

Chapter 2

Experimental Methods

2.1 Single-Crystal Growth

2.1.1 $\text{SrFe}_2(\text{As}_{1-x}\text{P}_x)_2$

Single crystals of $\text{SrFe}_2(\text{As}_{1-x}\text{P}_x)_2$ (P-Sr122) except for $x = 0$ and $x = 1$ were grown from a stoichiometric mixture of Sr, FeAs, and FeP powder. FeAs was prepared by reacting Fe powder and As grains at 850°C for 15 h in an evacuated quartz tube. FeP was prepared by reacting Fe powder and P powder at 700°C for 15 h in an evacuated quartz tube.

Sr, FeAs, and FeP were mixed in the atomic ratio $1:2(1-x):2x$, placed in an alumina crucible, and sealed in a silica tube with Ar gas at 0.2 bar and room temperature. It was heated up to 1300°C , kept for 12 h, and then slowly cooled down to 1050°C at a rate of 2°C/h .

SrFe_2As_2 ($x = 0$) was grown by the FeAs-flux method. Sr and FeAs were mixed in the atomic ratio 1:4, placed in an alumina crucible, and sealed in a silica tube with Ar gas at 0.2 bar and room temperature. It was heated up to 1200°C , kept for 12 h, and then slowly cooled down to 1050°C at a rate of 2°C/h .

SrFe_2P_2 ($x = 1$) was grown by the Sn-flux method. Sr, FeP, and Sn were mixed in the atomic ratio 1:2:20, placed in an alumina crucible, and sealed in a silica tube with Ar gas at 0.2 bar and room temperature. It was heated up to 1300°C , kept for 12 h, and then slowly cooled down to 600°C at a rate of 5°C/h . The Sn-flux was removed by a centrifuge.

For comparison, I grew single crystals of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ (P-Ba122) ($x = 0.20$ and 0.25) by the $\text{Ba}_2\text{As}_3/\text{Ba}_2\text{P}_3$ flux method described in Ref. [1].

The compositions of the obtained crystals were determined with an electron probe microanalyzer (EPMA) for P-Sr122 and a scanning electron microscope/energy dispersive x-ray spectroscopy (SEM-EDX) for P-Ba122.

2.1.2 $Ba(Fe_{1-x}TM_x)_2As_2$ ($TM=Cr, Mn, \text{ and } Co$)

Single crystals of $Ba(Fe_{1-x}TM_x)_2As_2$ ($TM=Cr, Mn, \text{ and } Co$) were grown by a self-flux method. MnAs was prepared by reacting Mn powder and As grains at 850 °C for 15 h in an evacuated double sealed quartz tube because it reacts with quartz. Particularly, it is necessary to pay attention to the synthesis of CrAs. If the same synthesis conditions as those for FeAs are adopted, the quartz tube explodes during the heating. To avoid this problem, a lower amount of the mixture of Cr and As (~ 3 g) was loaded into a quartz tube, and the tube was heated to 850 °C for 48 h and kept for 15 h at that temperature.

Ba, FeAs, and TMAs were mixed in the atomic ratio $1:4(1-x):4x$, placed in an alumina crucible, and sealed in a quartz tube. The tube was heated to 1200 °C, kept at that temperature for 10 h, and cooled to 1000 °C at a rate of 2 °C/h. The compositions of the grown crystals were determined by SEM-EDX analysis.

2.1.3 *Post Annealing Treatment*

In FeSC, the as-grown single crystals contain various amounts of disorders, lattice dislocations, or defects inside. In order to improve the crystal quality, a post annealing treatment is effective. The post annealing condition depends on the type and size of the crystal. Single crystals of $SrFe_2(As_{1-x}P_x)_2$ and $Ba(Fe_{1-x}TM_x)_2As_2$ ($TM=Cr, Mn, \text{ and } Co$) were sealed in an evacuated silica tube and annealed at 500 and 800 °C for several days, respectively.

2.2 Transport Measurement

2.2.1 *Resistivity Measurement*

A standard four-probe method was used for the resistivity measurement of twinned and detwinned single crystals.

2.2.2 *Hall Coefficient Measurement*

The Hall resistivity, ρ_{xy} , was measured with the electric current along the ab -plane and the magnetic field applied along the c -axis. The measurement was performed

for magnetic fields up to 7 T at various temperatures by using twinned crystals. The Hall coefficient, R_H , was determined by the polynomial fitting of the Hall resistivity with $\rho_{xy} = R_H H + aH^3$, where H is the magnetic field.

2.2.3 Resistivity Measurement with Detwinned Crystal

Below the structural transition temperature, T_s , the crystal tends to form structural twins, which prevent the measurement of the in-plane anisotropy of iron pnictide. To measure the in-plane anisotropy of the resistivity, a single-domain crystal is required. I detwinned the single crystals by applying a uniaxial pressure along the $[110]$ direction in the tetragonal lattice. The measurements of the in-plane resistivity along both the a - and b -axes of the orthorhombic lattice were performed on detwinned samples by a standard four-probe method. I repeated the resistivity measurements with increasing pressure and confirmed the saturation of the anisotropy. A schematic picture of the measurement method is shown in Fig. 2.1.

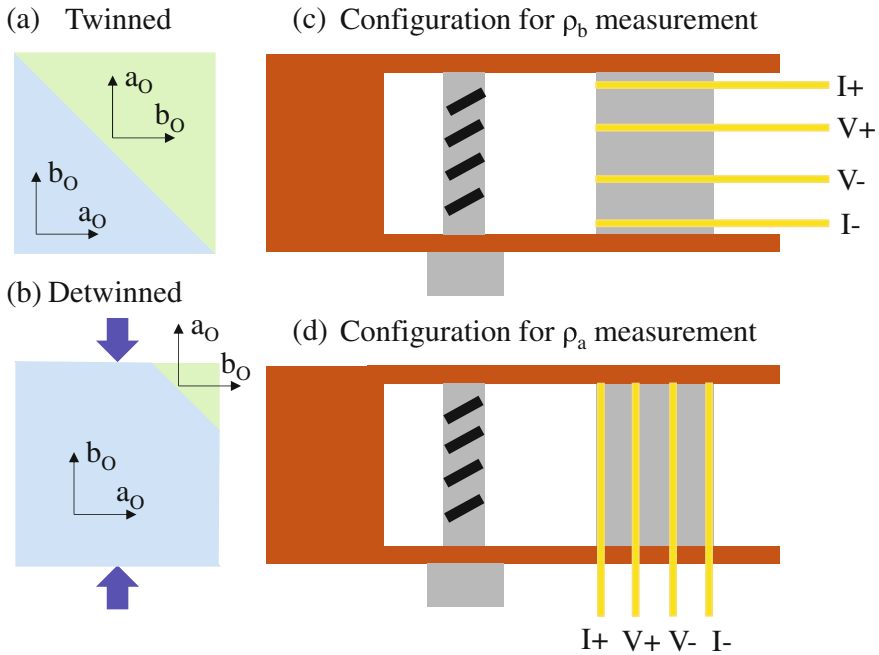


Fig. 2.1 Schematic picture of a twinned (a) and detwinned (b) crystal. Two sets of domains have the same population for the twinned crystal, whereas one set of domains have a dominant population for the detwinned crystal. c and d show a schematic picture of a four-probe measurement of the detwinned crystal on the detwinning device, respectively

2.3 Magnetization

Magnetization measurements from 1.8 to 300 K were performed using a Quantum Design magnetic property measurement system (MPMS). Zero-field-cooled (ZFC) and field-cooled (FC) data were taken at 10 Oe for superconducting samples.

2.4 X-Ray Diffraction Measurement

The x-ray diffraction experiment of single crystals for determining lattice constants was performed using a four-circle crystal x-ray diffractometer. The x-ray diffraction experiment for the structural analysis of single crystals was carried out using x-ray with 15 keV energy at BL-8A of the Photon Factory, KEK in Japan. In order to determine the atomic positions of $\text{SrFe}_2(\text{As}_{0.65}\text{P}_{0.35})_2$, I used those of SrFe_2As_2 as starting parameters and refined them by the least-squares method using Rigaku CRYSTALSTRUCTURE [2].

2.5 Specific Heat Measurement

Specific heat was measured by a relaxation technique down to 1.8 K under magnetic fields up to 14 T using a Quantum Design physical properties measurement system (PPMS).

2.6 Optical Measurement

The optical reflectivity $R(\omega)$ was measured on the ab plane of the mechanically polished samples using Al_2O_3 powder with a grain size of $0.3 \mu\text{m}$ and lapping film sheets. The measurement was performed at various temperatures in the frequency range $50\text{--}20000 \text{ cm}^{-1}$ by a Fourier transform infrared spectrometer at our laboratory, and in the frequency range $20000\text{--}320000 \text{ cm}^{-1}$ at UVSOR facility, Okazaki, Japan at room temperature. Below 50 cm^{-1} , the Hagen–Rubens formula ($R \propto 1 - \alpha\sqrt{\omega}$) was used to extrapolate the optical reflectivity. At a higher energy region (above 320000 cm^{-1}), extrapolation with $R \propto \omega^{-4}$ was used.

The optical conductivity was obtained using the Kramers–Kronig relation (KK-relation). The complex reflectivity $\hat{r}(\omega)$ can be obtained as follows.

$$\hat{r}(\omega) = \frac{1 - \sqrt{\hat{\epsilon}(\omega)}}{1 + \sqrt{\hat{\epsilon}(\omega)}} = \sqrt{R(\omega)} \exp(i\theta(\omega)). \quad (2.1)$$

Here, $\hat{\varepsilon}(\omega)$ is the complex dielectric function, and $\theta(\omega)$ is the phase. $\hat{\varepsilon}(\omega)$ is given as follows.

$$\hat{\varepsilon}(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega), \quad (2.2)$$

$$\varepsilon_1(\omega) - 1 = \frac{2}{\pi} P \int_0^\infty \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega', \quad (2.3)$$

$$\varepsilon_2(\omega) = -\frac{2\omega}{\pi} P \int_0^\infty \frac{\varepsilon_1(\omega')}{\omega'^2 - \omega^2} d\omega'. \quad (2.4)$$

Here, P denotes the principal value.

$R(\omega)$ is experimentally measured, following which the phase $\theta(\omega)$ can be calculated with the KK-relation as follows.

$$\theta(\omega) = -\frac{2\omega}{\pi} P \int_0^\infty \frac{\ln \sqrt{R(\omega')}}{\omega'^2 - \omega^2} d\omega'. \quad (2.5)$$

Once the real and imaginary part of the complex reflectivity are calculated, the complex dielectric function can be obtained.

The complex optical conductivity $\hat{\sigma}(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$ is obtained with dielectric functions as follows.

$$\sigma_1(\omega) = \frac{\omega \varepsilon_2(\omega)}{4\pi}, \quad (2.6)$$

$$\sigma_2(\omega) = \frac{\omega(1 - \varepsilon_1(\omega))}{4\pi}. \quad (2.7)$$

The Drude-Lorentz model for the dielectric function $\hat{\varepsilon}(\omega)$ was used to describe the optical conductivity.

$$\hat{\varepsilon}(\omega) = \varepsilon_\infty + \sum_j \frac{\omega_{p,D;j}^2}{\omega^2 + i\omega/\tau_{D,j}} + \sum_k \frac{\Omega_k^2}{\omega_k^2 - \omega^2 - i\omega\gamma_k}. \quad (2.8)$$

Here, ε_∞ is the real part of the dielectric function at a high frequency, and $\omega_{p,D;j}^2 = 4\pi n_j e^2 / m_j^*$ and $1/\tau_{D,j}$ are the square of the plasma frequency and scattering rate for the Drude carrier in the j th Fermi surface, respectively. n_j and m_j^* are the carrier density and carrier mass for the carrier in the j th Fermi surface, respectively. ω_k , γ_k , and Ω_k are the position, width, and strength of the k th vibration or excitation, respectively.

References

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<http://www.springer.com/978-981-10-4474-8>

Study of Electronic Properties of 122 Iron Pnictide
Through Structural, Carrier-Doping, and
Impurity-Scattering Effects

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2017, XII, 88 p. 56 illus. in color., Hardcover

ISBN: 978-981-10-4474-8