Low-temperature lattice structure anomaly in the $LaFeAsO_{0.93}F_{0.07}$ superconductor by x-ray absorption spectroscopy: Evidence for a strong electron-phonon interaction

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(Received 14 October 2008; published 24 December 2008)

The local lattice structure in $LaFeAsO_{1-x}F_x$ superconductors is studied by extended x-ray absorption fine-structure measurements. An anomalous upturn of the mean-square relative displacement of the Fe-As bond is detected below ~70 K as electron carriers are introduced, reflecting the occurrence of Fe-As bond local lattice fluctuation. Similar to that in cuprates, this lattice fluctuation exhibits an abrupt depression at the onset superconducting transition temperature. The results indicate that strong electron-lattice interaction is involved in the superconducting transition in oxypcnictide superconductors, putting a strict limitation on possible theoretical models.

DOI: 10.1103/PhysRevB.78.214513 PACS number(s): 74.81.−g, 61.05.cj, 64.60.−i, 74.72.Dn

I. INTRODUCTION

The recently discovered high-temperature superconductivity in fluorine-doped LaFeAsO has stirred new interest in the research of high-T_c superconductors[1] outside of the cuprate family.[2] Replacing oxygen by fluorine introduces charge carriers which is eventually transferred from the La-O(F) charge reservoir layer to the Fe-As conductive layer. Superconductivity emerges as the F-doping concentration is higher than 5%. Subsequent research suggests that replacing the lanthanum in LaFeAsO with other rare-earth elements such as cerium, samarium, neodymium, and praseodymium leads to superconductors with elevated critical temperature up to 55 K.[3–5]

The first and most important question about the LaFeAsO-based superconducting system is whether it has similar mechanism for superconductivity with cuprate superconductors or not. In cuprate superconductors, the antiferromagnetic properties of the parent compounds have provoked scenarios of purely electronically driven superconductivity, where lattice effects are mostly ignored.[6] On the other hand, various anomalous lattice effects have recently been observed in cuprates which closely correlate with the onset of superconducting transition, suggesting that lattice effects play an important microscopic role in the superconducting pairing mechanism.[7–12] In particular, extended x-ray absorption fine-structure (EXAFS) measurements have shown that doping causes local lattice distortion which occurs well above T_c.[7,8,11] Correlating data from inelastic neutron scattering and inelastic x-ray scattering, isotope effects, Raman spectroscopy, infrared-absorption spectroscopy, and femtosecond optical spectroscopy have been proving that the anomalous local lattice distortion observed by EXAFS measurements is correlated with the opening of pseudogap and the formation of polarons.[13–15] The change in dynamics, which is observed across the superconducting transition temperature, indicates an intimate link of the dynamics of these polarons with the mechanism of high-temperature superconductivity.[13] In LaFeAsO-based superconductors, evidence of pseudogap evolutions similar to the high-T_c cuprates has been reported.[16,17] However, there is a lack of experimental data on the lattice effects. In order to find the appropriate mechanism, lattice effects can provide key information. In this paper we present results from Fe and As K edge EXAFS measurements indicating that local Fe-As lattice fluctuation occurs well above T_c. Similar to that in cuprates, this local lattice fluctuation is closely correlated with the onset of superconducting transition, indicating that the local lattice fluctuation is involved in the superconducting coherence in both systems.

II. EXPERIMENT

Polycrystalline samples $LaFeAsO_{1-x}F_x$ ($x=0,0.07$) were prepared by solid-state synthesis as described elsewhere.[1] EXAFS measurements were performed at BL13B at Photon Factory, Tsukuba. Powder samples were mounted on an aluminum holder and attached to a closed-cycle helium refrigerator. The holder rotates on a high-precision goniometer (Huber 420) to change the incidence angle. A state-of-the-art Ge pixel array detector (PAD) with 100 segments was used in order to gain high throughput and energy resolution. The detailed description of PAD apparatus was reported elsewhere.[18] The experimental EXAFS, $\chi(k)$, was analyzed by the use of the IFEFFIT analysis package. The fitting to experimental data was performed in both R space and k space, and the uncertainties were determined from a reduced χ^2 using standard techniques of error analysis.

III. RESULTS AND DISCUSSION

The Fe and As K-edge EXAFS oscillations for $LaFeAsO_{1-x}F_x$ ($x=0,0.07$) are measured from 5 and 300 K. The EXAFS oscillations at the Fe and As K edges are converted into k space. Typical EXAFS oscillations are shown in Fig. 1(a) for the $x=0.07$ sample at the Fe K edge (lower panel) and the As K edge (upper panel). The Fourier-transform spectra at 20 K for the Fe and As K edges are shown as black curves in Fig. 1(b). The positions of the coordination atoms of the Fe and As atoms are also indicated

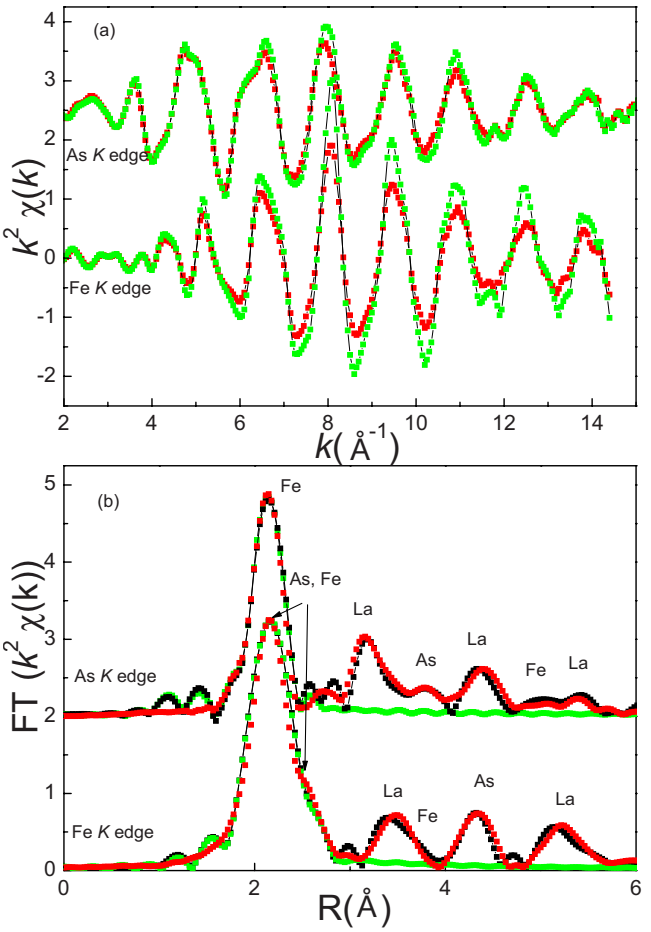

FIG. 1. (Color online) (a) Representative experimental EXAFS oscillations at Fe *K* edge (lower panel) and As *K* edge (upper panel) shown in *k* space. The red curves are taken at 20 K and the green curves at 300 K. The As *K* edge data are shifted by 2.5. (b) The complex Fourier-transform $\{|\mathrm{FT}[k^2\chi(k)]|\}$ magnitude functions of EXAFS oscillations at Fe and As *K* edges are shown as the black symbols. The simulated RDFs around Fe and As atoms are shown as the red curves. For Fe *K* edge, a comparison with the fitting curve using two shells (the first-shell Fe-As and second-shell Fe-Fe, green symbols) is given. For As *K* edge, a comparison with the fitting curve including As-Fe shell (green symbols) is given.

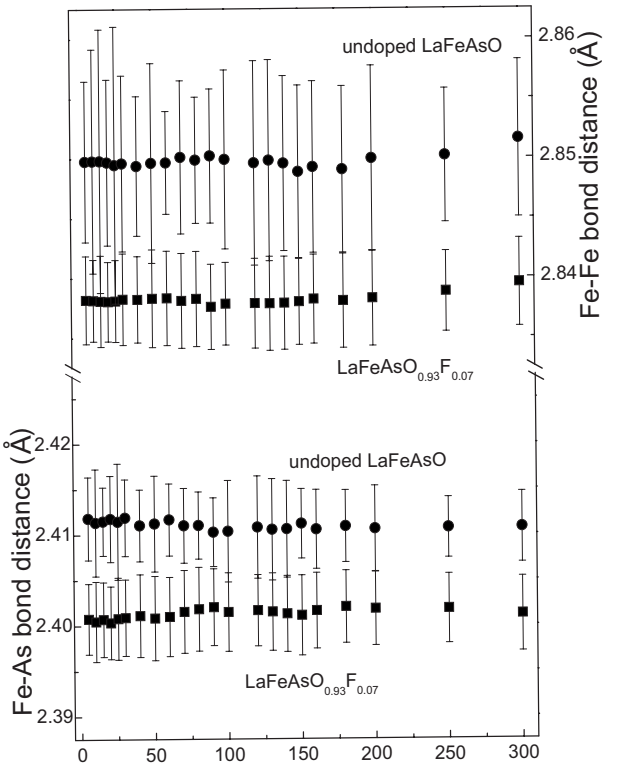

FIG. 2. Temperature dependence of Fe-As bond distances and Fe-Fe bond distances for undoped LaFeAsO and $LaFeAsO_{0.93}F_{0.07}$ samples. The error bars are also indicated which are taken from the quantitative uncertainty value from the EXAFS analysis.

which are slightly shifted due to the phase-shift effect. The atomic radial distribution function (RDF) around Fe and As atoms is simulated using FEFF7. In the simulation the structural parameters determined by Rietveld analysis are used and all possible scattering paths (including single-scattering and multiple-scattering paths) are included.[19] The simulated RDFs around Fe and As atoms are shown as the red curves in Fig. 1(b), which can reproduce all the main peaks in the experimental Fourier-transform spectra.

In the EXAFS data analysis process, coordination numbers are set to the values dictated by the average structure. For the Fe *K* edge, we fit the experimental data by including both the nearest-neighboring Fe-As and the next-nearest-neighboring Fe-Fe correlations. Typical fitting result is shown as the green curve in Fig. 1(b). It can be seen that the fitting curve can well reproduce the experimental data at $1.4 \leq R \leq 3.1$ Å range. For the As *K* edge, we fit the experimental data using a single-Gaussian As-Fe RDF. The result is shown in Fig. 1(b) as the green curve.

Figure 2 gives the temperature dependence of the Fe-As bond distances and the Fe-Fe bond distances for both samples. It is obvious that the F doping leads to a shrink of Fe-As bond distance. The slight decrease in Fe-As bond distance induced by F doping has been detected by synchrotron x-ray diffraction measurement.[19] The contraction of the Fe-As bond distance with F doping indicates that the bonding between Fe and As atoms strengthens covalent bonding. The contraction of the Fe-As bond distance is reminiscent of the shortening of the Cu-O bond distance in $La_{2-x}Sr_xCuO_4$ as charge carriers are introduced into the CuO_2 plane. In cuprate superconductors, the Cu-O orbital hybridization is strengthened with the shortening of the Cu-O bond. According to this fact, we can also suggest that the hybridization between the Fe 3*d* orbitals and the As 4*p* orbitals would be strengthened. The strengthening of the Fe-As orbital hybridization favors the flow of charge carrier in the Fe-As conductive layer. It is also obvious that the Fe-Fe bond distance is shortened in the F-doped sample, which indicates a decrease in the unit-cell volume. We notice a slight increase in the Fe-Fe bond distance below ~150 K in undoped LaFeAsO, which is consistent with the tetragonal to orthorhombic phase transition.[19] In F-doped sample, such a phase transition disappears. The temperature dependence of Fe-Fe bond distance for the F-doped sample shows little change in the whole temperature region.

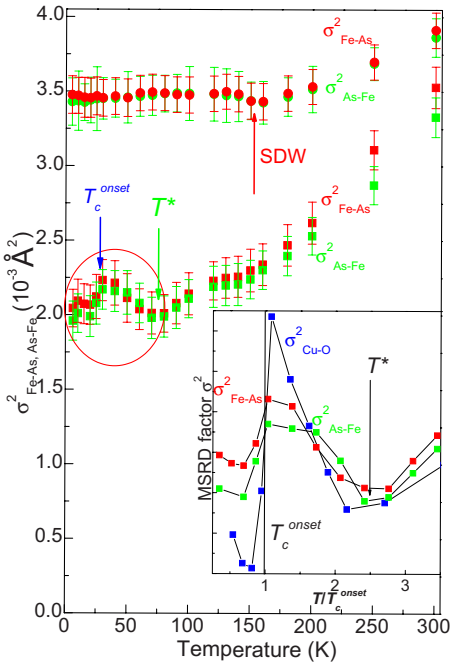

FIG. 3. (Color online) Temperature dependence of Fe-As bond mean-square relative displacements for $LaFeAsO_{0.93}F_{0.07}$ (squares) and LaFeAsO (circles). The red symbols are derived from Fe K edge EXAFS measurements and the green symbols are derived from As K edge EXAFS measurements. The inset shows an enlarged view of low-temperature (<100 K) MSRD for the $LaFeAsO_{0.93}F_{0.07}$ sample plotted as the function of normalized temperature (T/T_c^{onset}) and the comparison with the $La_{1.85}Sr_{0.15}CuO_4$ sample.

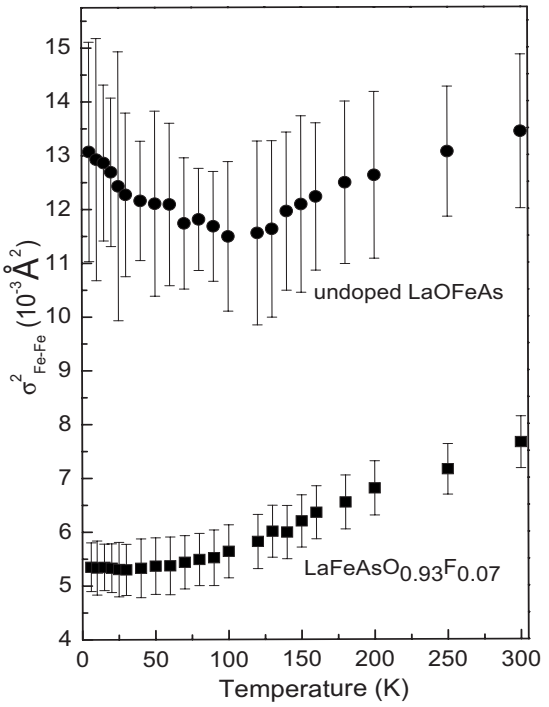

FIG. 4. Temperature dependence of Fe-Fe bond mean-square relative displacements for $LaFeAsO_{0.93}F_{0.07}$ (squares) and LaFeAsO (circles).

In Fig. 3 we plot the temperature dependence of the mean-square relative displacement (MSRD) for the nearest-neighboring Fe-As shell derived from both Fe K edge EXAFS (labeled as $\sigma^2_{\text{Fe-As}}$) and As K edge EXAFS (labeled as $\sigma^2_{\text{As-Fe}}$) for the $LaFeAsO_{1-x}F_x$ ($x=0.07$) sample together with that of the undoped LaFeAsO sample. As expected, the results give nearly the same $\sigma^2_{\text{Fe-As}}$ and $\sigma^2_{\text{As-Fe}}$ values at each temperature. At $T \geq 150$ K range, the $\sigma^2_{\text{Fe-As}}$ value decreases with decreasing temperature for both samples consistent with the noncorrelated Debye-type behavior. However, below 150 K the temperature dependence of $\sigma^2_{\text{Fe-As}}$ exhibits distinctly different behavior. For undoped LaFeAsO, the $\sigma^2_{\text{Fe-As}}$ value slightly increases with further decreasing temperature, which is related to the so-called spin-density-wave (SDW) transition.[19,20] For the F-doped sample, the increase in $\sigma^2_{\text{Fe-As}}$ at about 150 K is well suppressed. The $\sigma^2_{\text{Fe-As}}$ decreases further with decreasing temperature. Significantly, an anomalous upturn of $\sigma^2_{\text{Fe-As}}$ appears at $T \leq 70$ K. This anomaly occurs only in F-doped sample while no such anomaly is detected in undoped parent compound. This anomaly is accompanied by a sharp drop at the temperature where the onset of superconducting transition occurs ($T_c^{\text{onset}} \sim 29$ K). Similar anomalous behavior was previously found in $La_{2-x}Sr_xCuO_4$ samples where an upturn of $\sigma^2_{\text{Cu-O}}$ (mean-square relative displacement of the in-plane Cu-O bond) occurs at $T \leq 80$ K which is also accompanied by a sharp decrease in T_c^{onset}.[11] In order to clearly see the low-temperature local lattice instability and its relation to the T_c^{onset} value, we plot in the inset of Fig. 3 the normalized temperature (T/T_c^{onset}) dependence of the mean-square relative displacements for both $LaFeAsO_{0.93}F_{0.07}$ and $La_{1.85}Sr_{0.15}CuO_4$ samples. It can be seen that a sharp decrease in the mean-square relative displacement occurs exactly at T_c^{onset} in both systems. This result indicates that the local lattice instability might play an important role in the superconducting coherence in both systems.

In order to reveal whether or not this anomaly involves the Fe-Fe bond, we studied the temperature dependence of mean-square relative displacement for the Fe-Fe bond ($\sigma^2_{\text{Fe-Fe}}$) by fitting the Fe K edge EXAFS data including the multiple-scattering paths. Figure 4 shows the temperature dependence of $\sigma^2_{\text{Fe-Fe}}$ for the $LaFeAsO_{1-x}F_x$ ($x=0,0.07$) samples. The temperature dependence of $\sigma^2_{\text{Fe-Fe}}$ for the undoped LaFeAsO sample exhibits a slight increase below ~140 K, which may relate to the SDW transition.[19] It can be clearly seen that there is no anomaly in the mean-square relative displacement of the Fe-Fe bond in $x=0.07$ sample. Thus we conclude that the anomaly in $\sigma^2_{\text{Fe-As}}$ below 70 K in F-doped sample involves only the Fe-As bond. Comparing the mean-square relative displacements of the Fe-Fe bond in $LaFeAsO_{1-x}F_x$, one can find a rather strong F-doping effect, i.e., the displacement of Fe-Fe bond is strongly decreased upon F doping. The temperature dependence of $\sigma^2_{\text{Fe-As}}$ shows a complicated behavior related to a magnetic phase transition; that is, an increase in $\sigma^2_{\text{Fe-As}}$ occurs below 140 K in undoped LaFeAsO. In $LaFeAsO_{0.93}F_{0.07}$, the temperature dependence of $\sigma^2_{\text{Fe-As}}$ shows no anomaly in the whole temperature region consistent with the disappearance of phase transition in F-doped samples.

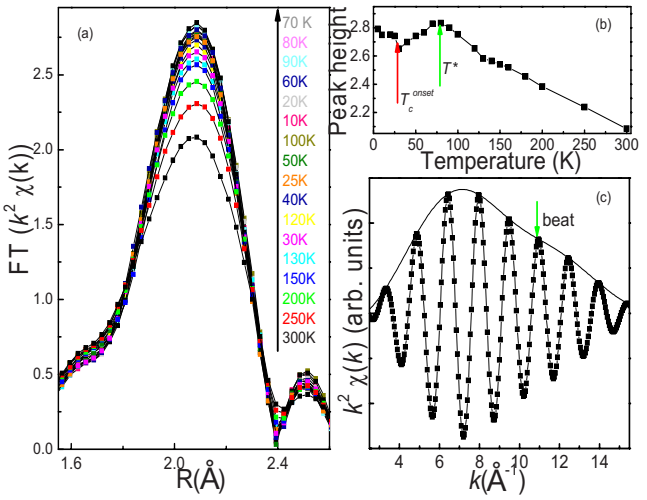

FIG. 5. (Color online) (a) The first-shell As-Fe bond radial distribution function for $LaFeAsO_{0.93}F_{0.07}$ sample from 300 to 10 K. (b) The absolute magnitude of the As-Fe peak taken from (a). (c) Fourier-filtered EXAFS oscillation and amplitude of the As-Fe bond at 40 K. A beat feature is built at about $k \sim 10.5$ Å^{-1}.

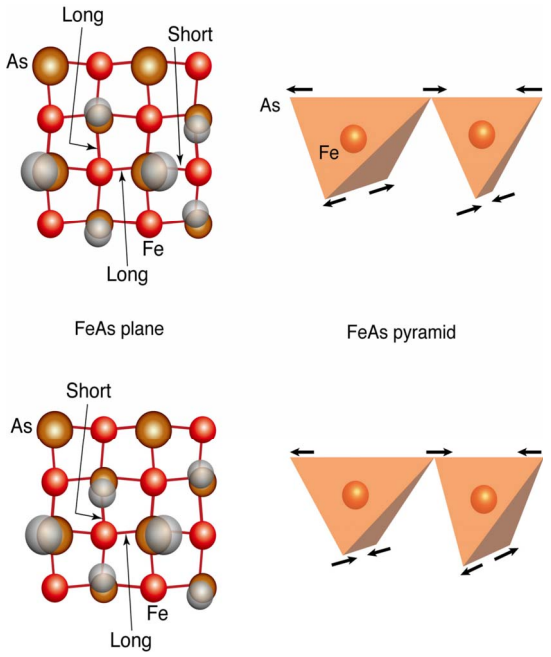

FIG. 6. (Color online) Two crystal structure models show the possible Fe-As bond distortion in $LaFeAsO_{0.93}F_{0.07}$.

To our knowledge macroscopic structural study on LaFeAsO-based system did not explore any structural transition near 70 K. However, in cuprate superconductors, a similar upturn of mean-square relative displacement of the in-plane Cu-O bond has been discovered, which is related to the splitting of the Cu-O bonds into elongated and shortened Cu-O bond distances.[7] Based on this fact, we suggest that a bond splitting of the Fe-As bond in F-doped LaFeAsO system also occurs below ~70 K. Consequently, some As ions are shifted forward or backward the adjacent Fe ions. This bond splitting would lead to a decrease in the magnitude of the Fe-As (As-Fe) RDF peak. In Fig. 5(a) we plot the Fourier-transform magnitude of the first-shell As-Fe bond. In order to compare the magnitude As-Fe peak quantitatively, we plot the absolute magnitude of the As-Fe peak in Fig. 5(b). The magnitude of the As-Fe peak increases with decreasing temperature which is followed by a decrease below 70 K consistent with the As-Fe bond splitting model.

In order to quantitatively determine the length scale of the Fe-As bond splitting, we plot the Fourier-filtered (backtransforming over $1.4 < R < 2.6$ Å) EXAFS oscillation and amplitude of the first-shell As-Fe bond at 40 K. The plot is shown in Fig. 5(c). From the EXAFS oscillation we notice that the local minimum in the amplitude and the irregularity in the phase near 10.5 Å^{-1} constitute a "beat," which signifies the presence of two As-Fe bond distances. Using the relation $\Delta R = \pi/2k$ between the separation of the two shells and the position of the beat, the As-Fe distances are determined to differ by ~0.15 Å. We notice that the beat feature is very weak, which possibly comes from two facts: one is that only small amount of Fe-As bonds is split while the other Fe-As bonds keep undistorted; another reason could be the unpolarized property of the powder sample used in the EXAFS measurements.

In doped cuprates, lattice instability is observed as local distortions (creation of elongated and shortened bonds) probed by EXAFS which reflects the presence of strong hole-lattice interaction.[7–11] In case of doped LaFeAsO system, similar behavior is found in both As and Fe K edge EXAFSs. We note that this distortion is of electronic origin and is different from crystallographic phase transition, as it is observed only after carrier doping at low temperature. The anomalous change below 70 K is explained using a local lattice distortion model having equal number of elongated and shortened Fe-As bonds separated by about 0.15 Å. Among the candidates of distortion models characterized by the elongated and shortened Fe-As bonds, we consider two cases in Fig. 6 which illustrates the distortion in the FeAs layer in F-doped LaFeAsO. The left panels show displacement of As atoms (gray ball) tetrahedrally coordinating with Fe atoms. In the right, fourfold coordination of Fe atoms is represented by pyramids where each corner indicates the location of As atom and the direction of displacement is indicated by an arrow. In the upper model all four Fe-As bonds in the same unit elongate and the shortening of bonds occurs in the adjacent unit, while in the lower model the elongation and shortening occur in the same unit. In analogy to doped cuprates, the former and latter models correspond to breezing[21] and Q_2 (Refs. 22 and 23) distortions proposed for $La_{1.85}Sr_{0.15}CuO_4$, respectively. In the LaFeAsO system, those two possible distortions may account for the detected distortion.

We now discuss the implications of the present results. First, the temperature dependence of mean-square relative displacement of the Fe-As bond shows remarkable similarity with that of cuprate superconductors.[8,11] That is, a significant upturn in the temperature dependence of $\sigma^2_{\text{Fe-As}}$ in F-doped LaFeAsO (or $\sigma^2_{\text{Cu-O}}$ in Sr-doped La_2CuO_4) occurs at a characteristic temperature T^*, which is related to the opening of pseudogap in cuprates.[9,13,24,25] In LaFeAsO(F) system, the opening of pseudogap was recently reported[16,17] consistent

with the observation of the onset of the upturn of $\sigma^2_{\text{Fe-As}}$. We interpret this anomaly as a signature of lattice instability that indicates the formation of polarons. Second, the increase in mean-square relative displacement continues until a sudden drop occurs at the onset of superconducting transition. The plot of mean-square relative displacement vs normalized temperature (T/T_c^{onset}) clearly indicates that the mean-square relative displacement exhibits a large decrease in the onset superconducting transition temperature in both Fe-based and cuprate superconductors, which indicates that the lattice effects might be important in both systems. However, whether or not the superconducting mechanism in these systems is driven by electron-lattice interaction needs further experimental and theoretical studies.

IV. CONCLUSION

In conclusion, we provide evidence from EXAFS measurements that local lattice instability occurs in F-doped LaFeAsO superconductor similar to that in cuprate superconductors. This local lattice distortion may reveal certain polaron formation well above T_c. The mean-square relative displacements of the Fe-As bond exhibit a sharp drop at the onset transition temperature, indicating the lattice effects might be important in this system.

ACKNOWLEDGMENTS

The authors express their greatest thanks to H. Koizumi for inspiring discussions. The EXAFS experiments were conducted under the Proposal No. 2007G071 at Photon Factory.

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