Tunable ($\delta \pi, \delta \pi$)-Type Antiferromagnetic Order in $\alpha$-Fe(Te,Se) Superconductors

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The recently discovered ferrous superconductors differ from phonon-mediated conventional superconductors in an important way: when the nonmagnetic La in LaFeAs(O,F) is replaced by magnetic lanthanides, $T_C$ increases from 26 K to as high as 55 K [1–4], in contrast to the breaking of the Cooper pairs by magnetic ions [5]. The La(O,F) “charge reservoir” layer turns out not to be a requirement for superconductivity and can be replaced by simple metal layers in (Ba/Sr/Ca,K/Na)Fe$_2$As$_2$ [6–9], or completely absent as shown more recently in the $\alpha$ phase of Fe(Se,Te) [10–12]. The common iron layer contributes dominantly to the electronic states at the Fermi level in these families of materials [13–17], which thus share similar quasi-two-dimensional Fermi surfaces with a nesting wave vector ($\pi$, 0) in the reciprocal Fe square lattice. The antiferromagnetic order observed in the parent compounds of both the LaFeAsO [18] and BaFe$_2$As$_2$ [19] families of materials, Fig. 1(c), has been predicted by the nesting spin-density-wave (SDW) mechanism [20]. In view of insufficient electron-phonon coupling [21–23], spin excitations from the only known mode at ($\pi$, 0) have been proposed as the bosonic “glue” mediating high $T_C$ superconductivity in these ferrous materials [13–17,20].

However, the weak-coupling SDW mechanism critically depends on the matching electron and hole Fermi surfaces in the parent compounds [14]. The nesting condition is lost when adding electrons or holes to the systems [24]. This expectation is confirmed in systematic doping [25–27] and pressure studies [28], which show the destruction of the SDW order well before the optimal superconducting state is established. Moreover, despite the same ($\pi$, 0) SDW order being predicted for $\alpha$-FeTe in first-principles theory [17], we observed a completely different antiferromagnetic order with the in-plane propagation vector ($\delta \pi, \delta \pi$) along the diagonal direction of the Fe “square” lattice, Fig. 1(b). The $\delta$ is tunable from an incommensurate 0.38 to the commensurate 0.5. Therefore, experimental results reported here call for a better understanding of the mechanism of magnetism and its role in superconductivity for the ferrous superconductors.

The single-phase Fe(Se, Te), material in the tetragonal PbO structure exists in a composition range near $z = 1$ [29]. In this $\alpha$ phase [10–12] (called $\beta$ phase in [29]), iron-chalcogen forms with the same edge-sharing antifluorite layers as found in the FeAs superconductors. The $\alpha$-FeSe with the nominal composition FeSe$_{0.88}$ was recently reported to superconduct at $T_C \approx 8$ K [10], which increases to 27 K at 1.48 GPa [30]. The isovalent series Fe(Te$_{1-x}$Se$_x$)$_2$, in the $\alpha$ phase with nominal $z = 0.82$ has been synthesized, and the $T_C$ is enhanced to 14 K at $x = 0.4$ at ambient pressure [11]. Similar results have also been reported for the nominal $z = 1$ series [12].

The end member $\alpha$-FeTe, is not superconducting, and bulk measurements indicate a phase transition at $T_S \sim 60–75$ K [11,12]. As a function of $z$, there exist two distinct types of transport behaviors in the low temperature phase: for $z \geq 0.90$ the samples change from a semiconductor to a metal, while for $z < 0.90$ the samples remain semiconducting [11]. Therefore, we selected a typical composition from each range of $z$ for this study, FeTe$_{0.82}$ and FeTe$_{0.90}$. For superconducting $\alpha$-Fe(Se, Te)$_2$, we chose the highest $T_C \approx 14$ K compound Fe(Se$_{0.6}$Te$_{0.4}$)$_2$. The high-resolution powder diffraction spectra of polycrystalline samples, weighing 15–16 g, were measured with
neutrons of wavelength 2.0785 Å using BT1 at NIST (Fig. 2). See Ref. [31] for a table listing the refined parameters. The high-temperature phase of these samples indeed has the tetragonal \( P4/nmm \) structure [10]; however, the chalcogen and Fe(1) sites of the PbO structure are fully occupied, and the excess Fe partially occupies the interstitial site Fe(2), see [31] and Fig. 1(a). Thus, the more appropriate formula for nominal \( \alpha\text{-Fe} (\text{Te}_{1-x} \text{Se}_x) \) is \( \text{Fe}_{1+y} (\text{Te}_{1-x} \text{Se}_x) \).

While \( \text{Fe}_{1.080} \text{Te}_{0.67} \text{Se}_{0.33} \) remains tetragonal in the superconducting state at 4 K [[31], Table I(c)], the parent compounds \( \text{Fe}_{1.141} \text{Te} \) and \( \text{Fe}_{1.076} \text{Te} \) experience a first-order magnetostructural transition, see Fig. 3, similar to that in \( \text{BaFe}_2 \text{As}_2 \) [19]. The semiconducting \( \text{Fe}_{1.141} \text{Te} \) distorts to an orthorhombic \( P_{mmm} \) structure below \( T_S \approx 63 \) K, with the \( a \) axis expanding and the \( b \) axis contracting, Fig. 3(c) and [31], Table I(a). This results in the splitting of the \((h0k)\) Bragg peaks of the high-temperature structure, Fig. 2(b). The orthorhombic distortion here, however, does not double the unit cell, different from that observed in either the \( \text{LaFeAsO} \) [32] or \( \text{BaFe}_2 \text{As}_2 \) [19]. The metallic \( \text{Fe}_{1.076} \text{Te} \) has a monoclinic \( P_{2_1}/m \) structure below \( T_S \approx 75 \) K, [31], Table I(b). In addition to the differentiation of the \( a \) and \( b \) axis [Fig. 3(d)], the \( c \) axis rotates towards the \( a \) axis to \( \beta = 89.2^\circ \). Thus, the monoclinic distortion not only splits the (200) but also the (112) Bragg peak, Fig. 2(d). In the weaker first-order transition of \( \text{Fe}_{1.141} \text{Te} \), a mixed phase exists in the pink-shaded region in Fig. 3(c). At 55 K upon warming, 85% of the sample is orthorhombic and 15% tetragonal. See Ref. [31] for the temperature dependence of distances and angles between various atoms.

The additional magnetic Bragg reflections of the monoclinic metal in Fig. 2(d) can be indexed by a commensurate magnetic wave vector \( \mathbf{q} = (\frac{1}{2} 0 \frac{1}{2}) \), as previously reported [33]. However, magnetic Bragg reflections of the orthorhombic semiconductor in Fig. 2(b) cannot be indexed by multiples of the nuclear unit cell. By performing single-
which are the directions of the antiferromagnetic alignment parallel to each other, and it expands in the $a$-$b$ plane to the next along the $c$ axis, for $\delta = 0.380$, for Fe$_{1.14}$Te. The $\mathbf{q}$ determines that magnetic moments in each row along the $b$ axis are parallel to each other. The rows of moments in an Fe plane modulate with the propagating vector $2\pi \delta/a$, which is 45° away from that of previous FeAs materials, see Figs. 1(b) and 1(c). From one plane to the next along the $c$ axis, magnetic moments simply alternate direction. In the same magnetostriction pattern as previously observed in the magnetic state of NdFeAsO [34] and BaFe$_2$As$_2$ [19], the lattice contracts in the $b$ axis, along which the magnetic moments are parallel to each other, and it expands in the $a$ and $c$ axis, which are the directions of the antiferromagnetic alignment. Once again, the unusual coupling between the lattice and magnetic degrees of freedom is what expected from multiple $d$-orbital magnetism [15].

The observed magnetic powder spectra can be refined by a collinear sinusoid model,

$$M'(\mathbf{R}) = M_i \mathbf{b} \cos(\mathbf{q} \cdot \mathbf{R} + \phi_R),$$

where $\mathbf{R}$ is the position of the Fe, $M_i$ the staggered magnetic moment, $\phi_R$ the additional phase at the Fe site. The unit vector $\mathbf{b}$ fixes the moment along the $b$-axis, and $\mathbf{q}$ is the observed magnetic wave vector. Refined magnetic parameters at low temperature are listed in Ref. [31] Table I(a) and (b). However, for an incommensurate $\mathbf{q}$, a spiral model with the moment rotating in the $ac$ plane,

$$M'(\mathbf{R}) = M_i[\hat{a} \cos(\mathbf{q} \cdot \mathbf{R} + \phi_R) + \hat{c} \sin(\mathbf{q} \cdot \mathbf{R} + \phi_R)],$$

offers an equivalent description of the unpolarized neutron diffraction results, with the relation between the respective neutron diffraction cross sections

$$2\sigma^2(\mathbf{Q})/M_i^2 = \sigma^2(\mathbf{Q})/\langle M_s \rangle^2.$$  

Thus, any linear combination of Eqs. (1) and (2) is also an equivalent description. On the other hand, $\sigma^1$ and $\sigma^s$ are partial cross sections for different channels of polarized neutron scattering [35]. Therefore, they can be readily determined using polarized neutrons.

We measured a Fe$_{1.14}$Te single-crystal sample, aligned in the $(h0l)$ horizontal scattering plane, using polarized neutron spectrometer Asterix at the Lujan Center of LANL. The neutron spin is controlled to align either perpendicular to the $(h0l)$ plane (VF) or parallel to the momentum transfer (HF). All four channels $(+, +, +, +, +, +)$ in both the VF and HF configurations were measured for the $(001)$ and $(\delta 0 1)$ Bragg peaks. The flipping ratio of the instrument is 10.3 as measured at the nuclear $(001)$ peak. The $(\delta 0 1)$ is proved magnetic by the spin-flip scattering in HF. The normalized intensity of $(\delta 0 1)$ in VF is 8.24(28) in the non-spin-flip (NSF) channels, and 4.13(20) in the spin-flip (SF) channels. After correcting for the finite flipping ratio of the instrument, we obtained $\sigma^1/\sigma^s = I_{NSF}/I_{SF} = 7.91(27)/3.37(16)$. Therefore, the incommensurate magnetic structure for Fe$_{1.14}$Te is

$$M(\mathbf{R}) = M_1 + M_s$$

$$= M_i[\mathbf{w} \mathbf{b} \cos(\mathbf{q} \cdot \mathbf{R} + \phi_R + \psi) + \hat{a} \cos(\mathbf{q} \cdot \mathbf{R} + \phi_R) + \hat{c} \sin(\mathbf{q} \cdot \mathbf{R} + \phi_R)],$$

where $\mathbf{w} = \sqrt{2}\sigma^1/\sigma^s = 2.17(6)$, $M = M_i/\sqrt{2 + w^2} = 0.76(2)\mu_B/\text{Fe}$ and $\psi$ is an arbitrary phase between the spiral and the sinusoidal components; see Fig. 1(b).

To understand whether the incommensurate magnetic structure in the orthorhombic semiconducting phase is locked or tunable, we examined another sample...
Fe$_{1.165(3)}$Te by powder diffraction at BT1, [31], Table I(d). The incommensurability is greatly affected and measures at δ = 0.346, despite no appreciable differences in either the moment or the phase φ from Fe$_{1.141}$Te in [31], Table I(a). Thus, δ can be tuned by varying the excess Fe in the orthorhombic phase, and it reaches a commensurate value $\frac{1}{4}$ for the composition Fe$_{1.076}$Te in the metallic monoclinic phase with less excess iron, see inset (a) of Fig. 4.

Having unveiled a tunable (δπ, δπ)-type of antiferromagnetic order in the parent compound Fe$_{1+y}$Te, it is natural to ask whether the new magnetic order survives in the optimal $T_C$ superconducting sample Fe$_{1.080}$Te$_{0.67}$Se$_{0.33}$. While there is neither long-range magnetic order nor structural transition, we observed pronounced short-range quasielastic magnetic scattering at the incommensurate wave vector (0.438, 0, $\frac{1}{4}$), Fig. 4, using SPINS at NIST. The temperature insensitive half-width-at-the-half-maximum 0.25 Å$^{-1}$ indicates a short magnetic correlation length of 4 Å, approximately only two nearest-neighbor Fe spacings. The concave shape of the peak intensity as a function of temperature in inset (b) indicates the expected diffusive nature of the short-range magnetic correlations. This is very different from the case of the (π, 0) SDW which is completely suppressed in the optimal $T_C$ FeAs samples [18,22,25,27].

To summarize, the α-Fe(Te,Se) shares a common electronic structure with the previously reported FeAs-based superconductor systems. Though the same (π, 0) SDW order has been predicted [17], we show the presence of a fundamentally different (δπ, δπ) antiferromagnetic order which propagates along the diagonal direction. The incommensurability δ in the orthorhombic semiconducting phase is easily tunable with excess Fe and locks into a commensurate $\frac{1}{4}$ in the monoclinic metallic phase. This magnetic order, which survives as short-range order even in the optimal superconducting state, cannot be the result of Fermi surface nesting, which is along the (π, 0) direction and delicately depends on electronic band filling for its existence.

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FIG. 4 (color online). Short-range magnetic order in superconducting Fe$_{1.080}$Te$_{0.67}$Se$_{0.33}$. The peak intensity as a function of temperature is shown in inset (b). Inset (a) shows the incommensurability δ as a function of y for Fe$_{1+y}$Te.