Crystallographic phase transition and high-$T_c$ superconductivity in LaFeAsO:F

T Nomura$^1$, S W Kim$^2$, Y Kamihara$^3$, M Hirano$^3$, P V Sushko$^{4,5}$, K Kato$^6$, M Takata$^6$, A L Shluger$^{4,5}$ and H Hosono$^{1,3,7,8}$

1 Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan
2 Secure Materials Center, Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan
3 ERATO-SORST, JST, in Frontier Research Center, Tokyo Institute of Technology, Yokohama 226-8503, Japan
4 London Center for Nanotechnology and Department of Physics and Astronomy, University of College London, Gower Street, London WC1E 6BT, UK
5 WPI Advanced Institute for Nanotechnology and Department of Physics, Tohoku University, Sendai 980-8577, Japan
6 RIKEN SPring-8 Center, Sayo-gun, Hyogo 679-5148, Japan
7 Frontier Research Center, Tokyo Institute of Technology, Yokohama 226-8503, Japan

E-mail: hosono@msl.titech.ac.jp

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Abstract

Undoped LaFeAsO, the parent compound of the newly found high-$T_c$ superconductor, exhibits a sharp decrease in the temperature-dependent resistivity at $\sim 160$ K. The anomaly can be suppressed by F doping with simultaneous appearance of superconductivity appears correspondingly, suggesting a close association of the anomaly with the superconductivity. We examined the crystal structures, magnetic properties and conductivity of undoped (normal conductor) and 14 at.% F-doped LaFeAsO ($T_c = 20$ K) by synchrotron x-ray diffraction (XRD), DC magnetic measurements, and ab initio calculations demonstrated that the anomaly is associated with a phase transition from tetragonal ($P4/\text{mmm}$) to orthorhombic (C$\text{mma}$) phases at $\sim 160$ K as well as an antiferromagnetic spin ordering transition at $\sim 140$ K. These transitions can be explained by spin configuration-dependent potential energy surfaces derived from the $ab$ initio calculations. The suppression of the transitions is ascribed to interrelated effects of geometric and electronic structural changes due to doping by F$^-$ ions.

Supplementary data are available from stacks.iop.org/SUST/21/125028

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The discovery of the high-$T_c$ superconductor LaFeAsO:F ($T_c = 26$ K) [1] has caused a recurrence of a new superconductivity boom similar to that caused by the finding of layered copper oxides. By either applying an external pressure of $\sim 3$ GPa [2] or replacing La with other rare-earth elements such as Sm [3], it has been possible to achieve $T_c$ beyond 55 K. The undoped LaFeAsO, which is the parent compound of the superconductor, is a member of the large LnTMPnO family, where Ln represents a 4f rare-earth element, M a transition-metal element with a more than half-filled 3d shell, and Pn a pnictogen element [4–8]. They have a common ZrCuSiAs-type crystal structure, belonging to the tetragonal $P4/\text{mmm}$ space group (figure 1(a)). The crystal is formed by an alternating stack of electrically charged LnO and $\text{T}_\text{MnPn}$ layers, and can also be represented as (LnO)$^{+2}$(T$_\text{M}$Pn)$^{-3}$. Several high-$T_c$ superconductors have also been discovered in other Fe-based analogous compounds including AFe$_2$As$_2$ (A is an alkali-earth-metal element such as Sr and Ba) [9, 10] and LiFeAs [11, 12]. This, together with the observed lower $T_c$ in LaFePO [13] and LaNiP(As)O ($T_c = 2–4$ K) [14–16],...
strongly suggests that the FeAs layers play a leading role in the appearance of the high $T_c$. This view is supported in part by theoretical analysis of the energy band structure based on density functional theory, revealing that five Fe 3d orbitals hybridized with As 4p contribute to the Fermi surface whereas the LaO, A and Li layers are blocking or spacer layers which act as a charge reservoir.

By changing the M element, the electronic and magnetic properties of the LnTmPnO compounds vary such that it is an antiferromagnetic insulator for $M = \text{Mn}$ [17], a superconductor for $M = \text{Fe}$ [1, 13, 18], a ferromagnetic metal for $M = \text{Co}$ [19], and again a superconductor for $M = \text{Ni}$ [14–16]. Further, the replacement of La with other 4f rare-earth elements having spin magnetic moments provides an additional magnetic interaction and facilitates antiferromagnetic ordering of the spins at low temperatures, which results in the coexistence of the superconductivity with antiferromagnetism for Ln = Ce, Nd, Pr and Sm, for instance; see [20]. More importantly, the substantial replacement of rare-earth elements with smaller ionic radii makes the lattice constants smaller and enables raising $T_c$ up to 56 K [21, 22].

High-$T_c$ superconductivity in LnFeAsO materials is realized upon doping with electrons; this can be achieved either by replacing $O^{2-}$ ions in the reservoir layers by $F^-$ ions or by forming oxygen vacancies [23, 24]. The doping can also be achieved by partially substituting Co for Fe in the FeAs layer [25, 26]. In contrast, AFe$_2$As$_2$ compounds can undergo the superconducting transition only after hole doping, which is achieved through the replacement of A elements with potassium.

Parent compounds of the high-$T_c$ superconductors show a rapid decrease in their electrical resistivity ($\rho$), which is clearly seen in the resistivity–temperature ($\rho$–$T$) curves with a kink at $\sim 160$ K ($T_{\text{nom}}$). This anomaly has been attributed to the combined effect of a crystallographic phase transition at $\sim 160$ K, and an antiferromagnetic ordering of the Fe spins at a slightly lower temperature of $\sim 140$ K [27–31]. Both transitions can be simultaneously suppressed by electron or hole doping, suggesting a close association of these phase transitions with the superconductivity observed in the doped compounds.

The Fe-based and the Cu-based superconductors have a common feature in that superconductivity is attained by providing itinerant electron or hole carriers to the two-dimensional transport layers containing 3d transition-metal elements. However, they differ distinctly from each other in that nine 3d electrons (one hole) are involved for Cu$^{2+}$, which forms an ionic bond with oxide ions, whereas six 3d electrons participate in the more complex interplay of Fe–Fe and Fe–As bonding.

In this study, we examine the crystal structures, magnetic properties and conductivity of undoped and 14 at.% F-doped LaFeAsO ($T_c = 20$ K) by Rietveld refinement of synchrotron x-ray diffraction (XRD) measurements, DC magnetic measurements, and $ab\ initio$ calculations. We demonstrate that the undoped LaFeAsO undergoes a phase transition from the tetragonal ($P4/nmm$) phase to the orthorhombic ($Cmma$) phase at $\sim 160$ K as well as an antiferromagnetic spin ordering transition at $\sim 140$ K. These transitions can be explained by spin configuration-dependent potential energy surfaces derived from the $ab\ initio$ calculations. Doping by F$^-$ ions in the LaO layers suppresses both transitions, which is ascribed to interrelated effects of geometric and electronic structural changes. Our results demonstrate how doping of electrons in the FeAs layer can increase the $T_c$, suggesting that the interplay between the charge and spin density fluctuations is responsible for the high $T_c$ in LaFeAsO:F.

2. Experimental and $ab\ initio$ calculation procedures

The undoped and 14% F-doped LaFeAsO samples employed in this study were prepared and the content of the F dopant in the samples was estimated by the same procedures as those described in previous studies [1, 2]. The synchrotron XRD measurements at various temperatures ranging from 300 to 25 K were conducted at the BL02B2 beamline of SPring-8, Japan, using a large Debye–Scherrer camera with a 286.5 mm camera radius [32]. The monochromatic x-ray wavelength was 0.05 nm and two-dimensional Debye–Scherrer images were detected by imaging plates. For measurements at low temperatures, capillaries containing ground samples were cooled using a dry N$_2$ or He gas-flow cooling device. The diffraction patterns ranging from 4$^\circ$ to 73$^\circ$ (N$_2$ gas cooling) or to 53$^\circ$ (He gas cooling) were obtained with a 0.01$^\circ$ step in 2$\theta$, which corresponds to 0.042 nm and 0.056 nm resolution, respectively. These diffraction patterns were then subjected to the Rietveld analysis. Electrical resistivity measurements with a DC four-probe technique were conducted at 1.8–300 K using a Quantum Design physical properties measurement system (PPMS) with a vibrating sample magnetometer (VSM) option at 1.9–370 K. The magnetization was measured using the same equipment under an external magnetic field up to 2 T. (More experimental information is available online at stacks.iop.org/SUST/21/125028.)

$ab\ initio$ calculations were carried out using density functional theory (DFT). We used the generalized gradient

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Figure 1. Crystal structure of LaFeAsO. (a) Schematic view of the crystal structure, demonstrating the layered structure. Distorted tetrahedrons of FeAs$_4$ are connected in an edge-sharing manner to form the FeAs layer. (b) Top view of the crystal structure from the $c$-direction. The inner square represents the unit cell in the tetragonal phase ($P4/nmm$). The outer square is that in the orthorhombic phase ($Cmma$). The unit cell of the orthorhombic phase rotates by 45$^\circ$ from that of the tetragonal phase and the lattice constants expands by $\sqrt{2}$, resulting in an increase in the number of chemical formula units in a unit cell from 2 to 4.
Figure 2. Electrical and magnetic properties of undoped and F-doped LaFeAsO. (a) Electrical resistivity ($\rho$) and magnetization per mol ($M_{\text{mol}}$) at a fixed magnetic field of 1 T as a function of temperature ($T$) for undoped LaFeAsO. (b) $M_{\text{mol}}$ as a function of magnetic field ($H$) for undoped LaFeAsO. (c) $\rho$ and $M_{\text{mol}}$ at a fixed $H$ of 1 T as a function of $T$ for 14% F-doped LaFeAsO. (d) $M_{\text{mol}}$ as a function of $H$ for 14% F-doped LaFeAsO. (e) Magnetic susceptibility ($\chi_{\text{mol}}$) as a function of $T$ in various F-doped LaFeAsO samples. Dotted lines represent estimated Pauli paramagnetic components, whereas dashed areas correspond to Curie–Weiss-like components. Data are rearranged from [31]. (f) Magnetic susceptibility ($\chi_{\text{mol}}$) as a function of F content ($x$) in LaFeAsO for several temperatures. The midpoint $T_c$ is also shown. Data are reproduced from [1].

approximation (GGA) density functional of Perdew and Wang (PW91) [33] and the projected augmented waves method [34], as implemented in the computer code VASP [35]. The plane-wave basis set cutoff energy of 600 eV was used. Supercells containing 8, 16, and 32 atoms were considered and the tested meshes containing 252, 132, and 36 $k$-points, respectively, were used for Brillouin zone integrations. The total energy was minimized with respect to the coordinates of all atoms. For the analysis of the electronic structure, the charge density was decomposed over the atom-centered spherical harmonics.

3. Results and discussion

3.1. Electrical and magnetic measurements

As reported previously [1], undoped samples exhibit an abrupt decrease in the resistivity at $\sim$160 K ($T_{\text{anom}}$) with a little hysteresis around $T_{\text{anom}}$, as shown in figure 2(a), but do not exhibit the superconducting transition down to 1.8 K. The magnetization ($M$) at a fixed magnetic field ($H$) of 1 T decreased gradually with lowering temperature from room temperature; the temperature dependence exhibited
isotropic atomic displacement parameter of each site. The increase sharply at \( T \approx 25 \) K. As shown in figure 2(b), the \( M-H \) curves above 25 K are almost straight whereas nonlinearity starts to appear at 10 K and becomes prominent at 1.9 K (figure 2(b)). The magnetic moment at \( H = 0 \) can be estimated to be \( \sim 4 \) emu/LaFeAsO or \( \sim 7 \times 10^{-5} \) \( \mu_B/\text{Fe} \) if one assumes the linear dependence of \( M \) on \( H \) in the \( H \) region of 1.5–2 T, but its origin remains unclear. The presence of magnetic impurity phases, such as FeAs, is a possible origin. (The contents of impurity phases estimated from the Rietveld analysis are shown in figure S1 (available at stacks.iop.org/SUST/21/125028)).

The anomaly at \( \sim 160 \) K disappears in 14% F-doped LaFeAsO, which undergoes a superconducting transition at \( \sim 20 \) K. The \( M \) value becomes negative in the superconducting state due to the Meissner effect (figure 2(c)). With increasing temperature it jumps to a fairly large value at a temperature just above \( T_c \), and then decreases monotonically with further increase of \( T \) and finally gradually increases again above room temperature, similar to the undoped sample. The \( M-H \) curves in the normal conducting state exhibit a straight line in the high-\( H \) region and they deviate a little down side from the line in the low-\( H \) region (figure 2(d)). Figure 2(e) summarizes the temperature-dependent magnetic susceptibilities as estimated from straight lines in figures 2(b) and (d), for LaFeAsO_{1-x}F_x with several \( x \) values. Further, comparison of the curves among the superconducting samples enables us to separate the temperature-sensitive Curie–Weiss-like (CW-like) component from the temperature-insensitive baseline in each sample. It is noteworthy that the CW-like component increases with the F content up to 5% and then decreases with further increase in the F content. This tendency is more clearly demonstrated in figure 2(f), where the \( \chi \) values are plotted against the value of \( x \) for three temperatures. It is, however, unlikely that this tendency is totally due to the magnetic impurity phases, such as FeAs, because the content of the dominant magnetic impurity phase of FeAs was observed to vary slightly with the F content. This tendency is not consistent with the almost constant value of \( T_c \) \( \sim 26 \) K over the F content of 5–11% [1]. In other words, the \( \chi \) value does not correlate with the generation of the superconductivity, provided that the contribution of the impurity phases to the observed \( \chi \) value is small.

### 3.2. Crystallographic analysis

All the diffraction peaks of the undoped sample at temperatures above \( T_{\text{anom}} \) and of the F-doped sample were assigned to the conventional ZrCuSiAs-type tetragonal crystal phase (space group \( P4/nmm \), except for the additional weak peaks, which were assigned to impurity phases. It is noteworthy that several peaks, including the 110, 111, 112, 211 and 322 reflections of the tetragonal phase, split into two when the temperature was lowered below \( T_{\text{anom}} \). The peak splitting is clearly demonstrated in figure 3(a), which shows the tetragonal 322 diffraction peak profiles at various temperatures around \( T_{\text{anom}} \). On the other hand, such splitting was never observed in the diffraction peaks for the 14% F-doped sample down to 25 K.

We analyzed these XRD patterns with a Rietveld analysis to refine the crystal structures of these samples. This analysis led us to the conclusion that the anomaly is associated with the crystallographic phase transition from the tetragonal (T) to orthorhombic (O) phase. The \( Cmma \) space group provided the smallest \( R_I \) and \( R_{wp} \) value of \( \sim 2.0\% \) and \( \sim 4.6\% \) for the O phase (the fitting results are available online). The resultant structure parameters are shown in tables 1 and 2. It is convenient to characterize the orthorhombic structure using a unit cell with \( a \) and \( b \) crystallographic axes rotated by 45° around the \( c \)-axis with respect to those of the original tetragonal cell. As a result, the number of the formula units in the orthorhombic unit cell (supercell) increases from 2 to 4, as illustrated in figure 1(b).

Cruz et al [28] have reported the crystal phase transition of undoped LaFeAsO, but they assigned the monoclinic \( P112/n \)

### Table 1. The structure parameters determined by Rietveld analysis for undoped LaFeAsO at (a) 300 K and (b) 120 K. \( B \) represents the isotropic atomic displacement parameter of each site.

| Atom | Site | Occ. | \( x \) | \( y \) | \( z \) | \( B (\text{Å}^2) \) |
|------|------|------|--------|--------|--------|----------------|
| (a) Undoped LaFeAsO at 300 K (\( P4/nmm, Z = 2 \)) |
| La   | 2c   | 1.000 | 0.25   | 0.25   | 0.141  | 0.476(4)  |
| Fe   | 2b   | 1.000 | 0.75   | 0.25   | 0.5    | 0.725(15) |
| As   | 2c   | 1.000 | 0.25   | 0.25   | 0.651  | 0.713(8)  |
| O    | 2a   | 1.000 | 0.75   | 0.25   | 0       | 0.67(7)   |
| (b) Undoped LaFeAsO at 120 K (\( Cmma, Z = 4 \)) |
| La   | 4g   | 1.000 | 0      | 0.25   | 0.141  | 0.275(3)  |
| Fe   | 4b   | 1.000 | 0.25   | 0      | 0.5    | 0.415(14) |
| As   | 4g   | 1.000 | 0      | 0.25   | 0.651  | 0.368(8)  |
| O    | 4a   | 1.000 | 0.25   | 0      | 0      | 0.39(6)   |
Figure 3. Crystallographic transition in LaFeAsO. (a) Diffraction profiles of tetragonal 322 reflections of undoped LaFeAsO for several temperatures ($T$) from 135 to 185 K. The split peaks below 165 K are indexed as 152 and 512 reflections in the orthorhombic symmetry. (b) $a$, $b$, and $c$-axis lengths of undoped and 14% F-doped LaFeAsO as a function of $T$. The axes of the undoped LaFeAsO are defined as the orthorhombic phase, and those in the 14% F-doped LaFeAsO are as the tetragonal phase. Closed and open circles are obtained in the heating process and the cooling process, respectively. (c) The temperature-dependent La–O, La–As and Fe–As bond lengths for undoped and 14% F-doped samples. Closed and open symbols in (b) and (c) represent cooling and heating processes, respectively.

Table 2. The structure parameters determined by Rietveld analysis for 14% F-doped LaFeAsO at (a) 300 K and (b) 120 K. Space group to the low-temperature phase. We checked our fitting results with the orthorhombic Cmma space group, but any peaks violating the extinction rule have not been found in the diffraction patterns down to 25 K. Structural studies of other LnFeAsO structures, such as CeFeAsO, NdFeAsO and SmFeAsO [20, 39–41], have also reported that the crystal symmetry of the low-temperature phase can be successfully assigned to the Cmma space group, citing our report. These results support our determination of the space group for the low-temperature phase.

The lattice parameters of the undoped LaFeAsO, shown in figure 3(b) as a function of $T$, confirm the existence of the crystallographic phase transition at $\sim$160 K ($T_{anom}$). On the other hand, the F-doped samples keep the tetragonal symmetry down to 25 K, although the lattice constants become smaller on lowering the temperature. The La–O, La–As and Fe–As bond lengths are shown in figure 3(c) for undoped and 14% F-doped samples as a function of $T$. (The Fe–O bond length is half of the $c$ crystallographic parameter; see figure 3(b).) All the bond lengths undergo small, but abrupt changes due to the phase transition. Further, it is noteworthy that, with the...
F doping, the Fe–As bond length changes only slightly (less than 0.1%), whereas the other distances change significantly: by comparison at 120 K, the La–O distance increases by ∼0.8%; on the other hand, the La–As and the Fe–O distances reduce by ∼1.4% and ∼0.6%, respectively. These results indicate that the F doping does not affect the geometry of the FeAs layer, in contrast to the significantly modified LaO layer. Additionally, the distance between the (LaO)\(^{+δ}\) and (FeAs)\(^{-δ}\) layers prominently decreases by F doping, suggesting that the electron doping of the FeAs layer enhances the polarization and the Coulomb interaction between the layers.

### 3.3. Ab initio calculations

To achieve further insight into the relation between the chemical composition, structure, magnetic properties and the superconductivity mechanism, we carried out ab initio calculations of both undoped and F-doped LaFeAsO using DFT and the PW91 density functional.

Our calculations suggest that the charge density distribution across the layers has (LaO)\(^{+δ}\)(FeAs)\(^{-δ}\) character with \(δ = 0.15\) per molecule. The density of states (DOS) near the Fermi energy (figure 5) is dominated by Fe 3d states with about 10% contribution of As 4p states. The total energy of the system depends on the configuration of the spins associated with Fe 3d electrons. For example, within the 16-atom \(\sqrt{2} \times \sqrt{2}\) supercell we calculated the total energies for four non-equivalent spin configurations: ferromagnetic (FM), and three antiferromagnetic (AF1, AF2a, AF2b) ones, where AF2a and AF2b are equivalent (see figure 4). For the lattice parameters and internal coordinates of the O phase determined both experimentally and by calculations using the PW91 density functional, we find that \(E_{\text{FM}} > E_{\text{AF1}} > E_{\text{AF2a}} = E_{\text{AF2b}}\) and that the relative energies of these configurations with respect to AF2a are 0.15 eV (AF1) and 0.40 eV (FM).

By minimizing the total energies with respect to the atomic positions as well as the lattice parameters, we find that the O structure has lattice parameter values \(a, b\) and \(c\) of 0.567, 0.573 and 0.869 nm, respectively, so \(a > b\) for AF2a and \(a < b\) for AF2b. In the AF2 configuration, the Fe 3d spins along the short Fe–Fe bonds have parallel orientation and those along the long Fe–Fe bond have antiparallel orientation. In contrast, the AF1 configuration relaxes to the T structure with \(a = b = 0.569\) nm and \(c = 0.862\) nm and remains by 0.15 eV less stable than AF2. The FM configuration becomes unstable and converges to AF1. We note that the relative energies of the spin configurations are expected to depend on the accuracy of the exchange–correlation functional, which needs to be investigated separately.

We analyzed the effect of the T–O transition on the electronic structure of LaFeAsO. Figure 5 shows the DOSs calculated using the PW91 functional near the Fermi level for the AF1 (T-phase) and AF2 (O-phase) configurations. It is clearly seen that the magnitude of the DOS near the Fermi energy is large in the AF1 configuration (T-phase). However, it transforms into a wide depression in the AF2 configuration (O-phase). We note that the DOS structure is mostly determined by the spin configuration rather than by the details of the atomic structure.

Integrating the PW91 spin density within the sphere near each Fe atom suggests that the magnetic moment per Fe in the AF2 configuration is \(\sim 1.6\ \mu_B\). The densities of spin-up

\[\text{Figure 4.} \text{ Schematic representations of Fe spin configurations in the FeAs layer of undoped LaFeAsO. The arrows indicate the spin states of the Fe 3d electrons. The upper images represent AF1 (checkerboard type) and AF2a and AF2b (spin stripe type) spin configurations in the tetragonal phase, whereas the lower images represent the spin configurations of AF1, AF2a and AF2b in the orthorhombic phase. The a-axis (x-direction) is longer than the b-axis (y-direction) in O1 and vice versa in O2.}\]

\[\text{Figure 5.} \text{Densities of states (DOSs) calculated for LaFeAsO}_{1-x}\_x\_F_x. (a) AF2 spin configurations in the orthorhombic phase of undoped LaFeAsO (x = 0), (b) AF1 spin configuration in the tetragonal phase of undoped LaFeAsO (x = 0), (c) paramagnetic state in the tetragonal phase for x = 0.125, (d) paramagnetic state in the tetragonal phase for x = 0.25.}\]
and spin-down electrons are almost equivalent, so the total magnetic moment per 16-atom supercell is about $4 \times 10^{-3} \mu_B$ and $\sim 10^{-3} \mu_B$ for the tetragonal and orthorhombic structures, respectively. Although these numbers are too small to be determined accurately with DFT, they indicate that: (i) the total magnetization of FeAs layers is small, and (ii) the total magnetic moment reduces during the T–O transition.

3.4. Phenomenological model for phase transitions

Figure 6 shows a schematic representation of the potential energy surfaces (PESs) calculated for undoped LaFeAsO and plotted with respect to the lattice parameters of the $C\text{mma}$ space group. The PES curves are calculated for two types of antiferromagnetic configuration, the checkerboard (AF1) and spin stripe type (AF2), and the latter is the more stable one, in agreement with the experimental observation [20]. The AF2 PES is represented by two equivalent parabolic curves with the minima at $O_1$ ($a < b$ region) and $O_2$ ($a > b$ region). The two curves split at the crossing point into upper (AF2U) and lower (AF2L) branches due to anharmonic electron–phonon interaction (tunneling interaction). The lower branch has a double minimum structure and, at low temperature (the $T_1$ region in figure 6(b)), the system is stabilized at one of the minima. This indicates that the orthorhombic phase is stable at low temperatures. The spins on Fe atoms along short Fe–Fe bonds couple ferromagnetically in the AF2U branch and antiferromagnetically in the AF2L branch, suggesting that the magnetostrictive interaction plays a major role in stabilizing the orthorhombic structure. On increasing the temperature (the $T_2$ region in figure 6(b)), the system migrates dynamically between the two minima due to the thermal energy, inducing the transition from the orthorhombic to tetragonal phase. The calculated double minima most likely arise from both the existence of degenerate states at the Fermi level (the energy band structure indicates that the two branches of the Fe 3d orbital are quasi-degenerate at the $\Gamma$ points) and the magnetostrictive interaction between the spins, which can be interpreted as the occurrence of a cooperative Jahn–Teller effect [42, 43].

In the reductively F-doped LaFeAsO$_{1−\delta}$F$_\delta$, F$^-$ ions substitute lattice O$^{2-}$ ions. This induces three main effects. First, the doping provides additional electrons to the FeAs layer and changes the calculated charge distribution to (LaO)$_{\delta}$+(FeAs)$_{3−\delta}$ in all considered cases ($x = 0.5$, 0.25, 0.125). The increased interlayer ionic bonding manifests itself in the shortening of the lattice vector along the $c$-axis, observed experimentally, and in the opening of a narrow gap at $\sim 2.5$ eV below the Fermi energy separating predominantly p and d states of the FeAs layers.

Second, the Fe magnetic moments decrease to $\sim 1.3 \mu_B$ for $x = 0.125$ and to below $\sim 0.1 \mu_B$ for $x = 0.25$. Interestingly, we found that F doping induces strong perturbation in the spin density distribution. In particular, in the $x = 0.25$ case, the spin-down 3d density is localized on a single Fe atom closest to the F$^-$ impurity, while the remaining three Fe atoms share the spin-up density. However, at a more realistic doping level ($x = 0.125$), the character of the spin distribution is much more complex: the spin density is predominantly antiferromagnetic but the local magnetic moments associated with Fe atoms become essentially disordered. Thus, we suggest that the F$^-$ doping induces a strong perturbation and may destroy the antiferromagnetic spin ordering.

Finally, relaxing the lattice parameters for the F-doped systems, we find that they have tetragonal structures. For example, the relaxed 16-atom supercell ($x = 0.25$) has tetragonal lattice structure with $a = b = 0.569$ nm, and $c = 0.849$ nm. This indicates that the F doping reduces the strength of magnetostrictive interaction and suppresses the transition into the orthorhombic phase.

The calculated DOS for the AF1 state shows a pronounced depression in the DOS of both tetragonal and orthorhombic LaFeAsO at the Fermi energy. However, the F doping shifts the Fermi energy so that it is at the local DOS peak for $x = 0.125$, which agrees well with the optimal doping level of $x = 0.11$ found experimentally for this material. This DOS peak is formed predominantly by d($xz$) and d($yz$) states, which couple the interaction between the Fe atoms in the Fe sheet with the Fe–As interaction across the FeAs layer. As the doping level increases to $x = 0.25$, the value of the DOS at the Fermi energy decreases again.

Finally, we note that the AF1 DOS in the undoped tetragonal and orthorhombic phases of LaFeAsO are virtually indistinguishable from each other, but they are very different from those found for AF2. This suggests that the effect of the structural change due to the phase transition alone is much smaller than the effects induced by the reorientation of Fe 3d spins. The latter are strongly affected by doping, which includes interrelated geometric, electronic and spin structure changes. In particular, the interaction between the LaO and FeAs layers increases, the Fermi level shifts to higher energies, and the DOS increases at the Fermi level.

F doping increases the electron density within the FeAs layers and the magnetic moments associated with the Fe atoms decrease as the F doping level increases, thus further decreasing the propensity of forming the orthorhombic structure.
4. Concluding remarks

Our experimental results clearly demonstrate that the anomaly in the $\rho$–$T$ curve of the undoped LaFeAsO is associated with the crystallographic phase transition between the tetragonal ($P4/nmm$) and orthorhombic ($Cmma$) phases. The transition starts to occur at $\sim 160$ K, in agreement with a kink in the anomaly. The temperature is a little higher than that of the magnetic transition. The magnetic moments of Fe in the orthorhombic phase exhibit a predominantly antiferromagnetic order, forming the spin stripe type configuration in the layer. Both transitions can be explained by spin configuration-dependent potential energy surfaces derived from the ab initio calculations.

On the other hand, Pauli paramagnetic and spin fluctuations contribute to the magnetic susceptibility in the normal conducting state, and both components are enhanced with the F doping, showing a maximum around F content of 5%. The F$^-$ ion doping at the O$^{2-}$ site suppresses the transitions and the antiferromagnetic ordering as the result of providing additional electrons confined to the FeAs layer, which modifies the DOS near the Fermi energy. These results suggest that the $T_c$ and the optimal doping level in LaFeAsO and related materials can be controlled in two ways: (i) the Fermi level can be shifted across the DOS peak (figure 5) by varying the dopant concentration, and (ii) the DOS value at this peak can be increased by higher localization of the Fe d($xz$) and d($yz$) states. The latter can be achieved by modifying the lattice constants via doping or vacancy formation [44] in the La and/or O sublattices or replacement of La with rare-earth elements with smaller ionic radii. Finally we note that the doping-induced structural modification (the overall reduction of the distance between layers and the increase in the distance between F$^-$ and La$^{3+}$ (0.249 nm) within the layer, as compared to the O$^{2-}$–La$^{3+}$ distance (0.236 nm)) may result in the stronger electron–phonon coupling and enhancement of both the spin and charge density fluctuations. Thus, the interplay between spin and charge density fluctuations [31, 45] can be responsible for the high $T_c$ in LaFeAsO-F.

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