Magnetism, Superconductivity and Stoichiometry in Single Crystals of Fe\(_{1+y}(\text{Te}_{1-x}\text{S}_x)\)_z

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We report synthesis of high quality Fe\(_{1+y}(\text{Te}_{1-x}\text{S}_x)\)_z single crystals and a comprehensive study of structural, magnetic and transport properties. There is high sensitivity to material stoichiometry which includes vacancies on the Te(S) site. Our results reveal competition and coexistence of magnetic order and percolative superconductivity for \(x \geq 0.03\), while zero resistivity is achieved for \(x \geq 0.1\).

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I. INTRODUCTION

All exotic superconductors exhibit Cooper pairing in proximity to a magnetic ground state, regardless of crystal structure and bonding type: cuprate oxides, heavy fermion intermetallics and organics. Recently discovered iron pnictide superconductors are no exception: magnetism in these materials is strongly influenced by subtle crystal structure changes. Binary iron chalcogenides FeSe and FeTe share square planar layers of tetrahedrally coordinated Fe with the Fe-As based superconductors, yet they crystalize in a simple crystal structure which is amenable to modeling by band structure calculations. FeSe hosts high \(T_c\)’s of up to 37 K under pressure and an isotropic superconducting state. Its crystal structure changes from high temperature tetragonal \(P4/nmm\) to low temperature orthorhombic \(Cnmm\) at 70 K. In Fe\(_{1.08}\)Te transition to monoclinic space group \(P2_1/m\) with commensurate AF order occurs between 65 and 75 K, whereas Fe\(_{1.14}\)Te exhibits weaker first-order transition to orthorhombic space group \(Pmmn\) and incommensurate AF order from 55 K to 63 K. In this work we examine the evolution of superconductivity and magnetism in single crystals of Fe\(_{1+y}(\text{Te}_{1-x}\text{S}_x)\)_z for \(x = (0 - 0.15), y = (0 - 0.14)\) and \(z = (0.94 - 1)\). We provide experimental evidence for structural parameters at the magnetic/superconducting boundary.

II. EXPERIMENTAL METHOD

Single crystals were grown from Te(S) flux and their composition was determined as previously described. Total scattering data from finely pulverized crystals were obtained at 80 K at 11-ID-B beamline of the Advanced Photon Source synchrotron using 58.26 keV x-rays (\(\lambda = 0.2128\,\text{Å}\)) selected by a Si 311 monochromator. 2D patterns for samples in 1mm diameter Kapton tubes were collected using a MAR345 2D-detector, placed perpendicular to the primary beam path, 188.592 mm away from the sample. An Oxford Cryosystem cryostream was used for temperature regulation. Details on experimental procedures, data processing, the atomic pair distribution function (PDF) method, and structural modeling can be found elsewhere. Electrical resistivity measurements were performed using a standard four probe method with current flowing parallel to the \(\hat{a}\)-axis of tetragonal structure. Magnetization and resistivity measurements were carried out in a Quantum Design MPMS-5 and a PPMS-9 instruments.

![FIG. 1: Fe\(_{1+y}(\text{Te}_{1-x}\text{S}_x)\)_z synchrotron Rietveld (a) and PDF refinement (b) results taken at \(T = 80\,\text{K}\). Inset shows two Te-Fe-Te bond angles illustrated on the FeTe\(_4\) tetrahedron.](image-url)

III. RESULTS

Typical synchrotron data (symbols), with fully converged \(P4/nmm\) structural model superimposed (solid lines), and corresponding difference curves (offset for clarity) are presented in Figure 1, featuring Fe\(_{1.12}\)Te\(_{0.83}\)S\(_{0.11}\). Panel (a) features a Rietveld refinement, with a corresponding PDF refinement shown in (b). The PDF is peaked at positions corresponding
TABLE I: Structural parameters from PDF refinement at $T = 80$ K, magnetic and superconducting properties of Fe$_{1+y}$Te$_{1-x}$S$_x$. Transition temperatures $T_1$ and $T_2$ are from $\partial \chi / \partial T$ data. Temperatures of $T_c$ onset and zero resistance are from resistivity data.

| Fe$_{1+y}$Te$_{1-x}$S$_x$ | $V (\AA^3)$ | $c/a$ | $\Theta(K)$ | $\chi^{\parallel}(\mu$B) | $T_1(K)$ | $T_2(K)$ |
|--------------------------|-------------|-------|-------------|-----------------|--------|---------|
| Fe$_{1.14(2)}$Te$_{0.01(1)}$ | 91.150(4) | 1.642(1) | 104(2) | 0.10(2) | 117.46(1) | 191(4) |
| Fe$_{1.09(2)}$Te$_{0.00(1)}$ | 91.017(4) | 1.640(1) | 102(2) | 0.09(2) | 117.15(1) | 191(4) |
| Fe$_{1.12(3)}$Te$_{0.00(1)}$ | 90.959(4) | 1.632(1) | 104(2) | 0.12(2) | 117.15(1) | 191(4) |
| Fe$_{1.13(3)}$Te$_{0.85(1)}$S$_{0.15(2)}$ | 90.932(5) | 1.632(1) | 104(2) | 0.12(2) | 117.15(1) | 191(4) |
| Fe$_{1.12(3)}$Te$_{0.83(1)}$S$_{0.17(2)}$ | 90.997(4) | 1.632(1) | 104(2) | 0.12(2) | 117.15(1) | 191(4) |
| Fe$_{0.96(4)}$Te$_{0.90(1)}$S$_{0.15(2)}$ | 89.900(5) | 1.632(1) | 104(2) | 0.12(2) | 117.15(1) | 191(4) |

Fig. 2 (a,b) shows the anisotropic temperature dependence of magnetic susceptibility for Fe$_{1+y}$Te$_{1-x}$S$_x$. The peak at 70 K for Fe$_{1.14(2)}$Te corresponds to an antiferromagnetic (AF) transition presumably coupled with structural and first order. The transition spans about 20 K for both field orientations. The magnetic susceptibility is isotropic above 70 K and $\chi^{\parallel}/\chi^{\perp}$ increases from 1 to 1.1 below the transition. The transition temperature is suppressed with sulfur doping down to 20 K by $x = 0.15$. A diamagnetic signal is observed for $x \geq 0.14$ (Fig. 2(a,b) insets), in apparent coexistence with a magnetic state. Magnetic susceptibility is Curie-Weiss like above 200 K. The effective moments estimated are between the low spin (2.94$\mu$B, $S = 1$) and high spin (4.9$\mu$B, $S = 2$) values of an Fe$^{2+}$ (3d$^6$) in a tetragonal crystal field (Table I). The high temperature effective moments decrease with the S-doping and with the reduction of excess Fe. Negative Curie-Weiss temperatures attest to the antiferromagnetic coupling between moments (Table I).

The in-plane electrical resistivity in zero field is shown in Fig. 2(c). Residual resistivity values at low temperatures for pure Fe$_{1+y}$Te and crystals with the highest sulfur concentration $x$ are comparable to single crystals grown by Bridgeman method but smaller by a factor of 3 - 4 than in polycrystalline materials due to the absence of grain boundaries and secondary phases. The grain boundaries are not transparent as in MgB$_2$ where intrinsic low values of $\rho_0$ in high quality polycrystals are often lower than in crystals. Therefore grain boundaries cannot be neglected when measuring resistivity on polycrystals of iron chalcogenide superconductors. The resistivity of Fe$_{1+y}$Te above the magnetic transition is poorly metallic, in agreement with measurements on
Figure 3(a) gives the temperature dependent specific heat $C_p$ and $M/H$ for Fe$_{1.14(2)}$Te and Fe$_{1.09(2)}$Te below 90 K. Both crystals show two lambda anomalies at magnetic/structural transition around $T_1 = 70$ K and $T_2 = 59$ K for Fe$_{1.14(2)}$Te and around $T_1 = 66$ K and $T_2 = 59$ K for Fe$_{1.09(2)}$Te. Above and below the transition region there is no difference in $C_p(T)$. A magnetic field of 90 kOe shifts both transition in both samples for $\Delta T = 1$ K. The entropy $\Delta S = 2.2$ J/mol associated with the transition is independent of the iron stoichiometry $y$ (Fig. 3(b)). This is smaller than estimated change of entropy in Fe$_{1.07}$Te of $\Delta S \sim 3.2$ J/mole(K)$^{12}$ The error is probably due to conventional PPMS heat capacity setup which introduces sizeable error in the vicinity of the first order phase transition.$^{23}$ Nevertheless, we can still compare the change in $\Delta S$ for Fe$_{1+y}$Te crystals with different $y$ caused by AF contribution which dominates $\Delta S$ in the transition region.$^{23}$ Assuming that total entropy is lost on the spin state transition $\Delta S = R \ln[(2S_H + 1)/(2S_L + 1)]$ and using $\mu_{eff} = \sqrt{4S(S + 1)}$, high temperature effective moment is $\mu_{eff}^H(Fe_{1.14(2)}Te) = 3.92 \mu_B$, $\mu_{eff}^H(Fe_{1.09(2)}Te) = 3.73 \mu_B$, we obtain the moment value below magnetic transitions in the ordered state $\mu_{eff}^H(Fe_{1.14(2)}Te) = 1.3 \mu_B$ and $\mu_{eff}^H(Fe_{1.09(2)}Te) = 1.2 \mu_B$. Larger relative entropy change for higher $y$ is related to the occupancy of iron in the interstitial sites which is expected to be strongly magnetic.$^{23}$ Interestingly, these numbers are very close to values for a spin moment of 1.3 $\mu_B$ associated with SDW transition calculated by DFT calculations.$^{25}$

The low temperature $C_p$ data for Fe$_{1.14}$Te can be fitted to the $C(T) = \gamma T + C_0 T^3$ power law below 15 K with $\gamma = 32$ mJ/moleK$^2$ and $\beta = 0.49$ mJ/moleK$^4$ from which a $\theta_D = 228$ K can be obtained (Fig. 3(c)). Specific heat shows a broad feature around $T_c$ (Fig. 3(c) inset) for superconducting samples, similar to other iron pnictides.$^{26}$ Due to high upper critical fields and apparent coexistence of superconductivity and long range magnetic order in our crystals, a reliable estimate of the normal state contribution to electronic specific heat $\gamma$ is rather difficult. Addition uncertainty in testing traditional isotropic weak coupling BCS value of $\Delta C_p/\gamma T_c$ in Fe$_{1+y}(Te_{1-x}S_x)_2$ is introduced by the percolative nature of superconductivity with up to 7% superconducting volume fraction (Fig. 2). Therefore we restrict ourselves to an estimate of the $C_p/T$ discontinuity associated with superconducting transition for material with the highest sulfur concentration and consequently the most pronounced jump in specific heat.$^{27}$ For $x = 0.15$ it is about 12 mJ/moleK$^2$ at $T_c = 8.8$ K, comparable to what is observed in Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ and Ba(Fe$_{1-x}$Ni$_x$)$_2$As$_2$ single crystals.$^{28}$

Closer inspection of the $(\partial \rho / \partial T)$ and $(\partial \rho / \partial T)^2$ (Fig. 4) for Fe$_{1.14(2)}$Te and Fe$_{1.09(2)}$Te unveils two transitions at temperatures $T_1$ and $T_2$ that correspond to specific heat anomalies in Figure 3(a) (Table I). With sulfur substitution both transitions are clearly observed only up to $x \leq 0.1$ (Fig. 4). For higher sulfur concentra-
FIG. 4: Fe$_{1.1+2}$Te and Fe$_{1.062}$Te as well as sulfur doped samples for $x \leq 0.1$ show two clear magnetization anomalies around SDW transition, as seen in derivatives $d(\chi(T))/dT$ and $d\rho/dT$ (inset). For higher sulfur content anomalies are broader (insets) and cannot be distinguished.

IV. DISCUSSION

The AF SDW in pure Fe$_{1+y}$Te is accompanied by a lattice distortion for all investigated values of $y$ as in the undoped Fe-As superconductors. DFT calculations have found that excess Fe donates charge as Fe$^+$ to FeTe layers, with strong tendency of moment formation on the excess Fe site. By comparing our C(T) data with the specific heat data taken on Fe$_{1.06}$Te crystals, it can be seen that the clarity of the two step anomaly increases with the increase of $y$ in Fe$_{1+y}$Te. It is absent for Fe$_{1.05}$Te and Fe$_{1.06}$Te, visible for Fe$_{1.06}$Te and rather pronounced for Fe$_{1.14}$Te with similar entropy under both transitions (Fig 3a,b). Magnetic measurements $(\partial \chi/\partial T)$ closely match thermodynamic data (Fig 3, Fig. 4). Whereas temperature of lower temperature transition $T_2$ (59 K) does not change with change in $y$, Fe$_{1+y}$Te with higher content of excess Fe $y$ has transition $T_1$ at higher temperature (70 K and 66 K, Table I). The Fermi level in Fe$_{1+y}$Te lies exactly at the sharp peak of the excess Fe density of states $N(E_F)$; therefore higher $T_1$ may be magnetically driven based on the Stoner criterion $N(E_F)I_\alpha I_\delta$. Increased $\rho$ values for Fe$_{1.14}$Te when compared to Fe$_{1.09}$Te are also consistent with this (Fig. 2). Higher level of excess Fe $y$ corresponds to larger size mismatch between cylindrical electron and hole Fermi surfaces. Therefore $T_2$ and $T_1$ transitions may correspond to successive SDW Fermi surface nesting of individual electron - hole cylindrical pieces. Recent work shows that the magnetic order in parent compounds of iron based superconductors is established below temperature of structural transition with up to 20 K difference in temperature of transition, as seen in CeFe$_{1-x}$Co$_x$AsF. It is unlikely that two transitions seen in our crystals correspond to individual magnetic and structural transitions since they have the same sensitivity to magnetic field.

Our findings are summarized in the electronic and structural phase diagrams shown in Fig. 5. The lattice contraction with isoelectronic sulfur substitution corresponds to a positive chemical pressure. The magnetic transition is suppressed from the ~ 58 – 70 K region to about 20 K. Signatures of percolative superconductivity were observed for all $x \geq 0.3$. Zero resistivity in fully percolating path was observed for $x \geq 0.1$. The superconducting transition width decreases with the increase of $x$ and $T_c$. Clearly, there is a competition between magnetic SDW order and the superconducting state since with increase in sulfur content $x$, $dT_1/dx$ and $dT_c/dx$ have opposite signs.

Having delineated the evolution of magnetic and superconducting properties, it is natural to ask what is the correlation with the structural parameters. The unit cell parameters $a$ and $c$ of $P_4/nmm$ crystal structure decrease smoothly at $T = 80$ K as sulfur is substituted in the place of tellurium (Table I). The $c/a$ ratio decreases to nearly constant value for $x \geq 0.1$ up to $x = 0.15$. After $x = 0.15$ we have observed formation of FeS in the hexagonal NiAs - type of structure in the same range of synthesis parameters. Close inspection of the tetrahedral angle $\alpha$ at $T = 80$ K (Fig. 5(b)) reveals an extremum near the superconducting percolation threshold. The angle $\alpha$ increases up to $x = 0.03$ and then decreases with further sulfur increase. The tetrahedral angle $\alpha$ therefore seems to be intimately connected with electronic transport properties which will be discussed next.

Both $x = 0$ crystals are metallic in the low temperature phase (Fig. 2(c)). On the other hand, two successive transitions have also been reported in FeTe$_{0.92}$ under high pressure in the intermediate regime between $P = (1 - 1.8)$ GPa as well as two distinct types of transport below the magnetic and structural transition: metallic for FeTe$_{0.09}$ and semiconducting for FeTe$_{0.82}$. We note that semiconducting contribution to $\rho$ below the magnetization anomaly for $x = 0.10$ and $x = 0.11$ (Fig. 1) coincides with Te(S) vacancies from synchrotron X ray refinement (Fig. 1, Table I). Crystals with no Te(S) vacancies within error bars have metallic or semimetallic contributions to $\rho$. This is in agreement with photomission studies that showed no visible energy gaps at the electron and hole Fermi surface for $y < 0.05$ in Fe$_{1+y}$Te. Increase of resistivity at the SDW AF transition signals small gap opening at the Fermi surface. The band structure of FeTe features intersecting elliptical cylindrical electron portions at the Brilloin zone corners compensated by hole sections with higher effective mass at the zone center. Our findings show that
the details of the nesting condition depend rather sensitively on the tetrahedral angle \( \alpha \) and vacancies on the ligand site. This points to importance of hybridization between Te \( p \) and Fe \( d \) bands in addition to excess stoichiometry \( y \) on Fe site.\footnote{Michael R. Norman, Physics 1, 21 (2008)} Our results strongly suggest that nanoscale inhomogeneity seems to be the key factor governing magnetic and electronic transport properties in Fe\(_{1+y}/(\text{Te}_{1-x}\text{S}_{x})_2\).

Finally we comment on the percolative nature of superconductivity found in our crystals. Superconducting volume fraction increases with sulfur stoichiometry \( x \). The \( 4\pi \chi_C \) reaches up to \(-0.07\) at \( T=1.8 \text{ K} \) \((\sim 0.26 T_C)\) for the highest \( x \) crystals where zero resistivity was observed to approach the \( T_C \) onset (Fig. 5). This signals granular superconducting state coexisting with SDW order, taking only a fraction of sample volume and stabilizing to fully percolating superconducting path by \( x = 0.14 \). Similar coexistence was observed in other iron based superconductors, CaFe\(_{1-x}\)Co\(_x\)AsF, SmFeAsO\(_1-x\)F\(_x\), SrFe\(_2\)As\(_2\) and BaFe\(_2\)As\(_2\).\footnote{Wei Bao, Y. Qiu, Q. Huang, M. A. Green, P. Zajdel, M. J. Carey, A. Bars天ow, Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. 130, 3296 2008 .} For example in the underdoped region of Ba\(_{1-x}\)K\(_x\)Fe\(_2\)As\(_2\) the superconducting volume fraction has been reported to be \((23\pm3\%)\%\) of \(-1/4\pi \) at ~0.06\( T_C \) increasing up to \( 50\% \) for nearly optimally doped material.\footnote{Yoshikazu Mizuguchi, Fumiaki Tomioka, Shunsuke Tsuda, Takahide Yamaguchi and Yoshihiko Takano, Appl. Phys. Lett. 94, 012503 (2009)} Since SDW magnetic order and superconductivity compete for the same Fermi surface, percolative nature of superconductivity may be associated with intrinsic mesoscopic real space phase separation as in cuprate oxides or CaFe\(_{1-x}\)Co\(_x\)AsF.\footnote{Alaska Subedi, Lijun Zhang, D. J. Singh and M. H. Du, Phys. Rev. B 78, 134514 (2008)} Consequently superconductivity may be mediated by magnetic fluctuations, consistent with small values of electron phonon coupling constant found in doped Fe\(_{1+y}\)Te and FeSe.

\[ \text{FIG. 5: (a) Electronic phase diagram of Fe}_{1+y}(\text{Te}_{1-x}\text{S}_{x})_2, \] showing paramagnetic (PM), antiferromagnetic (AFM) and superconducting (SC) ground states. Blue triangles pointing up and down correspond to \( T_2 \) and \( T_1 \) transitions respectively. For \( x = 0 \) both can easily be identified. Red circles denote onset of superconducting transition in \( \rho \) and zero resistance. Transition for \( x = 0.15 \) was estimated from heat capacity measurement. (b) Structural parameters at \( T = 80 \text{K} \).]

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