Superconductivity Induced in Iron Telluride Films by Low Temperature Oxygen Incorporation

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We report superconductivity induced in films of the non-superconducting, antiferromagnetic parent material FeTe by low temperature oxygen incorporation in a reversible manner. X-ray absorption shows that oxygen doping changes the nominal Fe valence state from 2+ in the non-superconducting 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 FeTe1−xSex. This work also suggests a convenient path for conducting doping experiments in-situ with many measurement techniques.

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The discovery of LaO1−xFxFeAs high-temperature superconductors [1] has aroused great interest in iron-based superconductivity. Besides the original 1111-type ReFeAsO (Re = rare earths), the 111-type AFAs (A = alkali metal), 122-type AeFe2As2 (Ae = alkaline earths), and 11-type FeX (X = chalcogens) are oxygen free. The latter system is structurally the simplest, consisting only of FeX 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 LaO1−xFxFeAs compound is charge doped versus the LaOFeAs parent compound. In contrast, pressure induces superconductivity in the undoped compounds of 1111-type LaOFeAs [2] and 122-type AeFe2As2 (Ae = Sr, Ba) [3, 4], and decreases the the critical temperature of 111-type LiFeAs [5].

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 [6, 7]. FeSe shows the most dramatic pressure effect among the Fe-based superconductors with the T_onset increases from 8.5 to 36.7 K under 8.9 GPa [8]. However, no form of charge doping or of physical pressure on FeTe has been shown to produce a superconductor. Recently, superconductivity has been reported in FeTe films and the result attributed to the in-plane lattice strain [10]. Exactly what aspect of doping induces superconductivity from a parent compound in the Fe-based superconductors is unknown. In the Fe-chalcogenide system the primary discussions have focused on the effects of distorting the lattice [6, 11, 12]. More broadly, there has been some discussion that since both isovalent distortions and charge doping can produce a superconductor, then the key feature must be avoiding the antiferromagnetically ordered state rather than reaching any particular place in a charge-strain phase diagram.

In this letter, 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, thus indicating a very different path towards achieving superconductivity from the FeTe parent than substitutionally doping Se on Te sites.

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 0C 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 40/°C/min in vacuum.

Film thickness was measured using a laser interferometer. The resistance of the films was measured by using the 4-point technique with silver paint contacts made at room tempera-

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Figure 2: X-ray diffraction profiles of FeTe films taken at room temperature. The wide range profiles show only the tetragonal (00L) peaks of FeTe films and the MgO substrate (002) peak, indicating c-axis preferred orientation. No sign of extra peaks of the (00L) peaks of FeTe films and the MgO substrate (002) peak, indicating c-axis preferred orientation. No sign of extra peaks of the (00L) peaks of FeTe films and the MgO substrate (002) peak, indicating c-axis preferred orientation.

Figure 3: Effects of exposure to various air components. Separate FeTe samples were annealed in 100 °C, 100 mTorr O2 (a), N2 (b), CO2 (c), vacuum and exposed to water (d) and shows that the structure does not break down as oxygen is incorporated and superconductivity sets in. Further, clear shifts of FeTe (00L) peaks were observed for the films annealed in oxygen atmosphere indicating that the c lattice constant increases with the incorporation of oxygen. The amount of increase in the c axis depends upon the amount of excess oxygen added, varying from 0.01 Å to 0.03 Å.

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 in O2, N2, CO2, vacuum and exposed to water. For comparison, the resistivity measurement of the as-grown FeTe films is shown in Fig. 3(a). The FeTe films annealed in pure O2 show a sharp drop of resistivity at around 10 K similar to the air exposed sample in-
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 Fig. 3(c), (d), and (e). Water exposed films show a substantial increase in resistivity but no sign of superconductivity, see Fig. 3(f). Repeated anneals improved the superconducting properties, most notably the sharpness and completeness of the transition. However, adding subsequent anneals of 50 minutes 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 doping is reversible. Fig. 3(g) shows the resistivity of an FeTe film that was first annealed 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 TEY and TFY results at the Fe L edges were identical (not shown), while the O K edge TEY looks similar to bulk FeOx (not shown) but the TFY 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 oxidation 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 total fluorescence yield (TFY) of 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 FeOx’s [15–17], see the inset [15]. In contrast, for the sample with the longest exposure to air (24 days), the TFY Fe L edge spectra look most like the $Fe_2O_3$. In particular, the spectra look most like $γ$-Fe2O3 rather than $α$-Fe2O3, but the two are quite similar compared to the changes we observe with doping 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, that ambient oxidation drives the initial 2+ Fe ions to a 3+ like nominal valence state. Our observation of the Fe valence states is different from the literature on iron pnictides. In iron pnictides, the Fe L edge spectra were reported to be metallic in nature; an indication of weak electronic correlations [13]. Our data are thus consistent with claims that the iron chalcogenides are more strongly correlated than the pnictides [19–20] and are also consistent with a larger moment in the chalcogenides [21, 22].

In Fig. 4(b), 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 pre-peak 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 O 2p orbitals, where the increase in pre-peak intensity is proportional to the exposure time to air.

Figure 4: X-ray absorption spectroscopy of FeTe films. (a). The Fe L-edges 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$_2$O$_3$ curves in the inset. (b). The O K-edge spectra show a pre-peak which is a direct result of Fe 3d orbitals hybridizing with O 2p orbitals [23]. The relative photon energy position of the FeO$_x$ pre-peak to the main MgO peak is in very good agreement with the peak spacing reported in XAS studies of Fe$_{1-x}$Mg$_x$O$_y$ [24].

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 [2, 11]. 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 [2, 11, 12]. Thus the overall picture that one must move away from a specific point in the phase diagram rather than moving toward a particular point receives strong confirmation in the FeTe system.

Experimentally, the ability to reversibly turn on superconductivity with suitable, low temperature annealing steps opens the door for 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. who found superconductivity in films of FeTe and attributed the result to in-plane, tensile strain. [10] 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 know and it could be possible that either mechanism could produce superconducting versions of FeTe.

In summary, by introducing excess oxygen at low temperature, superconductivity was induced in the FeTe films with an onset temperature near 10 K. The oxygen doping process is reversible. X-ray absorption spectroscopy indicates that the FeTe films become superconducting concurrent with a nominal Fe valence state increase from 2+ to 3+. This method for creating a superconductor is drastically different from the better known procedure of substituting isovalent Se or S for Te. Thus superconductivity occurs in at least two very different places in the phase space of strain and Fe valence. A proper theory for superconductivity in these materials must account for this new conceptual phase diagram.

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