Discovery of the Peculiar Structural Relationship in Iron-Based Superconductors

In this work, the crystal structure of an iron oxypnictide $LaFeAsO_{1-x}H_x$ is studied as a function of pressure using synchrotron X-ray diffraction. We found that the As–Fe–As angle of the $FeAs_4$ tetrahedron widens with application of pressure. This disputes a widely accepted structural guideline that superconductivity favors regular tetrahedron, even though the superconducting critical temperature (T_c) increases from 18 K (at ambient pressure) to 52 K (at 6 GPa) for x = 0.2. In addition, the second parent phase at x ~ 0.5 is suppressed by a pressure as low as ~1.5 GPa. This is in contrast to the first parent phase at x ~ 0, which exhibits robustness under pressure. We suggest that certain spin-fluctuation from the second parent phase is strongly related to the high T_c observed under pressure.

Iron pnictides are a new family of high-temperature superconductors, commonly termed as iron-based superconductors [1]. A significant number of studies on chemical substitution in iron pnictides have resulted in an empirical guideline that the superconducting critical temperature (T_c) is maximized when the geometry of FePn_4 (Pn = pnictogen) unit approaches the regular tetrahedron. The application of pressure is a direct and clean way to modify the local geometry of FePn_4 without the degradation of the crystal in comparison to the chemical substitution. Hence it is a significant method to study the interplay between the structure and the T_c.

One of the fascinating materials in iron pnictides is $LaFeAsO_{1-x}H_x$, which has a ZrCuSiAs-type structure with alternating stacks of conducting $FeAs_4$ and insulating (O,H)La_4 layers. As shown in **Fig.1**, $LaFeAsO_{1-x}H_x$ exhibits a unique phase diagram on hydrogen anion substitution, i.e., electron doping: two superconducting domes with T_c^{max} = 26 K at x ~ 0.08 (SC1) and T_c^{max} = 37 K at x ~ 0.35 (SC2), and two parent phases at x ~ 0 (PP1) and x ~ 0.5 (PP2) [2]. The SC2 and PP2 are rarely observed among high-T_c materials because they usually become normal metal in the heavily electron-doped region. Takahashi *et al.* have recently demonstrated that applying pressure on $LaFeAsO_{0.72}H_{0.18}$ induced a notable enhancement of the T_c from 18 K at ambient pressure to 52 K at 6 GPa [3].

To clarify the relation between the $FeAs_4$ geometry and the T_c, the synchrotron X-ray diffraction experiment of $LaFeAsO_{1-x}H_x$ (x = 0, 0.2, and 0.51) under pressure was examined at BL-8B and AR-NE1A. The results reveal that the $FeAs_4$ unit deviates from the regular tetrahedron on application of pressure, which is an unexpected finding that breaks the hitherto believed guideline of approaching a regular FePn_4 tetrahedron for increasing the T_c [4]. In addition, at high pressure, rapid suppression of the peculiar PP2 is found, while the conventional PP1 is robust against pressure. The pressure responses of the $FeAs_4$ deformation, the parent phases, and their correlation are previously unexplained peculiarities in 1111-type iron pnictides.

Figure 2 shows the contour plots of T_c against the As-Fe-As bond angle ($\alpha_{As\text{-}Fe\text{-}As}$) and Fe-As bond length ($d_{Fe\text{-}As}$) under pressure, where the values of T_c in the whole map are interpolated from ref. [3]. The pressure triggers a merger of the two SC domes at ambient pressure into a single SC dome along with the increase of T_c to 52 K at 6 GPa for x = 0.2. After the merge, the ridge line of T_c runs along the line for x = 0.20 as the pressure increased.

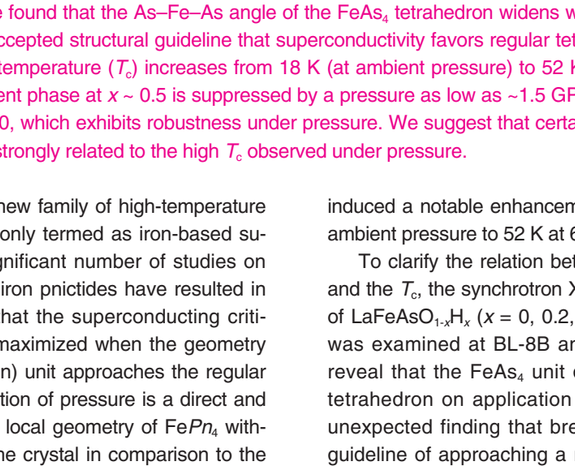

Figure 1: Phase diagram of $LaFeAsO_{1-x}H_x$ at ambient pressure and 6 GPa. Inset: crystal structure of $LaFeAsO_{1-x}H_x$. The carriers are located in the $FeAs_4$ layer.

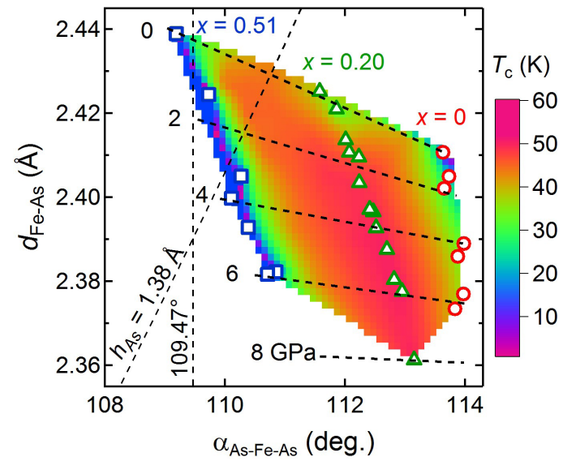

Figure 2: Contour plots of T_c for $LaFeAsO_{1-x}H_x$ as a function of the As-Fe-As bond angle ($\alpha_{As\text{-}Fe\text{-}As}$) and the Fe-As distance ($d_{Fe\text{-}As}$). The regular tetrahedron angle and the As height (h_{As}) = 1.38 Å in $FeAs_4$ are shown as broken lines.

In iron-based superconductors, the relation between the maximum T_c and structural parameters of $FeAs_4$ has been so far proposed as follows: the highest T_c is achieved when $\alpha_{As\text{-}Fe\text{-}As}$ approaches 109.5° as in a regular tetrahedron of $FeAs_4$ or when the As height from the Fe plane ($h_{As} = d_{Fe\text{-}As}\cos(\alpha_{As\text{-}Fe\text{-}As}/2)$) is ~1.38 Å. Theoretical argument has been advanced that antiferromagnetic spin- or orbital-fluctuation is maximized as $FeAs_4$ adopts a nearly regular tetrahedron geometry, leading to an optimum T_c. The former is strongly related to the number and topology of Fermi surfaces, while the latter is due to the electron-phonon interaction. In agreement with the above rule, $SmFeAsO_{0.78}H_{0.22}$, which has the highest T_c of 55 K in iron pnictides, has nearly ideal values of $\alpha_{As\text{-}Fe\text{-}As}$ (109.3°) and h_{As} (1.386 Å) at ambient pressure. Moreover, the $\alpha_{As\text{-}Fe\text{-}As}$ for $BaFe_2As_2$ and LiFeAs act toward and away from the regular tetrahedron of $FeAs_4$ along with increasing and decreasing the T_c, respectively. However, the results reveal that while $\alpha_{As\text{-}Fe\text{-}As}$ and h_{As} of $LaFeAsO_{0.8}H_{0.2}$ deviate from the optimum values with pressure (see **Fig. 2**), the T_c increases significantly. Thus, this work highlights the inconsistencies in the guides for increasing the T_c. The electronic state calculations illustrate that the Fermi surface topologies of $LaFeAsO_{0.8}H_{0.2}$ are unaltered on the application of pressure. Additionally, the bandwidth of Fe-3d widens with pressure because of the shortening of $d_{Fe\text{-}As}$, resulting in a decrease of the spin-fluctuation that should cause the T_c to decrease as well. Thus, the properties examined so far fail to account for the increase in T_c under pressure.

In general, the nature of the parent phase influences the superconducting state of high-T_c superconductors. That is, fluctuations derived from the parent phase may enhance the pairing of superconducting electrons. Thus, the origins of SC1 and SC2 adhering to PP1 and PP2, respectively, can be considered as the fluctuations from PP1 and PP2. Since the widely accepted structural guide for increasing the T_c is tied to the itinerant spin-fluctuation, the deviation from the regular tetrahedron by applying pressure means the reduction of the fluctuation from PP1. Consequently, the fluctuation from PP2 should be more significant for the superconductivity under pressure. This fluctuation is accompanied with a strongly localized character of PP2 as the orbital selective Mott phase. It is therefore suggested that the localized spin-fluctuation from PP2 is the principal origin for superconductivity under pressure. The relation between the present results and the other mechanism of orbital- or charge-fluctuations remains unclear. To identify the above suggestion, the investigation of spin/structural dynamics in this system is required.

REFERENCES

[1] Y. Kamihara, T. Watanabe, M. Hirano and H. Hosono, *J. Am. Chem. Soc.* **130**, 3296 (2008).
[2] M. Hiraishi, S. Iimura, K. M. Kojima, J. Yamaura, H. Hiraka, K. Ikeda, P. Miao, Y. Ishikawa, S. Torii, M. Miyazaki, I. Yamauchi, A. Koda, K. Ishii, M. Yoshida, J. Mizuki, R. Kadono, R. Kumai, T. Kamiyama, T. Otomo, Y. Murakami, S. Matsuishi and H. Hosono, *Nat. Phys.* **10**, 300 (2014).
[3] H. Takahashi, H. Soeda, M. Nukii, C. Kawashima, T. Nakanishi, S. Iimura, Y. Muraba, S. Matsuishi and H. Hosono, *Sci. Rep.* **5**, 7829 (2015).
[4] K. Kobayashi, J. Yamaura, S. Iimura, S. Maki, H. Sagayama, R. Kumai, Y. Murakami, H. Takahashi, S. Matsuishi and H. Hosono, *Sci. Rep.* **6**, 39646 (2016).

BEAMLINES

BL-8B and AR-NE1A

K. Kobayashi[1], J. Yamaura[2], S. Iimura[2], S. Maki[2], H. Sagayama[1], R. Kumai[1], Y. Murakami[1], H. Takahashi[3], S. Matsuishi[2] and H. Hosono[2] ([1]KEK-IMSS-PF/CMRC, [2]Tokyo Inst. of Tech., [3]Nihon Univ.)