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Superconductivity induced in iron telluride films by low-temperature oxygen incorporation

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We report superconductivity induced in films of the nonsuperconducting, antiferromagnetic parent material FeTe by low-temperature oxygen incorporation in a reversible manner. X-ray absorption shows that oxygen incorporation changes the nominal Fe valence state from 2+ in the nonsuperconducting state to mainly 3+ in the superconducting state. Thus superconductivity in O-doped FeTe occurs in a quite different charge and strain state than the more common $FeTe_{1-x}Se_x$. This work also suggests a convenient path for conducting doping experiments *in situ* with many measurement techniques.

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The discovery of $LaO_{1-x}F_xFeAs$ high-temperature superconductors[1] has aroused great interest in iron-based superconductivity. Besides the original 1111-type *Re*FeAsO (*Re*=rare earths), the 111-type *A*FeAs (*A*=alkali metal), 122-type $AeFe_2As_2$ (*Ae*=alkaline earths), and 11-type Fe*X* (*X*=chalcogens) are oxygen free. The latter system is structurally the simplest, consisting only of Fe*X*-buckled planes. For the Fe-based superconductor families, there are two different ways in which superconductivity was achieved: chemical or physical pressure and charge doping. The original $LaO_{1-x}F_xFeAs$ compound is charge doped versus the LaOFeAs parent compound. In contrast, pressure induces superconductivity in the undoped compounds of 1111-type LaOFeAs (Ref. 2) and 122-type AFe_2As_2 (A=Sr,Ba,Ca) (Refs. 3–5) but decreases the critical temperature of 111-type LiFeAs.[6]

For the iron chalcogenides, FeTe is considered the parent compound as it is antiferromagnetic but not superconducting. Chemical pressure via isoelectronic substitution of Se or S onto Te sites produces a superconductor.[7–9] FeSe shows the most dramatic pressure effect among the Fe-based superconductors where the T_{onset} increases from 8.5 to 36.7 K under 8.9 GPa.[10] However, no form of charge doping or of physical pressure on bulk FeTe has been shown to produce a superconductor. Recently, superconductivity has been reported in FeTe films with the result attributed to strain[11] though a separate report describes similar superconductivity in FeTe films as due to oxygen incorporated during growth.[12] In addition, there is recent work showing that the bulk-oxygen annealing enhances superconductivity in $FeTe_{0.8}S_{0.2}$.[13] It remains unknown just what aspect of doping induces superconductivity from a parent compound in the Fe-based superconductors and more detailed studies of the process are necessary.

In this Rapid Communication, we report a study of films of the parent compound FeTe which we make superconducting by incorporating oxygen after growth. We first observed superconductivity after long-term exposure to the ambient atmosphere at room temperature. Careful low-temperature annealing experiments confirm that superconductivity is established by the incorporation of excess oxygen in a reversible manner. The superconductivity we induce in FeTe films has an onset temperature around 10 K. Spectroscopic measurements confirm that oxygen is being taken up by the bulk of the film structure and alters the nominal Fe valency.

FeTe films were grown on MgO(001) single-crystal substrates by pulsed laser-deposition techniques, using a nominal 1:1 FeTe target. The base pressure of the system is around 7×10^{-8} torr. During deposition, the substrate temperature was kept at 380 °C in a vacuum of better than 2×10^{-7} torr. The deposition rate is around 1.7 nm per minute. After the deposition, the samples were cooled down to room temperature at a rate of 4 °C/min in vacuum. The data shown in this paper come from films of thickness 100 ± 5 nm. However, FeTe films with various thickness, ranging from 30 to 150 nm, show essentially identical results.

Crystalline quality and orientation were examined by a two-circle x-ray diffractometer with a Cu $K\alpha$ source and a four circle diffractometer with an area detector and a Cu $K\alpha$ source. High-resolution measurements of the lattice constants were taken at beamline X22C of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. X-ray absorption (XAS) experiments were performed at NSLS U4B beamline. The XAS spectra were recorded simultaneously in total electron yield (TEY) and total florescence yield (TFY).

Figure 1 shows the effect of exposure to air on the resistivity. Overall, the resistivity of these materials is weakly metallic, consistent with bulk materials.[9,14,15] In addition, all of the resistivity vs temperature curves show a broad peak around 70 K, an effect also seen in the bulk and associated with the concurrent antiferromagnetic and structural transition.[14–16] After two days of exposure to air, there is almost no change observed. However, a superconducting transition appears by 17 days of air exposure. The close up of the transition region in Fig. 1(b) shows that the superconducting transition continues to sharpen for up to two months in air reaching essentially zero resistance at 2 K. Figure 1(c) shows the field-cooled and zero-field-cooled diamagnetic signals for a superconducting film on a $SrTiO_3$ substrate. The magnetic transition is a few degrees lower than the occurrence of zero resistivity as seen by others.[12] The magnitude of the signal for samples on MgO is a little larger but are complicated by magnetic impurities in the MgO. The large value for $4\pi\chi$, especially for the field-cooled true Meissner signal, indicate that superconductivity exists in most of the film and is not a filamentary feature.

X-ray diffraction data confirm that the FeTe structure was

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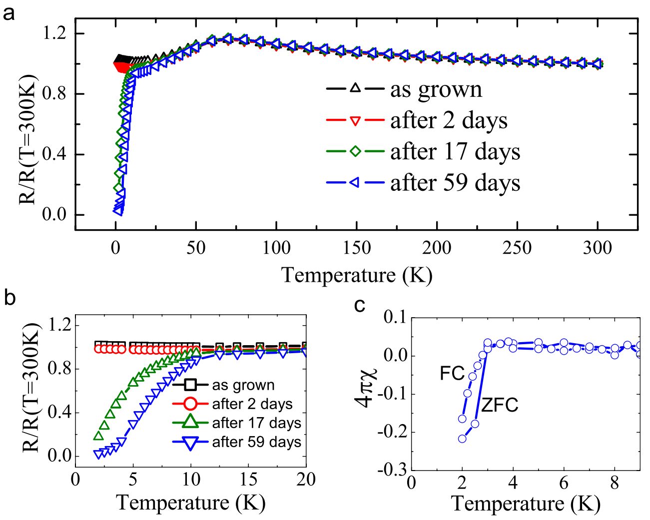

FIG. 1. (Color online) Resistivity measurements normalized to the value at 300 K for FeTe films with various amounts of air exposure. (a) The broad data set from 2–300 K. Superconductivity appears after 17 days. (b) Closeup of the transition region. (c) The diamagnetic response of a superconducting film on $SrTiO_3$ substrate.

always found to be a tetragonal phase consistent with bulk measurements. Figure 2 shows x-ray profiles in the (00L) direction for an as-grown FeTe film (nonsuperconducting) and after annealing the same film in oxygen atmosphere (superconducting). The only peaks observable are the tetragonal FeTe (00L) peaks and the substrate MgO (002) peak. This scan indicates the basic epitaxial nature of the film and shows that the structure does not break down as oxygen is incorporated and superconductivity sets in. High-resolution data obtained from the synchrotron light source gave the lattice constants for the as-grown FeTe film at room temperature as $a=b=3.8358(2)$ Å and $c=6.2734(1)$ Å. The oxygen-annealed film has $a=b=3.7782(1)$ Å, and $c=6.2835(1)$ Å. This indicates a small lattice change after the incorporation of oxygen, an increase in c but a decrease in a and b.

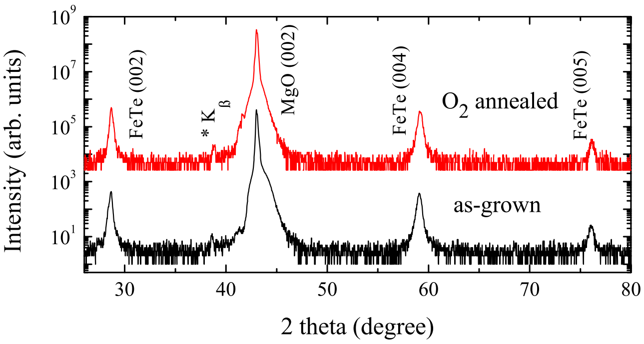

FIG. 2. (Color online) X-ray diffraction profiles in the (00L) direction of the as-grown and oxygen annealed FeTe films taken at room temperature.

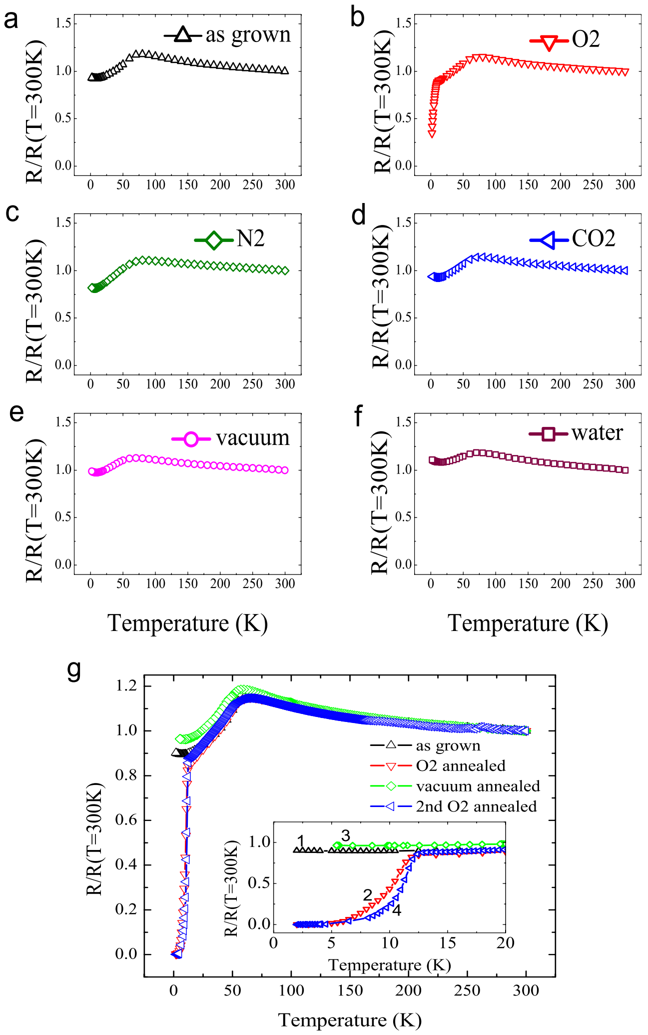

FIG. 3. (Color online) Normalized R vs T for FeTe films after exposure to different elements. The panels reflect (a) as-grown sample, and annealing in (b) O_2, (c) N_2, (d) CO_2, (e) in vacuum, and (f) exposure to water. Panel (g) shows the resistivity evolution after repeated oxygen and vacuum anneals, demonstrating the reversibility of the process.

In order to determine what aspect of the exposure in air caused the appearance of superconductivity, we conducted careful low-temperature annealing experiments. Separate FeTe samples were annealed at 100 °C, 100 mTorr O_2, N_2, and CO_2 atmosphere, as well as in 100 °C, 2×10^{-7} torr vacuum and exposed to 40 °C water. The FeTe films annealed in pure O_2 show a sharp drop of resistivity at around 10 K similar to the air exposed sample indicating the onset of the superconducting transition, see Fig. 3(b). FeTe films annealed in N_2, CO_2, or vacuum have no sign of superconductivity down to 2 K, see Figs. 3(c)–3(e). Water exposed films show a substantial increase in resistivity but no sign of superconductivity, see Fig. 3(f). Repeated anneals in O_2 improved the superconducting properties, most notably the sharpness and completeness of the transition. However, adding subsequent anneals of 50 min each increased both the room-temperature resistivity and degraded the superconducting transition. This degradation may indicate the possibility of overdoping or may indicate some degradation of the structure. Further, the oxygen incorporation is reversible. Figure 3(g) shows the resistivity of an FeTe film that was first an-

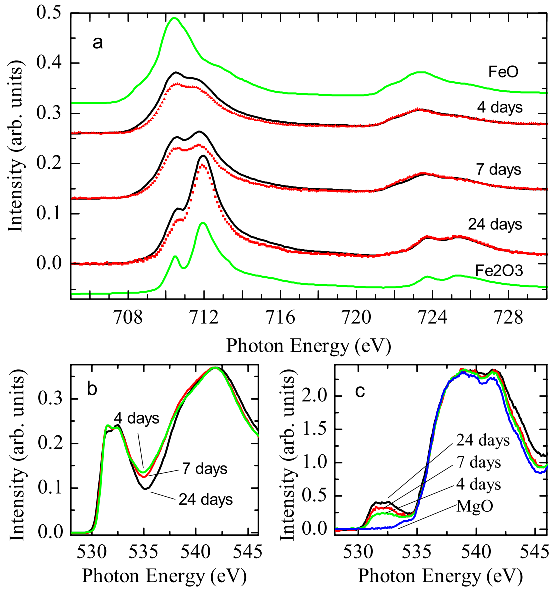

FIG. 4. (Color online) X-ray absorption spectroscopy of FeTe films. (a). The Fe *L* edges TEY (black or upper solid curve) and TFY (red or lower dashed curve) show that the nominal valence state of Fe increases with longer exposure to air, from 2+ to 3+, by comparing with the FeO and Fe_2O_3 curves. (b) shows the TEY of O *K*-edge spectra. (c) shows the TFY of O *K*-edge spectra.

nealed in O_2 to be superconducting. Subsequently, the sample was annealed in vacuum to drive out the excess oxygen and this film was not superconducting with a resistivity vs temperature approximately the same as as-grown samples. Finally, a further oxygen anneal restored the superconducting state. Taken together, this set of annealing experiments provides strong evidence that the fundamental change that leads to superconductivity in the FeTe films is the reversible incorporation of oxygen.

We pursued x-ray absorption experiments at the Fe *L* edge and O *K* edge to understand the role of the oxygen that is incorporated into the FeTe structure. The energy resolution was 0.34 eV for the Fe *L* edges and 0.18 eV for the O *K* edge. The TEY (black or upper solid curve) and TFY (red or lower dashed curve) results at the Fe *L* edges were identical except for the intensity variations due to the self-absorption effect in TFY.[17] The O *K* edge TEY shown in Fig. 4(b) looks similar to bulk FeO_x but the TFY shown in Fig. 4(c) is dominated by the MgO substrate demonstrating that TFY is sampling the entire bulk of the film. In Fig. 4(a) we display the results for samples at three different stages of oxygenation under ambient conditions: after 4, 7, and 24 days. FeTe is expected to be charge balanced such that Fe is in a nominal 2+ valence state. Consistent with this expectation, the TEY and TFY of the FeTe sample measured 4 days after growth has an Fe *L*-edge spectra which is closest in shape to that of FeO, compared to any of the other bulk FeO_x's.[18–21] In contrast, for the sample with the longest exposure to air (24 days), the TFY Fe *L*-edge spectra looks most like the Fe_2O_3. In particular, the spectra looks most like γ-Fe_2O_3 rather than α-Fe_2O_3 but the two are quite similar compared to the changes we observe with doped FeTe. The FeTe film with intermediate exposure to air (7 days) has an Fe *L* edge that appears to be a sum of roughly equal contributions from an FeO-like spectrum and an Fe_2O_3-like spectrum. The different crystalline environment for Fe in FeTe, compared to the oxides, rules out a reliable quantitative analysis of Fe^{2+} and Fe^{3+} contributions. However, the qualitative result is clear, the superconducting film consists primarily of Fe in a nominal 3+ oxidation state which is a large valence change from the nonsuperconducting film.

In Fig. 4(c), the TFY O *K*-edge spectra provide further evidence that oxygen is incorporated into the FeTe matrix. The bulk nature of the TFY measurement causes the spectra to be dominated by the MgO substrate which can be seen by comparison to the spectra from a bare MgO substrate. However, the prepeak in the energy range between 530 and 535 eV only appears with the FeTe films. Such a peak is a direct result of Fe $3d$ orbitals hybridizing with oxygen $2p$ orbitals.[22] The relative photon-energy position of the FeO_x prepeak to the main MgO peak is in very good agreement with the peak spacing reported in XAS studies of $Fe_{1-x}Mg_xO_y$.[23]

We performed a density-functional theory (DFT) calculation with the local-density approximation to study the possible interstitial sites for oxygen. The most stable sites for the interstitial O were found to be the unoccupied, symmetry-equivalent sites to the Te sites but situated closer to the Fe subplane. We note this is similar to the position of Li in LiFeAs. Details of the DFT studies of the crystal structure and electronic and magnetic properties will be discussed in a separate paper.

In summary, the key results are: (1) we can reversibly create superconductivity by incorporating oxygen, (2) the structure of the sample is only slightly altered from pristine FeTe (XRD), and (3) the superconducting sample exhibits Fe with a nominal 3+ valence (XAS). Does the valence state of Fe ions play an important role in creating superconductivity in the Fe-chalcogenide system? Previous studies seem to indicate that it does not. FeTe is a parent compound that while poorly conducting is antiferromagnetic and not superconducting. In previous work, creating a superconductor from FeTe involved substituting isovalent Se or S for some fraction of the Te ions.[8,24] This does not seem to involve changing the valence of Fe or the charge balance of the active Fe planes. However, the process for creating a superconductor we report here is quite different: turning FeTe films into superconductors involves incorporating oxygen into the structure interstitially and not substitutionally. That observation combined with the x-ray absorption data indicate that the nominal Fe valency changes as the film becomes superconducting. Apparently either route will create a superconductor out of the FeTe parent material. This is a fundamental difference from the physics of the copper oxide high-temperature superconductors where hole concentration is universally linked to the presence of superconductivity. It is, however, consistent with the full range of data on the Fe-based superconductors. The original Fe-based superconductor involved doping the parent LaOFeAs compound by substitutionally doping F onto the O site, a form of charge doping.[1] However, other Fe-based superconductors can be created with stoichiometry that does not include any apparent charge doping but presumably a lattice distortion from the parent compound.[7,16,24] The picture that emerges is that superconductivity depends upon a complex interplay between strain and charge balance: a correct balance of the two is necessary rather than a particular value for either alone.

Experimentally, the ability to reversibly turn on superconductivity with suitable, low-temperature annealing steps will enable a variety of interesting, well-controlled experiments. This could be particularly important for surface related probes such as photoemission to determine key electronic aspects of the superconducting state.

Our results are also important in light of a finding recently published by Han *et al.*[11] who found superconductivity in films of FeTe and attributed the result to in-plane, tensile strain. In our case, the annealing experiments make a clear case that superconductivity is induced by incorporation of oxygen. An examination of this reference does not seem to rule out a similar cause for superconductivity in their samples. Oxygen in those films was never measured and they were grown with a background pressure an order of magnitude higher than in our work. Our films covering the same range of thickness were never superconducting immediately out of the growth chamber. Of course direct measurements would be necessary to confirm whether both mechanisms might produce superconductivity in FeTe.

In summary, by introducing excess oxygen at low temperature, superconductivity was induced in the FeTe films. When the films are superconducting, XRD indicates only a small structural change and XAS indicates that the majority of the Fe has a nominal valence of 3+. This method for creating a superconductor is quite different from the better known procedure of substituting isovalent Se or S for Te. Thus superconductivity occurs in very different places in the phase space of strain and Fe valence and the correct combination of both appears to be necessary for superconductivity.

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