Tetragonal-Orthorhombic Phase Transition in LaFeAsO – Relevant to High-Temperature Superconductivity

The discovery of the high-temperature superconductor, F-substituted LaFeAsO (superconducting temperature: T_c = 26 K) [1] has caused a recurrence of a new superconductivity fever similar to that caused by the finding of the copper oxide superconductors. By replacing La with other rare-earth elements (ex. Sm, Gd), it has been possible to achieve T_c beyond 55 K, which convinced us that the Fe-based superconductors is the "second" high-T_c superconductors beyond the T_c limit of phonon-mediated superconductors (30~40 K).

LaFeAsO is formed by an alternating stack of positively charged LaO layer and negatively charged FeAs layer (Fig. 1) and belongs to the tetragonal *P4/nmm* space group at room temperature (Fig. 1(a)). It is noteworthy that the stoichiometric (parent) LaFeAsO does not exhibit any superconductivity, however, their resistivity and magnetic susceptibility show a sudden decrease at approximately 160 K (T_{anom}) as seen in Fig. 4(a) [1]. They disappear by the F-substitution for O, and coincidentally, the superconducting states appear. On the other hand, no such anomalies have been observed in isostructural low-T_c superconductors including LaFePO (T_c ~4 K), LaNiPO (T_c ~3 K) and LaNiAsO (T_c ~2.4 K), which implies that the phenomena are closely associated with the high-T_c superconductivity. Therefore, to search the origins of the anomalies was one of important missions in the studies of high-T_c superconductivity. In this study, the low-temperature crystal structures of parent and 14 at% F-substituted LaFeAsO (T_c ~20 K) were examined by synchrotron powder X-ray diffraction (XRD) analysis.

The high-resolution synchrotron XRD measurements at various temperatures were conducted at beamline **BL02B2**. All the diffraction peaks of the parent sample at temperatures above 170 K were consistently assigned to the conventional tetragonal phase (*P4/nmm*). However, several peaks including the 110, 111, 112, 211 and 322 reflections of the tetragonal phase start to broaden at around 170 K, and they clearly split into two peaks below 160 K (Fig. 2). On the other hand, such splitting was not observed in the diffraction peaks for the 14% F-substituted sample, which indicates that the superconductivity occurs in the tetragonal phase.

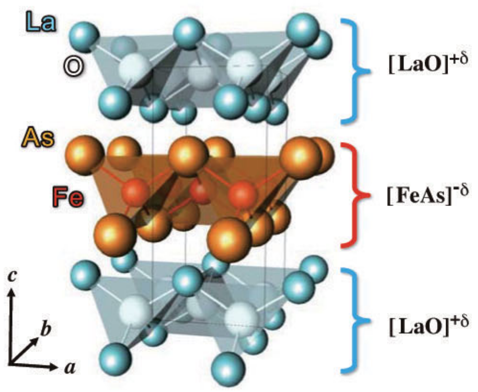

Fig. 1. Layered crystal structure of LaFeAsO. In each layer, the O/Fe atoms are tetrahedrally coordinated by the La/As atoms, respectively.

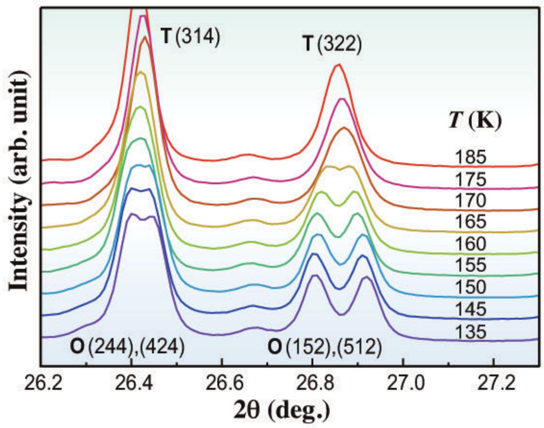

Fig. 2. Diffraction profiles of tetragonal (**T**) 314 and 322 reflections of parent LaFeAsO over the temperature range from 135 K to 185 K. The split peaks below 165 K are indexed as 244, 424 and 152, 512 in the orthorhombic (**O**) symmetry, respectively.

The Rietveld fitting results of each sample at 300 K and 120 K are shown in Fig. 3. The XRD patterns of the F-substituted sample were well fitted with the *P4/nmm* space group over the measured temperature range. For the parent LaFeAsO, the patterns measured above 170 K were also fitted with the tetragonal symmetry; however, the symmetry should be lowered to fit the doublet peaks of the patterns measured below 165 K. The orthorhombic *Cmma* space group provided the smallest R_I and R_{wp} values of 2.1% and 4.6% for the data at 120 K (Fig. 3(b)). Figure 4(b) clearly shows that the *a*-axis lengths split and grow at around 160 K, which corresponds to the temperature where anomalies occur (Fig. 4(a)). The results led us to the conclusion that the anomaly is associated with the crystallographic phase transition from the tetragonal to orthorhombic phase.

As a result of the transition, the *a*- and *b*-axes were rotated by 45° along the *c*-direction relative to those of the tetragonal phase and the lattice constants expand by a multiple of $\sqrt{2}$, although the axis lengths are no longer unequal (Fig. 4(c)). The symmetry of the *Cmma* space group is obtained by removing the confinement of "*a* = *b*" from the symmetry of *P4/nmm*, while keeping the other symmetry elements. Cruz *et al.* have reported the structure phase transition of parent LaFeAsO from the result of the neutron diffraction measurement, but they assigned the monoclinic *P*112/*n* space group for the low-temperature phase [2]. We checked our fitting results with the orthorhombic *Cmma* space group, but no peaks violating the extinction rule have been found in the diffraction patterns down to 25 K. The structural studies of other LnFeAsO structures, such as CeFeAsO [3] and so on, have also shown that the crystal symmetry of the low-T phase can be successfully assigned to the *Cmma* space group, citing our report [4]. These results support our determination of the space group.

The neutron diffraction measurement also revealed that a stripe-type antiferromagnetic phase transition occurs at 140 K, a slightly lower temperature than the T_{anom}, and some *ab initio* calculations [4,5] also supported the stability of the antiferromagnetic Fe-spin ordering in the orthorhombic phase. Such tetragonal-orthorhombic and antiferromagnetic phase transitions are common in the parent phases of other high-T_c Fe-based superconductors, and considering the similarity to antiferromagnetic order in the parent phase of copper oxide superconductors, the phase transitions would be closely associated with the appearance of high T_c. Further experimental and theoretical studies are expected to reveal the mysteries of the high-T_c superconductivity.

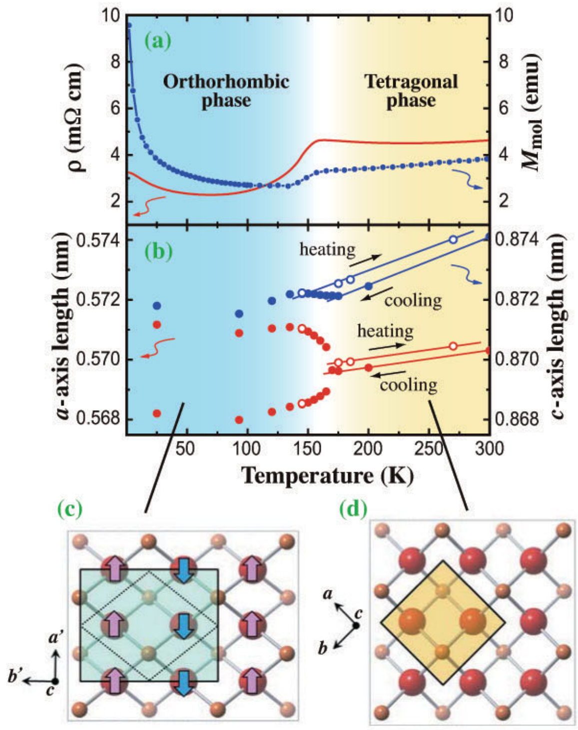

Fig. 4. **(a)** Temperature-dependent resistivity (ρ) and molar magnetization (M_{mol}) of parent LaFeAsO. **(b)** Temperature-dependent *a*-, *b*- and *c*-axis lengths of parent LaFeAsO. The *a*-axis lengths of tetragonal phases are multiplied by $\sqrt{2}$ for comparison with the orthorhombic phases. Closed and open symbols represent heating and cooling processes, respectively. **(c)**,**(d)** A view from *c*-direction of the FeAs layer for orthorhombic **(c)** and tetragonal **(d)** phases. The arrows in **(c)** represent the stable strip-type spin configuration on Fe atoms determined by DFT calculation [4,5].

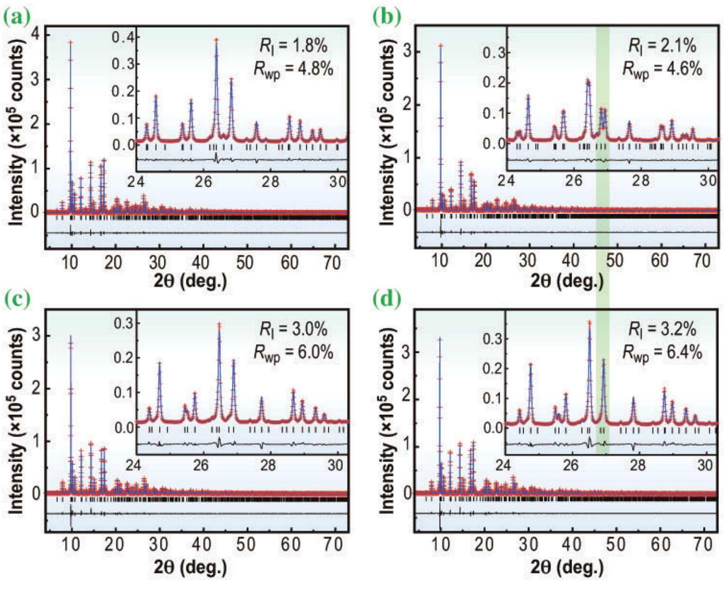

Fig. 3. Rietveld fitting results of the diffraction patterns of the parent LaFeAsO at **(a)** 300 K and **(b)** 120 K, and those of the 14% F-substituted LaFeAsO at **(c)** 300 K and **(d)** 120 K. The XRD patterns of the parent LaFeAsO below 160 K were fitted with the orthorhombic *Cmma* space group. Insets show magnified view ranging from 24° to 30°. The structure phase transition (i.e., peak split) of the parent sample is suppressed in the F-substituted sample (the green shade).

Takatoshi Nomura* and Hideo Hosono

Materials and Structures Laboratory,
Tokyo Institute of Technology

*E-mail: t-nomura@lucid.msl.titech.ac.jp

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