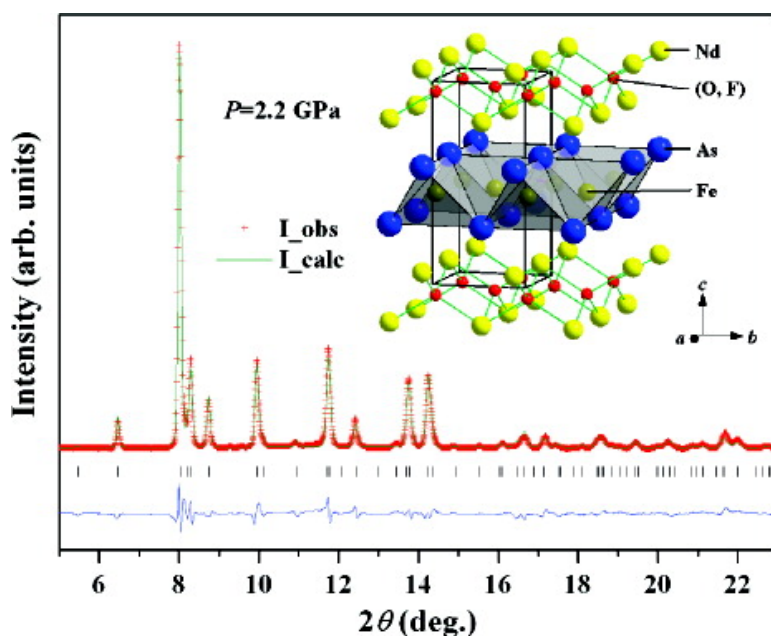


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Structure Stability and Compressibility of Iron-Based Superconductor Nd(O_{0.88}F_{0.12})FeAs under High Pressure

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Very recently, La(O_{1-x}F_x)FeAs ($x = 0.05-0.12$) was found to be an electron-doped superconductor with the transition temperature T_c at about 26 K, by doping with F ions at the O-site in LaOFeAs.¹ Substituting other small-radius lanthanide ions for La ions in La(O_{1-x}F_x)FeAs evidently increases the T_c .²⁻⁴ It was reported the T_c is ~ 55 K for Sm(O_{0.9}F_{0.1})FeAs,³ which clearly shows the chemical inner pressure effect on the superconducting property. All these compounds adopt the ZrCuSiAs type structure with the space group $P4/nmm$.⁵ Arranged alternately along the c -axis, the Ln₂(O, F)₂ layer (Ln = lanthanide elements) and Fe₂As₂ layer are the charger reservoir layer and conduction layer, respectively. There is a relatively large interspace between the two neighbor layers along the c -axis, indicating that high pressure will remarkably adjust their structures and consequently tailor their physical behaviors.

Some *in situ* high-pressure experiments on these compounds have been performed. For example, the T_c of F-doped LaOFeAs was reported to increase with pressure and reach a maximum of ~ 43 K at 4 GPa, obtained from electrical resistance measurements under high pressure.⁶ However, the behavior of structural stability and the equation of state of these iron-based superconductors under high pressure still remain unknown. It is important to understand the structural evolution of these new iron-based superconductors under pressure. Among these new iron-based superconductors, Nd(O_{1-x}F_x)FeAs is a good candidate for this study since it is a sister compound with La(O_{1-x}F_x)FeAs and crystallizes into the similar structure with a larger T_c of near 50 K at $x = 0.12$.⁴ In this report, we present the discovery of pressure-induced structural transition on this iron-based superconductor by using a diamond anvil cell (DAC) technique combined with an *in situ* angle-dispersive synchrotron X-ray diffraction (AD-XRD) experimental technique.

The Nd(O_{1-x}F_x)FeAs samples were synthesized by a solid-state reaction method using NdAs, NdF₃, Fe, FeAs, Fe₂As, and Fe₂O₃ as starting materials.⁴ The *in situ* high-pressure AD-XRD experiments were carried out at room temperature at the X17B3 beamline of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, with the wavelength of incident X-ray 0.040 41 nm. The samples were loaded into the sample chamber in the T301 stainless steel gasket. The pressure was measured by using the ruby fluorescence method.⁷ Silicone oil was used as the pressure-transmitting medium, which can generate a fine quasi-hydrostatic pressure environment within the pressure scope in this study.⁸

The unit cell parameters of Nd(O_{0.88}F_{0.12})FeAs at 0–32.7 GPa are calculated from Le Bail refinements based on the previous

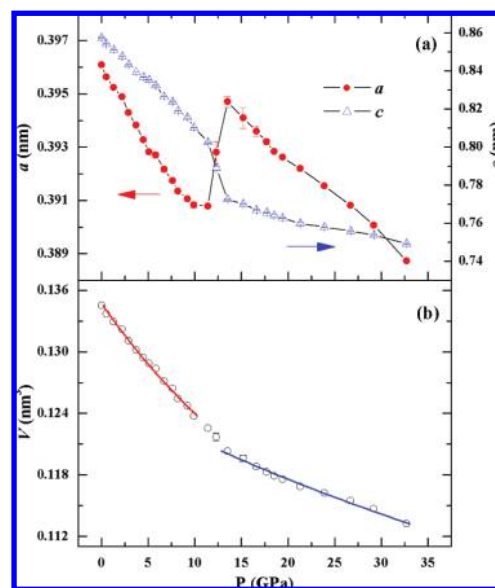


Figure 1. Pressure dependences of (a) lattice parameters and (b) unit cell volume of Nd(O_{0.88}F_{0.12})FeAs. The solid lines in (b) are the fitting results according to the second-order Birch equation of state (EoS).

reported structure,⁴ as shown in Figure 1a. Below 9.9 GPa, both the a - and c -axis shrink with increasing pressure. Then following abnormal changes, the value of the a -axis is increasing with pressure while that of c -axis is drastically decreasing with pressure within the pressure range 9.9–13.5 GPa. When pressure is higher than 13.5 GPa, both a and c are decreasing smoothly up to the maximal experimental pressure. These results show an isostructural phase transition starts at ~ 10 GPa. At ~ 13.5 GPa, Nd(O_{0.88}F_{0.12})FeAs completely transforms to a high-pressure tetragonal (HPT) structure within the same space group of $P4/nmm$ but with a larger a -axis and smaller c -axis, from the primary low-pressure tetragonal (LPT) structure below 9.9 GPa.

Figure 1b shows the pressure dependences of the unit cell volume for Nd(O_{0.88}F_{0.12})FeAs, where the solid lines are the fitting results for the LPT phase and HPT phase using the second-order Birch equation of state (EoS).⁹ With B_0' fixed as 4, we obtained the ambient pressure isothermal bulk modulus $B_0 = 102(2)$ and $245(9)$ GPa for the LPT phase and HPT phase, respectively. The fitted unit cell volume V_0 of the two forms at ambient conditions is equal to $0.1347(1)$ and $0.1262(3)$ nm³, respectively. The range 9.9–13.5 GPa is a transitional region between the LPT and HPT structure. Obviously, there is a turning point at 13.5 GPa in the V - P curve,

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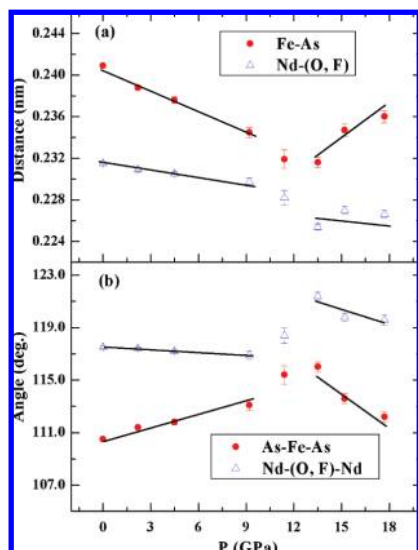


Figure 2. Pressure dependences of (a) selected bond distances and (b) bond angles for $\text{Nd}(\text{O}_{0.88}\text{F}_{0.12})\text{FeAs}$. Lines are guides for the eye.

which indicates that this isostructural phase transition induced by pressure is a process without a large volume drop.

The XRD patterns of $\text{Nd}(\text{O}_{0.88}\text{F}_{0.12})\text{FeAs}$ were analyzed with Rietveld refinements by using the GSAS program package,¹⁰ to study the pressure effect on the structural properties of the sample down to the atomic level. The refinement results are limited to relatively lower pressure cases below 17.7 GPa in this report, since it is difficult to obtain physically meaningful refinement results from the relatively poor quality XRD patterns when pressures are higher than that data point. A typical refinement result at 2.2 GPa conditions was shown in the Table of Contents, in which the fitted residuals R_p and R_{wp} were 4.08% and 5.69%, respectively. Figure 2 shows the pressure dependences of selected bond distances and angles, which are not continuous in the range 9.9–13.5 GPa. For the LPT phase, both the Fe–As and Nd–(O, F) distances are decreasing with increasing pressure. When the pressure is higher than 13.5 GPa, the Nd–(O, F) distance is basically decreasing with pressure, while the pressure dependence of the Fe–As distance is contrary to that of the Nd–(O, F) one. The Nd–(O, F)–Nd angle is decreasing with pressure for the LPT phase and then is increasing at the transitional region, while the As–Fe–As angle is increasing with pressure below 13.5 GPa. For the HPT phase, both As–Fe–As and Nd–(O, F)–Nd angles are decreasing with increasing pressure.

The structural evolution of the Fe_2As_2 layer and $\text{Nd}_2(\text{O}, \text{F})_2$ layer with pressure are clearly different. For the Fe_2As_2 layer, the pressure dependences of the Fe–As distance and As–Fe–As angle of the HPT phase are contrary to those of the LPT phase. For the $\text{Nd}_2(\text{O}, \text{F})_2$ layer, however, the relationships of the Nd–(O, F) distance and Nd–(O, F)–Nd angle versus pressure of the HPT phase are similar to those of the LPT phase. In the Fe_2As_2 layer, Fe and As ions could constitute an FeAs_4 tetrahedron because of the smaller ionic radius of Fe compared with As.¹¹ At ambient pressure, the FeAs_4 tetrahedron is close to an ideal one with the As–Fe–As angle at $110.5(1)^\circ$. According to the As–Fe–As angle evolution with pressure, the distorted degree of the FeAs_4 tetrahedron is increasing below 13.5 GPa and then is decreasing under higher pressure. When the pressure is higher than 13.5 GPa, the Fe–As distance enlarges with pressure to reduce the distorted degree of the FeAs_4 tetrahedron for the HPT phase, in which the As–Fe–As angle drops to $112.2(4)^\circ$ at 17.7 GPa from the value $116.0(4)^\circ$ at

13.5 GPa. In the $\text{Nd}_2(\text{O}, \text{F})_2$ layer, Nd and (O, F) ions do not form a tetrahedron. Instead, Nd ions have eight ligands including four (O, F) and four As ions, which form a distorted double tetraprism with a large Nd–As distance. The different coordination types from different ionic types contribute to the dissimilar compression behavior between the Fe_2As_2 and $\text{Nd}_2(\text{O}, \text{F})_2$ layers.

Upon compression, a relative displacement increasing between Nd and As ions was observed in $\text{Nd}(\text{O}_{0.88}\text{F}_{0.12})\text{FeAs}$ due to the mismatch of the two ions and the interspace between the Fe_2As_2 layer and $\text{Nd}_2(\text{O}, \text{F})_2$ layer. This is a plausible reason for the isostructural phase transition at ~ 10 GPa and the enlargement of the FeAs_4 tetrahedron for the HPT phase. Further study on the mechanism of pressure-induced phase transition requires *in situ* high-pressure experiments and theoretical calculations on these iron-based superconductors.

Based on the reported positive pressure dependence of T_c in the F-doped LaOFeAs case,⁶ the different microstructural evolution trend of the LPT and HPT phases of $\text{Nd}(\text{O}_{0.88}\text{F}_{0.12})\text{FeAs}$ under compression found in this communication implies that the T_c of $\text{Nd}(\text{O}_{0.88}\text{F}_{0.12})\text{FeAs}$ will reach its maximum before phase transition at ~ 10 GPa and then will have a negative pressure dependence for the HPT phase. Work is in progress to investigate in greater detail the pressure dependence of T_c in this sample from *in situ* electrical resistance measurements under pressure. Indeed, the preliminary results indicate that the T_c of the high pressure phase decreases with increasing pressure.

In summary, the discovery of the isostructural phase transition in iron-based superconductor $\text{Nd}(\text{O}_{0.88}\text{F}_{0.12})\text{FeAs}$ under high pressure was reported in this communication. Notably, this kind of phase transition may be more common in these iron-based superconductors. Moreover, the results of atomic structure evolution upon compression for a high pressure phase provide the essential structure information for the origin of the pressure dependence of its T_c . Finally, the high pressure phase found in this work has a negative pressure dependence for its T_c , which offers new insight to design and synthesize other element doping superconducting systems with a reversal “chemical internal pressure effect” similar to that for this system.

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