CONDENSED MATTER PHYSICS

Tuning across the BCS-BEC crossover in the multiband superconductor Fe$_{1+y}$Se$_x$Te$_{1-x}$: An angle-resolved photoemission study

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INTRODUCTION

The Bardeen-Cooper-Schrieffer (BCS) to Bose-Einstein condensation (BEC) crossover (1) has emerged as a new paradigm for pairing and superfluidity in strongly interacting Fermi systems, which interpolates between two well-known limiting cases: BCS theory for fermions with a weak attractive interaction and a BEC of tightly bound bosonic pairs. This crossover has now been extensively investigated in ultracold Fermi gas experiments (2–4), where the strength of the attraction between Fermi atoms is tuned using a Feshbach resonance. This has led to a number of new insights (5–7) into the strongly interacting unitary regime that lies in between the BCS and BEC limits. One of the key characteristics of the crossover regime is that the ratio of the pairing gap $\Delta$ to the bandwidth or Fermi energy $E_F$ is of order unity, as opposed to the BCS limit, where $\Delta/E_F = 1$.

From this perspective, most superconducting (SC) materials, even strongly correlated systems such as the cuprates, are much closer to the BCS limit than in the crossover regime. A key obstacle to realizing the BCS-BEC crossover in quantum materials is that one does not have the ability to continuously tune the strength of the pairing interaction that controls $\Delta$. We offer an alternative path to the realization of the BCS-BEC crossover: Instead of trying to change $\Delta$, we tune $E_F$ by chemically doping carriers and drive the system through the BCS-BEC crossover.

We focus on the Fe-based superconductor Fe$_{1+y}$Se$_x$Te$_{1-x}$, which is a nearly compensated semimetal (8–10), and tune the Fermi energies of various pockets by changing the excess Fe concentration $y$. Using angle-resolved photoemission spectroscopy (ARPES), we systematically map out the evolution of the electronic excitation spectrum to demonstrate that we traverse the BCS-BEC crossover in the solid state. Our work raises fundamentally new questions about the crossover in multiband superconductors, which go beyond those addressed in the context of cold atoms.

RESULTS

Our main results are summarized in Fig. 1, where we show the ARPES intensity at 1 K, well below SC $T_c$, for a hole band near the $\Gamma$ point of the Brillouin zone. The top three panels (Fig. 1, A to C) correspond to three samples in order of decreasing $y$, the amount of excess Fe. We deduce the following important results from these data.

(i) From the electronic dispersion far from the chemical potential, which is the same in the normal and SC states, we estimate $E_F$, the unoccupied bandwidth for this hole pocket, and show that it systematically decreases with decreasing $y$.

(ii) We measure the SC energy gap $\Delta$ from the coherence peaks in the spectra, which correspond to the Bogoliubov quasiparticles. We find $\Delta = 3 \pm 0.5$ meV for all three samples. We conclude that the dimensionless measure of the pairing strength $\Delta/E_F = 0.16, 0.3$, and 0.5 increases monotonically with decreasing $y$, exhibiting a crossover from a BCS to a BEC regime.

(iii) As $\Delta/E_F$ increases, we see that the dispersion of the coherence peak changes from being BCS-like dispersion, with characteristic backbending near $k_F$, to the unusual BEC-like dispersion, with a minimum gap at $k = 0$. This can also be viewed as the shrinking of the “minimum gap locus” (11) from a contour enclosing a finite area in the large $y$ BCS regime to a single point in the small $y$ BEC regime, consistent with the prediction (12) of the crossover theory for multiband SCs (13, 14). We show in Fig. 1 (D to F) the spectral function obtained from a simple model and describe below how it captures important features of the BCS-BEC crossover.

Our work builds on recent experimental progress in Fe(Se$_x$Te). We have previously shown (15) that a small $y$ sample had a tiny $E_F$ of a few millielectron volts and a large $\Delta/E_F$ that places it well outside the weak coupling BCS limit. The small value of $E_F$ in Fe$_{1+y}$Se$_x$Te$_{1-x}$ has also been reported by Okazaki et al. (16), which focused on an unoccupied electron band just above $E_F$. Small values of $E_F$ were also found in FeSe (17), together with the observation (18) of anomalously large SC fluctuation effects attributed to preformed pairs above $T_c$. The results presented here go beyond these earlier works in that we show how a systematic change in $E_F$ via doping permits us to tune across the BCS-BEC crossover.

Materials and transport data

Bulk FeSe has been intensively investigated. It exhibits nematic ordering without antiferromagnetic long-range order (in contrast to other Fe pnictides) (19) and becomes a $T_c = 65$ K superconductor in monolayer thin-film form on various substrates (20–22). Here, we focus on the
lower $T_c$ bulk material Fe(Se,Te), which is nevertheless the most strongly correlated in this family with the largest $\Delta/e_F$ ratios, as we show below.

A series of Fe$_{1+y}$Se$_{1-x}$Te$_x$ samples were prepared using the modified Bridgman method. We chose to fix $x = 0.4$ near the maximum $T_c \approx 15$ K for $y$ near zero. The composition $x$ was measured by energy-dispersive x-ray (EDX) analysis. Recently, it was shown that, by annealing in oxygen, it is possible to reduce $y$, the amount of excess Fe (23–27). Attempts, made by us and other groups, to quantify $y$ using standard techniques, such as EDX, x-ray diffraction, and inductively coupled plasma, have resulted in inconclusive results. It seems that the only reliable way to measure $y$ is to simply count the number of excess Fe atoms using a scanning tunneling microscope (27). We note that a quantitative determination of $y$ in our samples is not essential to our study, because we will focus on the resulting systematic changes in $\varepsilon_F$ measured by ARPES, as shown below.

The result of reducing $y$ is an increase in $T_c$ and a change in the resistivity as a function of temperature. In addition, it was found that the annealing process changes the sign of the Hall resistivity at low temperatures. The samples shown in Fig. 1 are ordered from large value of $y$ (BCS) to small value of $y$ (BEC) based on their $T_c$ and resistivity curves.

In Fig. 2 (B and C), we show dc transport data for two samples: The small $y$ sample (red curve) has an SC $T_c = 14$ K, whereas the large $y$ sample (blue curve) has $T_c = 12$ K. Using a SQUID magnetometer, we verified that all the crystals used have a full SC shielding volume fraction. Note that the entire $T$ dependence of the resistivity in Fig. 2B is different for the two samples.

The Hall resistance $R_{HI}$ for the same samples shown in Fig. 2C also depends strongly on $y$. At low temperatures, the small $y$ sample has a negative $R_{HI}$, whereas the large $y$ sample has a positive $R_{HI}$, in agreement with previous reports (23). A quantitative analysis of the Hall data is difficult in view of the multiple bands involved.

**Electronic structure**

To understand our ARPES results, it is useful to first look at the schematic of the band structure of Fe(Se,Te) (see Fig. 2A). In bulk FeSe, Fe$^{2+}$ is in a 3$d^5$ configuration. With an even number of electrons per unit cell, FeSe is a compensated semimetal, which should be unaffected by the isovalent substitution of Se by Te. Changing $y$ in Fe$_{1+y}$Se$_{1-x}$Te$_x$ alters the balance between electrons and holes in what was an almost perfectly compensated semimetal (23–25, 28).

In Fig. 2A, we show the three hole bands $\alpha_i \ [i = 1, 2, 3]$ in the notation of Tamai et al. (29) near the $\Gamma$ point and two electron bands (due to zone folding) near the $M$ point of the Brillouin zone. The red curves in Fig. 2A denote the bands for the small $y$ sample, whereas the blue curves correspond to the large $y$ sample. The main focus of our attention in this paper is the light-hole band $\alpha_2$, but we will also discuss some features of the heavy-hole band $\alpha_3$ (which remains at or just below the chemical potential) and the electron band near $M$. The $\alpha_1$ band is always well below the chemical potential. A key observation below is that changing excess Fe does not just shift the chemical potential in a rigid band structure. Some bands shift in energy, whereas other do not. In addition, changing $y$ leads to mass renormalizations.

**ARPES data for electron and hole bands**

In Fig. 3 (A to D), we compare ARPES data for the electron pocket around the $M$ point for the two samples in Fig. 2. We show the ARPES intensity in Fig. 2A and the momentum distribution curves (MDCs) in Fig. 2C for the small $y$ sample, whereas Fig. 2 (B and D) shows the corresponding data for the large $y$ sample. The green lines in Fig. 2
structure and the effect of curves correspond to the small and large bands as the excess Fe is changed. In Fig. 3 (E and F), we show the ARPES intensities for the small y (E) and large y (F) samples measured along a cut going through the Γ point, using a vertically polarized 22-eV light. In this polarization, only the α₁ dispersion can be seen. The blue curves represent the dispersion of α₂, and the green lines represent that of α₃.

In contrast to the electron and α₂ hole bands, we do not find any significant shift in α₁ and α₃ bands as the excess Fe is changed. In Fig. 3 (E and F), we show the ARPES intensities for the small y (E) and large y (F) samples measured along a cut going through the Γ point, using a vertically polarized light. In this polarization, only the α₁ and α₃ bands can be seen (and not α₂). For all the samples that we have measured, the top of the α₁ band is at 22 ± 2 meV, that is, deep on the occupied side, in agreement with Lubashevsky et al. (15), Tamai et al. (29), and Miao et al. (30).

(A and B) represent the best parabolic fits to the MDC maxima shown in Fig. 2 (C and D, respectively). We see that the Fermi energy (occupied bandwidth for the electron band) changed from 20 meV (small y sample) to 14 meV (large y sample), whereas the effective mass is 3.7 m_e for both. We can compare the change in the electron pocket dispersion (green lines in Fig. 2, A and B), with excess Fe content y, to the corresponding α₂ dispersion (shown as red curves). The latter is obtained from the measured α₂ MDC peaks around the Γ point (see Fig. 4). With increasing y, as the electron dispersion moves up in energy near the M point, so does the hole dispersion near Γ. This is qualitatively consistent with the increasing hole-like character of the Hall data in Fig. 2, with increasing y. We note that, in the ARPES geometry that we use (vertical polarization along the Γ − M direction), we observe only one of the electron pockets, and we do not observe any coherence peaks in the SC state spectra.
We finally describe the central results of this paper for the large sample to 16 \text{meV} for the \( \alpha_3 \) band, which is well below the chemical potential \( \text{Chemical Potential} \) or \( \text{Chemical Potential} \). The effective mass \( m^* \) changes with excess Fe from 26 \( m^* \) for the small \( y \) sample to 16 \( m^* \) for the large \( y \) sample. Effective mass changes of the \( \alpha_3 \) band were reported also in studies of the effect of Se-Te substitution on the band structure in Fe\(_{1+y}\)Se\(_y\)Te\(_{1-x}\) (32).

**ARCES evidence for BCS-BEC crossover**

We finally describe the central results of this paper for the \( \alpha_3 \) hole band (highlighted in Fig. 1). We show in Fig. 4 (A to C) the energy distribution curves (EDCs) for the three samples in Fig. 1 (A to C, respectively). The large \( y \) sample in Fig. 4A and the small \( y \) sample in Fig. 4B are the same ones for which we presented transport data above. The sample in Fig. 4C has the smallest value of \( y \), the smallest amount of excess Fe, and a \( T_c = 14.5 \text{K} \). The data in Figs. 1 and 4 were obtained using linearly polarized 22-eV photons at a temperature of 1 K (well below the SC \( T_c \)'s of the samples) using a horizontal light polarization \( l = \text{light polarization} \).

To understand the effect of excess Fe on \( \varepsilon_F \) (the unoccupied bandwidth of the \( \alpha_3 \) band), we analyze MDCs away from the low-energy region with the SC gap. The MDC peak positions from –5 to –50 meV are shown as red dots in Fig. 4 (D to F), with the three panels corresponding to the data in Fig. 1 (A to C, respectively). We note that the MDC peaks are the same, within our resolution, below and above \( T_c \). Parabolic fits to the MDC peak dispersion are shown as red curves in Fig. 4 (D to F) and lead to \( \varepsilon_F \) estimates of 19, 10, and 6 meV for the three samples in order of decreasing \( y \). The uncertainty in \( \varepsilon_F \) obtained from the fit (95% confidence bounds) was lower than 1.5 meV for all samples.

We determine the SC energy gap from the EDC peaks in Fig. 4 (A to C), which correspond to the coherent Bogoliubov quasiparticles in the spectral function below \( T_c \). The dispersion of the EDC coherence peaks is shown as blue dots in Fig. 4 (D to F). Let us denote the experimentally determined Bogoliubov dispersion by \( \tilde{E}(k) \). The SC gap \( \Delta \) is given by the minimum of \( |\tilde{E}(k)| \) for \( k \approx k_F \) along a \( k \)-space cut perpendicular to the normal-state Fermi surface (here, a radial cut through \( \Gamma \)).

The SC gap for all three samples is \( \Delta = 3 \pm 0.5 \text{meV} \), in agreement with Lubashevsky et al. (15) and Miao et al. (30). We thus find \( \Delta/\varepsilon_F = 0.16 \) (large \( y \)), 0.3 (small \( y \)), and 0.5 (smallest \( y \)). Thus, the important dimensionless ratio \( \Delta/\varepsilon_F \), which characterizes the pairing strength, increases monotonically with decreasing excess Fe, going from the BCS regime at large \( y \) to the BEC regime at small \( y \).

Another important evidence for the BCS-BEC crossover comes from the characteristic change in the coherence peak dispersion. In the BCS regime, we expect a bending back of \( E(k) \) for \( k \approx k_F \), whereas in the BEC regime, the dispersion is qualitatively different with a minimum gap at \( k = 0 \) (see the Supplementary Materials). This evolution is evident in both the raw ARPES data of Fig. 1 and the EDC peak dispersion in Fig. 4 (blue dots).

We can understand this better from the Bogoliubov dispersion

\[
\tilde{E}(k) = \sqrt{(\varepsilon_k - \mu)^2 + \Delta^2},
\]

where \( \varepsilon_k = \hbar^2 k^2/2m^* \), \( \mu \) is a renormalized chemical potential, and \( \Delta \) is the SC gap, which is assumed to be \( k \)-independent for simplicity. Exact numerical calculations (34) have shown that this form of the dispersion, well known from the mean-field theory, is accurate across the BCS-BEC crossover, provided one allows for renormalization of \( m^* \) and \( \mu \) due to interaction effects. In the weak coupling BCS limit, \( \mu = \varepsilon_F \), and the dispersion shows back-bending at \( k_F \). More generally, in the BCS regime, where \( \mu > 0 \), \( E_k \) exhibits back-bending at \( k^* = (2m^*\mu)^{1/2} \). As one goes through the crossover, \( k^* \) decreases, which can also be described as the shrinking of the minimum gap locus (17). In the BEC regime, when \( \mu < 0 \), the locus has shrunk to a single point so that the dispersion has a minimum gap at \( k = 0 \).

We use the BCS-inspired spectral function

\[
A(k, \omega) = \frac{\Delta^2}{(\omega - \varepsilon_F)^2 + \Delta^2},
\]

with broadened delta functions, as a simple way to model our ARPES data (see the Supplementary Materials for details). In Fig. 1 (D to F), we plot \( A(k, \omega) \) without the Fermi function that cuts off the ARPES intensity for unoccupied states at positive energies. We choose \( \varepsilon_F = 20, 10, \text{and} 2.5 \text{meV} \) in Fig. 1 (D, E, and F, respectively), with a fixed \( \Delta = 5 \text{meV} \). We adjust the chemical potential using \( \mu = \varepsilon_F - \Delta^2/4\varepsilon_F \), the mean-field result for the two-dimensional BCS-BEC crossover (35).

We see from Fig. 1 (D to F) that this simple model captures the evolution of SC state dispersion in the ARPES data. This analysis also gives insight into the ARPES spectral weight, which is controlled by the momentum distribution \( n(k) \). On the BCS side of the crossover, low-energy coherence peaks have significant spectral weight only near \( k \approx k_F \), whereas on the BEC side, there is significant spectral weight in a large momentum range around \( k = 0 \). The fact that we focus on a hole band,
as opposed to an electron band, makes it much easier to observe the BEC-like regime using ARPES (see the Supplementary Materials).

**DISCUSSION**
Our main results are summarized in the Introduction, and we conclude with a discussion of the interesting open questions about the BCS-BEC crossover in multiband superconductors raised by our work. In contrast to the extensive theoretical literature (5–7) on the BCS-BEC crossover in single-band systems, motivated in large part by ultracold atom experiments, the crossover theory for multiband systems, especially nearly compensated semimetals, is much less developed [see, however, Lee Loh et al. (12), Leggett (1), and Chubukov et al. (14)].

We note that the evolution of the minimum gap locus from a contour in the BCS regime to a point in k space is a general consequence of the BCS-BEC crossover even in a multiband system (12). This also points to the interesting possibility that the crossover can be band-selective, namely, the pairing could be in a BEC regime on one band while in the BCS regime on another. This could well be the case for Fe1+xSe0.41Te0.6 where we focused only on the crossover in the a2 band. We found that, as the Fermi energy of the a2 hole band near \( \Gamma \) is reduced, that on the electron band near \( M \) is increased. However, in the polarization geometry used, we do not see any SC state coherence peaks on the electron band, and new experiments are needed to see how the SC gap on that band changes with excess Fe.

The SC state BCS-BEC crossover reported in this paper raises several vital questions about the normal state. Do preformed pairs exist above \( T_c \) in Fe(Se,Te)? Is there a pairing pseudogap above \( T_c \)? We conclude with a discussion of the significance and implications of these issues.

A normal-state pseudogap was first observed in the underdoped high \( T_c \) superconductors, with ARPES playing a key role. We now understand that the cuprate pseudogap (36) has many facets, including the proximity to the Mott insulator, short-range singlet correlations, charge density wave fluctuations, and preformed pairing. In contrast, the pseudogap in the single-band BCS-BEC crossover originates from pairing. The normal state thus evolves from a Fermi liquid in the BCS limit to a normal Bose liquid in the BEC limit via the appearance of a pairing pseudogap in the crossover regime, as predicted early on (37). This pseudogap has been observed in the ultracold Fermi gases using a spectroscopic technique (4) analogous to ARPES.

For a multiband superconductor, such as Fe(Se,Te), the question is more complex than in the one-band case. Although the gaps, Fermi energies, and dispersions can be examined separately on each band by ARPES, there are fundamental properties of superconductors, such as the transition temperature \( T_c \) and the superfluid density \( \rho_s \) that depend on all the bands and their mutual coherence. An understanding of how \( \rho_s \) and \( T_c \) evolve with Fe doping would shed light on the important questions of SC fluctuations and pseudogap above \( T_c \). We note that recent diamagnetism experiments (17) on FeSe provide evidence for a large SC fluctuation regime above \( T_c \). To date, however, there is no spectroscopic evidence for, or against, a pseudogap above \( T_c \). This key question deserves further investigation.

**MATERIALS AND METHODS**
High-quality single crystals of Fe1+xSe0.41Te0.6 were grown using the modified Bridgman method. The stoichiometric amounts of high-purity Fe, Se, and Te powders were grinded, mixed, and sealed in a fused silica ampoule. The ampoule was evacuated to a vacuum better than \( 10^{-5} \) torr, and the mixture was reacted at 750°C for 72 hours. The resulting sinter was then regrinded and put in a double-wall ampoule that was again evacuated to a vacuum better than \( 10^{-5} \) torr.

The ampoule was placed in a two-zone furnace with a gradient of 5°C/cm and slowly cooled from 1040°C to 600°C at a rate of 2°C/hour, followed by a faster cooldown to 360°C for 24 hours. The resulting boule contained single crystals that could be separated mechanically. To change the amount of excess Fe, we annealed the crystals for 48 hours in ampoules that were evacuated and then filled them with different pressures of oxygen.

Transport measurements were performed using a homebuilt setup based on an Oxford Teslatron system. The resistivity and Hall resistance were measured using the van der Pauw method between room temperature and 2 K.

High-resolution ARPES measurements were performed at the UE112_PGM-2b-1^3 beamline at BESSY (Berlin, Germany) and at the CASSIOPEE Beamline at SOLEIL (Saint-Aubin, France) using a photon energy of 22 eV. The samples were cleaved in vacuum better than \( 5 \times 10^{-4} \) torr at base temperature and measured for not more than 6 hours. The base temperature at BESSY was 1 K and at SOLEIL was 7 K. The energy resolution was 4 meV in both beamlines.

**SUPPLEMENTARY MATERIALS**
Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/4/e1602372/DC1

**Comparison between superconducting and normal state ARPES data**

**Modeling the spectral function**

**fig. 51. ARPES spectra above and below \( T_c \).**

**fig. 52. Bogoliubov dispersion from BCS to BEC.**

**References**


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