Rapid Communication

Observation of lateral long range order in superconducting FeTe thin films*

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We find that the superconductivity in the thin films of the formerly believed non-superconducting parent compound FeTe is accompanied by an emergence of second order with a correlation length of 742 nm and 258 nm at 10 K and 300 K, respectively. The structural phase transition found in iron pnictide superconductors, in non-superconducting FeTe bulk samples, and in FeSe superconducting thin films is not observed in the superconducting FeTe thin films. The interplay between superconductivity and long range order may suggest the crucial role of competition between electronic localization and itinerancy which leads to strong quantum fluctuations in the FeTe system.

Keywords: superconducting materials, surface phase transitions and critical phenomena, superconducting films, x-ray determination of structures

PACC: 7470, 6842, 7475, 6110

1. Introduction

The discovery of iron-based superconductors[1−6] stirs the condensed matter physics society not only because of its relatively high transition temperature but also because it provides an alternative material platform to revisit a set of formidable problems in condensed matter physics, e.g., mechanism of high temperature superconductivity, interplay between magnetic ordering and superconducting condensation, and competition between electronic localization and itinerancy. Consensus was soon reached on that superconductivity comes from doping induced suppression of a spin density wave (SDW) ground state in iron pnictides, leading to a phase diagram[7,8] analogous to that of cuprate superconductors in which case the parent compound being doped to superconduct is a Mott insulator. However, argument still remains because of inconsistent experimental results between pnictides and chalcogenide parent compound FeTe on many different issues,[9−12] e.g., Fermi surface nesting[9] and antiferromagnetic ordering.[10] For detailed discussions readers are referred to Refs. [13] and [14]. Furthermore, very recently FeTe thin films were found to be superconducting at 13 K although bulk FeTe was previously believed as a ground state material in iron chalcogenides,[15] the fact naturally calls into questions such as, if FeTe is truly an end member and the parent compound in iron chalcogenide, how electrons pair and condensate in the superconducting FeTe thin films? if structural phase transitions exist above superconducting transition being the same as those in iron pnictide superconductors,[16] in non-superconducting FeTe bulk samples,[17] and in FeSe superconducting thin films.[18]

On the other hand, one major task of the condensed matter physics is to unravel the correlations inside each particular state of matter, i.e., to understand the formation and behaviour of a tremendous amount of phases existing in nature. For decades, second correlation length and central peak were heavily studied experimentally and theoretically in a wide variety of material systems, e.g., prototypical material $SrTiO_3$ for second order phase transition which under-

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goes an antiferrodisplacive transition at 105 K,[19−22] perovskite $RbCaF_3$,[23] and antiferromagnetic Ho[24] and Tb.[25] The origin of the second correlation length scale was thoroughly examined experimentally, recognized as a long range strain induced phenomenon related to a surface disorder which is localized within a near surface skin region.[26−28]

2. Experiment and discussion

In this paper, we present the x-ray diffraction (XRD) results on superconducting FeTe thin films, and report for the first time the second correlation length scale existed in thin film and its impact on the superconductivity as well. The structural phase transition found in iron pnictide superconductors, in non-superconducting FeTe bulk samples, and in FeSe superconducting films is not observed in the FeTe films. However, weak structural changes still remain at $\sim$ 80 K, around which a first order transition occurs in FeTe bulk samples.

Distinct from their counterparts in chalcogenides, i.e., the Fe(Se,Te) thin films and FeSe thin films, two components of (00L) diffractions can be clearly identified in the FeTe thin films, which reveal two different lateral correlations and orders. The narrow component which corresponds to correlation lengths of 742 nm and 258 nm at 10 K and 300 K, respectively, is sitting atop a broad one which corresponds to $\sim$ 48 nm at all measured temperatures from 300 K to 10 K. Although the films growths are epitaxial, i.e., FeTe(001) is parallel to the (001) of the cubic lattices of the substrates, reciprocal space mapping (RSM) reveals that (101) and (202) diffractions are in fact formed by two parts, one corresponding to film Bragg diffraction matched in-plane to those of the substrates, i.e., FeTe (100) being parallel to the (100) of the substrates, while the other misaligned with the substrate in-plane lattice. Combining the volume analyses of superconductivity, long range correlation order, and in-plane matched lattice, we conclude that the emergence of the long range order in the FeTe thin film plays a crucial role in introducing superconductivity in this formerly believed ground state material. The relationship established between long range order and superconductivity may suggest strong quantum fluctuations because of the competition between electronic localization and itinerancy.

An FeTe film grown on $SrTiO_3$ (001) was heavily studied. Its thickness calibrated by fringes observed in x-ray reflectivity (XRR) is 75 nm (not shown). Details regarding the film deposition and characterization have been reported elsewhere.[15] Its onset transition temperature, zero resistance transition temperature, and superconducting fraction at 2 K are 13.0 K, 6.8 K, and 5%, respectively, are taken from dc magnetization and ac susceptibility measurements (not shown). The XRD was performed on a laboratory diffractometer equipped with a closed cycle helium refrigerator covered with a beryllium window, and also at two different beamlines of Beijing and Shanghai Synchrotron Radiation Facilities (BSRF and SSRF) operated at 8 keV and 10 keV, respectively, for RSM experiments in surface diffraction mode.

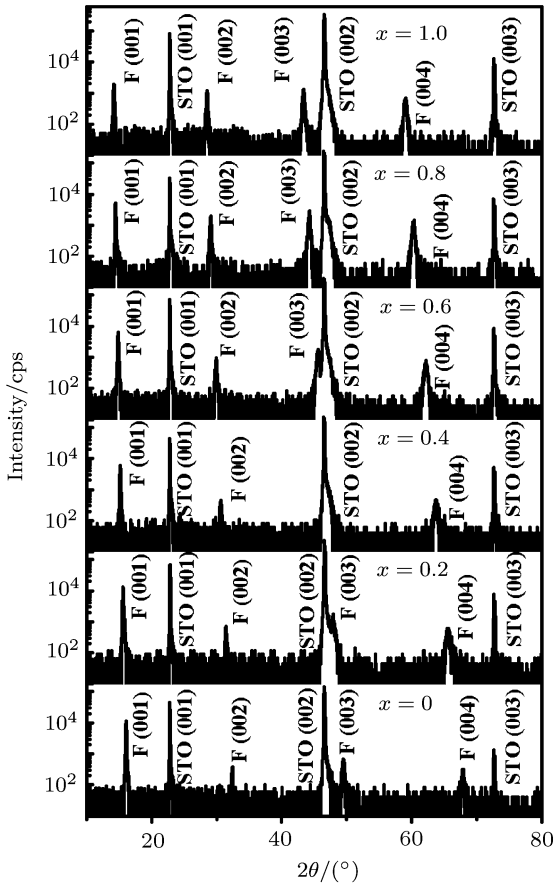


Fig. 1. The x-ray diffraction spectra of $FeSe_{1-x}Te_x$ films on $SrTiO_3$ with x = 0, 0.2, 0.4, 0.6, 0.8, and 1.0, measured at room temperature. The films are all epitaxial, single-phased, and (001) oriented. Note that (003) peak of $FeSe_{1-x}Te_x$ (x = 0.4) merges into the STO(002) peak.

For comparison reasons, a set of $FeSe_{1-x}Te_x$ films on $SrTiO_3$ with x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9 were prepared and measured by $\theta-2\theta$ scan and (001) rocking curve scan at 300 K, some of which are reproduced in Figs. 1 and 2(a). The rest given in Figs. 1 and 2 are similar scans for FeTe film taken at room temperature, and examples of a whole set of low temperature (001) rocking curve scans for FeTe

film. There are two main findings from results given in Fig. 2. First, the phase transition documented previously in iron pnictide,[16] non-superconducting bulk FeTe,[17] and superconducting FeSe films[18] cannot be seen in the superconducting FeTe films. Second, and most important, it is clear that there exist two components in rocking curves of superconducting FeTe films, while only one component in the other superconducting $FeSe_{1-x}Te_x$ films with $x \neq 1$. Similar two-component feature in rocking curve scan was also found in an FeTe film on MgO substrate.[1)]

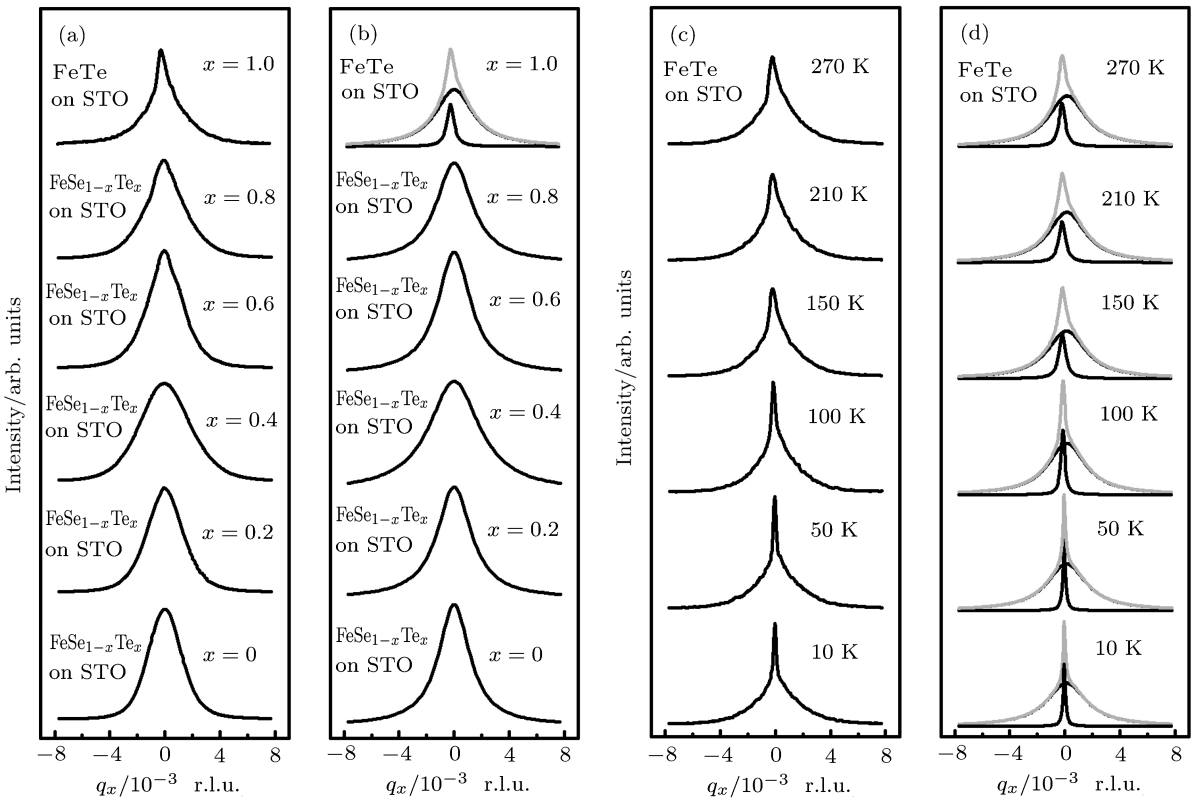


Fig. 2. (a) Experimental data of rocking curves of $FeSe_{1-x}Te_x$ films on $SrTiO_3$ at room temperature. (b) Lorentzian fits of (a). (c) Parts of the experimental data of the rocking curve scans of the FeTe film taken at low temperatures down to 10 K. (d) Lorentzian fits of (c). It is clear that single peak Lorentzian fits are applicable to $FeSe_{1-x}Te_x$ films with $x \neq 1$, while double peak Lorentzian fits (light gray as summations) must be used for FeTe films.

Prior to the rocking curve scans as reproduced in Fig. 2(b), a θ–2θ scan was taken at each set of temperatures (not shown) after it was stabilized longer than 15 min in order to allow sample to reach thermal equilibrium. The temperature dependency of lattice constant of the $SrTiO_3$ substrate is plotted in Fig. 3(a), clearly indicating that it shrinks linearly down to ∼120 K, around which a second order phase transition occurs.[19−22,29] The c-axis lattice of the FeTe film also shrinks linearly, however in this case down to ∼ 70 K. Volume fraction η of the narrow component in the film as a function of temperature is deduced from the amounts of integrated intensities of the two components, given in Fig. 3(b). Note that the volume fraction keeps almost constant at ∼ 8% when the temperature is lower than 70 K, a phenomenon corresponding to ∼ 70 K lattice constant anomaly shown in Fig. 3(a).

From a sketch given in Fig. 3(c), it is clear that,[30]

$$q_z = k[\sin\omega + \sin(2\theta - \omega)] = 2k\sin\theta\cos\delta, \quad (1)$$

$$q_x = k[\cos\omega - \cos(2\theta - \omega)] = 2k\sin\theta\sin\delta. \quad (2)$$

[1)] Low temperature (LT) XRDs were performed on 5 superconducting FeTe films in total, 4 on $SrTiO_3$ and 1 on MgO. Emergence of second, long range order was observed in all 5 superconducting films. For the film on $SrTiO_3$ described in this paper, after the LT XRD during which the film was kept in a vacuum chamber of the refrigerator, a systematic survey on XRRs and XRD RSMs performed at BSRF and SSRF exposing the film under air more than 60 hours does deteriorate the superconductivity of the film, which is found accompanied by the disappearance of the second, long range order. This fact provides another evidence that the lateral long range order is responsible for superconductivity in the FeTe films.

And therefore,

$$\Delta q_z = k[\cos\omega \cdot \Delta\omega + \cos(2\theta - \omega) \times (\Delta(2\theta) - \Delta\omega)], \quad (3)$$

$$\Delta q_x = k[-\sin\omega \cdot \Delta\omega + \sin(2\theta - \omega) \times (\Delta(2\theta) - \Delta\omega)]. \quad (4)$$

For rocking curve scans with detector 2θ fixed while rocking ω, taken on a specular reflections, i.e., $\delta = 0$,

$$\Delta q_x = -2k \sin\omega \cdot \Delta\omega, \quad (5)$$

$$\Delta q_z = 0. \quad (6)$$

Obviously ω scan is same as the q_x scan, and gives lateral correlation of the materials examined. We take the product of x-ray wavelength and full width at half maximum (FWHM) as the correlation length ξ, the upper limit of which can be detected using a laboratory diffractometer is ~ 1 μm.[30] It is interesting to point out that the width of the narrow component varies a lot with temperature, corresponding to a monotonic increment of ξ from 258 nm at 300 K to 742 nm at 10 K, while the broad ones keep almost constant, corresponding to ξ of 48 nm ± 2 nm from 300 K all the way down to 10 K. This fact reveals that the narrow component solely relies on the correlation inside the materials, but not depending on film microstructures, e.g., grain size, strain, etc.

In Fig. 3(d), we plot in logarithmic scales the temperature dependency of ξ of the narrow component, deduced from the data as examples shown in Fig. 2(b). Reduced temperatures were transformed by employing critical temperature as 13 K, where the superconducting transition begins. Two distinct features can be seen clearly. First, ξ keeps almost constant for temperatures lower than 80 K. Second, ξ changes dramatically at around 80 K, i.e., the correlation length $\xi = \xi_0 \cdot t^{-\nu}$ diverges as the associated critical temperature $T_c = 80$ K is approached, where $\xi_0 = 742$ nm is the correlation length in superconducting state, $t = (T - T_c)/T_c$ is the reduced temperature, and ν is the critical exponent.[31,32] We replot in Fig. 3(e) the data shown in Fig. 3(d) for those higher than 80 K, in this case replacing $T_c = 13$ K with $T_c = 80$ K, leading to $\nu = 0.518$, a value reminiscent of scaling law of mean field theory applicable to 3-dimensional (3D) behaviours.

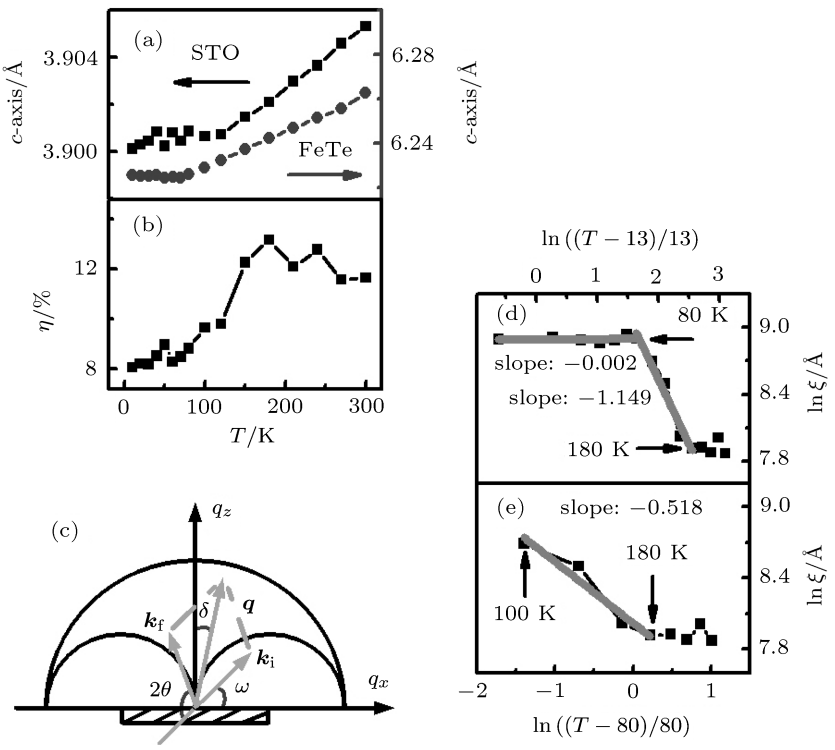


Fig. 3. (a) Temperature dependencies of c-axes lattice constants of $SrTiO_3$ and FeTe films, which show anomalies at ~ 120 K and ~ 70 K, respectively. (b) Volume fraction η of narrow component in FeTe film, which reaches a constant of $\sim 8\%$ when temperatures lower than 70 K. (c) Schematic illustration interpreting the rocking curve scan in the reciprocal space, with 2θ being the angle between incident wave vector $\boldsymbol{k}_i$ and scattered wave vector $\boldsymbol{k}_f$, ω between $\boldsymbol{k}_i$ and scattering plane q_x, and δ between scattering vector $\boldsymbol{q}$ and surface normal q_z. δ equals $\theta - \omega$. Scattering plane q_x and surface normal q_z define the laboratory coordinate system. (d) Correlation length ξ as function of temperature with critical temperature set as superconducting temperature 13 K. (e) Replot of (d) with critical temperature set as 80 K (1 Å=0.1 nm).

One important conclusion which can be drawn from results shown in Fig. 3 is, although in FeTe superconducting thin films a first order phase transition at $\sim$ 70 K is smeared out[15] and no evident structural phase transition[16−18] can be identified from our present work either, some weak structural change can be distinguished at $\sim$ 80 K, and this 80-K structural change is closely related to the superconducting condensation since the long range correlation length scale keeps constant from 80 K down to 10 K (c.f., Figs. 3(a), 3(b), 3(d), and 3(e)).

Mappings of the RSM scans were reproduced in Fig. 4. Surprisingly, in addition to a Bragg peak which corresponds to film lattice parallel to that of $SrTiO_3$ not only in c-direction but also in a- and b-directions, there exists a "polycrystalline", "powder ring like" feature. This is in contradiction with ordinary expectations for epitaxial thin films, that is, only an intensified Bragg diffraction should appear on the integer lattice spot in reciprocal space, and for the most, with some weak ordered satellite peaks arranged regularly and separately along some specified directions with high symmetry.[33] The Bragg diffration from the "ring like" feature reflects that a portion of film is epitaxial growth but not in-plane aligned. Its intensity is even stronger than that of the former, the lattice in-plane matched one. Similar RSM feature was also observed in an FeTe film on MgO substrate. Taking four-fold symmetry of FeTe (101) and (202) into account, one can estimate roughly that the volume fraction of the lattice in-plane matched portion in the film is $\sim$9% at room temperature, which is close to $\sim$ 12%, the volume fraction of narrow component (c.f. Fig. 3(b)).

One possible scenario is, the second correlation in the FeTe films is responsible for the appearance of superconductivity, given the coincidence among superconducting volume fractions at 2 K (5%), η (12% at 300 K and 8% at 10 K, c.f. Fig. 3(b)), and in-plane lattice matched Bragg diffraction (9% at 300 K, c.f. Fig. 4). This long range correlated part undergoes a 3D weak structural change ($\nu = 0.5$) at $\sim$ 80 K, where the film may enter a low temperature state not superconducting but related state (c.f., Fig. 3(d)), e.g., precursor state or pseudogap opening.[34] More theoretical and experimental studies are called on to verify the above speculations (c.f. footnote 1)).

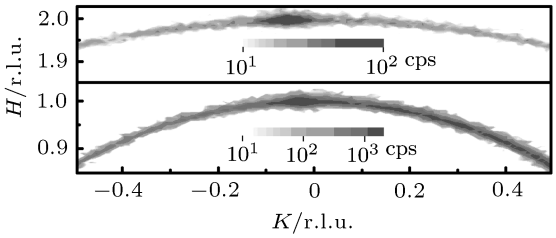


Fig. 4. Reciprocal space mappings of FeTe films at room temperature taken at (lower panel) around FeTe (101) and (upper panel) around FeTe (202). The matrices were defined in a way that FeTe is parallel to the substrate.

Another fact observed in the RSM, i.e., a great portion of the FeTe film lattice being in-plane misaligned however still epitaxial (c.f. Fig. 4) and possessing a correlation temperature independence with ξ of $\sim$ 48 nm (broad component shown in Fig. 2(b)), tells more about the superconducting FeTe films. Obviously it results from misalignment among the Fe–Te lattice planes since the interaction between adjacent lattice planes is very weak.[15] Although in-plane misaligned broad component seems not responsible for superconductivity, it does compete with the superconducting, lattice in-plane matched to substrate, long range correlated narrow component.

3. Conclusions

The most important findings of the present paper may be the second correlation length found in the thin film, and also its crucial role in the introduction of superconductivity into non-superconducting ground state. It seems that two portions of FeTe with different correlation scales mix spatially to each other and compete with each other, and eventually drive the film into a low temperature state ($T < 80$ K) which is related to superconductivity at $T < 13$ K. Such a scenario suggests a strong quantum fluctuation and may help understanding the competition between electronic localization and itinerancy in the iron-based superconductors,[13,14,35] e.g., in a quantitative way.

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