Discovery of the Peculiar Structural Relationship in Iron-Based Superconductors

In this work, the crystal structure of an iron oxypride LaFeAsO$_x$H$_y$ is studied as a function of pressure using synchrotron X-ray diffraction. We found that the As–Fe–As angle of the FeAs$_x$ tetrahedronwidens with application of pressure. This disrupts a widely accepted structural guideline that superconductivity favors regular tetrahedra, 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 FeAs$_x$ (P$_0$ = prichtgen) unit approaches the regular tetrahedron. The application of pressure is a direct and clean way to modify the local geometry of FeAs$_x$, 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 LaFeAS$_x$OH$_y$, which has a ZrCuSiAs-type structure with alternating stacks of conducting FeAs$_x$ and insulating (OH)$_2$La$_2$ layers. As shown in Fig. 1, LaFeAsO$_4$H$_y$ exhibits a unique phase diagram on hydrogen anion substitution, i.e., electron doping: two superconducting domains with $T_c$ = 26 K at $x = 0.08$ (SC1) and $T_c$ = 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$_4$H$_y$ induces a notable enhancement of the $T_c$ from 18 K at pressure to 52 K at 6 GPa [3].

To clarify the relation between the FeAs$_x$ geometry and the $T_c$, the synchrotron X-ray diffraction experiment of LaFeAsO$_4$H$_y$ ($x = 0, 0.2$, and $0.51$) under pressure was examined at BL-8B and AR-NE1A. The results reveal that the FeAs$_x$ 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 FeAs$_x$ 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$_x$ 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 ($\alpha$) and Fe–As bond length ($d_{Fe-As}$) under pressure, where the values of $\alpha$ 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 $x = 0.2$ as the pressure increased.

In iron-based superconductors, the relation between the maximum $T_c$ and structural parameters of FeAs$_x$ has been so far proposed as follows: the highest $T_c$ is achieved when $\alpha_{As-Fe-As}$ approaches 109.5° as in a regular tetrahedron of FeAs$_x$ or when the As height from the Fe plane ($h_As = d_{Fe-As} \cdot \sin(\alpha_{As-Fe-As})$) is ~1.38 Å. Theoretical arguments have been advanced that antiferromagnetic spin- or orbital-fluctuation is maximized as FeAs$_x$ 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, high FeAsO$_4$H$_y$ with the highest $T_c$ of 55 K in iron pnictides, has nearly ideal values of $\alpha_{As-Fe-As}$ (109.3°) and $h_As$ (1.386 Å) at ambient pressure. Moreover, the $\alpha_{As-Fe-As}$ for BaFe$_2$As$_2$, FeAs$_x$, and LiFeAs$_x$ trigger toward and away from the regular tetrahedron of FeAs$_x$ along with increasing and decreasing the $T_c$, respectively. However, the results reveal that while $\alpha_{As-Fe-As}$ and $h_As$ of LaFeAsO$_4$H$_y$ deviate from the optimum values with pressure (see Fig. 2), the $T_c$ increases significantly. This work highlights the inconsistencies in the guides for increasing the $T_c$. The electronic state calculations indicate that the Fermi surface topologies of LaFeAsO$_4$H$_y$ are unaltered on the application of pressure. Additionally, the bandwidth of Fe-3d states with pressure because of the shortening of $d_{Fe-As}$ resulting in a decrease of 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-charge fluctuations remains unclear. To identify the above suggestion, the investigation of spin/structural dynamics in this system is required.

REFERENCES

BEAMLINES
BL-8B and AR-NE1A