0 K even in the SC state at $x = 0.8 - 0.9$. This suggests that a phase separation into SC and normal-state regions takes place at $x = 0.8 - 0.9$. Otherwise, there might remain a normal-state pocket at the Fermi surface even in the SC state.

1. Introduction
Recently discovered iron-based superconductors have vigorously been studied owing to their high superconducting (SC) transition temperature, $T_c$, and the variety of crystal structures, as in the case of copper-based superconductors. Among the iron-based superconductors, FeSe$_{1-x}$Te$_x$ has attracted interest, because this compound has the simplest crystal structure. It has been reported that $T_c$ of FeSe$_{1-x}$Te$_x$ increases with increasing $x$, shows a maximum 14 K at $x = 0.6$ [1,2] and that the superconductivity disappears at $x = 1$ because of the appearance of an antiferromagnetic order [3,4].

As for single crystals of FeSe$_{1-x}$Te$_x$ $(0.5 \leq x \leq 1)$, Sales et al. [5] have reported that only single crystals of $x \sim 0.5$ exhibit bulk superconductivity. On the other hand, our magnetic-susceptibility and specific-heat measurements have revealed that single crystals of $x = 0.5 - 0.9$ annealed at 400°C for 100 h in vacuum exhibit bulk superconductivity [6,7]. In this paper, we have prepared FeSe$_{1-x}$Te$_x$ $(0.6 \leq x \leq 1)$ single-crystals annealed at different temperatures for different times in vacuum and investigated the superconductivity and electronic state from the specific-heat measurements.
2. Experimental

Single crystals of Fe$_{1-x}$Te$_x$ were grown by the Bridgman method. The details are described in the literature [6]. As-grown crystals obtained thus were annealed at 300 - 500°C for 100 - 200 h in vacuum. Specific-heat measurements were carried out by the thermal-relaxation method, using a commercial apparatus (Quantum Design, PPMS).

3. Results and discussion

Figure 1 shows the temperature dependence of the specific heat of FeSe$_{1-x}$Te$_x$ (0.6 $\leq$ x $\leq$ 0.9) single-crystals as-grown and annealed at 400°C for 100 h and 200 h. It is found that a jump of specific heat is clearly observed at $T_c$ for annealed crystals of x = 0.6 - 0.9, indicating that bulk superconductivity appears in these crystals. This is consistent with our magnetic-susceptibility results [6]. It is remarkable that the specific-heat jump at $T_c$ of x = 0.7 is clearer in the 200 h annealed crystal than in the 100 h annealed crystal, while the specific-heat jump of x = 0.9 is not different between 100 h and 200 h annealed crystals.

In order to estimate the electronic specific heat, $C_{el}$, the phonon specific heat, $C_{ph}$, must be subtracted from experimental values of the specific heat, C. In order to estimate $C_{ph}$, we prepared a non-SC annealed single-crystal of Fe$_{0.95}$Cu$_{0.05}$Se$_{0.4}$Te$_{0.6}$ also and measured the specific heat. The specific heat was well fitted using the equation, $C = \gamma_n T + \beta T^3 + \delta T^5 + \varepsilon T^7$. Values of $\beta$, $\delta$ and $\varepsilon$ obtained...
by the fit were used to estimate $C_{ph}$ for annealed single-crystals of FeSe$_{1-x}$Te$_x$, namely, $C_{ph} = \beta(\alpha T)^3 + \delta(\alpha T)^3 + \varepsilon(\alpha T)^3$. Here, $\alpha$ is a parameter reflecting the difference in the atomic mass between Fe$_{0.92}$Cu$_{0.08}$Se$_{0.06}$Te$_{0.04}$ and FeSe$_{1-x}$Te$_x$ and is nearly unity. Then, $C_{el}$ of the SC annealed single-crystals was obtained as $C_{el} = C - C_{ph}$. The value of the electronic specific-heat coefficient in the normal state, $\gamma_n$, was also estimated as $C_{el}/T$ above $T_c$. In this process, $\alpha$ and $\gamma_n$ were determined taking into account the so-called entropy balance that the electronic entropy in the SC state accords with that in the normal state at the onset temperature of superconductivity, $T_{onset}$.

Figure 2 shows the $x$ dependence of $\gamma_n$ and the residual electronic specific-heat coefficient at 0 K in the SC state, $\gamma_0$, for FeSe$_{1-x}$Te$_x$ ($0.6 \leq x \leq 1$) single-crystals annealed at 400°C for 100 h and 200 h. The $\gamma_n$ values are one order of magnitude larger than those estimated from the band calculation: 3.055 mJ/molK$^2$ in FeSe and 4.783 mJ/molK$^2$ in FeTe [8]. They increase with increasing $x$ for $x = 0.6 - 0.9$. The large value of $\gamma_n$ is guessed to be due to the enhancement of the effective mass related to spin fluctuation and/or orbital fluctuation. The decrease in $\gamma_n$ above $x = 0.9$ is due to the antiferromagnetic ordering around $x = 1$.

As for the $\gamma_0$ value, it is nearly zero for $x = 0.6$ and 0.7 annealed for 200 h, meaning that there is no normal-state region at 0 K in these crystals. In contrast, it is finite for $x = 0.8$ and 0.9 annealed for 100 h and 200 h also, indicating that there remain normal-state carriers at 0 K even in the SC state. Compared with the annealing for 100 h, the annealing for 200 h is found to be most effective for $x = 0.7$, because the $\gamma_0$ value has decreased to zero and the specific-heat jump at $T_c$ has become clear with increasing annealing-time. Through the long annealing, it seems that the distribution of Se and Te in the crystal of $x = 0.7$ has become homogeneous so that the SC state has become homogeneous in the crystal [9]. For $x = 0.8$ and 0.9, on the other hand, it does not seem that the SC state becomes homogeneous through further long annealing, because the effects of the annealing for 200 h are not so different from those of the annealing for 100 h. Therefore, it is guessed that a phase separation into SC and normal-state regions inevitably takes place at $x = 0.8 - 0.9$. Otherwise, inhomogeneity might appear in the momentum space, namely, there might remain a normal-state pocket at the Fermi surface even in the SC state at $x = 0.8 - 0.9$. According to our recent muon-spin-relaxation experiment, the normal state is guessed to be a magnetic one related to the antiferromagnetic ordering around $x = 1$ [10].

**Figure 2.** Dependences on $x$ of the electronic specific-heat coefficient in the normal state, $\gamma$, and the residual electronic specific-heat coefficient at 0 K in the SC state, $\gamma_0$, for FeSe$_{1-x}$Te$_x$ single-crystals annealed at 400°C for 100 h and 200 h.

Finally, we estimate several SC parameters from the data of $C_{el}$ for annealed single-crystals of FeSe$_{1-x}$Te$_x$. The SC condensation energy at 0 K, $U_0$, is estimated using the equation,

$$U_0 = \frac{\gamma_0}{2} \left( T_{onset} - \int_0^{T_{onset}} \frac{C_{el}}{T} dT \right).$$

The SC gap at 0 K, $\Delta_0$, is estimated using the equation, $\Delta_0 = \left\{ \frac{4 \pi^2 k_B^2 U_0}{3( \gamma_n - \gamma_0 )} \right\}^{1/2}$. Here, $k_B$ is the Boltzmann constant. As shown in Fig. 3, it is found that the superconductivity is strongest for $x = 0.7$ annealed for 200 h. In this crystal, $2\Delta_0/k_B T_c$ and $\Delta C/(\gamma_n - \gamma_0) T_c$ are as large as 4.29 and 2.38, respectively, indicating that the superconductivity is strong-coupling. As for $x = 0.8$ and 0.9, the
superconductivity is found to become weak with increasing x, which will be due to the coexistence of SC and normal-state carriers.

4. Summary
We have investigated the superconductivity and electronic state of annealed FeSe$_{1-x}$Te$_x$ (0.6 $\leq$ x $\leq$ 1) single-crystals from the specific-heat measurements. The appearance of bulk superconductivity has been confirmed at x = 0.6 - 0.9. The superconductivity is strongest at x = 0.7 and it is strong-coupling. The $\gamma_n$ value has been found to be large and increase with increasing x at x = 0.6 - 0.9, which is guessed to be due to the enhancement of the effective mass related to spin fluctuation and/or orbital fluctuation. At x = 0.8 - 0.9, it has been suggested that a phase separation into SC and normal-state regions takes place; otherwise there might remain a normal-state pocket at the Fermi surface even in the SC state.

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