

## Synchrotron X-Ray Diffraction Study of Fe-1111 Type Superconductor *AeFeAsF* (*Ae* = Ca and Sr): Possibility of Higher $T_c$

Since the discovery of superconductivity in F-doped LaFeAsO with  $T_c = 26$  K, Fe-based layered compound systems have been intensively studied as candidates for high- $T_c$  superconductors. With these efforts,  $T_c$  is increased to  $\sim 55$  K in *LnFeAsO* (Fe-1111 type: *Ln* = La, Ce, Pr, Nd, Sm,...). The Fe-1111-type superconductors consist of an  $(\text{FeAs})^{\delta-}$  layer forming a tetragonal iron lattice sandwiched by a  $(\text{LnO})^{\delta+}$  layer and suffer from the crystallographic transition from tetragonal to orthorhombic, accompanied by an antiferromagnetic spin order at 120-160 K. The electron or hole doping to the  $(\text{FeAs})^{\delta-}$  layer through the doping of fluorine to  $(\text{LnO})^{\delta+}$  suppresses the crystallographic and magnetic phase transitions, and induces superconductivity. Therefore, the relationship among the structural and magnetic instabilities, and superconductivity have been studied, and much effort has been made for the synthesis of related compounds composed of similar iron lattices with the aim of increasing the  $T_c$ .

Recently, we have succeeded in the synthesis of a new member of the Fe-1111 type compounds *AeFeAsF* (*Ae* = Ca, Sr), in which the  $(\text{LnO})^{\delta+}$  layers in *LnFeAsO* are replaced by  $(\text{AeF})^{\delta+}$  layers (Fig. 1) [1,2]. These compounds exhibit the superconductivity induced by the partial substitution of Fe with Co, which is regarded as a direct electron doping to the  $(\text{FeAs})^{\delta+}$  layer. It is noteworthy that  $T_c = 22$  K, which is realized

for a Co content of 10% ( $\text{CaFe}_{0.9}\text{Co}_{0.1}\text{AsF}$ ), is higher than the optimal  $T_c$  in Co-substituted *LnFeAsO* (LaFeAsO: 13 K; SmFeAsO: 15 K), while the optimal  $T_c$  in Co-substituted SrFeAsF is below 4 K.

In this study, we have performed synchrotron X-ray powder diffraction measurements of  $\text{CaFe}_{1-x}\text{Co}_x\text{AsF}$  and  $\text{SrFe}_{1-x}\text{Co}_x\text{AsF}$  ( $x = 0, 0.06, 0.12$ ) at beamline **BL02B2** to confirm that the tetragonal to orthorhombic crystallographic transition also occurs in the *AeFeAsF* system, as observed in the *LnFeAsO* system and to analyze the relationship between  $T_c$  and crystal structure [3].

Tetragonal-to-orthorhombic phase transitions were observed at  $\sim 120$  K for unsubstituted CaFeAsF and at  $\sim 180$  K for unsubstituted SrFeAsF; such transition temperatures agree with kinks observed in temperature-dependent resistivity curves (Fig. 2). Although the transition temperature decreases, the structural phase transitions were observed below 100 K in both samples of  $x = 0.06$ , and finally, they were suppressed at the doping level of  $x = 0.12$ . The crystal structures refined by Rietveld analysis reveal that distortions of the  $\text{FeAs}_4$  tetrahedron from the regular tetrahedron are likely to originate from mismatches in atomic radii among the constituent elements (Fig. 3). In this system, the enlarged  $\text{FeAs}_4$  tetrahedron, resulting from the fact that the radius of Sr is larger than that of Ca, is flattened along the

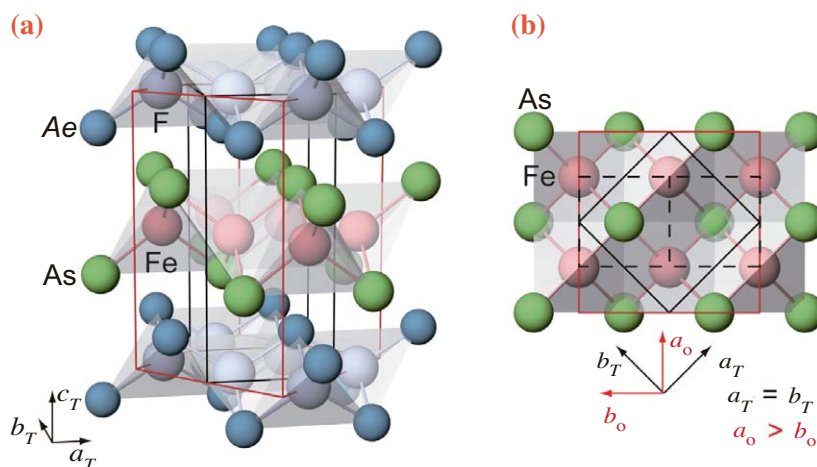


Fig. 1. Crystal structure of *AeFeAsF* composed of alternate stacking of  $(\text{AeF})^{\delta+}$  and  $(\text{FeAs})^{\delta-}$  layers. Owing to the tetragonal-to-orthorhombic transition, the unit cell setting is changed from a lattice (indicated by black solid lines) that is deformed to an orthogonal lattice (indicated by red lines.).

*ab* plane, and the smaller radius of Ca makes the tetrahedron closer to a regular one; their characteristic shapes are further enhanced by Co substitution. The positive relationship between the optimal  $T_c$  and regularity of the  $\text{FeAs}_4$  tetrahedron is observed in various FeAs-based superconductors [4]. Furthermore, it is also observed that the optimal  $T_c$  in the Fe-1111 system realized by Co substitution is lower than that induced by F-doping. Our results suggest that the  $\text{CaFeAsF}$  compound is a promising candidate for a higher- $T_c$  superconductor, if a substitutional doping to a  $(\text{CaF})^{\delta+}$  layer yielding an indirect electron doping to a  $(\text{FeAs})^{\delta-}$  layer is realized.

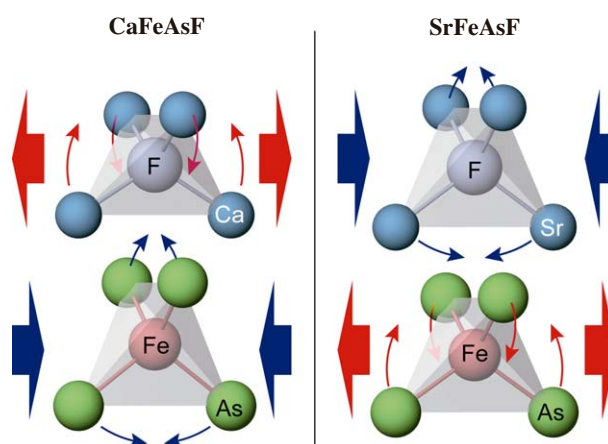


Fig. 3. Distortion of  $\text{Ae}_4\text{F}$  and  $\text{FeAs}_4$  tetrahedra. For lattice-space matching between the  $(\text{AeF})^{\delta+}$  and  $(\text{FeAs})^{\delta-}$  layers, the As-Fe-As and Ae-F-Ae bond angles are changed from those of the regular tetrahedron to compensate for the difference in bond length ( $r_{\text{Sr-F}} > r_{\text{Fe-As}} > r_{\text{Ca-F}}$ ).

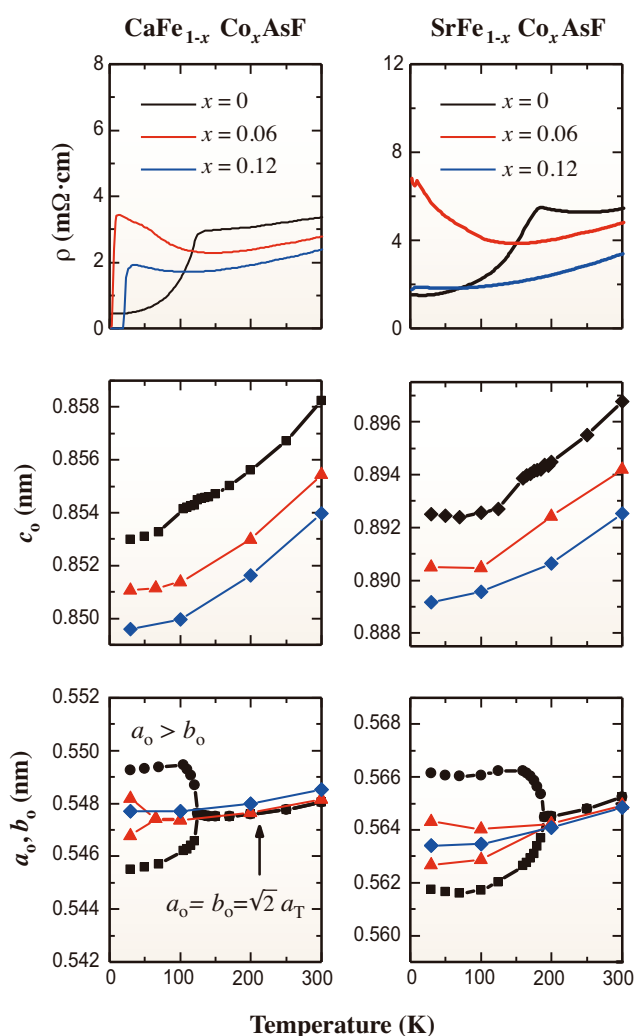


Fig. 2. Temperature dependences of electrical resistivity ( $\rho$ ) and lattice constants ( $a_0$ ,  $b_0$ ,  $c_0$ ) of  $\text{AeFe}_{1-x}\text{Co}_x\text{AsF}$  ( $\text{Ae} = \text{Ca}, \text{Sr}$ ;  $x = 0, 0.06, 0.12$ ).

Satoru Matsuishi<sup>a,\*</sup> and Hideo Hosono<sup>a,b</sup>

<sup>a</sup> Frontier Research Center,  
Tokyo Institute of Technology  
<sup>b</sup> Materials and Structures Laboratory,  
Tokyo Institute of Technology

\*E-mail: satoru@lucid.msl.titech.ac.jp

## References

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