Local lattice response in LaFeAsO$_{0.93}$F$_{0.07}$ probed by x-ray absorption spectroscopy: Evidence for carrier-induced lattice distortion

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Abstract. Carrier-induced lattice distortion (signature of strong electron-lattice interaction) in oxypnictide superconductors is found by a local structural study using extended x-ray absorption fine structure (EXAFS). Local lattice instability (polaron formation) is detected as an anomalous upturn of the mean-square relative displacement for the nearest neighbor distances (Fe-As) in LaFeAsO$_{1-x}$F$_x$ ($x=0.07$), implying a local lattice distortion that develops below 70 K and disappears at the superconducting critical temperature. Comparing the results with the lattice response in cuprate superconductors, intimate correlation between local lattice mode and superconductivity is revealed. The results suggest that strong electron-lattice interaction is present as a common ingredient in the microscopic mechanism of superconducting transition.

1. Introduction

Although more than 20 years have passed since the discovery of high temperature superconductivity (HTSC) [1], the microscopic mechanism is still far from convergence, despite intensive research efforts. Recently reported superconductivity in fluorine-doped LaFeAsO (LFAO), a typical oxypnictide [2], however, has revived keen interests in the research of HTSC mechanism. Replacing oxygen by fluorine or oxygen vacancy control introduces charge (electrons) carriers which are transferred from the La-O(F) “charge reservoir” layer to the Fe-As conducting layer. Superconductivity emerges as the F-doping concentration exceeds about 5% close to the antiferromagnetic (AFM) phase. The mechanism of superconductivity is still a puzzling question, allowing diversity and contradictions in theoretical interpretations; a conventional phonon mechanism is unlikely as the DFT calculations indicated a weak electron-phonon coupling, yet, the purely electronic mechanism [3] is also less likely than the case of cuprates [4] as the onsite correlation is not large ($U\sim5eV$) [5].

A polaron is formed when an electron is strongly coupled to the atoms in a crystal. In manganites, coherent polaron condensation is believed to be the driving mechanism of colossal magnetoresistance (CMR) phenomena [6]. Here we describe lattice effects in oxypnictide [7] studied by means of a local probe, extended x-ray absorption fine structure (EXAFS) compared with the results for La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) [8]. Unusual carrier-induced local displacement found for LSCO was interpreted as a nanometer-scale self-organization (stripe) [9]. We take local lattice distortion as a signature of polarons [7] as predicted by theoretical models [10-13].

2. Experimental
Here we use segmented fluorescence monitoring to discriminate signal from noise. A novel germanium 100-pixel array detector (PAD) developed for this purpose is used collecting signals over a segmented solid angle [14]. All EXAFS data were recorded for polycrystalline LFAO(F) samples at the Photon Factory. The energy and maximum electron current of storage ring were 2.5 GeV and 400–500 mA, respectively. A directly water-cooled silicon (111) double-crystal monochromator was used, covering the energy range 4–25 keV. The energy resolution was better than 2 eV at 9 keV, calibrated from the near-edge features of copper metal at the Fermi energy, $E_f$ (8.9803 keV). Single crystal sample was attached to an aluminum holder with a strain-free glue and cooled down using a closed-cycle He refrigerator (cooling power 2 W at 20 K, stability ±0.1 K) on a high-precision goniometer (Huber 420). As a typical magnitude of normalized EXAFS oscillations is several %, each data set must have photon statistics better than 0.1% or 10^6 photons. For reliable data taking, non-statistic (systematic) error should be minimized for which segmented x-ray detection and repeated scans are useful. Fluorescence yield spectra for all channels of PAD were monitored in real time and the effect of scattering was inspected. By choosing a proper incidence angle, the substrate scattering effect was completely removed. A typical LSCO bulk single crystal grown by TSFZ method was 2 mm x 2 mm x 1 mm in dimension [8]. Using a closed cycle He refrigerator, sample temperature is controlled to a temperature error within 1 K. Polycrystalline samples LaFeAsO$_{1-x}$F$_x$ ($x$=0, 0.07) were prepared by solid-state synthesis as described elsewhere [2] and unpolarized EXAFS data were recorded at various temperatures [7].

3. Results and Discussion

Parent LFAO has a double layer structure where the conducting FeAs layer is adjacent to the reservoir LaO layer in close similarity with LSCO where more two-dimensional CuO$_2$ and LaO planes play their roles [1, 2]. In the FeAs layer, Fe and As atoms are tetrahedrally coordinated each other resulting in a more three-dimensional network while in LSCO, copper atoms are four-fold coordinated by oxygen atoms within the plane and two apical oxygen atoms along the c-axis. As EXAFS is an “incoherent” (in the sense of much faster time scale than lattice vibrations) local probe, local distortions of near neighbor atoms with static and dynamic nature are sensitively detected as an interference (beat) of $k$-dependent oscillations ($k <15$ Å$^{-1}$) where $k$ is a wave vector of photoelectron. Complex Fourier transform (FT) of EXAFS oscillations relates to the radial distribution function (RDF) with a correction of phase-shift (Fig.1). Experimental EXAFS oscillations around Fe and As atoms are compared to those simulated by FEFF7 [15] based on the structural parameters determined by Rietveld analysis and all possible scattering paths including single-scattering and multiple-scattering paths [7].

Contributions of the first nearest neighbor shell are back Fourier transformed into $k$-space and analyzed, providing the Fe-As distance and mean square relative displacement (MSRD) $\sigma_{Fe-As}^2$. In the inset, the Fe-As displacement $\sigma_{Fe-As}^2$ in doped LFAO is compared with that of in-plane $\sigma_{CuO}^2$ in LSCO as a function of normalized temperature. Carrier doping creates a remarkable effect on the Fe-As MSRD, i.e., the Fe-As MSRD in undoped sample shows no anomaly below the spin-density-wave (SDW) transition temperature [16] whereas lattice instability $\sigma_{Fe-As}^2$ variation with temperature) newly arises as magnetic instability is suppressed in the F-doped sample.

Here lattice instability is defined as usual behavior of $\sigma_{Fe-As}^2$, a deviation from a smooth non-correlated Debye-like function, which appears as carriers are doped. The increase of $\sigma_{Fe-As}^2$ is usually taken as an increase of disorder but here it describes the interference (beat) of bonds having different (short and long) bond lengths. Elongation of bonds is an outcome of local distortion (polaron formation). The inset of Fig. 2 shows that a sharp drop of $\sigma_{Fe-As}^2$ occurs at $T_c$ onset in LFAO(F) and LSCO systems, indicating that local lattice response directly relates to the microscopic mechanism of superconductivity (development of coherence) while the onset of polaron formation coincides with $T^*=$70-80 K.
Fig. 1. Fourier transform magnitude functions for the Fe K- and As K-edge EXAFS for LaFeAsO$_{1-x}$F$_x$ ($x=0.07$). Red marks indicate the simulated curve and black marks represent the experimental data. Blue marks denote the nearest neighbor contribution, taken from ref. 7.

Fig. 2 Temperature dependence of the Fe-As bond mean-square relative displacements for LaFeAsO$_{0.93}$F$_{0.07}$ (squares) and LaFeAsO (circles). The red and green symbols denote the results for the Fe K edge and the As K edge EXAFS data respectively, taken from ref. 7. The inset shows an enlarged view plotted as the function of normalized temperature ($T/T_{c\text{onset}}$).

We take this lattice instability starting at about $1.5 T_c$ ($T^* \sim 1.5 T_c$) as a signature of polaron, rather than charged magnetic domains with incommensurate spacings (stripes), although nanoscale polarons have strong similarity with stripes in cuprates as the underlying nature has a similar origin (large Hubbard U). Let us discuss implications of lattice fluctuation. It may arise from softening of LO phonons [17]. Bond-stretching-type LO phonon mode strongly couples with doped holes as a result of $d$-$p$ mixing or Cu-O charge transfer and spin correlation. Femtosecond quasi-particle (QP) lifetime experiments indicated phonon-assisted charge transfer and charge inhomogeneity [18]. Nanometer-scale charge inhomogeneity is one of the fundamental properties of cuprates. Although polarons are expected localized in nature but tunneling [13, 18] or percolation [19] may results in extended states with a longer QP lifetime. Here we only note that the two polaron models with different types of in-plane modes (pseudo JT vs. Qz-type JT) are consistent with the experimental observation. The former model (pseudo JT distortions with the two CuO$_6$ units) gives $R=1.82$ Å and 1.96 Å in good agreement with the EXAFS results [20].

4. Conclusion

The local lattice of LaFeAsO$_{1-x}$F$_x$ superconductors was studied by EXAFS. We find an anomalous upturn of the mean-square relative displacement of the nearest neighbor (Fe-As) distance below $T^*$ as electron carriers are introduced. The Fe-As local lattice fluctuation reveals the formation of two
distinct bond lengths $R_1$ and $R_2$ where $\Delta R = R_1 - R_2 \sim 0.1\text{Å}$. The onset of lattice effects coincides with the opening of pseudogap. The results indicate that oxynitride superconductors have a signature of polaron formation similar to that of HTSC cuprates. Whether polaron works to perturb spin configurations leading to spin vortices growing into spin loop current [13] or it enhances strong coupling of spin, charge and lattice [12] is an open question.

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