First-order magnetic and structural phase transitions in Fe$_{1+y}$Se$_x$Te$_{1-x}$

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We use bulk magnetic susceptibility, electronic specific heat, and neutron scattering to study structural and magnetic phase transitions in Fe$_{1+y}$Se$_x$Te$_{1-x}$. Fe$_{1.068}$Te exhibits a first order phase transition near 67 K with a tetragonal to monoclinic structural transition and simultaneously develops a collinear antiferromagnetic (AF) order responsible for the entropy change across the transition. Systematic studies of FeSe$_{1-x}$Te$_x$ system reveal that the AF structure and lattice distortion in these materials are different from those of FeAs-based pnictides. These results call into question the conclusions of present density functional calculations, where FeSe$_{1-x}$Te$_x$ and FeAs-based pnictides are expected to have similar Fermi surfaces and therefore the same spin-density-wave AF order.

I. INTRODUCTION

Superconductivity was recently discovered in $\alpha$-phase FeSe$_x$ system [1], shortly after the discovery of superconductivity in FeAs-based pnictides [2-6]. The $T_c$ of the Fe$_{1+y}$Se$_x$Te$_{1-x}$ system can reach up to 14 K at ambient pressure [7-10] and 27 K at a pressure of 1.48 GPa [11]. Contrary to the earlier prediction of a low-$T_c$ conventional superconductor [12], density functional calculations of the electronic structure, magnetism and electron-phonon coupling for the superconducting phase of Fe$_{1+y}$Se$_x$Te$_{1-x}$ suggest that superconductivity in this class of materials is unconventional and mediated by spin fluctuations [13]. Furthermore, the calculated Fermi surface of Fe$_{1+y}$Se$_x$Te$_{1-x}$ is very similar to that of the iron pnictides such as LaFeAsO and SrFe$_2$As$_2$. If the observed collinear antiferromagnetic (AF) order in the parent compounds of the FeAs-based pnictides [14-16] is due to the spin-density-wave (SDW) instability of a nested Fermi surface [22, 23, 24, 25], one would expect to find the same AF structure or SDW instability in the nonsuperconducting Fe$_{1+y}$Se$_x$Te$_{1-x}$. For FeAs-based materials such as LaFeAsO, CaFeAsO, and PrFeAsO, neutron scattering experiments have shown that the system exhibits a tetragonal to orthorhombic lattice distortion followed by a collinear AF order with moment direction along the orthorhombic long ($a$) axis (Fig. 1c) [14, 15, 16, 17, 18, 19, 20, 21]. In the case of Fe$_{1+y}$Se$_x$Te$_{1-x}$, although Fe$_{1+y}$Te also undergoes a structural distortion along with the establishment of a long-range AF order near 67 K [26, 27], the temperature structure is monoclinic and the magnetic structure can be either commensurate [26] or incommensurate [27], much different from the commensurate AF structure of FeAs-based pnictides.

To understand this apparent discrepancy, we carried out systematic neutron scattering studies of the Fe$_{1+y}$Te system. We find that excess Fe ions in Fe$_{1+y}$Te sitting in the octahedral sites [26, 28, 29] have magnetic moments [26]. Although stoichiometric FeTe is difficult to synthesize [28], the Fe spins in Fe$_{1.068}$Te form a collinear AF structure with moments confined within the $a$-$b$ plane of the monoclinic structure as shown in Fig. 1(b). Consistent with earlier measurements [30, 31], we find that the AF phase transition is first-order with an entropy change of $\sim 3.2$ J/(mol-K). Systematic studies of FeSe$_{0.287}$Te$_{0.713}$ and FeSe$_{0.568}$Te$_{0.432}$ reveal that the differences in lattice distortions between FeSe$_{1-y}$Te$_x$ and LaFeAsO can account for the differences in their magnetic structures. These results are difficult to explain within the previous density functional calculations, where FeTe, FeSe, and LaFeAsO are expected to have similar Fermi surfaces and therefore similar SDW-type AF order [13]. However, more recent density functional calculations suggest that the excess Fe in Fe$_{1+y}$Te is strongly magnetic and is also an electron donor, which might account for the observed differences in magnetic structures of Fe$_{1+y}$Te and other FeAs-based pnictides [32].

II. EXPERIMENTAL RESULTS AND DISCUSSIONS

We prepared powder samples of Fe$_{1+y}$Se$_x$Te$_{1-x}$ with nominal composition of $x = 0, 0.3, 0.5$ using the method described elsewhere [3]. Fe$_{1+y}$Te is non-superconducting while the other two samples have $T_c$ of $\sim 14$ K. Powder neutron diffraction data were taken on the BT-1 powder diffractometer at the NIST Center for Neutron Research (NCNR). The nuclear and magnetic structure transitions were further studied on the BT-7 triple-axis spectrometer at the NCNR. We define the nuclear wave vector $\mathbf{Q}$ at $(q_x, q_y, q_z)$ as $(H, K, L) = (2\pi, q_x/2\pi, 2\pi, q_y/2\pi, 2\pi, q_z/2\pi)$ reciprocal lattice units (r.l.u.) in both the tetragonal and monoclinic unit cells. We used commercial SQUID and PPMS systems to measure the DC susceptibility and specific heat of the samples used for neutron measurements.

We first discuss the nuclear and magnetic structures of the non-superconducting Fe$_{1+y}$Te. At 80 K, Fe$_{1+y}$Te has...
Fe$_{1.06}$Te

T = 5 K

(a) Neutron powder diffraction data of Fe$_{1.06}$Te at T = 5 K collected on the BT-1 diffractometer with Ge(311) monochromator and an incident beam wavelength $\lambda = 2.0785 \text{Å}$. The lattice structure is described by the monoclinic space group $P2_1/n$ above $T_N$, as illustrated schematically in the inset. (b) Schematic in-plane spin structure of Fe$_{1.06}$Te. The solid arrows and hollow arrows represent two sublattices of spins, which can be either parallel or antiparallel. The shaded area indicates the magnetic unit cell. (c) Schematic in-plane spin structure of SrFe$_2$As$_2$ from Ref. 20.

A tetragonal crystal structure with space group $P4/nmm$ and no static magnetic order. Our Rietveld analysis reveals that the system actually has excess Fe with $y = 0.068$. On cooling to 5 K, the nuclear structure changes to monoclinic with the space group $P2_1/m$, as shown by the neutron powder diffraction data in Fig. 1(a) and refinement results in Table I. For oxypnictides such as LaFeAsO and CeFeAsO, the lattice distortion changes the symmetry from tetragonal to orthorhombic [14, 13]. In the case of Fe$_{1+y}$Te, the lattice distortion is from tetragonal to monoclinic with the $\beta$ angle between $a$ and $c$ axis being reduced to less than 90 degrees while the nearest Fe-Fe distance is unchanged.

Figure 1(c) shows the in-plane spin structure of LaFeAsO and SrFe$_2$As$_2$, where the Fe moments form a collinear AF structure with spin directions along the $a$-axis of the orthorhombic direction. This magnetic structure appears to be ubiquitous for parent compounds of FeAs-based superconductors [14, 13, 16, 17, 18, 19, 20, 21]. Our refinement on Fe$_{1.06}$Te suggests that the spin structure in this system is also collinear, and consists of two sublattices with a major component of the moment along the tetragonal $b$ axis as shown in Fig. 1(b). Based on our powder diffraction data, we cannot conclusively determine the relative spin directions between the two sublattices (they may be parallel or antiparallel).

The in-plane spin directions in Fe$_{1.06}$Te are rotated 45 degrees from those in the Fe-As materials. This is different from the prediction of the density functional calculations [13], where Fermi surfaces of these two materials are expected to be very similar.

In addition to the large moment (1.97 $\mu_B$) along the tetragonal $b$-axis direction, we find that the projections of the moment along the $a$ and $c$-axes were -0.56 $\mu_B$, and 0.25 $\mu_B$, respectively. Although the total moment is similar in Fe$_{1.06}$Te and Fe$_{1.125}$Te, the $c$-axis component of the moment in Fe$_{1.125}$Te is 1.36 $\mu_B$ [20]. This difference may be related to the excess Fe ions in the octahedral sites [20, 28, 29], which is expected to be strongly magnetic [32]. Since the moments of the excess Fe ions are randomly distributed between the Fe-Fe layers, the Fe moments in Fe$_{1.125}$Te tend to cant toward the $c$-axis. With further addition of excess Fe into the system, the static antiferromagnetic order actually becomes incommensurate [27]. The reduction of the excess Fe drives the system toward the stoichiometric FeTe and decreases the influence of the excess Fe, this in turn favors the commensurate AF spin structure in Fig. 1(b).

To understand the nuclear and magnetic phase transitions, we focus on the (1,1,2)/(1,1,-2) nuclear and
(1,0,1)$_M$ magnetic Bragg peaks. As shown in the inset of Fig. 2(a), the (1,1,2)/(1,1,2) reflections split into two peaks due to the tetragonal-monoclinic structural transition. By fitting with one and two Gaussian peaks at high and low temperatures, respectively, we find that the structural phase transition happens near 67 K. Figure 2(b) shows that the temperature dependence of the (1,0,1)$_M$ magnetic peak is clearly associated with the structural phase transition. In addition, the full width at half maximum (FWHM) of the (1,0,1)$_M$ peak is larger than the resolution due to the splitting of the (1,0,1)$_M$ and (1,0,-1)$_M$ peaks.

To see if the 67 K phase transition is first or second order, we measured the magnetic susceptibility using a SQUID. Figure 2(c) shows that DC susceptibility with field-cooled (FC) process and an applied magnetic field of 20 Oe has a clear hysteresis near the structural/magnetic phase transition. The first-order nature of the structural/magnetic phase transitions is shown unambiguously in the heat capacity measurement. Similar to the previous study in Fe$_{1.11}$Te [31], a sharp peak is found around the phase transition temperature [Fig. 2(d)]. Since the heat capacity option of the PPMS does not to work accurately in the vicinity of the first-order transition [32], the inset of Fig. 2(d) shows the raw data of the calorimeter, where the plateaus in the heating and cooling processes clearly reveal the heat absorption and liberation during the first-order phase transition. Based on these data, we estimate that the latent heat of the phase transition is $\sim$215 J/mol, meaning a change of entropy of $\Delta S \sim 3.2$ J/(mol-K) through the transition. If we assume that the Fe moment in FeTe is about 3.87 $\mu_B$ in the paramagnetic state [33] and 1.7 $\mu_B$ below $T_N$, the change of the entropy across the transition based on an Ising model is about 3.5 J/(mol-K). This result suggests that the major contribution to the entropy change at the phase transition arises from the spin ordering, which supports the view that the first order phase transition is driven by the magnetism [32].

Finally, we discuss the lattice distortions and magnetic structure in Fe$_{1+y}$Se$_{1-x}$Te$_x$ as superconductivity is induced by replacing Te with Se [8, 10]. Although we find no static long range ordered magnetic Bragg peaks in the superconducting FeSe$_{0.287}$Te$_{0.743}$ and FeSe$_{0.568}$Te$_{0.432}$ similar to the Fe-As based materials [14, 13, 14, 16, 15, 18, 19, 20, 21], short-range spin fluctuations with correlation length of 9.4 Å were found in FeSe$_{0.287}$Te$_{0.743}$ at $Q = 0.938$ Å$^{-1}$ as shown in Fig. 3(b). The $Q$ value is slightly less than the $Q$ value 0.974 Å$^{-1}$ at the commensurate position (0,0,1)$_M$, which is likely due to the variation of the magnetic form factor as well as a possible variation of the magnetic structure factor. However, one has to be vigilant for impurity phases [34, 36]. For example, we can clearly see the strong (1,1,0) cubic Fe impurity peaks in Fig. 3(a) in both superconducting samples, which suggests the nonstoichiometry of our samples and the possible existence of other phases. We therefore cannot conclude unambiguously that these magnetic fluctuations originate in the superconducting phase, although that is likely the case.

Figure 3 and Table I summarize the doping evolution of some structural parameters for Fe$_{1+\delta}$Se$_{1-x}$Te$_x$. The nearest Fe-Te distance linearly increases with increasing Te concentration, as shown in Fig. 3(c). On the other hand, the Fe-Te/Se-Fe angles [Fig. 3(d)] decrease with increasing Te concentration. For Fe$_{1.068}$Te, the Fe-Te/Se-Fe angle along the a axis is much smaller than that along the b axis. Because of the low-temperature monoclinic structure, the perfect Fe-Te/Se tetrahedron is distorted, resulting in a slight difference in the Fe-Te/Se-Fe angles between the nearest Fe ions, labeled as 1 and 2 in Fig. 3(d). This distortion of the Fe-Te/Se tetrahedron is also illustrated by the Fe-Te/Se distances, which increase with increasing Te concentration [Fig. 3(e)].

To put these results in a proper context, we note that the density functional calculations predicted a similar Fermi surface for Fe$_{1+\delta}$Te and FeAs-based materials [13]. Therefore, within the itinerant electron picture where the observed AF order in these two classes of materials arises from the same Fermi surface nesting, one should expect a similar spin density wave instability, in contrast to the experimental observation. However, the presence of a large magnetic moment on the excess Fe ion in between the ordered Fe-layers in Fe$_{1+\delta}$Te might resolve this inconsis-

FIG. 3: (a) Evolution of the (1,1,2)/(1,1,2) and (2,0,0)/(0,2,0) peaks at low temperatures in Fe$_{1.068}$Te, FeSe$_{0.287}$Te$_{0.743}$ and FeSe$_{0.568}$Te$_{0.432}$. (b) Short-range AF fluctuations at $Q = 0.938$ Å$^{-1}$ with FWHM = 0.67 Å$^{-1}$ in FeSe$_{0.287}$Te$_{0.743}$. (c)-(e) doping dependence of nearest-neighbor Fe-Fe distance, the angles of Fe-Te/Se-Fe, and Fe-Te/Se distances, respectively.
Experimental results [37]. In fact, the difference between magnetic exchange interactions can well explain the extency [32]. Alternatively, a model based on the localized FeSe structure. The difference between angles 1 and 2 due to the monoclinic lattice distortion may give rise to different nearest neighbor couplings $J_{1a}$ and $J_{1b}$. This could in turn stabilize the proposed spin structure in Fig. 1(b) where a spin is actually frustrated by the four nearest spins in a perfect rectangle [38].

### III. Conclusions

In conclusion, we have systematically studied the structural and magnetic phase transitions in $\alpha$-phase Fe$_{1+x}$Se$_2$Te$_{1-x}$ system. In the pure Fe$_{1+y}$Te, we find structural and magnetic phase transitions are intimately connected and first order in nature. The spin structure in Fe$_{1+x}$Te is different from all other FeAs-based materials. Our results show the important role played by the excess Fe ions in determining the magnetic structure of Fe$_{1+y}$Te and suggest that the magnetic ordering can provide enough energy for driving the first order phase transition. Our systematic neutron diffraction measurements suggest that magnetic structure evolution might be consistent with a local moment picture in Fe$_{1+x}$Se$_2$Te$_{1-x}$.

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| TABLE I: Refinement of powder diffraction data |
|-----------------------------------------------|
| Fe$_{1.086}$Te(5 K), P2$_1$/m, $\alpha^2=1.559$, $\beta=89.212(3)$° |
| $\alpha = 3.83435(8)$Å, $b = 3.78407(7)$Å, $c = 6.25705(8)$Å |
| Atom site | x  | y  | z  | occupancy |
| Fe(1)     | 2b | 0.75 | 0.25 | 0.0035(7) | 0.995(11) |
| Fe(2)     | 2a | 0.25 | 0.25 | 0.2798(6) | 1 |
| Fe$_{1.066}$Te(80 K), P4/nmm, $\alpha^2=1.399$ |
| $\alpha = 3.81234(8)$Å, $b = 3.81234(8)$Å, $c = 6.25172(4)$Å |
| Atom site | x  | y  | z  | occupancy |
| Fe(1)     | 2b | 0.75 | 0.25 | 0.2829(4) | 1 |
| Fe(2)     | 2a | 0.25 | 0.25 | 0.7350(3) | 0.068(3) |
| Fe$_{0.28}$Te$_{0.432}(10$ K), P4/nmm, $\chi^2=3.649$ |
| $\alpha = 3.8030(4)$Å, $b = 3.8030(4)$Å, $c = 6.0836(3)$Å |
| Atom site | x  | y  | z  | occupancy |
| Fe        | 2b | 0.75 | 0.25 | 0 |
| Se        | 2a | 0.25 | 0.25 | 0.2708(4) | 0.287 |
| Te        | 2a | 0.25 | 0.25 | 0.2708(4) | 0.743 |
| Fe$_{0.56}$Te$_{0.432}(5$ K), P4/nmm, $\chi^2=1.985$ |
| $\alpha = 3.7924(1)$Å, $b = 3.7924(1)$Å, $c = 5.9551(3)$Å |
| Atom site | x  | y  | z  | occupancy |
| Fe        | 2b | 0.75 | 0.25 | 0 |
| Se        | 2a | 0.25 | 0.25 | 0.2715(3) | 0.568 |
| Te        | 2a | 0.25 | 0.25 | 0.2715(3) | 0.432 |


tendency [32]. Alternatively, a model based on the localized magnetic exchange interactions can well explain the experimental results [37]. In fact, the difference between the Fe-Se/Se-Se angles along the $a$ and $b$-axes should result in different next-nearest neighbor couplings $J_{2a}$ and $J_{2b}$ that are responsible for the observed collinear AF structure. The difference between angles 1 and 2 due to the monoclinic lattice distortion may give rise to different nearest neighbor couplings $J_{1a}$ and $J_{1b}$. This could in turn stabilize the proposed spin structure in Fig. 1(b) where a spin is actually frustrated by the four nearest spins in a perfect rectangle [38].

[1] F.-C. Hsu, J.-Y. Luo, K.-W. Yeh, T.-K. Chen, T.-W. Huang, P.M. Wu, Y.-C. Lee, Y.-L. Huang, Y.-Y. Chu, D.-C. Yan, et al., Proc. Natl. Acad. Sci. U.S.A. 105, 14262 (2008).
[2] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. 130, 3296 (2008).
[3] X. H. Chen, T. Wu, G. Wu, R. H. Liu, H. Chen, and D. F. Fang, Nature 453, 761 (2008).
[4] G. F. Chen, Z. Li, D. Wu, W. Z. Hu, J. Dong, P. Zheng, J. L. Luo, and N. L. Wang, Phys. Rev. Lett. 100, 247002 (2008).
[5] Z.-A. Ren, G.-C. Che, X.-L. Dong, J. Yang, W. Lu, W. Yi, X.-L. Shen, Z.-C. Li, L.-L. Sun, F. Zhou, et al., Europhys. Lett. 83, 17002 (2008).
[6] M. Rotter, M. Tegel, and D. Johrendt, Phys. Rev. Lett. 101, 107006 (2008).
[7] H. H. Wen, G. Mu, L. Fang, H. Yang and X. Zhu, Europhys. Lett. 82, 17009 (2008).
[8] K.-W. Yeh, T.-W. Huang, Y.-L. Huang, T.-K. Chen, F.-C. Hsu, P. M. Wu, Y.-C. Lee, Y.-Y. Chu, C.-L. Chen, J.-Y. Luo, D. C. Yan, and M. K. Wu, Europhys. Lett. 84, 37002 (2008).
[9] S. Margadonna, Y. Takabayashi, M. T. McDonald, K. Kasperkiewicz, Y. Mizuguchi, Y. Takano, A. N. Fitch, E. Suard, and K. Prassides, Chem. Commun., 2008, DOI: 10.1039/b813076k.
[10] M. H. Fang, H. M. Pham, B. Qian, T. J. Liu, E. K. Vehstedt, Y. Liu, L. Spinu, Z. Q. Miao, arXiv:0807.3775 (2008).
[11] Y. Mizuguchi, F. Tomioka, S. Tsuda, T. Yamaguchi, and Y. Takano, Appl. Phys. Lett. 93, 152505 (2008).
[12] S. Atzori and G. Mula, Solid State Commun. 13, 157 (1973).
[13] A. Subedi, L. Zhang, D. J. Singh, and M. H. Du, Phys. Rev. B 78, 134514 (2008).
[14] C. de la Cruz, Q. Huang, J. W. Lynn, J. Li, W. Ratcliff, J. L. Zarestky, H. A. Mook, G. F. Chen, J. L. Luo, N. L. Wang, Pengcheng Dai, Nature 453, 899 (2008).
[15] J. Zhao, Q. Huang, C. de la Cruz, J. W. Lynn, Y. Chen, M. A. Green, G. F. Chen, G. Li, Z. Li, J. L. Luo, N. L. Wang, and Pengcheng Dai, Nature Materials (Published online: 26 October 2008; doi:10.1038/nmat2315).
[16] Y. Chen, J. W. Lynn, J. Li, G. Li, G. F. Chen, J. L. Luo, N. L. Wang, Pengcheng Dai, C. dela Cruz, H. A. Mook,
[17] S. A. J. Kimber, D. N. Argyriou, F. Yokaichiya, K. Habicht, S. Gerischer, T. Hansen, T. Chatterji, R. Klingeler, C. Hess, G. Behr, A. Kondrat, and B. Büchner, Phys. Rev. B 78, 140503(R) (2008).

[18] J. Zhao, Q. Huang, C. de la Cruz, J. W. Lynn, M. D. Lumsden, Z. A. Ren, Jie Yang, Xiaolin Shen, Xiaoli Dong, Zhongxian Zhao, and Pengcheng Dai, Phys. Rev. B 78, 132504 (2008).

[19] Q. Huang, Y. Qiu, W. Bao, J. W. Lynn, M. A. Green, Y. Chen, T. Wu, G. Wu, X. H. Chen, arXiv:0806.2776v2.

[20] J. Zhao, W. Ratcliff, J. W. Lynn, G. F. Chen, J. L. Luo, N. L. Wang, J. Hu, and Pengcheng Dai, Phys. Rev. B 78, 140504 (2008).

[21] A. I. Goldman, D. N. Argyriou, B. Ouladdiaf, T. Chatterji, A. Kreyssig, S. Nandi, N. Ni, S. L. Bud’ko, P. C. Canfield, and R. J. McQueeney, Phys. Rev. B 78, 100506 (2008).

[22] Z. P. Yin, S. Lebègue, M. J. Han, B. P. Neal, S. Y. Savrasov, and W. E. Pickett, Phys. Rev. Lett. 101, 047001 (2008).

[23] I. I. Mazin, D. J. Singh, M. D. Johannes, and M. H. Du, Phys. Rev. Lett. 101, 057003 (2008).

[24] J. Dong, H. J. Zhang, G. Xu, Z. Li, G. Li, W. Z. Hu, D. Wu, G. F. Chen, X. Dai, J. L. Luo, it et al., Europhys. Lett. 83, 27006 (2008).

[25] F. Ma, Z.-Y. Lu, and T. Xiang, arXiv:0804.3370.

[26] D. Fruchart, P. Convert, P. Wolters, R. Madar, J. P. Sene- au, and R. Fruchart, Mat. Res. Bull. 10, 169 (1975).

[27] W. Bao, Y. Qiu, Q. Huang, M. A. Green, P. Zajdel, M. R. Fitzsimmons, M. Zherenkov, M. Fang, B. Qian, E. K. Vehstedt, et al., arXiv:0809.2058.

[28] F. Grønvold, H. Haraldsen, J. Vihovde, Acta Chem. Scand. 8, 1927 (1954).

[29] J. B. Ward and V. H. McCann, J. Phys. C: Solid State Phys. 12, 873 (1979).

[30] I. Tsubokawa and S. Chiba, J. Phys. Soc. Jpn. 14, 1120 (1959).

[31] E. F. Westrum, C. Chou, and F. Grønvold, J. Chem. Phys. 30, 761 (1959).

[32] L. Zhang, D. J. Singh, and M. H. Du, arXiv:0810.3274

[33] J. C. Lashley, M. F. Hundley, A. Migliori, J. L. Sarrao, P. G. Pagliuso, T. W. Darling, M. Jaime, J. C. Cooley, W. L. Hults, L. Morales, et al., Cryogenics 43, 369 (2003).

[34] K. L. Komarek and P. Terzieff, Monatsh. Chem. 106, 145 (1975).

[35] C. Fang, H. Yao, W. F. Tsai, J. Hu and S. A. Kivelson, Phys. Rev. B 77, 224509 (2008).

[36] P. Terzieff, Physica B+C 103, 158 (1981).

[37] F. Ma, W. Ji, J. Hu, Z.-Y. Lu, and T. Xiang, arXiv:0809.4732.

[38] C. Fang, B. A. Bernevig and J. Hu, unpublished