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Spin density wave transition of Fe1 zigzag chains and metamagnetic transition of Fe2 in TaFe_{1+y}Te_3

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The mixed-metal-network layered compound TaFe_{1+y}Te_3 with a “sandwich” TaFeTe_3 layer has partial iron atoms Fe2 randomly occupying these interstitial sites of tetrahedral (Ta, Fe)Te, similar to that in iron-based high-$T_c$ superconductor Fe_{1+y}Te. The antiferromagnetic (AFM) transition of Fe1 zigzag chains and spin-flop of these interstitial Fe2 under high magnetic field are studied through susceptibility, magnetoresistance (MR), Hall effect and specific heat measurements in high-quality single crystal TaFe_{1+y}Te_3. These properties suggest that the high temperature AFM transition of the TaFeTe_3 layers should be a spin-density-wave type AFM order. Below $T_N$, the spin-flop of these interstitial Fe2 from antiferromagnetism to ferromagnetism induces an sharp drop on resistivity and an anomalous Hall effect. It can be inferred from the spin-flop of Fe2 that the local moment of Fe2 atom is about 4 $\mu_B$/Fe. The possible magnetic structure of TaFe_{1+y}Te_3 is proposed from the susceptibility, MR and Hall effect. The properties related to the spin-flop of Fe2 supply a good opportunity to study the coupling between Fe1 and Fe2 in these TaFe_{1+y}Te_3 or Fe_{1+y}Te compounds with interstitial Fe2.

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I. INTRODUCTION

The discovery of iron-based high temperature superconductors has generated great interests in exploring layered Fe-based pnictides and chalcogenides. The superconducting transition temperature ($T_c$) in iron chalcogenides $\alpha$-FeSe increased from initial 8 K4 to 15 K by partial Te substitution for Se5,6, and up to 37 K under high pressure7,8. Recently, the new intercalated iron selenides $A_x$Fe$_{2-y}$Se$_2$ ($A = K$, Rb, Cs and Tl)$^9$12 were reported to have $T_c$ around 32 K, even 43 K. Although the presently known maximum critical temperatures are lower than that of the iron pnictides, these iron chalcogenides have attracted considerable attention due to the fact that it is virulent As free, and that they have very interesting coexistence and competition relation between magnetism and superconductivity$^{13,14}$. The observation of spin resonance below $T_c$ and enhancement of spin fluctuation near $T_c$ in iron chalcogenides suggest a superconducting pairing mechanism mediated by spin fluctuation. The high pressure and muon spin rotation ($\mu$SR) experiments indicate the static magnetic phase macroscopically coexists with superconductivity in FeSe$_{1-x}$ under pressure. In addition, the magnetic order temperature ($T_N$) and superconducting transition temperature ($T_c$) are both enhanced by pressure$^{13,14}$. In the intercalated iron selenides, $\mu$SR$^{15,17}$, neutron scattering$^{16}$ and high temperature magnetization and resistivity$^{18}$ also indicate that superconductivity coexists with antiferromagnetism (AFM) with high $T_N$ ($T_N = 470 - 550$ K) and large magnetic moment 2-3.3 $\mu_B$/Fe$^{16,17}$. Furthermore, Fe$_{1+y}$Te has the most simple crystal structure in iron based superconductors. It is stacked with anti-PbO-type FeTe layer along c-axis, in which iron atoms (Fe1) form a square plane in the edge-sharing FeTe tetrahedral layer. Fe$_{1+y}$Te always contains excess iron atoms (Fe2), which randomly occupy the interstitial sites of FeTe layer and directly couple with the four nearest neighbor Fe1 atoms in the iron square plane$^{19,20}$. This structural characteristic is analogous to that of PbFCl-type Fe$_2$As, where one half iron atoms (Fe1) and As form edge-sharing tetrahedral network, and the other half of iron atoms (Fe2) fully occupy these interstitial sites between anti-PbO type FeAs layers. Fe$_2$As compound also has a spin-density-wave (SDW) type AFM order at 353 K$^{21}$, which is higher than $T_N$ in FeAs-based parent compounds.

The Fe$_{1+y}$Te is not superconducting until Te atoms are partially replaced by Se or S and excess iron atoms (Fe2) are also removed simultaneously$^{5,6}$. Similar to iron-pnictides, Fe$_{1+y}$Te exhibits a structural and AFM transition simultaneously near $T_N \sim 60 - 70$ K. The different $T_N$ arise from the different contents of excess partial iron atoms (Fe2)$^{4,6,19,20}$. However, its AFM structure is distinct from that in FeAs-based parent compounds. A collinear commensurate AFM order with Fe moment along a-axis has been identified in the iron-pnictides$^{22,31}$, while Fe$_{1+y}$Te has a bicollinear and 45° rotated AFM order$^{24,25}$. In addition, neutron scattering experiment found that interstitial Fe2 could tune the AFM wave vector from commensurate to incommensurate in Fe$_{1+y}$Te when y is increased to above 0.076. Theory suggests that the interstitial Fe2 with a valence near Fe$^+$ donates charge to the FeTe layers$^{26}$. There is also a very strong tendency toward moment formation on the Fe2, then these interstitial Fe2 with a large local moment will interact with the magnetism of the FeTe layers, complicating the magnetic order$^{24 - 27}$. Here we report a mixed-metal-network layered compound TaFe$_{1+y}$Te$_3$, which has also partial iron atoms Fe2 randomly occupying these interstitial sites of tetrahedral (Ta, Fe)Te$^{28 - 30}$, similar to...
that in Fe$_{1+y}$Te. TaFe$_{1+y}$Te$_3$ has a SDW-type AFM order ($T_N$) at 160 - 200 K depending on the contents of interstitial Fe$_2$ atoms. In addition, below $T_N$, these Fe$_2$ atoms directly couple with the three nearest Fe$_1$ atoms of Ta-Fe1 mixed network layers and also form AFM alignment, but external magnetic field ($H_{ext}$) is able to break the coupling between Fe$_1$ and Fe$_2$, and cause Fe$_2$ to take a spin-flop and form ferromagnetic (FM) alignment from AFM alignment. It offers an interesting opportunity to investigate the interplay between excess Fe$_2$ and magnetism and transport properties of Ta-Fe mixed network layer.

II. EXPERIMENTAL DETAILS

Single crystals of TaFe$_{1+y}$Te$_3$ were grown by chemical vapor transport method$^{28,29}$. Ta (3N) powder, Fe (3N) powder and Te (4N) powder were accurately weighed according to the stoichiometric ratio of TaFe$_{1+y}$Te$_3$ ($y = 0 - 0.25$), then thoroughly grounded and pressed into pellets. The 2 g mixture pellets and 30 mg transport agent TeCl$_4$ were sealed in evacuated 18 cm long × 15 mm diameter quartz tube. The sealed tubes were placed in multi-zones tube furnace and slowly heated to temperature with the hot end at 690 °C and the cool end at 630 °C. After 150 hours, the furnace was shut off and cooled down to room temperature. The long narrow crystals were obtained, but in different temperature zones the samples had different contents of interstitial Fe$_2$. The sample preparation process except for annealing was carried out in glove box in which high pure argon atmosphere is filled. Single crystal X-ray diffraction (XRD) was performed by MAC MXPAHF X-ray diffractometer (Japan) at room temperature. Elemental analysis obtained by Energy Dispersive X-ray Spectroscopy (EDX). Magnetic susceptibility measurement was performed by a SQUID magnetometer (Quantum Design MPMS-XL7s). Magneto-resistance (MR), Hall coefficient ($R_H$), heat capacity and thermoelectric power (TEP) were measured by using Quantum Design PPMS.

III. RESULTS AND DISCUSSION

A. Crystal structure

The structure of TaFe$_{1+y}$Te$_3$ is shown in the right inset of Fig. 1a. The structure of TaFe$_{1+y}$Te$_3$ features a Ta-Fe bonded network, and the mixed metal network lies between tellurium layers, forming a FeTaTe$_3$ “sandwich”$^{28,29,31}$, similar to that of anti-PbO type FeTe layer. It is stacked with FeTaTe$_3$ “sandwich” along ($-l$ 0 $l$), and crystallizes in P$_2_1$/m monoclinic symmetry with lattice constants $a = 7.4262$ Å, $b = 3.6374$ Å, $c = 9.9925$ Å and $\beta = 109.166$ °. According to literatures$^{28,30}$, there are always partial excess iron atoms, which randomly occupy the interstitial sites of FeTaTe$_3$ layers$^{30}$, similar to that in Fe$_{1+y}$Te. Fig. 1a shows XRD pattern of the platelet-shaped TaFe$_{1+y}$Te$_3$ single crystal at room temperature. Only ($-l$ 0 $l$) reflections are observed in XRD pattern, indicating that the FeTaTe$_3$ “sandwich” plane parallels to the surface of the long piece-like single crystal. The full width of half maximum (FWHM) in the rocking curve of the ($-3$ 0 3) reflection is 0.1 °, shown as the left inset of Fig. 1a, suggesting it is a high quality single crystal. A view of the FeTaTe$_3$ “sandwich” structure along b-axis is shown in Fig. 1b. There are two unique zigzag chains that are parallel to the b-axis. The view nearly perpendicular to the Ta-Fe mixed network layer is

![FIG. 1: (a) The single crystal X-ray diffraction pattern for TaFe$_{1+y}$Te$_3$. The left inset shows the rocking curve at the (-3 0 3) reflection. The crystal structure is shown in the right inset; (b) A view of the TaFeTe$_3$ “sandwiched” structure along b-axis. There are two unique zigzag chains that are parallel to the b-axis; (c) A view of the mixed metal network TaFeTe$_3$ along (-l 0 l); (d) The zigzag chain is made up of Fe centered edge-sharing tetrahedra, similar to the FeTe$_4$ tetrahedra of anti-PbO type Fe$_{1+y}$Te. The partial Fe$_2$ atoms randomly occupy the interstitial sites of the (Ta,Fe)/Te layers; (E) The structure of anti-PbO type Fe$_{1+y}$Te. The partial Fe$_2$ atoms also randomly occupy the interstitial sites of anti-PbO type FeTe layers.](image-url)
The Sandwich layer and Fe$^{1+}$ atoms. The (Ta,Fe)Te$_3$ ing randomly in square pyramidal sites formed by five Te$^4$. The susceptibility under low field shows a sharp antiferromagnetic transition at $T_N \sim 160$ K, which is lower than $T_N = 200$ K of polycrystalline sample TaFe$_{1.25}$Te$_3$. Elemental analysis of the single crystal with $T_N = 160$ K obtained by EDX indicates that interstitial iron is about 0.21. This suggests that interstitial iron atoms Fe$^2$ have strong effect on the magnetism of the Fe zigzag chains. Less excess iron will result in lower $T_N$. When external magnetic field is perpendicular to the Ta-Fe mixed metal network, the AFM order temperature $T_N$ is weakly suppressed from $T_N = 160$ K at 0.1 T to $T_N = 150$ K at 7 T, and the more interesting thing is that high field induces ferromagnetic behavior in susceptibility below $T_N$. Below $T_N$ susceptibility firstly keeps constant with temperature decreasing, then sharply drops at certain temperature $T_M$, which depends on the value of external field $H$. At 160 K Fe$^1$ of zigzag chains form AFM order, and also induce that excess Fe$^2$ of interstitial sites to form antiferromagnetic order simultaneously due to the direct coupling of Fe$^1$ and Fe$^2$. Below $T_N$ magnetic moment of excess Fe$^2$ tends to align along the direction of external field $H$, and forms ferromagnetic order due to the coupling of Fe$^2$ and external field. This is the reason why susceptibility keeps a constant under higher vertical magnetic field below $T_N$. The external field...
is in the ascendant in tuning Fe2 to form FM alignment at high temperature, while the inner field will be in the ascendant with temperature decreasing further, which also induces the susceptibility to drop sharply at certain temperature. The susceptibility of single crystal has strong anisotropic magnetic properties at low field below $T_N$, suggesting that the magnetic easy axis of Fe1 zigzag is along the $[−1 0 1]$. Fig. 2c and 2d show field dependence of magnetization $M$ at various temperature with field perpendicular and parallel to Ta-Fe mixed network, respectively. When external magnetic field is perpendicular to Fe1 zigzag of Ta-Fe mixed network, magnetization $M$ increases linearly with the external field $H_{ext}$ at low field and shows sharp ferromagnetic-like transition at certain field $H_C$. But the magnetic hysteresis is not observed in $M$-$H$ curves at Fig. 2c and 2d. It also arises from the result that the external field $H_{ext}$ competes with the inner field $H_{int}$ formed by Fe1 zigzag chains for tuning the direction of Fe2 spin.

Figure 3 shows temperature dependence of resistivity in various magnetic field $H$. The resistivity shows a metal behavior and has an abnormal transition at $T_{S1} \sim 160$ K under low field, corresponding to the drop of magnetic susceptibility. When external magnetic field is parallel to the Ta-Fe mixed metal network, the abnormal transition temperature $T_{S1}$ has almost no change at different fields. However, under high field perpendicular to the single crystal plane $T_{S1}$ is weakly suppressed to low temperature ($T_{S1} \sim 150$ K for $H > 6$ T) and the resistivity has another abnormal transition simultaneously at certain low temperature $T_{S2}$, which depends on the magnitude of external field $H$. These abnormal behaviors of resistivity can be easily seen in these inters of Fig. 3. The $T_{S1}$ and $T_{S2}$ in resistivity correspond with the AFM transition temperature $T_N$ of Fe1 and the metamagnetic transition temperature $T_M$ of Fe2 in magnetic susceptibility, respectively.

To confirm the origin of the anomalous in resistivity, isothermal magnetoresistance (MR) at different temperature is shown in Fig. 4. One can easily see that they have negative MR effect under parallel field for all temperature and under vertical field for higher than $T_N$. For
vertical field, they have small positive MR below the certain field $H_C$, and it shows a sharp negative MR around $H_C$, which should be ascribed to spin-flop of Fe2 at certain field $H_C$. The largest negative MR effect appears with local moment Fe (4 $\mu_B$) in Fe2, which is the same type FeTe layers. Empirically, the change of Hall coefficient $R_H$ has a strong change around $T_N$, which is almost two times larger than that of Fe1 (2.25 $\mu_B$) in the anti-PbO type Fe layers.

C. Hall coefficient and thermoelectric powder

It is well known that Hall effect arises from two parts—normal Hall effect and anomalous Hall effect in ferromagnetic metals, in which anomalous Hall resistivity is proportional to the magnetization $M$. Empirically, one finds Hall resistivity $ho_H = \rho_{OH} + \rho_{AH} = R_H^N + R_H^A \pi \mu M$, where $\rho_{OH}$ is the normal Hall resistivity due to the Lorentz force in a perpendicular magnetic field $B$, $\rho_{AH}$ the anomalous Hall resistivity, $R_H^N$ the normal Hall coefficient, and $R_H^A$ the anomalous Hall coefficient. To confirm the origin of the AFM transition of Fe1 zigzag chains and field inducing FM transition of Fe2, the transverse resistivity $\rho_{xy}$ is measured by sweeping field from -9 T to +9 T at various temperature, and the accurate Hall resistivity $\rho_H$ is obtained, as shown in Fig. 6a, by using $[\rho_{xy}(+H) - \rho_{xy}(-H)]/2$, where $\rho_{xy}(\pm H)$ is $\rho_{xy}$ under positive or negative magnetic field. Similar to the isothermal MR at various temperature, $\rho_H$ also shows a steep rise at certain field $H_C$ below $T_N$, which arises from the jump magnitudes of magnetization $M$ due to the spin-flop of excess Fe2 induced by external field $H$. The normal Hall coefficient $R_H^N$ is obtained from these $H$-linear term of $\rho_H$ below the “coercive” field $H_C$. $R_H^N$ dependence of temperature is shown in Fig. 5. The $R_H^N$ is positive, indicating the carrier is hole. Above $T_N$, $R_H^N$ decreases distinctly with temperature increasing and almost has a linear dependence of temperature. It may arise from the strong magnetic fluctuation above $T_N$ in this system. Empirically, the change of $R_H^N$ is weakly dependent on temperature above $T_C$ in general ferromagnetic metal. $R_H^N$ shows a pronounced dip at $T_N$. It should be ascribed to that the magnetic fluctuation is suppressed completely and the transport lifetime $\tau$ has a strong change around the fermi surface below $T_N$. The Hall number density $n_{xy} = 1/e R_H^N$ varies from the minimal value $1.3 \times 10^{21}$ cm$^{-3}$ at 155 K to $1.4 \times 10^{22}$ cm$^{-3}$ at 75 K. The normal Hall coefficient $R_H^N$ is the same to that of Fe1 $\chi(\pi M)$ in Fe1+$y$Te($H$). The thermoelectric power (TEP) is positive and has the same sign of the Hall coefficient. As shown in Fig. 6b, TEP shows a weak temperature depen-

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**FIG. 5:** Magnetization of Fe2 $M$ vs $T$ (Left Y-axis) and magnetoresistance $\Delta \rho(T)/\rho(T)$ vs $T$ (Right Y-axis). $M$ vs $T^2$ (Up X-axis) shows $\Delta M(T)/M(0) \propto T^2$ up to 160 K.
FIG. 6: (a) Field dependent Hall resistivity $\rho_H$ at various temperatures are obtained by using $(\rho_{xy}(+H) - \rho_{xy}(-H))/2$, where $\rho_{xy}$ is $\rho_{xy}$ under positive or negative magnetic field. (b) The temperature dependence of anomalous Hall coefficient $R_H^A$, normal Hall coefficient $R_H^N$ and thermolectric power $S$. $R_H^A$ is inferred from the jump in $\rho_H$ at “coercive” field $H_C$, while $R_H^N$ is inferred from the $H$-linear portions of $\rho_H$ below $H_C$.

FIG. 7: Temperature dependence of specific heat for TaFe$_{1.23}$Te$_3$ under different fields perpendicular to sample plane.

D. Heat capacity

In order to confirm the AFM transition, the heat capacity was measured by a relaxation-time method with a Quantum Design PPMS. One can clearly see a pronounced anomaly peak of $C_p(T)$ at 185 K for zero field in Fig. 7. The temperature is different from the $T_N$ inferred by susceptibility due to different samples with different magnitude of excess Fe. The sample measured specific heat has 0.23 interstitial Fe2 confirmed by EDX. The temperature of specific heat peak is shifted from 185 K to 170 K at 9 T in excellent agreement with the previous susceptibility and MR under high field. They consistently confirm that high magnetic field suppress the AFM order of Fe1 zigzag chains distinctly. In the low-temperature region the specific heat is of the form $C_p = \gamma T + \beta T^3$. The Debye temperature can be estimated from the equation $\beta = (12\pi^4 N k_B)/\Theta_D^3$, where $N$ is the number of atoms per formula unit. From the plot of $C_p/T$ vs. $T^2$ data between 2 and 14 K, we can estimate a Sommerfeld coefficient $\gamma = 25.86$ mJ K$^{-2}$ mol$^{-1}$, $\beta = 1.496$ mJ K$^{-4}$ mol$^{-1}$ and $\Theta_D = 189$ K for TaFe$_{1.23}$Te$_3$.

The electron specific heat coefficient $\gamma$ is close to that of Fe$_{1+y}$Te ($\gamma = 27$ mJ K$^{-2}$ mol$^{-1}$) [37]. The above resistivity and normal Hall coefficient $R_H^N$ also show that Fe$_{1+y}$Te and TaFe$_{1+y}$Te$_3$ have the same order of magnitude. It suggests that Fe$_{1+y}$Te and TaFe$_{1+y}$Te$_3$ have almost the same density of states near the Fermi energy level.

E. Models of magnetic structure

Based on the above results of susceptibility, MR and Hall effect, possible magnetic structures for the spins of Fe1 and Fe2 are proposed shown in Fig. 8a and 8b.
low $T_N$, Fe1 atoms of zigzag chains form antiferromagnetic alignment. The magnetic easy axis of Fe1 should be perpendicular to the Ta-Fe mixed metal network layers with a very large anisotropy energy. Since excess Fe2 directly couples with Fe1 of zigzag chains, the random excess Fe2 forms ferromagnetic alignment with nearest two Fe1 due to the inner field $H_{\text{int}}$ induced by Fe1 in zigzag chain below $T_N$. Furthermore, the inner field and the coupling energy between Fe2 and Fe1 are both enhanced with temperature decreasing. On the other hand, the external field $H_{\text{ext}}$ has very weak suppression on the AFM transition of Fe1 in zigzag chains, but strongly tunes the direction of Fe2 spin as long as $H_{\text{ext}} > H_{\text{int}}$. Since the especial crystal structure and magnetic structure shown in Fig. 8, the inner field will induce the excess Fe2 up and down among Fe1 zigzag chains to form AFM alignment between Fe2(up) and Fe2(down). That is why the whole Fe form AFM alignment below $T_N$ under low field. However, the external field prefers the all excess Fe2 to be parallel with each other along external field. When the external field overcomes the inner field with temperature increasing, it will tune Fe2 atoms which are antiparallel to external field to reverse their spins. This causes the fact that susceptibility sharply increases at the certain temperature $T_M$ or certain field $H_C$, as shown in Fig. 2.

IV. CONCLUSION

In summary, we systematically study the AFM order of Fe1 zigzag chains and spin-flop of excess Fe2 under high magnetic field $H$ through the susceptibility, MR, Hall effect and specific heat measurements in high-quality single crystal TaFe$_{1+y}$Te$_3$. These properties suggest that the high temperature AFM transition of the TaFeTe$_3$ layers should be a SDW-type AFM order. Below $T_N$, Fe1 antiferromangetic chains will induce a inner magnetic field $H_{\text{int}}$ to excess Fe2 and lead Fe2 to form an AFM alignment, in which the magnetic coupling strength between Fe1 and Fe2 is enhanced by decreasing temperature. On the other hand, the external magnetic field $H_{\text{ext}}$ competes with the inner magnetic field $H_{\text{int}}$ induced by AFM order of Fe1 zigzag chains and inclines to tune excess Fe2 to form FM alignment along $H_{\text{ext}}$. The excess Fe2 has a spin-flop at the "coercive" field $H_C$, where $H_{\text{ext}}$ can overcome the $H_{\text{int}}$. Based on spin-flop of Fe2, the local moment of Fe2(4 $\mu_B$/Fe) can be obtained from $\Delta M$ around "coercive" field $H_C$ in $M$-$H$ curves. The possible magnetic structure of TaFe$_{1+y}$Te$_3$ is also proposed. The properties related to the spin-flop of Fe2 supply a good opportunity to study the coupling between Fe1 and Fe2 in these TaFe$_{1+y}$Te$_3$ or Fe$_{1+y}$Te compounds with excess Fe2.

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