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Pressure effects in iron oxypnictide superconductor $LaFeAsO_{1-x}H_x$

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1 Introduction

$LaFeAsO_{1-x}H_x$ is the hydrogen anion substituted version of the pioneering iron oxypnictide superconductor $LaFeAsO_{1-x}F_x$, that unveils a unique phase diagram of two superconducting (SC) domes and two parent phases [1-2]. The undoped LaFeAsO exhibits, an antiferromagnetic (AF) ordering at T_{N1} = 155 K, subsequently a tetragonal to orthorhombic (T-O) structural transition at T_{S1} = 137 K: this is a first parent phase, PP1. The PP1 is suppressed on increasing x *i.e.* doping the electron, and then two SC domes appear with the maximum temperature of the SC transition $T_{c,max}$ = 26 K at x ~ 0.08 (SC1) and 37 K at x ~ 0.35 (SC2). Instead of the SC phase, an AF ordering reappears over x > 0.45, eventually the AF ordering exhibits at T_{N2} = 89 K with a T-O structural transition at T_{S2} ~ 95 K for x = 0.51, ascribed to a second parent phase (PP2). The PP2 has a non-centrosymmetric structure in contrast to a centrosymmetric structure of the PP1. The magnetic moment 1.21 μ_B in the PP2 is twice as large as 0.63μB in the PP1, implying that the strong electron correlation exists, albeit heavily electron-doped. Such the characteristic PP2s were observed only in the series of 1111-type compounds, REFeAsO$_{1-x}$H$_x$ (RE = rare earth).

Applying pressure to $LaFeAsO_{1-x}H_x$ induces a notable effect that the two SC domes are merged into a single SC dome, along with the significant enhancement of T_c from 18 K at ambient pressure to 52 K at 6 GPa in x = 0.18, close to the highest class of T_c = 55 K in Sm1111 among the iron-based superconductors [3]. Our research is aimed at which crystal structures of $LaFeAsO_{1-x}H_x$ are determined experimentally under pressure in the wide range of hydrogen contents x.

2 Experiment

The synchrotron X-ray diffractions (sXRD) for x = 0, 0.20 and 0.51 were carried out at room temperature up to ~8 GPa at the beamline NE1A of PF-AR, KEK. Pressure was generated by a diamond anvil cell (DAC). Very fine powder indicates a perfect Debye ring of reflections on the two-dimensional image. The DAC, in which the anvils are supported by the 45° tapered slit window without the backing plate, has an advantage for reducing the background scatter and simplifying the absorption correction of diamond. The measured wavelength of λ = 0.4217 Å and the wide open angle of DAC can approach the d-spacing of d < 0.7 Å, enables to determine accurate atomic positions. The pressure values were calibrated by the ruby fluorescence method. The two-dimensional images collected by RIGAKU R-AXIS on the curved imaging plate were integrated to yield 2θ-intensity data. Crystal structures were refined by Rietveld method based on the space group $P4/nmm$, and the residual factors in the refinements are R_{wp} = 3.9-6.6%. We moreover traced the PP2 by means of the sXRD down to 8 K up to 3.2 GPa at beamline BL-8B of PF, KEK, measured at λ = 0.8267 Å. Pressure values were monitored by lattice constants of NaCl at various temperatures. A 4:1 methanol-ethanol mixture was used as a pressure transmitting medium in all the experiments.

3 Results and Discussion

Figure 1(a) shows lattice constants of a and c as a function of pressure for $LaFeAsO_{1-x}H_x$ (x = 0, 0.20, 0.51) at room temperature. In the whole pressure range, any peak broadenings were not observed, indicating that the tetragonal systems are preserved. The a and c in all the compositions decrease monotonically up to ~8 GPa with the linear compressibilities of k_a = 2.54~2.62×10^{-3} GPa^{-1} and k_c = 5.50~5.64×10^{-3} GPa^{-1}, respectively. The bulk modules B_0, estimated by the empirical Murnaghan equation of state (EOS) $V/V_0 = (1+p(B'_0/B_0))^{-1/B'0}$, where V_0 is the volume of ambient pressure and B_0' was fixed to 4.2, were about 100(1) GPa in all the compounds.

Figures 1(b)-(d) plot the pressure dependence of geometrical parameters of $FeAs_4$ tetrahedron, where the $d_{Fe\text{-}As}$, $\alpha_{As\text{-}Fe\text{-}As}$, and h_{As}, are the Fe-As bond length, the As-Fe-As bond angle and the As height from Fe plane, respectively. Pressure induces the $d_{Fe\text{-}As}$ reduction and the h_{As} lowering, and the $\alpha_{As\text{-}Fe\text{-}As}$ spreading in all the compositions. The degree of the pressure variation in $\alpha_{As\text{-}Fe\text{-}As}$ as well as h_{As} develops with growing the hydrogen contents of x, for instance the pressure variation of $\alpha_{As\text{-}Fe\text{-}As}$ for x = 0.51 is four times larger than that for x = 0.

The contour plots of T_c for the $\alpha_{As\text{-}Fe\text{-}As}$ and the $d_{Fe\text{-}As}$ under pressure are illustrated in Fig. 2, where the values of T_c in the whole map are interpolated from the reported ones [3]. The relation of the $d_{Fe\text{-}As}$, $\alpha_{As\text{-}Fe\text{-}As}$, and h_{As} is expressed by the equation of $h_{As} = d_{Fe\text{-}As}\cos(\alpha_{As\text{-}Fe\text{-}As}/2)$. In iron-based superconductors, the optimum T_c lines based on the structural parameters of $FeAs_4$ are hitherto proposed: the highest T_c realizes on the regular tetrahedron of $FeAs_4$ or the optimum value of h_{As} ~ 1.38 Å. Actually, $SmFeAsO_{0.78}H_{0.22}$ with the highest T_c = 55 K gives the optimum values of the $\alpha_{As\text{-}Fe\text{-}As}$ = 109.3° and the h_{As} = 1.386 Å at ambient pressure. While, the experimental findings that the ridge line of T_c runs along the variation for x = 0.20 as the pressure increased reveal

that the shape of $FeAs_4$ tetrahedron deviates from the optimum T_c lines.

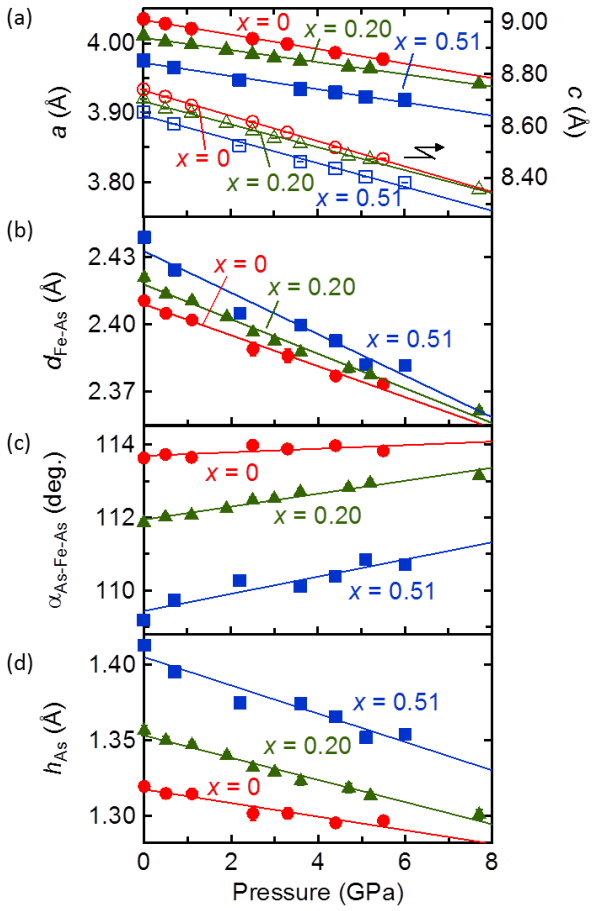

Figure 1. Pressure dependence of structural parameters of (a) the lattice constants, (b) the Fe-As bond length, d_{Fe-As}, (c) the As-Fe-As bond angle, $\alpha_{As-Fe-As}$, (d) the As height, h_{As}, for $LaFeAsO_{1-x}H_x$ with $x = 0$ (red circles), 0.20 (green triangles), 0.51 (blue squares).

We turn to investigate how it going the parent phases under pressure. Figure 3 shows the temperature dependence of the full width at half maximum (FWHM) of 220 reflection for $x = 0.51$, which is a good indicator to pursuit the T-O structural transition [2]. The structural transition temperatures of T_{S2} are indicated by arrows estimated from the power law fitting. At 0.5 and 0.9 GPa, the broadenings of FWHMs start moderately in high-temperature region as extensive fluctuations in vicinity of the structural transitions. At 1.5 GPa, only the slight broadening exhibits at low-temperature, not implying the structural transition but the precursory phenomenon near the phase boundary. Any broadening was not observed at 3.2 GPa. Takahashi *et al.* presented that an anomaly in resistivity, presumably corresponding to T_{N2}, for $x = 0.51$ was suppressed near 2 GPa [3]. This denotes that the T_{N2} as well as the T_{s2}, *i.e.* the PP2 was obscured by low-pressure although the PP1 being up to 20 GPa (T_{N1}) and 30 GPa (T_{s1}) is robust to pressure.

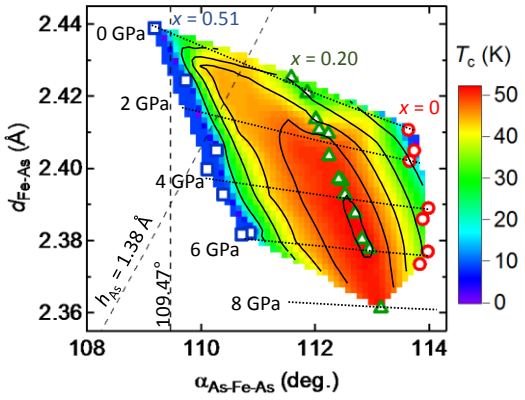

Figure 2. Contour plots of T_c for $LaFeAsO_{1-x}H_x$ as a function of the $\alpha_{As-Fe-As}$ and the d_{Fe-As}. Broken lines represent the regular tetrahedron of $FeAs_4$ and the h_{As} = 1.38 Å as empirically believed structural parameters of the highest-T_c.

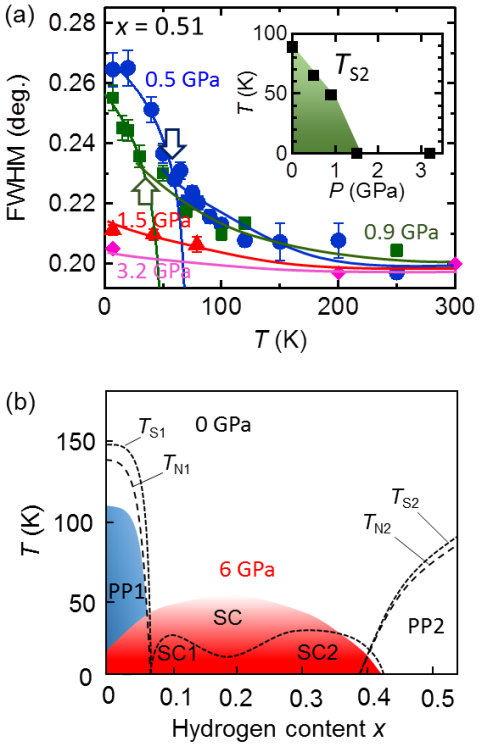

Figure 3. (a) Temperature dependence of FWHM of 220 reflections at several pressures for $LaFeAsO_{0.49}H_{0.51}$. The arrows indicate the T-O structural transitions of T_{S2}. Inset shows the phase diagram of T_{s2} under pressure. (b) Phase diagram of the parent phases (PP) and superconducting phases (SC) for $LaFeAsO_{1-x}H_x$ at 0 and 6 GPa. The PP1 and SC are drawn for blue and red colorings, respectively.

In summary, we established a map of the structural parameters in the wide range of doping and pressure for $LaFeAsO_{1-x}H_x$ by means of synchrotron X-ray diffraction experiments. Pressure deforms the $FeAs_4$ tetrahedron

shrunk and flattened, revealing inconsistent to the earlier believed structural guides for developing T_c. We found that the second parent phase, located in the heavy electron-doped region, is lost by low-pressure, contrary to the sluggish reaction to pressure in undoped parent phase. We speculate a certain fluctuation from the second parent phase reinforces the T_c under pressure.

References

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