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Structural transition and anisotropic properties of single-crystalline SrFe2As2

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**Abstract**
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Structural transition and anisotropic properties of single-crystalline SrFe$_2$As$_2$

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Platelike single crystals of SrFe$_2$As$_2$, as large as 3 × 3 × 0.5 mm$^3$ have been grown out of Sn flux. The SrFe$_2$As$_2$ single crystals show a structural phase transition from a high-temperature tetragonal phase to a low-temperature orthorhombic phase at $T_c$=198 K, and do not show any sign of superconductivity down to 1.8 K. The structural transition is accompanied by an anomaly in the electrical resistivity, Hall resistivity, specific heat, and the anisotropic magnetic susceptibility. In an intermediate temperature range from 198 to 160 K, single-crystal x-ray diffraction suggests a coexistence of the high-temperature tetragonal and the low-temperature orthorhombic phases.

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The recent discovery of high transition temperature ($T_c$) superconductivity in fluorine-doped ReFeAsO (R = rare earth) and K-doped Fe$_2$As$_2$ (A = Sr and Ba) has attracted extensive attention in scientific community.1–4 ReFeAsO with the ZrCuSiAs-type structure and Fe$_2$As$_2$, with the ThCr$_2$Si$_2$-type structure share the same structural unit of (Fe$_2$As$_2$)$_2$ layers. The (Fe$_2$As$_2$)$_2$ layers are separated by (R$_2$O$_3$)$_2$ layers in ReFeAsO and by simple A layers in Fe$_2$As$_2$. Partial substitution of A by K or Cs$^+$ induces superconductivity with $T_c$ up to 38 K.5,6 Studies of polycrystalline samples have revealed phase transitions at $T_c$=140 and 205 K for BaFe$_2$As$_2$ and SrFe$_2$As$_2$, respectively.5,6 At $T_c$=140 K for BaFe$_2$As$_2$, the structural transition from a high-temperature tetragonal phase to a low-temperature orthorhombic phase is thought to be accompanied by a magnetic phase transition.7

However, whether a similar structural transition takes place in SrFe$_2$As$_2$ at $T_c$=205 K concomitantly with the magnetic anomaly is still an open question. Indeed, C. Krellner et al.8 suggests the occurrence of a similar combination of a structural and a magnetic transition based on unpublished results measured on polycrystalline samples. This question is of great importance due to the fact that a similar combination of structural and magnetic phase transitions was observed in ReFeAsO.9

High quality, sizable single crystals are necessary in order to study the anisotropic properties of the compounds and details of the crystallographic structure. Ni et al.8 successfully grew BaFe$_2$As$_2$ single crystals out of Sn flux and studied the crystallographic, anisotropic magnetic, and transport properties. However, ~1% Sn was incorporated into the BaFe$_2$As$_2$ lattice and modifies the physical properties relative to those of polycrystalline samples. Whether SrFe$_2$As$_2$ lattice is susceptible to Sn incorporation remains to be clarified. Here, we report the growth of SrFe$_2$As$_2$ single crystals out of Sn flux and subsequent measurements of the anisotropic physical properties, including x-ray diffraction studies of the structural transition.

Single crystals of SrFe$_2$As$_2$ were grown out of Sn flux. Elemental Sr, Fe, and As were fired at 850 °C for 12 h and 900 °C for 20 h with intermediate grinding. The prefired pellet, which contains mainly SrFe$_2$As$_2$ with ~5% FeAs impurity, was broken into smaller pieces and added to Sn flux in the ratio of [SrFe$_2$As$_2$]:Sn=1:48 and placed in a 2 ml crucible. A catch crucible containing quartz wool was mounted on top of growth crucible and both were sealed in a silica ampoule under approximately 1/3 atmosphere of argon gas. The packing and assembly of the growth ampoule were performed in air since the prefired pellet is stable in air. The sealed ampoule was heated to 1000 °C and cooled over 36 h to 500 °C in a programmable furnace. At 500 °C, the Sn was decanted from the SrFe$_2$As$_2$ crystals. We note that some pieces of the prefired pellets are still undissolved in the growth crucible. Raising the ratio of [SrFe$_2$As$_2$]:Sn leads to more residual undissolved SrFe$_2$As$_2$.

As-grown crystals are platelike with a typical dimension of 1–2 × 1–2 × 0.1–0.5 mm$^3$. Some crystals manifest linear dimensions as large as 3–4 mm as shown in the inset of Fig. 1. Room-temperature powder x-ray diffraction confirmed that the crystals are single phase with lattice parameters of $a=3.926(3)$ Å and $c=12.42(1)$ Å, consistent with previous reports.8 Wavelength-dispersive x-ray analysis (WDS) was performed on a JEOL JXA-8200 electron microprobe at 15 kV acceleration voltage and ~10 nA beam current. Elemental analysis confirmed the atomic ratio of 1:2:2 and observed about 0.3% (atomic) Sn in the bulk, a factor of 3 times less Sn than the BaFe$_2$As$_2$ crystals grown in a similar manner.8

Single-crystal x-ray diffraction measurements were performed on a standard four-circle diffractometer using Cu $K_a$ radiation from a rotating anode x-ray source, selected by a Ge(1 1 1) monochromator. For these measurements, a plate-like single crystal with dimensions of 3 × 2 × 0.5 mm$^3$ was selected. The sample was mounted on a flat copper sample holder in a closed cycle diplex cryogenic refrigerator with the (001)–(110) reciprocal-lattice plane coincident with the scattering plane. The diffraction patterns were recorded for temperatures between 10 and 300 K. The mosaicity of this crystal was 0.035° full width at half maxima for the (0 0 10) reflection, indicating the excellent quality of the single crystal.

Magnetic properties were measured with a Quantum design (QD) magnetic property measurement system (MPMS).
The temperature dependent specific heat as well as magnetic-field and temperature dependent electrical transport data were collected using a QD physical property measurement system (PPMS). Electrical contact was made to the samples using Epotek H20E silver epoxy to attach Pt wires in a four-probe configuration. Hall measurements were performed in a QD PPMS instrument using the four probe ac ($f=16$ Hz, $I=1$ mA) technique with the current flowing in the $ab$ plane approximately parallel to the $a$ axis and the field parallel to the $c$ axis. To eliminate the effect of a misalignment of the voltage contacts, the Hall measurements were taken for two opposite directions of the applied field, $H$ and $-H$, and the odd component, $[\rho_{xy}(H)-\rho_{xy}(-H)]/2$, was taken as the Hall resistivity.

As shown in Fig. 1, magnetic measurements clearly show the anisotropy in the magnetic susceptibility $\chi=M(T)/H$ and a transition at $T_c=198$ K. The transition temperature is slightly lower than that observed for polycrystalline samples.\textsuperscript{5} Compared with the temperature dependence for polycrystalline samples, three prominent features are noteworthy: (1) Over the whole temperature range, there is a clear anisotropy with $\chi_{ab}>\chi_c$. (2) Below room temperature, both $\chi_{ab}$ and $\chi_c$ decrease linearly as the sample is cooled with a small slope until $T_c$. At $T_c$, they show a steplike change. Below $T_c$, both curves show a minimum in the temperature interval $100$ K $< T < 150$ K. This temperature dependence is different from that of polycrystalline samples reported by Krellner et al.,\textsuperscript{5} but agrees with that by Pfisterer and Nagorsen.\textsuperscript{3} (3) Below $\sim 100$ K the susceptibility becomes even more anisotropic, with a clear Curie-Weiss-like tail for $H\parallel ab$. The effective moment associated with this tail is $0.35$ $\mu_B$/f.u. The fact that this tail is so anisotropic argues that it is not associated with polycrystalline impurities within the residual Sn flux on the surface, but rather associated with the bulk, crystalline sample.

Figure 2(a) presents the temperature dependence of the in-plane electrical resistivity $\rho(T)$. $\rho(T)$ decreases with cooling and shows a sudden drop at $T_c=198$ K. The residual resistivity ratio (RRR) of $\rho_{300}$ K/$\rho_2$ K $\sim 6$ is smaller than the value of 32 of polycrystalline samples and larger than $\sim 3$ of similar single crystals grown out of Sn flux.\textsuperscript{10} The application of a magnetic field of 140 kOe parallel to the $c$ axis has no effect on the phase transition at $T_c=198$ K but slightly enhances the resistivity below $\sim 150$ K. On the other hand, the application of a 140 kOe field perpendicular to the $c$ axis shifts the transition upward by as much as $\sim 10$ K.

The inset of Fig. 2(a) shows the field dependence of the magnetoresistivity (MR) measured at 2 K. When the magnetic field is applied along the $c$ axis, the MR increases with field and reaches $\sim 27\%$ by 140 kOe. In contrast, the MR starts to increase only for $H>30$ kOe and only reaches $\sim 18\%$ by 140 kOe when the magnetic field is applied in the $ab$ plane. The observed value is consistent with the experimental results in Ref. 10 for field applied in the $ab$ plane.
SrFe$_2$As$_2$ material in comparison to the reported BaFe$_2$As$_2$ significantly less Sn is incorporated into the single crystalline consistent with the WDS analysis which indicates significant Sn flux. The Debye temperature data deviate from linearity possibly associated with residual Sn flux. The Debye temperature determined from the magnetization is 198 K which is consistent with that determined from magnetic and transport measurements. The transition temperature determined from the magnetization is 198 K (lower inset) indicates the transition temperature which is consistent with that determined from magnetic and transport measurements. The upper inset to Fig. 3 shows the low-temperature Cp/T data plotted as a function of T$^2$. The data follow the standard power law, Cp/T = $\gamma T + \beta T^2$. Below $T^2 < 20$ K$^2$ the data deviate from linearity possibly associated with residual Sn flux. The Debye temperature $\Theta_D$ could be estimated from $\beta = 12\pi^4 n k_B (5\Theta_D)$, where $n = 5$ is the number of atoms per formula unit for SrFe$_2$As$_2$. The fitting for $20 < T^2 < 45$ K$^2$ yields $\gamma = 33$ mJ/mol K$^2$ and $\beta = 0.64$ mJ/mol K$^4$ ($\Theta_D = 248$ K) similar to those of BaFe$_2$As$_2$.8

The temperature dependent specific-heat data are presented in Fig. 3. A sharp feature at $T = 198$ K (lower inset) indicates the transition temperature which is consistent with that determined from magnetic and transport measurements. The upper inset to Fig. 3 shows the low-temperature Cp/T data plotted as a function of T$^2$. The data follow the standard power law, $C_p/T = \gamma T + \beta T^2$. Below $T^2 < 20$ K$^2$ the data deviate from linearity possibly associated with residual Sn flux. The Debye temperature $\Theta_D$ could be estimated from $\beta = 12\pi^4 n k_B (5\Theta_D)$, where $n = 5$ is the number of atoms per formula unit for SrFe$_2$As$_2$. The fitting for $20 < T^2 < 45$ K$^2$ yields $\gamma = 33$ mJ/mol K$^2$ and $\beta = 0.64$ mJ/mol K$^4$ ($\Theta_D = 248$ K) similar to those of BaFe$_2$As$_2$.8

The transition temperature determined from the magnetization, electrical resistivity, Hall resistivity, and specific-heat measurements agrees with each other. The SrFe$_2$As$_2$ single crystals have comparable lattice parameters and similar transition temperatures as the polycrystalline material.8 This is consistent with the WDS analysis which indicates significantly less Sn is incorporated into the single crystalline SrFe$_2$As$_2$ material in comparison to the reported BaFe$_2$As$_2$ crystals.8 To determine whether there is a structural transition at $T_s$ as observed in the isostructural BaFe$_2$As$_2$, we performed a single-crystal x-ray diffraction study. As illustrated in Fig. 4, below 160 K, the splitting of the (1 1 10) reflection was observed in (ξξ0) scans, whereas the shape of the (0 0 10) reflection is unchanged in both (ξξ0) and (00ξ) scans. This behavior is consistent with a tetragonal-to-orthorhombic phase transition with a distortion along the diagonal (110) direction and a transition from the space group I4/mmm to Fmmm, similar to that observed in the BaFe$_2$As$_2$ compound.8 In an intermediate temperature range between 190 and 160 K, reflections related to the orthorhombic phase appear to coexist with reflections related to the tetragonal phase as shown in the (ξξ0) scans in Fig. 4. However, no significant difference was observed between measurements with decreasing and increasing temperatures as might be expected from a hysteretic first-order transition as reported in Ref. 6. We note that the split reflections are not equal in intensity or width at low temperatures, perhaps indicating an unequal “twin domain” population. However, we also note that a crystallographic structure with symmetry lower than the orthorhombic can yield a similar diffraction pattern at low temperature and cannot be excluded by the present study.

The lattice parameters have been determined by measurements of selected scans for the (0 0 10) and (1 1 10) reflections. By analyzing the position of the (0 0 10) reflection in longitudinal (00ξ) scans, the c-lattice parameter can be determined. The in-plane a and b-lattice parameters have been calculated based on the distance between the reflections close...
The characteristic reflections. Between 10 and 160 K, the difference in the orthorhombic $a$- and $b$-lattice parameters decreases monotonically with increasing temperature. Surprisingly, the difference between the in-plane lattice parameters stays nearly constant between 160 K and the transition to the tetragonal phase above 190 K. In the same intermediate temperature range, however, the sign of the thermal-expansion coefficient for the orthorhombic $b$ direction changes, coincident with the abrupt appearance of the central reflection related to the tetragonal phase at 160 K (see inset in Fig. 5). These observations suggest a more complex nature for this phase transition even though the transition from the space group $I4/mmm$ to $Fmmm$ can be second order. We also note that while the structure in this intermediate temperature range can be described in terms of a coexistence between the high-temperature tetragonal phase and the low-temperature orthorhombic phase, a complex superstructure of the high-temperature phase with an additional order parameter could likewise yield the observed set of three reflections. It should be noted that measurements of $M(T)/H$ on the crystal used for Figs. 4 and 5 showed only one transition at $T_c = 198$ K.

In conclusion, we have successfully grown sizable single crystals of SrFe$_2$As$_2$ out of Sn flux and studied anisotropic thermodynamic and transport properties as well as the structural transition. Electrical resistivity, Hall resistivity, specific heat, and the anisotropic magnetic susceptibility demonstrate a transition at $T_c = 198$ K. The magnetic susceptibility, $\chi = M/H$, is anisotropic, with $\chi_{ab} > \chi_c$ for 2 K < $T$ < 300 K. While the transition appears to be insensitive to $H||c = 140$ kOe, it does shift upward by ~10 K for $H||ab = 140$ kOe. As evidenced by the single-crystal x-ray diffraction study, a similar structural phase transition as in BaFe$_2$As$_2$ from a high-temperature tetragonal phase to a low-temperature orthorhombic phase takes place at $T_c = 198$ K.

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