The interplay of topology magnetism and superconductivity has been studied in the FeTe$_{1-x}$Se$_x$ family of Fe-based superconductors using high resolution laser-based photoemission. At the superconducting transition a gap is observed to open at the Dirac point in a topological surface state. The associated mass acquisition points to time reversal symmetry breaking probably associated with the formation of ferromagnetism in the surface layer. Such a coupling of two phases, triplet and singlet spin states, has previously been predicted in 2D superconductors, as at a surface, in the presence of strong spin-orbit coupling. The presence of intrinsic ferromagnetism combined with strong spin-orbit coupling provides an ideal platform for the Quantum Anomalous Hall effect.

Magnetism and superconductivity represent emergent ground states in condensed matter systems that often compete. In the high Tc cuprates for example, the phase diagram is characterized by magnetism at low doping and superconductivity at higher doping levels. There is some tendency for these two regions to overlap in the related Fe-based superconductors but note that the magnetic ground state is anti-ferromagnetic with neighboring spins anti-parallel as in the configuration associated with the Cooper pairs in superconductivity. Ferromagnetism on the other hand with neighboring spins aligned parallel most definitely appears to counter the possibility of the normal spin alignment associated with superconductivity, at least for systems characterized by singlet pairing. However, this idea has been challenged in the context of 2-D superconductivity in the presence of spin-orbit coupling, as might be found, for example, in the surface region of a superconductor. Indeed, Govkov and Rashba proposed that in a 2D-superconductor with strong spin-orbit coupling the latter can lead to the coupling of singlet and triplet spin systems. The very same spin-orbit interaction is associated with the formation of protected surface electron states on the surface of topological insulators. A recent example being the recent demonstration that the high Tc superconductors, FeTe$_{1-x}$Se$_x$, supports topological surface states reflecting the large spin-orbit interaction on the ligand Te atoms. Indeed, in our
own previous studies of the FeTe$_{1-x}$Se$_x$ system we showed that spin-orbit effects$^6$ combined with the local moments$^5$ associated with the paramagnetic state resulted in an inverted gap at the zone boundary capable of supporting a topological state. Here, we examine the interaction between magnetism, superconductivity and topology in this fascinating and complex system. With the superconducting transition we observe a gap opening at the chemical potential, a characteristic of superconductivity reflecting the formation of Cooper pairs but with the same transition, we also find evidence of a second gap opening, now at the Dirac point associated with the topological surface state. Such mass acquisition points to the breaking of some symmetry associated with the initial formation of the topological state, either inversion or time reversal. There is no evidence for the breaking of inversion in the system and thus we are led to conclude that the time reversal symmetry is broken, consistent with the formation of ferromagnetism or triplet pairing as proposed elsewhere.$^3$ The observation of the development of ferromagnetism is highly suggestive that this system could prove an ideal platform for the demonstration of the Quantum Anomalous Hall effect which is reliant on the presence of intrinsic magnetism and strong spin-orbit interaction.

In figure 1(a) we show the photoemitted spectral intensity from FeTe$_{0.7}$Se$_{0.3}$ in the normal state. As in previous studies, the plot is characterized by two features, the bulk band dispersing downwards away from the $\Gamma$ point and the topological state represented by the cone-like structure dispersing upwards. In the same figure we show the photoemission spectra recorded from the material near the center of the zone as a function of the incident light polarization and temperature, corresponding in (b) to the normal state and in (c) the superconducting state. In the latter state, the development of the peak associated with the superfluid density is clearly visible for p-polarized light across the entire range of $k_\parallel$ measured. For s-polarized light, on the other hand, the onset of superconductivity is only visible in the vicinity of the topological state at the center of the zone. As discussed in the Supplementary Information, in the correct geometry, matrix element effects in the photoemission process allow the identification of the orbital character of the initial state. In the present case, the observation that the state associated with the superconducting transition is evident only with p-polarized light would suggest that the onset of superconductivity is orbital selective. However, it is important to note that more detailed calculations imply that in the experimental geometry used in the present experiment, any emission from an orthogonal orbital,
say $d_{xz}$ as opposed to $d_{yz}$, might not in fact be observable with either polarization. In studies of a related system FeSe$_{0.4}$Te$_{0.6}$, a Spectroscopic Imaging Scanning Tunneling Microscopy (SI-STM) study reported evidence for orbital ordering which the authors correlated with superconductivity. Orbital ordering or selectivity has also been invoked in separate SI-STM and associated theoretical studies of the related FeSe. Here we would comment that in our earlier study we proposed that spin-orbit coupling would lift the degeneracy between the $d_{xz}$ and $d_{yz}$ orbitals in these materials. Thus the spin-orbit interaction results in two bands, $\alpha_1$ and $\alpha_2$, split by some energy reflecting the latter interaction and having the character $d_{xz} + id_{yz}$ and $d_{xz} - id_{yz}$. The $\alpha_2$ band defines the smallest hole pocket associated with the bulk band structure at the center of the zone. The observation that there appears some form of orbital ordering or selectivity suggests that a symmetry is broken as the system goes superconducting and that the associated nematicity is such that the bands above and below the chemical potential will be orthogonal to each other, consistent with the observations of the SI-STM study. The important observation is that unlike the FeSe system which undergoes a structural phase transition from tetragonal to orthorhombic with cooling, the FeTe$_{0.7}$Se$_{0.3}$ system shows no structural transition down to 0K. Thus any symmetry breaking if it exists, must be electronic in nature.

We make one further observation relating to the peak associated with the superconducting state as observed in the spectrum taken with p-polarized light. Basically it is observed across the entire zone center. This represents unusual behavior as pointed out in an earlier study of superconductivity in the material Fe$_{1+y}$SexTe$_{1-x}$, where the possibility of a Bose-Einstein Condensation (BEC) type transition as opposed to a BCS type transition was discussed. The authors of that study noted that a BEC transition would result in a superfluid peak at $q = 0$ or the center of the zone as observed in the present study. A peak at the center of the zone contrasts with the BCS mechanism where we expect to see the Bogolyubov quasiparticles showing their peak intensity around $k_F$ away from the zone center. As noted by the authors of Ref. 10, the crossover from BCS to BEC behavior reflects the ratio of $\Delta/E_F$ where again $\Delta$ represents the superconducting gap and $E_F$ is the Fermi energy. The Bogolyubov dispersion associated with pairing in the topological state would be expected to disperse downwards at the Fermi wavevector crossing of ~0.03 Å$^{-1}$ and away from the zone center. The dispersion associated with pairing in the bulk $\alpha_2$ band could potentially initially disperse towards the zone center but the Fermi crossing for that
band is much further out at approximately 0.15Å⁻¹.⁶ In fact if, as shown in the SM, we compare the relative ratio of the intensity of the peak immediately below the chemical potential as excited by p- and s-polarized light it becomes clear that the intensity is much stronger in the p-excited channel as one moves away from the center of the zone and that it is equal at the center of the zone. This suggests that the behavior at the center of the zone is dominated by the topological state and the behavior away from the center by the bulk superconductivity. We therefore chose to use s-polarized incident light to examine the properties of the topological state in detail.

Fig. 2 compares the temperature dependence of the photoemission spectra recorded along the surface normal, corresponding to k∥ = 0, using s-polarized light for temperatures from 20K down through the superconducting transition at T_c=14K to 6K, well into the superconducting state for (a) FeTe₀.₅₅Se₀.₄₅ and (b) FeTe₀.₇Se₀.₃. The spectra in (a) could be interpreted simply as the development of a peak associated with the superconducting transition as is evidenced in many superconducting materials. There are however notable differences between the two systems. At 20K the increase in Te concentration on moving from Te₀.₅₅ to Te₀.₇ results in a shift in binding energy of the lower binding energy peak and an increase in intensity, clearly showing it is related to the Te concentration. With the development of superconductivity, although more obvious in the 70% Te material, in both cases the two most prominent features in the spectra appear to be pushed apart as the temperature goes below the bulk T_c; the one at lower binding energy moving towards the chemical potential and the second at a binding energy beyond the Dirac point being pushed to higher binding energy. However, there are also differences between the peaks at low binding energy in the two systems. The peak in (a) is sharper with a width probably determined by the overall experimental resolution of 2.5 meV. The peak in (b) on the other hand is broader with a substructure suggesting the presence of more than one peak. Fig. 2(c) focuses specifically on the peak closer to E_F in 2(b) over the same temperature range. The peak again continuously changes its structure, indicating different components, one appearing to have its development associated with the superconducting transition. This is particularly noticeable in the 10K spectrum where at least two peaks are clearly resolved.

In figure 3(a) we show a series of measured spectral intensities at the center of the zone, as a function of temperature above and below the superconducting transition. The spectral images
clearly show the opening of a gap at the Dirac point at the transition temperature \( T_c \). As we have discussed elsewhere, there is already a small gap above \( T_c \) in the normal state. This gap may reflect superconducting fluctuations above \( T_c \) or the possible presence of ferromagnetism in the surface layer as observed in a previous study of a doped topological insulator, also in the paramagnetic state in the bulk.\(^\text{11}\)

The development of a larger temperature dependent gap at the Dirac point and associated mass-acquisition, is an indicator of some form of time reversal symmetry breaking associated with the bulk superconducting transition. To investigate this further we start with the assumption that the observed electron spectrum at the surface has only one Fermi pocket. This is different from the bulk, where the Fermi surface has multiple sheets. Hence the surface quasiparticles can be described by \( \psi_\sigma(k) \), \( \psi^*_\sigma(k) \), where \( \sigma \) represents the index of a “Kramers doublet”, or, “an effective spin and \( k \) the 2-dimensional momentum. Since photoemission shows well defined quasiparticle excitations, we treat them as surface modes not propagating into the bulk. Furthermore, the mass term for a single Dirac cone (Weyl fermion) breaks time reversal and therefore requires an internal magnetic field. Another important factor is the strong spin-orbit coupling, \( \lambda \), caused presumably by the strong electric field on the surface (the Rashba effect). We therefore use a model that represents the continuum limit of the model adopted by Mascot et al.\(^\text{12}\).

Discussed in more detail in the SM, the standard approach to the description of superconductivity is to use the Nambu notation. Thus we introduce the Nambu spinor \( \Psi^T(k) = (c_\uparrow(k), c_\downarrow(k), c_\downarrow((-k)), -c_\uparrow((-k))) \), so that the Hamiltonian \( H \) is given by

\[
H = \sum_k \bar{\Psi}^+(k) \hat{H}(k) \Phi(k)
\]

where the Hamiltonian can be written as

\[
H(k) = \epsilon(k) \tau^z \otimes I + \lambda \tau^x \otimes (k_y \sigma^y - k_x \sigma^y) + h \tau^z \otimes \sigma^z + (\text{Re}\Delta) \tau^x \otimes I + (\text{Im}\Delta) \tau^y \otimes I.
\]

Here the Pauli matrices \( \tau^z \) act in the particle-hole space and the \( \sigma^z \) matrices act in the spin space. \( \epsilon_0(k) = k^2/2m \), the bare dispersion, \( \mu \) is the binding energy of the Dirac point and \( h \) the Weiss field generated by the presumed ferromagnetic ordering in the surface region. As discussed in the SM, diagonalizing equation (4) results in the energy spectrum:
\[ E_{\pm}^2 = (\varepsilon_0(k) - \mu)^2 + \lambda^2 k^2 + h^2 + \Delta^2 k^2 \pm 2[(\varepsilon_0(k) - \mu)^2(\lambda^2 k^2 + h^2) + |\Delta|^2 \lambda^2 k^4]^{1/2} \quad (3) \]

In the vicinity of the Dirac point, well removed from the chemical potential equation (3) reduces to \[ E_{\pm} = (\varepsilon_0(k) - \mu) \pm \sqrt{\lambda^2 k^2 + h^2}. \] Thus to get some idea of the magnitude of the magnetic field \( h \) we fit the measured dispersion in the vicinity of the Dirac point with the expression

\[
E_{\pm} = \pm \sqrt{\lambda^2 k^2 + h^2}.
\]

(4)

We could have simply made the assumption that the gap has the magnitude \( 2h \). However, we believe that the close proximity of the bulk bands to the bottom of the gap renders such an approach less accurate.

Fitting the measured spectral plots as shown in fig. 3(a) provides us with a measure of \( h(T) \), the temperature dependence of the gap at the Dirac point. At the lowest temperatures the full opening of the gap is of the order of 8 meV. However, as noted earlier a gap of approximately 3.0 meV exists above \( T_c \). We therefore associate the additional 5.0 meV with the development of superconductivity. By contrast, the full gap at the chemical potential directly associated with the cooper pairing in the superconducting state is of the order of 4.0 meV. This is to be compared with the full gap of 3.6 meV measured in the earlier ARPES study \(^4\) and 3.8 meV measured in a recent STM study.\(^{13}\) In Fig. 4 we compare the temperature dependence of the gap at the Dirac point determined in the present study with the topological superconducting gap measured in the earlier ARPES study.\(^4\) We also show the mean field temperature dependence of the superconducting gap measured in the close lying bulk \( \alpha_2 \) hole band. The latter is out of range of the present laser study but \( \Delta_0 \) has been reported elsewhere.\(^{14}(18)\) In plotting \( \Delta(T) \) for the bulk band we use the expression

\[
\Delta(T) = \Delta(0) \tanh[\alpha \left( \frac{T_c}{T} - 1 \right)^{\frac{1}{2}}]
\]

(5)

where \( \alpha \) is such that \( \Delta(0) = \alpha kT_c.\(^{15}\) The agreement between the different measurements is quite striking and consistent with proximity induced superconductivity in the topological state.

Armed with the experimentally determined temperature dependence for the different gaps, we show in fig. 3(b) representative dispersions calculated from equation 3, compared with the experimentally observed behavior shown in fig. 3(a). We have not attempted to account for the 3
meV observed above Tc but rather show the opening of the gaps at the Dirac point and at the chemical potential with the onset of superconductivity. The agreement is again quite satisfying. We can make one further important observation regarding the plots shown in fig. 3(b). Elsewhere we did not rule out the possibility that the gap observed above Tc at the Dirac point could be simply due to sample misalignment. However we note from fig. 3(b) that as we move away from the Dirac point the effects of temperature occur at lower and lower temperatures. Thus the any change in the gap size would not have its onset at Tc if the entire effect was due to misalignment.

Our study thus reveals a number of new and important observations. As noted earlier, the opening of a gap at the Dirac point, indicative of time reversal symmetry breaking, points to the development of some form of ferromagnetic order in the surface region associated with the superconducting transition. Within the Ginsburg-Landau formulism TRSB requires mixing between two gap functions resulting in a complex order parameter. Such a possibility has been discussed before although to date there has been no experimental verification. Through spin-orbit coupling the complex order parameter can induce spin magnetization as described in the SM and explained in detail elsewhere.16 We note that alternative theories that may explain the appearance of the gap at the Dirac point have also been suggested.17,18 The presence of ferromagnetism in the surface region associated with strong spin-orbit coupling would potentially make this system the ideal platform for supporting the Quantum Anomalous Hall effect.

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Author contributions. P.D.J. conceived the experiment. N.Z. performed the experiment with advice from P.D.J. P.D.J. wrote the paper with assistance from N.Z., A.T., and C.W. G.G. synthesized the samples.

Competing interests. The authors declare no competing interests.

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Figure Captions:

Fig. 1. Photoemitted spectral intensities measured in the normal and superconducting states. (a) Spectral intensity measured in the vicinity of the Γ-point (k|| = 0) from FeTe0.7Se0.3. The total intensity corresponds to the sum of that measured with p-polarized and s-polarized light. (b) Energy Distribution Curves measured in a region ± 0.08Å around the Γ-point from FeTe0.7Se0.3 using p-polarized light and with the sample in the normal state at 20K. (c) The same as in (b) but now with s-polarized light. (d) and (e) are respectively the same as (b) and (c) but now with the sample held in the superconducting state at 6K.

Fig. 2. Temperature dependence of the photoemission spectra along the surface normal. (a) and (b) represent the temperature dependence from 20K to 6K of the measured spectra recorded along the surface normal from FeTe0.55Se0.45 and FeTe0.7Se0.3 respectively. (c) shows an expanded view of the temperature dependence of the peak immediately below the Fermi level for the spectra in (b).

Fig. 3. Measured dispersions in the vicinity of the Γ-point as a function of temperature. Spectral intensity measured in the vicinity of the Γ-point as a function of temperature. (a)-(d) correspond to 20K, 14K, 12K and 10K respectively. Superimposed over the measured intensities, the white curves show the peak intensities, the red dashed curve shows the Dirac cone and the solid red curves show the Dirac cone but now with a gap at the Dirac point determined by fitting with equation (4). (e)–(h) The calculated equivalent of (a)-(d) using the expression given in equation (3).

Fig. 4. Temperature dependence of the different gap magnitudes. Temperature dependence of the superconducting gap (red squares) from reference 4 and the gap at the Dirac point from the present study (blue circles) compared with the temperature dependence of the bulk superconductivity as determined for the α2 band as determined in reference 14.
Fig. 1.
Fig. 2.
Fig. 3.

(a)  (b)  (c)  (d)  

(e)  (f)  (g)  (h)
Fig. 4.
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