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Annealing effects on the crystal structure and physical properties of $FeSe_{1-x}Te_x$ ($0.6 \leqq x \leqq 1$) single crystals

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ABSTRACT

Annealing effects of $FeSe_{1-x}Te_x$ ($0.6 \leqq x \leqq 1$) single crystals have been investigated from measurements of the powder X-ray diffraction and specific heat. Through the annealing, several peaks of powder X-ray diffraction have become sharp and a clean jump of the specific-heat at the superconducting (SC) transition temperature, T_c, has been observed for $x = 0.6$–0.9, indicating bulk superconductivity. For annealed single-crystals of $x = 0.6$–0.8, the SC condensation energy, U_0, and the SC gap, Δ_0, at 0 K have been estimated as ~1.8 J/mol and 2.3–2.5 meV, respectively. The value of $2\Delta_0/k_BT_c$ is 3.9–4.5, indicating a little strong-coupling superconductivity. Both the electronic specific-heat coefficient in the normal state, γ_n, and the residual electronic specific-heat coefficient in the SC state, γ_0, have been found to show significant x dependence. The values of γ_n are much larger than those estimated from the band calculation.

1. Introduction

Recently discovered iron-based superconductors have attracted great interest owing to their high superconducting (SC) transition temperature, T_c. Among iron-based superconductors, $FeSe_{1-x}Te_x$ has the most simple crystal structure. It has been found that T_c of $FeSe_{1-x}Te_x$ increases with increasing x, shows a maximum 14 K at $x \sim 0.6$ [1,2] and that the superconductivity disappears at $x = 1$ because of the appearance of an antiferromagnetic order [3,4].

Sales et al. [5] have reported that only $FeSe_{1-x}Te_x$ crystals with $x \sim 0.5$ exhibit bulk superconductivity from the electrical resistivity, magnetic susceptibility and specific-heat measurements. On the other hand, our magnetic susceptibility 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]. In this paper, we have investigated annealing effects on the crystal structure and physical properties of $FeSe_{1-x}Te_x$ single crystals from measurements of the powder X-ray diffraction and specific heat.

2. Experimental

Single crystals of $FeSe_{1-x}Te_x$ were grown by the Bridgman method. Powders of Fe, Se and Te prescribed in the nominal composition were thoroughly mixed in an argon-filled glove box and sealed in an evacuated quartz tube. Since the quartz tube often cracked upon cooling, the tube was sealed into another large-sized evacuated quartz tube. The doubly sealed quartz ampoule was stood in a furnace, heated up to 950–1050 °C and cooled down. As-grown crystals obtained thus were annealed at 400 °C for 100 h in vacuum. Crystals were characterized by the X-ray back-Laue photography and the chemical composition was determined by the inductively coupled plasma atomic emission spectroscopy (ICP-AES). The details are described in literature [6]. The powder X-ray diffraction was performed at room temperature using Cu Kα radiation (MAC Science, M03XHF^{22}). Specific-heat measurements were carried out by the thermal relaxation method (Quantum Design, PPMS).

3. Results and discussion

Fig. 1 shows the powder X-ray diffraction patterns of as-grown and annealed single-crystals of $FeSe_{0.2}Te_{0.8}$. As seen in the inset clearly, several diffraction peaks have become sharp through the annealing. We speculate that the inhomogeneity of the distribution of Se and Te and/or the lattice distortion have been improved through the annealing.

Fig. 2 shows the temperature dependence of the specific heat of as-grown and annealed single-crystals of $FeSe_{1-x}Te_x$ ($0.6 \leqq x \leqq 1$). It has been found that a jump of the specific heat at T_c is clearly observed for annealed crystals with $0.6 \leqq x \leqq 0.9$, indicating that bulk superconductivity appears for these crystals. This is consistent with our results of magnetic susceptibility [6].

Here, in order to estimate some electronic parameters, we extract the electronic specific heat, C_{el}, from the specific heat, C, by subtracting the phonon specific heat, C_{ph}, for annealed single-crystals. 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 in which the supercon-

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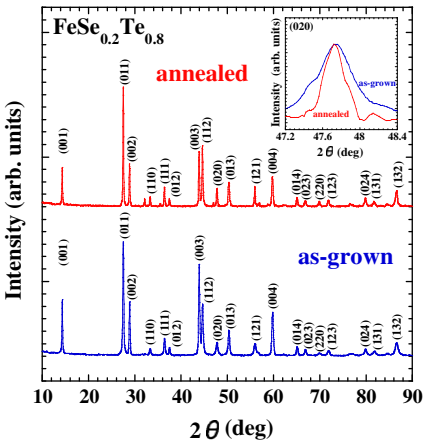

Fig. 1. Powder X-ray diffraction patterns of as-grown and annealed single-crystals of $FeSe_{0.2}Te_{0.8}$. The inset shows an enlarged view of the (0 2 0) reflection.

ductivity is suppressed by the partial substitution of Cu for Fe. The specific heat shown in Fig. 2 was well fitted using the following equation:

$$C = \gamma T + \beta T^3 + \delta T^5 + \varepsilon T^7. \quad (1)$$

Here γT is the electronic specific heat, and $\beta T^3 + \delta T^5 + \varepsilon T^7$ is the phonon specific heat. Values of β, δ and ε obtained by the fit were used to estimate C_{ph} for annealed single-crystals of $FeSe_{1-x}Te_x$. Here, it is noted that these values were not so different from those obtained by the same fit for as-grown single-crystals of $FeSe_{1-x}Te_x$ with $x = 0.6$–0.9 showing no clear specific-heat jump at T_c.

Fig. 3 shows the temperature dependence of thus obtained C_{el} divided by temperature for the annealed single-crystal of $FeSe_{0.4}Te_{0.6}$. The γ_0 obtained by extrapolating values of C_{el}/T to 0 K is the residual electronic specific-heat coefficient in the SC state. The γ_n is the electronic specific-heat coefficient in the normal state determined taking into account the entropy balance. That is, the

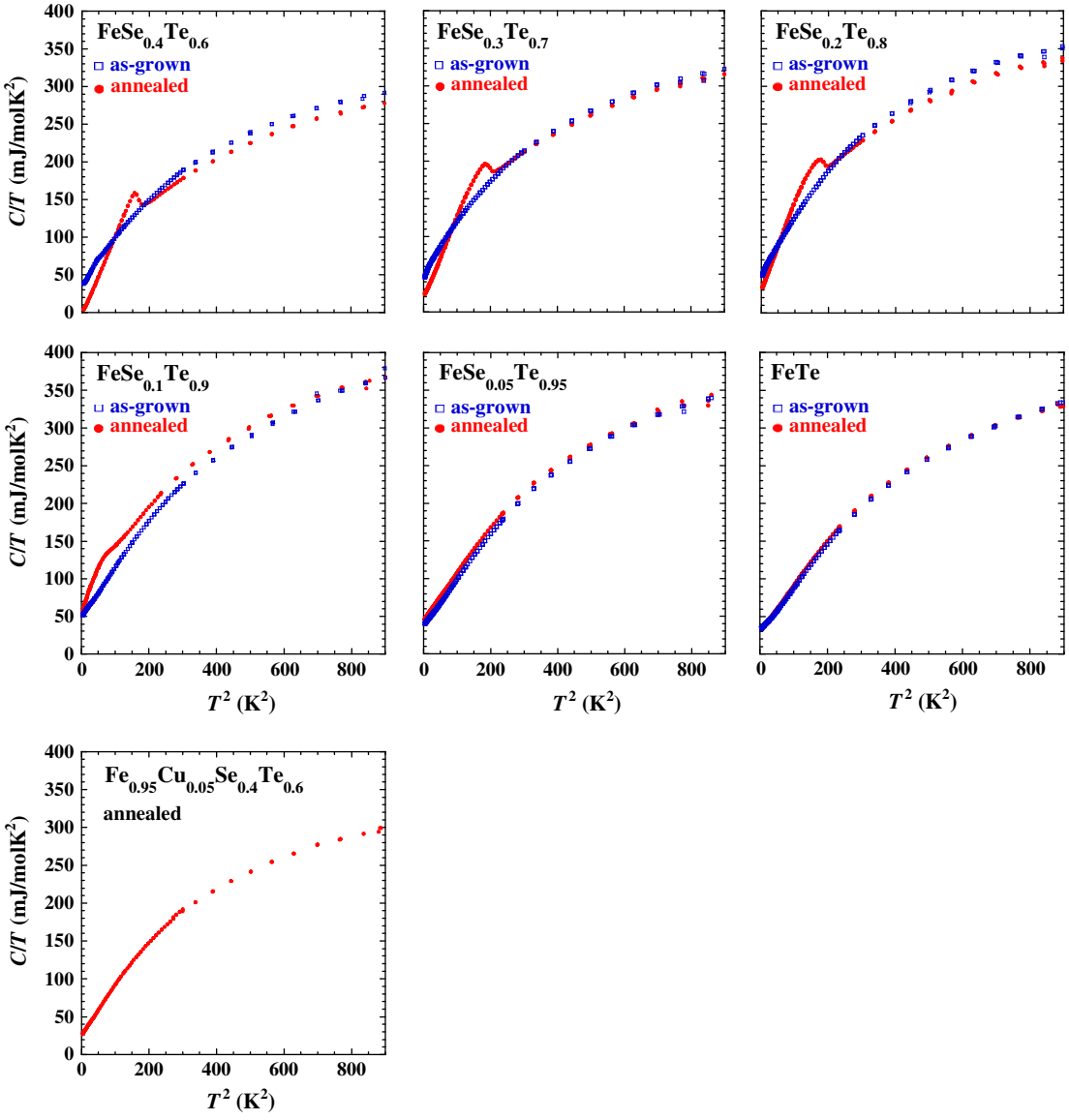

Fig. 2. Temperature dependence of the specific heat, C, of as-grown and annealed single-crystals of $FeSe_{1-x}Te_x$ ($0.6 \leqq x \leqq 1$) and an annealed single-crystal of $Fe_{0.95}Cu_{0.05}Se_{0.4}Te_{0.6}$ plotted as C/T vs. T^2.