Thermal expansion of LaFeAsO$_{1-x}$F$_x$: Evidence for high-temperature fluctuations

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We present measurements of the thermal expansion coefficient α of polycrystalline LaFeAsO$_{1-x}$F$_x$ ($x \leq 0.1$). The magnetic and structural transitions of the samples with $x \leq 0.04$ give rise to large anomalies in $\alpha(T)$ while the onset of superconductivity in the crystals with $x \geq 0.05$ is not resolved. Above the structural transition, the thermal expansion coefficient of LaFeAsO is significantly enhanced. This is attributed to fluctuations, which also affect the electrical transport properties of the compound. The complete absence of these fluctuations in the superconducting samples even for $x = 0.05$ is taken as evidence for an abrupt first-order type of suppression of the structural and magnetic transitions upon F doping.

I. INTRODUCTION

The family of layered FeAs materials has been extensively studied since the discovery of superconductivity with transition temperatures T_C up to 28 K in LaFeAsO$_{1-x}$F$_x$.[1] In the meantime, T_C has been increased to above 50 K (Refs. 2–6) by replacing La with other rare earths. Superconductivity has also been found in several related materials, such as Ba$_{1-x}$K$_x$Fe$_2$As$_2$,[7] LiFeAs,[8,9] or FeSe.[10] Interestingly, the evolution of superconductivity in LaFeAsO$_{1-x}$F$_x$ seems to be related to the suppression of a magnetically ordered orthorhombic phase, which has been found in the undoped parent compound.[11,12] In LaFeAsO, long-range magnetic order probably of a spin-density wave (SDW) type evolves below 137 K (Refs. 13 and 14) while an orthorhombic distortion of the tetragonal high-temperature phase has been observed at 156 K. The SDW ground state has also been established for isostructural rare earth (R)-based LaFeAsO$_{1-x}$F$_x$ (Ref. 15) and even in the parent materials of other iron-pnictide superconductors such as Ba$_{1-x}$K$_x$Fe$_2$As$_2$ with a different crystal structure but similar Fe$_2$As$_2$ layers.[7,16,17] However, while the structural and magnetic phase transitions are separated by about 20 K in the RFeAsO systems, they coincide for compounds of AFe$_2$As$_2$ type.

In this paper, we investigate polycrystalline LaFeAsO$_{1-x}$F$_x$ ($x \leq 0.1$) by means of thermal expansion measurements which sensitively probe the volume changes in the material. Large anomalies of the coefficient of linear thermal expansion α are found at the structural and magnetic transitions of the samples with $x \leq 0.04$. For comparison we studied superconducting LaFeAsO$_{1-x}$F$_x$ with $x = 0.05$ and 0.1, which exhibits neither the structural nor the magnetic phase transition. Interestingly, strong differences between the $\alpha(T)$ curves for the magnetic and the superconducting samples extend to temperatures well above the structural transition. We analyze these findings in view of our specific heat, x-ray diffraction (XRD), and resistivity data. Our data provide clear evidence for strong fluctuations in LaFeAsO$_{1-x}$F$_x$ ($x \leq 0.04$) over a large T range above the structural transition temperature T_S. By contrast, no indication of fluctuations is found in the superconducting samples. We discuss the impli-

cations for the phase diagram of LaFeAsO$_{1-x}$F$_x$, particularly at the crossover from a magnetic to a superconducting ground state.

II. EXPERIMENTAL METHODS

The preparation and characterization of our polycrystalline samples has been described in detail in Ref. 18. For the thermal expansion measurement a three-terminal capacitance dilatometer was utilized, which allows an accurate study of crystal length changes. To be specific, we measured the macroscopic length $L(T)$ of the samples and calculated the coefficient of linear thermal expansion $\alpha = 1/L \cdot dL/dT$, which is the first temperature derivative of $L(T)$. The specific heat was studied in a Quantum Design PPMS by means of a relaxation technique. Electrical resistivity measurements were performed using a standard four-probe technique.

III. RESULTS

Figure 1 shows the linear thermal expansion coefficient α of LaFeAsO between 5 and 300 K. In the whole investigated temperature range, α is found to be positive. This is in agreement with XRD data, which revealed a monotonically increasing lattice volume V_{uc} upon heating.[18] For our polycrystalline samples the volume expansion coefficient β is given as $\beta = 3\alpha$. Taking the volume at 300 K as an initial value we calculated the temperature dependence $V_{uc}(T)$, which agrees with the unit-cell volume determined from XRD data published in Ref. 18 [cf. inset of Fig. 2(a)]. Below 30 K a small plateau is seen in our $\alpha(T)$ data, which is also present for the F-doped samples discussed below. The origin of this structure is unclear. However, it does not affect the discussion of our data, which focuses on the temperature region above 100 K.

In Fig. 1, $\alpha(T)$ of LaOFeAs is shown in comparison to specific heat data $c_p(T)$. Below 120 K and above 200 K, α roughly tracks the temperature dependence of c_p, indicating an only weakly T-dependent Grüneisen ratio α/c_p. This observation implies a single energy scale in this temperature range and agrees to the assumption that mainly phonon de-
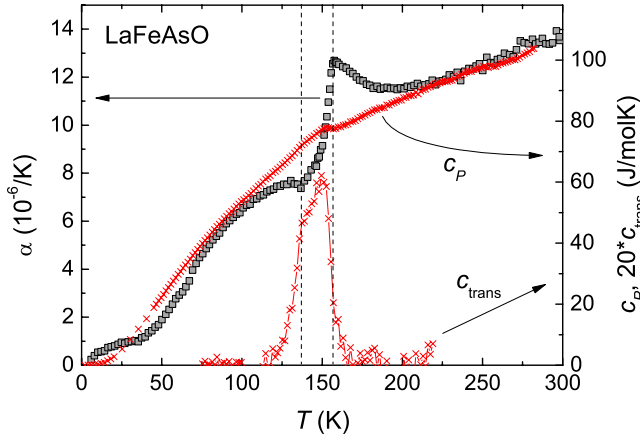
FIG. 1. (Color online) Temperature dependence of the coefficient of linear thermal expansion, $\alpha(T)$, of LaFeAsO in comparison to the specific heat, $c_p(T)$, of this compound. Two subsequent phase transitions are found in both quantities at similar temperatures, as indicated by the vertical lines. In addition, the specific heat contribution arising from the phase transitions, c_{trans}, is shown on a larger y scale.

grees of freedom are relevant. Around 150 K both quantities exhibit anomalous contributions, which do not obey a Grüneisen scaling. The thermal expansion coefficient exhibits two huge anomalies with opposite sign while the specific heat evolves rather smoothly with a small additional contribution, as will be discussed below. The anomalies in $\alpha(T)$ can be attributed to the structural and SDW transitions of the compound. The transition temperatures determined from the positions of the extrema are 137 and 157 K, respectively. These values are close to those found in many other properties on the same samples, such as XRD, resistivity, magnetic susceptibility,[18] μSR, and Mössbauer spectroscopy.[14,12] Both transitions are also visible in the specific heat data, which signals anomalous entropy changes in this temperature re-

FIG. 2. (Color online) Coefficient of linear thermal expansion, α, vs temperature, T, of LaFeAsO$_{1-x}$F$_x$ for different fluorine content x. For clarity, not all investigated samples are shown. The inset compares the temperature dependence of the unit-cell volume, $V_{uc}(T)$, for $x=0$ obtained from XRD (Ref. [18]) to the one calculated from α using the XRD value at 300 K as initial value. The orthorhombic unit cell is used in the whole T range.

gime. The anomalous specific heat c_{trans} can be determined by subtracting the phononic and electronic background estimated from a polynomial approximation of the data well above ($T > 170$ K) and below ($T < 120$ K) the transitions.[19] The result of such a procedure is shown in Fig. 1 on an enhanced scale, where the two anomalies at T_N and T_S, respectively, are clearly visible.

The SDW formation at $T_N = 137$ K generates a negative anomaly in the thermal expansion coefficient. For a second-order phase transition, the slope dT_N/dp can be determined from the jump height at T_N in the specific heat Δc_p and the volume thermal expansion coefficient $\Delta\beta = 3\Delta\alpha$ using the Ehrenfest relation

$$\frac{\partial T_N}{\partial p} = TV_{mol}\frac{\Delta\beta}{\Delta c_p} \qquad (1)$$

with the molar volume V_{mol}. However, for the given compound a determination of Δc_p and $\Delta\alpha$ is not possible with satisfactory accuracy due to the proximity of the structural and SDW transitions. Nevertheless, according to Eq. (1) the negative anomaly in $\alpha(T)$ at T_N qualitatively clearly implies a negative hydrostatic pressure dependence of T_N. This finding is in line with resistivity investigations on LaFeAsO showing a lowering of T_N under pressure with an initial slope of $dT_N/dp|_{p=0} \approx -1.5$ K/kbar.[20]

Contrary to the magnetic ordering, the structural transition at $T_S = 157$ K gives rise to a positive anomaly in $\alpha(T)$. This anomaly is very broad, extending to temperatures far above T_S. Extrinsic effects, in particular, those originating from grain boundaries, cannot cause this broadening. The grain size of our polycrystalline material has been determined from electron microscopy to be some tens of micrometer.[18] This renders a major contribution from grain boundaries to the thermal expansion coefficient as observed occasionally in nanocrystalline material[21] unlikely. Moreover, while the grain size is rather unaffected by F doping the width of the anomaly at T_S changes systematically upon substitution of O by F, as shown below, which also confirms the intrinsic nature of the broadening. By contrast, the corresponding anomaly in c_p is sharp, which excludes also the possibility of a smeared transition, e.g., due to sample inhomogeneities, as origin of the broadening. A sharp anomaly is likewise visible in our previously published $\partial(\chi T)/\partial T$ data.[14] Specific heat, magnetization, and XRD data indicate a second-order phase transition at T_S. Therefore, one expects a jump in the thermal expansion coefficient at the phase transition. From our data it is however not possible to determine the anomalous volume changes at the transition itself so that an analysis even of the sign of the pressure dependence dT_S/dp is hardly possible.

In order to understand the behavior of $\alpha(T)$ of LaFeAsO above T_S we studied the linear thermal expansion coefficient of LaFeAsO$_{1-x}$F$_x$ with nominal $x=0.02$, 0.04, 0.05, and 0.1. Upon fluorine substitution for $x \leq 0.04$ the structural and magnetic phase transitions are only weakly affected, i.e., they are slightly shifted to lower temperatures. At higher F content $x \geq 0.05$ both transitions are completely suppressed and a superconducting ground state is found.[12] Thus, F doping strongly affects the electronic properties of the series, especially at low temperatures, as well as the structural prop-
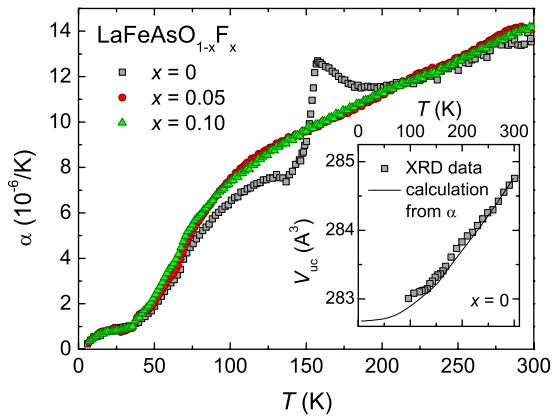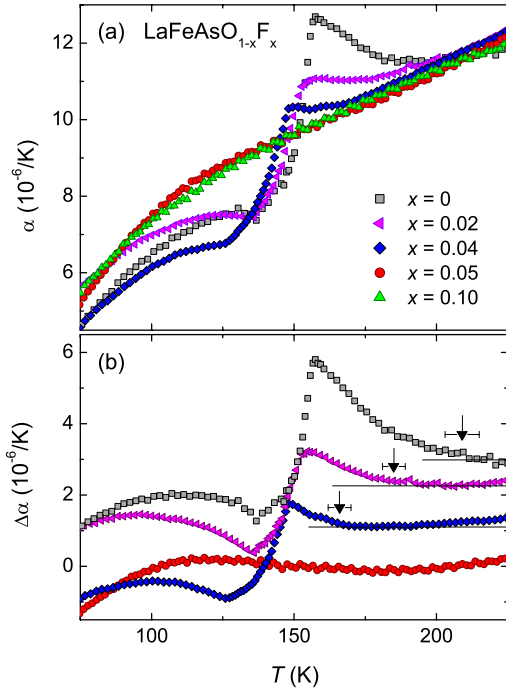
FIG. 3. (Color online) (a) Enhanced view of the linear thermal expansion coefficient vs temperature, $\alpha(T)$, of LaFeAsO$_{1-x}$F$_x$ between 80 and 220 K. (b) Determination of the temperature $T_{\rm fl}$ below which the thermal expansion data point at the presence of fluctuations. For this purpose, the data for $x=0.1$ have been subtracted and the curves shifted by multiples of 10^{-6}/K. Arrows with error bars mark $T_{\rm fl}$.

erties below $T_{\rm S}$. By contrast, the properties of the atomic lattice above $T_{\rm S}$, such as the phonon spectrum, are expected to be relatively insensitive to the fluorine content. Figure 2 compares the coefficient of linear thermal expansion of LaFeAsO$_{1-x}$F$_x$ for different F content $x=0$, 0.05, and 0.1. An enhanced view of the T region between 80 and 220 K for all investigated F concentrations is shown in Fig. 3(a). Upon F doping with $x\leq0.04$, the anomalies arising from the magnetic and structural transitions are shifted to lower temperatures, as expected from the lowering of $T_{\rm S}$ and $T_{\rm N}$. For $x \geq 0.05$ these transitions are suppressed. At high ($T > 210$ K) and low ($T \lesssim 70$ K) temperatures, α is almost independent of the composition. In particular, the superconducting transitions at $T_{\rm C}=20.6$ K ($x=0.05$) and $T_{\rm C}=26.8$ K ($x=0.1$), which are clearly visible in the resistivity, are not seen in $\alpha(T)$. Although our data in this temperature range are influenced by the small plateau of unknown origin, the existence of large anomalies at $T_{\rm C}$ appears unlikely given the close agreement of the curves for different F content. Regarding the T range above the structural transition of LaFeAsO$_{1-x}$F$_x$, Fig. 3(a) clearly reveals a significantly enhanced α for the magnetic samples compared to the superconducting ones. This difference cannot be explained by a simple change in the phonon spectrum upon F doping due to the larger atomic mass of fluorine compared to oxygen since the samples with $x=0.05$ and 0.1 exhibit almost identical $\alpha(T)$ curves. Instead, the enhanced α for $x\leq0.04$ suggests the presence of strong fluctuations preceding the structural transitions at $T_{\rm S}$.
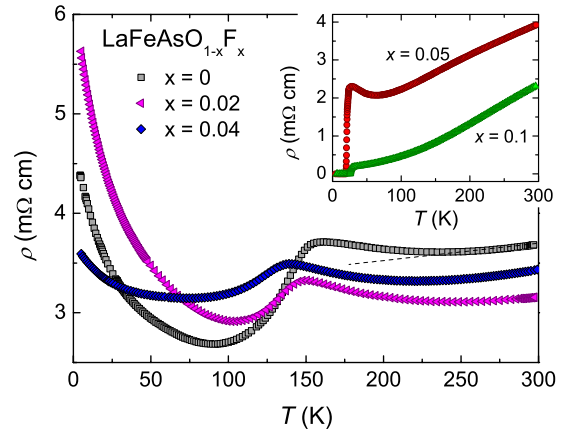

FIG. 4. (Color online) Temperature dependence of the resistivity, ρ, of LaFeAsO$_{1-x}$F$_x$. The main plot shows the data for the magnetic samples with $x\leq0$ while the superconducting samples ($x\geq0.05$) are shown in the inset. A dashed line to the eye highlights the regime with positive slope $d\rho/dT$ for $x=0$.

Indications for fluctuations are also found in the electrical transport properties of LaFeAsO$_{1-x}$F$_x$. Figure 4 shows the electrical resistivities $\rho(T)$ for $x\leq0.1$ taken from Ref. 22. At room temperature all samples exhibit metal-like resistivities with a positive slope $d\rho/dT$. Upon cooling, the resistivities of the superconducting samples continue to decrease, except for an upturn just above the superconducting transition for $x=0.05$, the origin of which is still not clear. Transitions to a superconducting state are found at $T_{\rm C}=20.6$ K ($x=0.05$) and $T_{\rm C}=26.8$ K ($x=0.1$). By contrast, the resistivities of LaFeAsO$_{1-x}$F$_x$ ($x\leq0.04$) increase below approximately 230 K and reach maxima at $T_{\rm S}$. This negative temperature dependence indicates enhanced scattering of charge carriers from fluctuations above $T_{\rm S}$. Consistently, below the transition, ρ drops as the fluctuations die away.

In Fig. 5 we plot the characteristic temperatures obtained from our thermal expansion measurements in the phase diagram of LaFeAsO$_{1-x}$F$_x$ established from magnetic susceptibility, μSR, and resistivity experiments.[12,22,23] The values for $T_{\rm S}$ and $T_{\rm N}$ taken as the positions of the extrema in $\alpha(T)$ fit well into this phase diagram. In addition we plot the temperature $T_{\rm fl}$, below which indications for fluctuations are found in the thermal expansion coefficient. For this purpose the data for $x=0.1$ have been subtracted from $\alpha(T)$ for $x \leq0.05$. The results are shown in Fig. 3(b) as $\Delta\alpha=\alpha(x)-\alpha(0.1)$ vs T, whereas the curves have been shifted by multiples of 10^{-6}/K. For $x\leq0.04$, $T_{\rm fl}$ is determined as the temperature, below which $\Delta\alpha$ exhibits a negative slope. With increasing fluorine content, $T_{\rm fl}$ is lowered. Extrapolating $T_{\rm fl}(x)$ and $T_{\rm S}(x)$ linearly to higher x would suggest a vanishing of the fluctuation regime around $x=0.06$. Nevertheless, already for the sample with $x=0.05$ no indication of fluctuations is found in $\alpha(T)$.

IV. DISCUSSION

The linear thermal expansion coefficient turned out a very sensitive probe for the phase transitions in LaFeAsO$_{1-x}$F$_x$
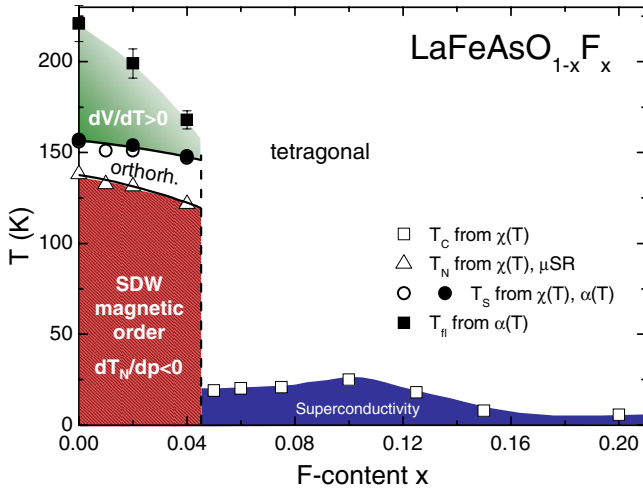
FIG. 5. (Color online) Phase diagram of LaFeAsO$_{1-x}$F$_x$ showing the change of the characteristic temperatures with F content x. The onset of superconductivity in the magnetic susceptibility at T_c (Refs. 22 and 23) and the temperatures of the orthorhombic distortion, T_S, and magnetic ordering, T_N, determined from magnetic susceptibility (Ref. 23) and μSR data (Ref. 12) are marked with open symbols. Closed symbols label the characteristic temperatures determined from thermal expansion measurements in this work.

($x \leq 0.04$). Large positive and negative anomalies are found in $\alpha(T)$ at T_S and T_N, respectively. By contrast, the small changes in the unit-cell volume related to T_S and T_N cannot be resolved directly from XRD measurements. Nevertheless, the close agreement between the $V_{uc}(T)$ curves for LaFeAsO determined from XRD and $\alpha(T)$ shown in the inset to Fig. 2(a) confirms the reliability of our thermal expansion data. The sizeable jumps in α at T_N reflect the strong coupling of the magnetic transition to the crystal lattice. The shape of the anomalies deviates from the one expected for second-order phase transitions, which is attributed to the closeness of the transitions and a contribution from fluctuations above T_S. So far, the origin of these fluctuations is unknown. A straightforward interpretation is to attribute them to a competing instability in vicinity to the actual ground state. One might speculate that this instability is of magnetic origin as suggested in Ref. 24. Based on a Hartree-Fock approximation and a Landau theory, Lorenzana *et al.*[24] find an orthomagnetic phase competing to the modulated magnetic stripes which are experimentally observed. In this scenario, long-range order of the competing, possibly magnetic phase is hindered by the orthorhombic distortion, whereas the increase in the corresponding anomalous positive contribution to the thermal expansion coefficient is truncated by the structural transition at T_S. Another model that accounts for the anomalous thermal expansion coefficient above T_S comprises ferro-orbital ordering accompanied by a lattice distortion at T_S.[25] In this picture, the enhanced α is suggested to arise from short-range orbital correlations above T_S. Interestingly, the experimentally observed onset temperature of the short-range order strongly depends on the F content. As visible in Fig. 5(b), the fluctuation regime is much stronger suppressed for larger x than T_N and T_S. Further investigations are necessary to determine the exact nature of the fluctuations above T_S.

In contrast to the structural and SDW transitions, the superconducting transitions of LaFeAsO$_{1-x}$F$_x$ with $x=0.05$ and 0.1 are not seen in $\alpha(T)$. The expected magnitude of $\Delta\alpha$ can be estimated from Eq. (1) using literature data. No anomaly was observed at T_C in the specific heat of LaFeAsO$_{1-x}$F$_x$.[26] As a rough estimate we take the difference of the curves measured in 0 and 9 T on LaFeAsO$_{0.9}$F$_{0.1-\delta}$ of $\Delta c_p / T \approx 5$ mJ/mol K^2. The derivative $\partial T_c / \partial p |_{p=0}$ of LaFeAsO$_{0.89}$F$_{0.11}$ was found to be on the order of 3 K/GPa.[27] Thus, the anomaly in α is estimated to $\Delta\alpha \approx 3 \times 10^{-8}$/K. This value, which is too small to be resolved with our setup, is in line with the absence of large anomalies in $\alpha(T)$ at T_C. However, it should be noted that we measure a directional average of the coefficient of linear thermal expansion on our polycrystalline samples which is associated to the hydrostatic pressure dependence. An almost complete cancellation of the contributions for different crystallographic directions was observed on single crystals with the related ThCr$_2$Si$_2$ structure, namely, Ba(Fe$_{0.88}$Co$_{0.12}$)$_2$As$_2$.[28] Measurements on single crystals of LaFeAsO$_{1-x}$F$_x$ are therefore necessary to decide whether the small magnitude of $\Delta\alpha$ is due to a similar effect.

The superconducting ground state in the $x=0.05$ sample is formed at the expense of an abrupt suppression of the structural and magnetic phase transitions observed in samples with $x \leq 0.04$. The change from the magnetically ordered to the superconducting ground state upon F doping has been proposed to be abrupt first orderlike.[12,22] Our thermal expansion data clearly support this picture. While fluctuations give rise to an enhanced thermal expansion coefficient over an extended T region for the sample with $x=0.04$, no indication of fluctuations is found for $x=0.05$. Instead, the thermal expansion coefficient of this sample is almost identical to the one for $x=0.1$, which lies well in the superconducting regime of the phase diagram. Moreover, the disappearance of the fluctuation regime around $x=0.045$ cannot be explained by a smooth convergence of T_{fl} and T_S with increasing F content, as seen from the phase diagram Fig. 5(b). Therefore, our data corroborate a first-orderlike scenario for the transition toward superconductivity upon doping.

V. SUMMARY

We performed measurements of the linear thermal expansion coefficient of LaFeAsO$_{1-x}$F$_x$ with $x \leq 0.1$ in the temperature range between 5 and 300 K. The structural and SDW transitions of the compounds with low F content $x \leq 0.04$ give rise to large anomalies in $\alpha(T)$, whereas fluctuations are present also well above T_S. By contrast, the superconducting transitions of the samples with $x \geq 0.05$ are not observable. Moreover, no indications for residual fluctuations in the superconducting samples are found at elevated temperatures, not even at the lowest F content $x=0.05$. This finding supports the idea of an abrupt first-order-type transition between the magnetic and superconducting ground states upon fluorine substitution.

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