Magnetic fluctuations and specific heat in Na$_x$CoO$_2$ near a Lifshitz transition

This item was submitted to Loughborough University’s Institutional Repository by the/an author.


Additional Information:

- This article was published in the journal, Physical Review Letters [© American Physical Society]. It is also available at: http://dx.doi.org/10.1103/PhysRevLett.114.066403.

Metadata Record: https://dspace.lboro.ac.uk/2134/18324

Version: Accepted for publication

Publisher: © American Physical Society

Rights: This work is made available according to the conditions of the Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International (CC BY-NC-ND 4.0) licence. Full details of this licence are available at: https://creativecommons.org/licenses/by-nc-nd/4.0/

Please cite the published version.
Magnetic fluctuations and specific heat in Na$_x$CoO$_2$ near a Lifshitz Fermi surface topological transition

Sergey Slizovskiy,$^1$ Andrey V. Chubukov,$^2$ and Joseph J. Betouras$^1$

$^1$Department of Physics, Loughborough University, Loughborough LE11 3TU, UK
$^2$Department of Physics, University of Wisconsin-Madison, Madison, WI 53706, USA

We analyze the temperature and doping dependence of the specific heat $C(T)$ in Na$_x$CoO$_2$. This material was conjectured to undergo a Lifshitz-type topological transition at $x = x_c = 0.62$, in which a new electron Fermi pocket emerges at the $\Gamma$ point, in addition to the existing hole pocket with large $k_F$. The data show that near $x = x_c$, the temperature dependence of $C(T)/T$ at low $T$ gets stronger as $x$ approaches $x_c$ from below and then reverses the trend and changes sign at $x \geq x_c$. We argue that this behavior can be qualitatively explained within the spin-fluctuation theory. We show that magnetic fluctuations are enhanced near $x_c$ at momenta around $k_F$ and their dynamics changes between $x \leq x_c$ and $x > x_c$, when the new pocket forms. We demonstrate that this explains the temperature dependence of $C(T)/T$. We show that at larger $x$ ($x > 0.65$) the system enters a magnetic quantum critical regime where $C(T)/T$ roughly scales as $\log T$. This behavior extends to progressively lower $T$ as $x$ increases towards a magnetic instability at $x \approx 0.75$.

**Introduction** The layered cobaltates Na$_x$CoO$_2$ have been the subject of intense studies in recent years due to their very rich phase diagram and associated rich physics. Their structure is similar to that of copper oxides and consists of alternatively stacked layers of CoO$_2$ separated by sodium ions. The Co atoms form a triangular lattice. The hydrated compound Na$_x$CoO$_2$·$y$H$_2$O with $x \sim 0.3$ shows superconductivity, most likely of electronic origin. The anhydrous parent compound Na$_x$CoO$_2$ exhibits low resistivity and thermal conductivity and high thermopower for $0.5 < x < 0.9$ and magnetic order for $0.75 < x < 0.9$ (Refs.[6,7,10,11]). In the paramagnetic phase Na$_x$CoO$_2$ shows a conventional metallic behavior at $x \leq 0.6$ and at larger $x$ displays strong temperature dependence of both spin susceptibility and specific heat down to very low $T$. This change of behavior has been attributed to a putative Lifshitz-type topological transition (LTT) at $x_c \approx 0.62$, in which a small three-dimensional (3D) electron Fermi pocket appears around $k = 0$, in addition to the already existing quasi-2D hole pocket with large $k_F$ (Ref.[14]), see Fig. 1. Although the small pocket has not yet been observed directly, ARPES measurements at smaller $x$ did find a local minimum in the quasiparticle dispersion at the $\Gamma$ point. Similar topological transitions have been either observed or proposed for several solid state [16–23] and cold atom systems [24], and the understanding of the role played by the interactions near the LTT transition is of rather general interest to condensed matter and cold atom communities.

The subject of this paper is the analysis of interaction contributions to the specific heat $C(T)$ in Na$_x$CoO$_2$ at around the critical $x_c$ for LTT. The experimental data show (see Figs. 3 and 4) that for doping near $x_c$, the temperature dependence of $C(T)/T$ is more complex than the $C(T)/T = \gamma_1 + \gamma_3T^2 + O(T^4)$ expected in an ordinary Fermi liquid (FL). The FL behavior itself is not broken in the sense that $\gamma_1$ remains finite. However the $T$ dependence at $x = x_c$ is stronger than $T^2$, as evidenced by the fact that the fits of the data on $C(T)/T$ to $\gamma_1 + \gamma_3T^2$ behavior in finite intervals around different $T$ yield larger $\gamma_3$ as $T$ goes down (see Ref.[36]). This does not allow one to interpret $\gamma_1$ directly as a density of states, and the full computation is needed to compare the data with the theory. For doping levels $0.65 < x < 0.75$ the data show that, to a good approximation, $C(T)/T \propto \log T$ in a wide range of temperatures $T \sim 1 \sim 10$ K, see Fig. 4a. This logarithmic temperature dependence progressively spans over larger temperature range as $x$ approaches 0.75, where a magnetic order develops (Refs.[6,7,10,11]).

Some qualitative features of the experimental data of $C(T)$ at $x \sim x_c$ are reproduced by the free-fermion formula for specific heat, with the quasiparticle dispersion taken from first-principle calculations (Fig. 2a). In particular, $\gamma_1$ increases and $\gamma_3$ passes through a maximum around $x = 0.62$, see Fig. 3b,c. However, the magnitudes of $\gamma_1$ and $\gamma_3$ are much smaller than in the data and the maxi-
maximum in $\gamma_3$ is too shallow. A strong temperature dependence of $C(T)/T$ may potentially come from phonons, but $\gamma_3$ due to phonons is highly unlikely to become singular at $x = x_c$. This implies that the observed features of $C(T)$ are most likely caused by electron-electron interactions. Interactions with a small momentum transfer $q$ give rise to linear in $T$ dependence of $C(T)/T$ in 2D due to non-analyticity associated with the Landau damping. That a linear in $T$ term has not been observed in Na$_x$CoO$_2$ near $x_c$ implies that small-$q$ fluctuations are weak near this doping. Interactions with a finite momentum transfer $q \approx k_{F1}$ are expected to be strong and sensitive to the opening of a new piece of electron FS as the static fermionic polarization operator $\Pi(k_{F1})$ gets enhanced as $x$ approaches $x_c$. An enhancement of $\Pi(k_{F1})$ generally implies that spin fluctuations at $k_{F1}$ get softer and mediate fermion-fermion interaction at low energies.

The spin-fluctuation contribution to $\gamma_3$ has been analyzed before for systems with a single 3D FS. In this situation, the sign of $\gamma_3$ is negative. This negative sign can be traced back to positive sign of the prefactor for the $\alpha^2$ term in the dynamical spin susceptibility $\chi(q, \omega)$. The latter behaves at small frequencies and at momenta $q < 2k_F$, which connects points on the FS, as $\chi^{-1}(q, \omega) \propto \xi^{-2} + b\omega^2 - i\gamma\omega$ with $b \propto 1/q^2 > 0$. We show that in our case relevant momenta are around $k_{F1}$ and situation with $b > 0$ holds for $x > x_c$, when a small 3D pocket emerges and $k_{F1}$ connects fermions at the two FSs. For $x < x_c$, when only 2D FS is present, we found that the sign of $b$ is negative. This gives rise to positive $\gamma_3$ at $x \leq x_c$ and negative $\gamma_3$ at $x > x_c$, consistent with the data in Na$_x$CoO$_2$ (see Fig. 3b,c). We further show that $b$ is singular at small $\mu$ and this gives rise to non-monotonic behavior of $\gamma_3$ around $x_c$ - it increases upon approaching $x_c$ from below, passes through a maximum and then rapidly decreases and changes sign at $x \geq x_c$ (Fig. 3c). We argue that this behavior is fully consistent with the data.

When the temperature exceeds $1/(\xi^2\gamma)$, the system enters into a quantum-critical regime. We found that in this regime, the specific heat can be well fitted by $C(T)/T \propto \log T$ (see Fig. 4). The lower boundary of quantum-critical behavior extends to lower $T$ as $x$ increases towards the onset of a magnetic transition at $x \approx 0.75$. This is again consistent with the experiment which observed $C(T)/T \propto \log T$ down to $0.1$ K at $x = 0.747$.

**The model.** We follow earlier works and consider fermions with the tight-binding dispersion $\epsilon(k)$ on a triangular lattice with hopping up to second neighbors in $xy$ plane and to nearest neighbors along $z$-direction. The dispersion, shown in Fig. 1, has a hole-like behavior at large momentum ($\partial \epsilon(k)/\partial k < 0$) and a local minimum at the $\Gamma$ point $k = 0$. At $\mu < 0$, ($x < x_c = 0.62$) the Fermi surface consists of a single quasi-2D hole pocket with large $k_F = k_{F1}$. As $\mu$ crosses zero and becomes positive, a new 3D Fermi pocket appears, centered at the $\Gamma$ point (see Fig. 1). For the specific heat analysis at small $|\mu|$ we can approximate the dispersion near $k = 0$ by $\epsilon(k) = k^2/(2m) + k_z^2/(2m_z)$ and approximate the large Fermi surface by an effectively 2D dispersion $\epsilon(k) \approx v_{F1}(k - k_{F1})$, where $k = \sqrt{k_x^2 + k_y^2}$. In our analysis, we do not consider
Na charge ordering. Such an ordering does indeed develop at intermediate dopings. However, the experimenters, who performed the measurements on quenched samples of Na$_x$CoO$_2$ at $x \geq 0.6$, did not observe time-dependent phenomenon and argued that their quenched samples are in quasi-equilibrium state.

$C(T)$ for free fermions. To set the stage for the analysis of interaction effects we first compute the specific heat for free fermions with non-monotonic dispersion $\epsilon(k)$. The grand canonical potential is given by

$$\Omega(T,\mu,V) = -T \int \rho(\epsilon) \ln(1 + e^{-(\epsilon-\mu)/T}) d\epsilon,$$  \hspace{1cm} (1)

Evaluating the entropy $S(T,\mu,V)$, extracting $\mu = \mu(T,V)$ from the condition on the number of particles and expanding $C(T) = C_V(T) = T \left( \frac{\partial S}{\partial T} \right)_V$ in temperature, we obtain at the lowest $T$

$$C(T)/T = \gamma_1 + \gamma_3 T^2 + O(T^4)$$

$$\gamma_1 = \frac{\pi^2 \rho}{3}, \quad \gamma_3 = \frac{\pi^4}{30} \left( \frac{7\rho\rho'' - 5(\rho')^2}{\rho} \right)$$  \hspace{1cm} (2)

where $\rho(\mu)$ and its derivatives over $\mu$ are computed at $T = 0$. The low-T expansion in (2) is valid for $T < |\mu|$. Analyzing (2), we find that for $\mu < 0$, when there is no electron pocket, the $T$ dependence comes from a large hole pocket and is non-singular. For $\mu > 0$, the electron pocket appears with $\rho(\mu) \propto \sqrt{|\mu|}$. This gives rise to negative $\gamma_3$, which diverges as $\mu \to 1/3^{3/2}$. At $\mu = 0$ the analytic expansion in powers of $T^2$ doesn’t work even at the lowest T. We found that in this case

$$\frac{C(T)}{T} = \gamma_1 + 2.88 \frac{m\sqrt{2m}}{\pi^2} \sqrt{T} + O(T)$$  \hspace{1cm} (3)

The same behavior holds at a finite $\mu$, when $T > |\mu|$. Observe that the prefactor for $\sqrt{T}$ term is positive, opposite to that of $T^2/\mu^{3/2}$ term. This implies that the temperature dependence of $C(T)/T$ changes sign at some positive $\mu$. The actual $T$ dependence of $C(T)/T$, obtained without expanding in $T$, is presented in Fig. 2a, and $\gamma_1$ and $\gamma_3$ extracted from fitting this $C(T)/T$ by $\gamma_1 + \gamma_3 T^2$ in different windows of $T$ are shown in Fig.3b,c and in Ref.36. We see that both $\gamma_1$ and $\gamma_3$ depend on where the $T$ window is set, and $\gamma_3$ as a function of doping changes sign at some $x > x_c$, i.e., at some positive $\mu$, as expected.

Interaction contribution to $C(T)$. At a qualitative level, the free-fermion formula for $C(T)$ is consistent with the data. At the quantitative level, it strongly differs from the measured $C(T)$, even if we would use a renormalized dispersion with larger effective density of states. To see the inconsistency, we compare in Fig.3b,c the theoretical and experimental doping dependence of $C(T)$ and particularly the values of $\gamma_1$ and $\gamma_3$ fitted over various temperature ranges. We see that the magnitude of $C(T)/T$ for free fermions and the strength of doping variation of $\gamma_3$, extracted from it, is much smaller than in the data. These discrepancies call for the analysis of interaction contributions to $C(T)$.

A fully renormalized fermion-fermion interaction can be decomposed into effective interactions in the charge and in the spin channel. For systems with screened Coulomb repulsion, the effective interaction in the spin channel get enhanced and, if the system is reasonably close to a Stoner instability, can be viewed as mediated by spin fluctuations. Na$_x$CoO$_2$ does develop a magnetic order at $x > 0.75^{6,7,10,11}$, and it seems reasonable to expect that magnetic fluctuations develop already at $x \approx x_c$.

The spin-fluctuation contribution to the thermodynamic potential is given by

$$\Omega = \Omega_0 + \int \frac{d\omega}{\pi} n_B(\omega) \int \frac{d^2q}{(2\pi)^3} \text{Im} \chi^{-1}(q,\omega)$$  \hspace{1cm} (4)

where $\Omega_0$ is the free-fermion part, $n_B$ is the Bose function, and $\chi(q,\omega)$ is fully renormalized dynamical spin susceptibility.

To obtain $\chi(q,\omega)$ we use the same strategy as in earlier works: compute first the static spin susceptibility $\chi_0(q,\omega = 0)$ of free fermions, then collect RPA-type renormalization and convert $\chi_0(q,\omega = 0)$

FIG. 4: Experimental data for doping $x = 0.63, 0.65, 0.72$ from Ref.12 (a) and theoretical (spin-fluctuation) result (b) for $C(T)/T$ in semi-logarithmic temperature scale. The dashed lines correspond to $C(T)/T \propto \log T$ fit. The prefactor of the $\log T$ depends on magnetic correlation length $\xi$. 

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{Experimental data for doping $x = 0.63, 0.65, 0.72$ from Ref.12 (a) and theoretical (spin-fluctuation) result (b) for $C(T)/T$ in semi-logarithmic temperature scale. The dashed lines correspond to $C(T)/T \propto \log T$ fit. The prefactor of the $\log T$ depends on magnetic correlation length $\xi$.}
\end{figure}
into full static $\chi(q, \omega = 0)$, and then compute the bosonic self-energy coming from the interaction with low-energy fermions and obtain the full dynamical $\chi(q, \omega)$ at low frequencies. The result is \[ \chi^{-1}(q, \omega) = \frac{\chi}{\varepsilon^2 + (q - k_{F1})^2 + b_0^2 - i\gamma\omega} \] (5)

where $\chi$ is a magnetic correlation length and the last term is the Landau damping. The sign of $\gamma_3$ term in $C(T)$ depends on the sign of $b$ -- the prefactor for the $\omega^2$ term (see Eq. (9) below). To obtain $b$ in our case we first evaluated the susceptibility of free fermions $\chi_0(q, \omega)$ and then obtained $\chi(q, \omega)$ using RPA. For most relevant $q \approx k_{F1}$ we obtained (see [36] for details)

$\chi_0(q, \omega) = \frac{\sqrt{m_{mz}}}{4\pi^2 v_{F1}} [(\omega - \tilde{\mu}) \log(|\omega - \tilde{\mu}|) + 
- (\omega + \tilde{\mu}) \log(|\omega + \tilde{\mu}|)] + \ldots$ (6)

where $\tilde{\mu} = \mu - (q - k_{F1})^2/(2m)$ and dots stand for regular terms. Expanding in $\omega$ and substituting into RPA formula we obtain

$\gamma = \frac{\sqrt{m_{mz}}}{4\pi^2 m a_0 v_{F1}} \theta(\tilde{\mu}) + \frac{1}{\sqrt{3} v_{F1}^2 m a_0 a_z}$. (8)

where $a_0$ is of order of lattice spacing in $xy$ plane, $a_z$ is inter-layer spacing. Note that near $\mu = 0$ the quadratic coefficient $b$ is singular and its dependence on $q$ becomes important. The $1/\mu$ dependence of $b$ originates from the singularity in the derivative of density of states at the Lifshitz transition. The $T^3$ term in $C(T)$ at $x < x_c$ and small $T$ ($T < |\mu|$ and $T < 1/(\xi^2 \gamma)$) comes from expanding $\text{Im} \ln \chi^{-1}$ in (4) to order $\omega^3$ and integrating over $q$ near $q = k_{F1}$. When $|\mu| > \xi^{-2}/m$ the $q$-dependence of $b$ and $\gamma$ may be neglected and we obtain

$\gamma_3 = \gamma_{k_{F1}} \xi^3 \pi^3 \frac{-4b - (\gamma\xi)^2}{10}$ (9)

The eq.(7) for $b$ suggests a singular behavior of $\gamma_3$ near $\mu = 0$. For small $|\mu| < \xi^{-2}/m$ the singularity is smoothed by $q$-dependence of $\gamma$ and $b$ and eq.(9) needs to be replaced by the result of numerical integration. The results, in particular a sharp maximum in $\gamma_3$ near $x_c$, are in good agreement with experiment, see Fig.3b,c.

At higher temperatures, when $T > 1/(\xi^2 \gamma)$ we find that the system enters into a quantum-critical regime where the system behavior is the same as at $\xi^{-1} = 0$. The form of $C(T)/T$ at such temperatures in principle depends on the effective dimensionality of spin fluctuations around $q = q_0$ (see Ref.[36]). We find, however, that such dimension-specific behavior holds only at high $T$, while in the intermediate regime $T \gtrsim 1/(\xi^2 \gamma)$, $C(T)/T$ can be well fitted by $\log T$ even for effectively 1D spin fluctuations. This agrees with the data which show a $\log T$ behavior even at doping $x = 0.65$, see Fig. 4. As $\xi$ and $\gamma$ increase at larger $x$, the lower boundary of $\log T$ behavior of $C(T)/T$ stretches to progressively smaller $T$ and a prefactor of $\log T$ grows, in agreement with the experiments at higher doping (Ref. [3,12]).

For quantitative comparison with the data we compute the dynamical part of particle-hole bubble without expanding in frequency and use (4) to compute the thermodynamic potential and the specific heat. To estimate $\xi$ we use the experimental data for $\chi(0,0)/\gamma_1$ at $x \approx x_c$ and our numerical RPA result for the prefactor for $(q - q_0)^2$ term in $\chi^{-1}(q, \omega)$. Extracting $\xi$ from these data we obtain $\xi \approx \xi_0$ near $x = 0.62$ and it grows with the doping. For better comparison we subtract from the data the contribution from phonons $C_{ph} \approx T^3 \cdot 0.07 m K^{-2} mol^{-1}$, which only weakly depends on doping$^{41}$. The results are shown in Fig. 2b and Fig. 3b,c. We see that theoretical and experimental $C(T)$ agree quite well over a wide range of temperatures, and the agreement between $\gamma_1$ and $\gamma_3$, extracted from the data and from spin-fluctuation theory, is also very good. We emphasize that the doping variation of $\gamma_3$ is not affected by the phonon contribution and thus measures solely the contribution to $C(T)$ from spin fluctuations. From this perspective, a good agreement with the data is an indication that magnetic fluctuations with large $q = k_{F1}$ are strong in Na$_x$CoO$_2$ near the LTT. The $\log T$ behavior of $C(T)/T$, which we found at $T \sim 3 - 10 K$ for $x \approx 0.7$ is also consistent with the data, see Figs.4. Finally, we note that the experimental data on $\gamma_1$, fitted at $T \sim 10 K$, show a small discontinuity as a function of doping, Figs.3b,c, which is expected if the LTT is first order$^{42}$. The jump in $\mu$ is estimated to be 5 to 10 meV. When we take this into account, we obtain a sharper doping dependence of $\gamma_3$, leading to an even better agreement with the data.

Conclusions.

In this work we have analyzed the specific heat in the layered cobaltate Na$_x$CoO$_2$. Near $x = 0.62$ the system exhibits a non-analytic temperature dependence and strong doping variation of the specific heat coefficient $C(T)/T$. We explained the data based on the idea that at $x_c = 0.62$ the system undergoes a LTT in which a new electron pocket appears. We demonstrated that the non-analytic temperature dependence of $C(T)/T$ at $x = x_c$, and its strong doping variation is quantitatively reproduced if interaction is mediated by spin fluctuations peaked at the wave-vector which connects the original and the emerging Fermi surfaces. We argued that the observed $\log T$ behavior of $C(T)/T$ at larger dopings $0.65 \lesssim x < 0.75$ is an indication that the system enters into the magnetic critical regime.

We acknowledge useful discussions with S. Carr,
where hole-like and electron-like excitations, we obtain 

dispersion near $\Gamma$ as a 3D parabola. Evaluating the 

effective mass $m_{F}$ at the hole FS and $\Gamma$ point 

to be computed numerically and are effectively 

carried from the particle-hole processes with total mo-

densities coming from low fermion energies.

We take the momenta $q > x$, $x > k_{F}$, $k_{F}$, $v_{F}$, $a_{x}$, 

and assume $\bar{\mu} = 0$, and the singularity in $\chi_{1}(\omega)$ 

where $\bar{\mu} = 0$. In explicit form:

$$\chi_{1}(\omega) = \frac{2\chi_{0}}{\sqrt{3}k_{F}v_{F}a_{x}} = \frac{1}{\pi\sqrt{3}v_{F}a_{x}}$$

$$\text{Re} \chi_{1}(\omega) \approx \frac{k_{F}}{2\pi v_{F}a_{x}}$$

where $a_{x}$ is inter-layer lattice spacing. This $\chi_{1}$ does not carry any interesting frequency or chemical potential dependence.

On the contrary, the susceptibility $\chi_{12}(q, \omega)$, coming from the particle-hole processes with total momen-
tum $q = k_{F}$, depends non-trivially on $\omega$ and $\mu$. We take the momenta $q$ to be near the distance between Fermi momentum for the hole FS and $\Gamma$ point 

where electron FS emerges for $x > x_{c}$, i.e., consider $q = k_{F} + \tilde{q}$ and assume $\tilde{q}$ to be small. Because $k_{F}$ for the electron pocket is either zero ($x = x_{c}$) or very small ($x > x_{c}$), we deal with a special case when the frequency may exceed the Fermi energy of the small pocket. This gives rise to a non-linear frequency dependence of the imaginary part of the susceptibility at $q \approx k_{F}$. To simplify the discussion, we approximate the hole dispersion as purely 2D and the dispersion near $\Gamma$ as a 3D parabola. Evaluating the imaginary part of the particle-hole bubble involving hole-like and electron-like excitations, we obtain

$$\text{Im} \chi_{12}(q, \omega) = \frac{1}{16\pi^{2}v_{F}}S$$

Here $S$ is the area in the $k_{y}, k_{z}$ plane, where $\mu - \omega < \tilde{q}^{2}/(2m) + k_{y}^{2}/(2m) + k_{z}^{2}/(2m) < \mu + \omega$. This area is a ring for $|\omega| < \tilde{q}^{2}/(2m) \equiv \tilde{\mu}$ and an ellipse otherwise; the ellipse shrinks to an empty set if $\tilde{\mu} + |\omega| < 0$. In explicit form:

$$S = 2\pi\sqrt{mm_{z}}((\tilde{\mu} + \omega)\theta(\tilde{\mu} + \omega) - (\tilde{\mu} - \omega)\theta(\tilde{\mu} - \omega))$$

where $\tilde{\mu} = \mu - \tilde{q}^{2}/(2m)$. We also need an extra factor of 2, if we add the contribution from the opposite patch of the large pocket.

Analyzing $S(\omega, q = 0)$, we find that it has a linear frequency dependence at the lowest frequencies at $\mu > 0$, when the small pocket is present, then there is a cusp at $\omega = \mu$, and then another linear dependence, with twice smaller slope. For $\mu < 0$, when there is no pocket but the dispersion has a local minimum at $\Gamma$, the slope is zero at $\omega < -\mu$ and becomes finite only after the cusp at $-\mu$, see Fig.5.

At a nonzero $\tilde{q}$ the results are the same as at $\tilde{q} = 0$ if one replaces $\mu$ by $\tilde{\mu}$.

The frequency-dependent part of $\text{Re} \chi_{12}(q, \omega)$ can be computed elegantly from Kramers-Kronig transformation. As the second frequency derivative of the imaginary part is a delta-function at the cusp, it is easy to compute the second frequency derivative of the real part:

$$\partial_{q}^{2}\text{Re} \chi_{12}(\omega) = \frac{\sqrt{mm_{z}}}{4\pi^{2}v_{F}} \left( \frac{1}{\omega - \tilde{\mu}} - \frac{1}{\omega + \tilde{\mu}} \right)$$

This expression is singular at frequencies $\omega = \pm \tilde{\mu}$, see Fig. 5. It is essential for our analysis that $\partial_{q}^{2}\text{Re} \chi_{12}(\omega) > 0$ for $\tilde{\mu} < 0$ and that it diverges when $\tilde{\mu} \rightarrow 0$.

Integrating Eq. (14) over $\omega$ we obtain the full analytic expression for the frequency dependence of susceptibility:

$$\chi_{12}(q, \omega) = \chi_{12}(q, 0) + \frac{\sqrt{mm_{z}}}{4\pi^{2}v_{F}} \left[ (\omega - \tilde{\mu}) \log(\omega - \tilde{\mu}) + +\tilde{\mu} \log(\tilde{\mu}^{2}) - (\omega + \tilde{\mu}) \log(-\omega - \tilde{\mu}) \right]$$

The result is presented in Fig. 5. At $\tilde{q} = \pm k_{F}$, $\tilde{\mu} = 0$, and the singularity in $\chi_{12}(\omega)$ is located at zero frequency. The static part

$$\chi_{12}(q, 0) \approx a_{0}m_{z}(q - q_{0})^{2} + \text{const}$$

has non-universal high energy contributions which have to be computed numerically and are effectively included in our calculations through the value of the correlation length. The parameter $a_{0}$ is of the order of the lattice spacing in $xy$ plane.

B. Direct derivation of the prefactor of the $\omega^{2}$ term in spin susceptibility at $q = k_{F}$.

In this section, we offer an alternative derivation of the prefactor $b$. Consider the case $\mu < 0$ and $q = k_{F}$.
FIG. 5: The frequency dependence of the susceptibility $\chi_{12}(\omega)$

along the x-axis. Working in Matsubara formalism we obtain for the free-theory susceptibility at $T = 0$:

$$\chi_0(k_{F1}, i\Omega) = -\int \frac{d^4k}{(2\pi)^4} G(k, i\omega) G(k + k_{F1}, i\omega + i\Omega)$$  \hspace{1cm} (17)

The Green’s functions are

$$G(k, i\omega) = \frac{1}{i\omega + v_{F1}k_x}$$  \hspace{1cm} (18)

$$G(k, i\omega) = \frac{1}{i\omega + v_{F1}k_x}$$  \hspace{1cm} (19)

One Green’s function is taken near the $k = 0$ (where the small pocket is due to appear) and another is near the large hole pocket. The contribution is doubled to account for the reverse situation. Expanding in $\Omega$ we get the quadratic term:

$$\chi_0^{(2)}(k_{F1}, i\Omega) = +2\Omega^2 \int \frac{dk_x}{(2\pi)^3} \int_0^\infty \frac{d\omega}{(2\pi)^4} \frac{1}{(i\omega - \frac{k_x^2 + k_y^2}{2m} + \frac{k_z^2}{2m_z} + |\mu|)}$$

for $k_x > 0$ the frequency integration contour passes between the poles and we get

$$\chi_0^{(2)}(k_{F1}, i\Omega) = -2\Omega^2 \int \frac{dk_x}{(2\pi)^3} \int_0^\infty \frac{d\omega}{(2\pi)^4} \frac{1}{(v_{F1}k_x + \frac{k_x^2 + k_y^2}{2m} + \frac{k_z^2}{2m_z} + |\mu|)}$$

(20)

for small $|\mu|$ the integration is peaked at small $k$ and we can neglect $k_x^2 / (2m)$ term compared to $v_{F1}k_x$. Then defining $x = k_x v_{F1} / |\mu|$, $y = k_y / \sqrt{2|\mu|m}$ and $z = k_z / \sqrt{2|\mu|m_z}$ we get:

$$\chi_0^{(2)}(k_{F1}, i\Omega) = -2\Omega^2 \frac{\sqrt{m m_z}}{v_{F1}|\mu|} \int_0^\infty dx \int_0^\infty dy \int_0^\infty dz \cdot \frac{1}{\sqrt{x^2 + y^2 + z^2 + 1}}$$

for $x, y, z > 0$.

The continuation to real frequencies provides a positive coefficient of $\Omega^2$ in $\chi_0$, which behaves as $1/|\mu|$ for $\mu < 0$. This coincides with the more general eq.(14), if we set $\omega = 0$ and $q = k_{F1}$ in eq.(14). This unconventional result appears because the momentum $q$ connects a Fermi-surface with a region where all states are above the Fermi level. When the small pocket appears and fermions are connected by the vector $q$ simultaneously at the Fermi-surface, an opposite sign is obtained.

C. Temperature expansion of the specific heat.

At low temperatures, when $|\omega| < |\mu|$ and $T < \mu$, we can expand the full free-particle susceptibility

$$\chi_0(q, \omega) = \chi_1(q, \omega) + \chi_{12}(q, \omega)$$

in frequency as

$$\chi_0(q, \omega) = \chi_0 - m_z a_0 (q - q_0)^2 + b_0 \omega^2 + i\gamma \omega$$  \hspace{1cm} (23)

From eqs.(10,15) we extract:

$$\gamma_0 = \frac{\sqrt{m m_z}}{2\pi v_{F1}} \theta(\tilde{\mu}) + \frac{1}{\sqrt{3\pi \nu_{F1}^2 a_z}}$$

$$b_0 = -\frac{\sqrt{m m_z}}{4\pi^2 v_{F1} \tilde{\mu}}$$

where $\chi \chi q, \omega / (1 - U\chi_0(q, \omega)$ is then expressed as

$$\chi(q, \omega) = \frac{\sqrt{m m_z}}{2\pi m_z a_0 v_{F1} \tilde{\mu}} + \frac{1}{\sqrt{3\pi \nu_{F1}^2 m_z a_0 a_z}}$$

The spin-fluctuation contribution to the grand thermodynamic potential is:

$$\Omega_{int} = \int \frac{d\omega}{\pi} n_B(\omega, T) \int \frac{d^2q}{(2\pi)^2} \text{Im} \ln \chi^{-1}$$

(29)

(29)

$$n_B(\omega, T),$$

however the form of temperature dependence of $\Omega_{int}$ depends on the frequency dependence of $\chi(q, \omega)$. Expanding the integrand in frequency and differentiating $\Omega_{int}$ over $T$ we obtain the temperature expansion of the interaction contribution to the entropy $S = -\theta_{int} / \partial T$:

$$S = \frac{T}{15(\pi)^5} \int \frac{\gamma d^3q}{(\xi^2 + (q - q_0)^2)^2} - \int \frac{T^3}{15(\pi)^5} \left( \int \frac{\gamma d^3q}{(\xi^2 + (q - q_0)^2)^2} + \frac{1}{3} \int \frac{d^3q}{(\xi^2 + (q - q_0)^2)^2} \right)$$

(30)
The momentum integral is peaked at $q = q_0 \approx k_F$, and we assume that it is cylindrically symmetric (the actual dispersion suggests that $q_z = \pi$ may be more important than other values of $q_z$, but this only changes the overall prefactor). Extracting $C(T)$ from the entropy we obtain $C(T) = \gamma_3 + T^3\gamma_3$, where, if we neglect $q$-dependence of $\gamma$ and $b$,

$$\gamma_3 = \gamma k_F \xi^3 \frac{\pi^3}{10} (-4b - (\gamma \xi)^2)$$

(31)

These are the expressions used in the main text. If we are close to $\mu = 0$, then $b$ is singular, so we cannot neglect its $q$ dependence. The integration has been done numerically, while the qualitative analytic picture is given below. At small enough $\mu$, $1/\mu$ has to be replaced by $-2m/(q - k_F)^2$. Typical $q - k_F$ is of order $\xi^{-1}$, hence $b$ saturates at the value of order $\xi^2 (m^3 m_v)^{1/2}/(m_q k_F)$. Note that the ratio $4b/(\gamma \xi)^2$ does not depend on $\xi$. This ratio exceeds one, for the dispersion we consider, hence, according to eq.(31), $\gamma_3 > 0$. A positive $\gamma_3$, which increases as $x$ approaches $x_c$ from below, is precisely what the data show (see Figs.6 c,d).

At $\mu > 0$ ($x \gtrsim x_c$), when the new pocket appears, $\gamma$ changes by a finite amount and $b$ evolves from a negative constant at $\mu = 0$ to a positive $b \propto 1/\mu$ given by (27) for $\mu > \xi^{-2}/(2m)$. The positive $b$ is consistent with earlier result\(^\text{31}\) for a single 3D FS as in both cases $q \approx k_F$ connects points on the FS and our small pocket is three-dimensional. As a result, $\gamma_3$ rapidly decreases as $x$ increases above $x_c$, changes sign and becomes negative. This is again consistent with the data.

D. Specific heat of free fermions for $|\mu| \ll T$.

Let us fix $x = x_c$, so that $\mu(T = 0) = 0$. The 3D pocket produces a singularity in the density of states:

$$\rho = B + A\sqrt{\theta}(\mu)$$

(32)

where in our case $B = \frac{k_F^2}{\pi^2}$, and $A = \frac{m\sqrt{2m}}{\pi^2}$. The grand canonical potential is $\Omega = -\int \rho(e) n_F((e - \mu)/T)de$, where $\rho(e) = \int \rho(e)de$. Then the entropy is $S = -T^{-2} \int \rho(e) n_F((e - \mu(T))/T)(e - \mu)/T)de = -\int \rho(e) n'_F(e - \mu(T)/T)de$. The specific heat is obtained by substituting $\mu(T)$ and evaluating $C/T = \left(\frac{\partial S}{\partial T}\right)_N$.

The condition on the chemical potential $\mu(T)$ is

$$\int \left(\frac{e - \mu(T)}{T} - \theta(-e)\right)B + A e^{1/2} \theta(e)de = 0$$

(33)

this equation can be expanded in series in $\mu(T)/T$:

$$\mu(T) = -0.678 AT^{3/2} + 0.536 A \sqrt{T} + O((\mu/T)^2)$$

(34)

This expansion is valid for moderate temperatures, where $A\sqrt{T} \ll B$, then, indeed $\mu/T \ll 1$, the actual expansion parameter is $A\sqrt{T}/B$.

For the specific heat we obtain

$$C/T = \frac{\pi^2}{3} B + 2.88 A\sqrt{T} \frac{8.84}{B} + O\left(\frac{A\sqrt{T}}{B}\right)^3$$

(35)

E. Quantum criticality near the transition to ordered phase.

If the small pocket and the large pocket have parts with matching curvatures, the susceptibility will be strongly peaked at the momentum vector connecting them, which may result in spin density wave magnetic order. This is indeed what happens when the small pocket has grown sufficiently large at $x > 0.75\text{.}\text{14,32}$ For smaller doping, the nesting is not good enough for magnetic order, but magnetic correlation length $\xi$ is nevertheless large. When $T \ll \xi/\eta$ and $T \ll \mu$, a regular Fermi-liquid expansion of $C(T)/T$ in powers of $T^2$ works. At slightly higher temperatures, when $\xi^{-2}$ cannot be assumed large (see eq.(38)) this expansion does not hold. This temperature regime is relevant to the description of the behavior of $C(T)/T$ at intermediate $T$ at $x = x_c = 0.62$ and down to quite low $T \sim 0.1K$ at $x = 0.747$ (Ref. 3), which is very close to $x = 0.75$ at which $\xi = \infty$. The fact that critical behavior extends to such low temperatures is remarkable.

For analytic estimate, we set $\omega$ to be of order $T$ and using earlier results obtain

$$C(T) \sim -\int d^3q \Im \left(\log \left(\xi^{-2} + \left(\sqrt{q_x^2 + q_y^2} - k_{F1}\right)^2 - i\gamma\omega\right)\right)\bigg|_{\omega \approx T}$$

(36)

where $\gamma$ is given in eq.(28). Here we integrate over cylindrical shell of momenta near the vectors that connect $\Gamma$-point with large pocket. Here we assumed the large pocket to be cylindrical, but this assumption can be easily relaxed not changing the result. There is a whole 2D surface of important momenta that contribute to near-critical spin fluctuations (kinetic part $(\sqrt{q_x^2 + q_y^2} - k_{F1})^2$ is degenerate in $q_x$ and angle). When $T \gtrsim \xi^{-2}/\gamma$, the system enters the critical region. Deep in this regime, the specific heat behaves as

$$\frac{C(T)}{T} \sim \frac{1}{T} \Im \sqrt{\xi^{-2} + i\gamma^2} \to \gamma \sqrt{T}$$

(37)

This behavior can be traced back to the fact that the dispersion of spin fluctuations near $q = q_0$ is effectively one-dimensional since it is independent on the direction of $q$ in the $xy$ plane and on $q_z$. For effectively 2D dispersion, we would obtain $C(T)/T \propto$
log $T$, and for 3D dispersion $C(T)/T$ would remain finite.

We have found, however, that in our, effectively one-dimensional, case the $1/\sqrt{T}$ dependence of $C(T)/T$ holds only at high $T$, while in a wide range of temperatures the function $\operatorname{Im}(\sqrt{a+iT})/T$ can be well approximated numerically by $(0.44 - 0.095 \log \frac{T}{a})/\sqrt{a}$. This behavior holds at $a \lesssim T \lesssim 40a$. In our case $a = \xi^{-2}/\gamma$ and we expect a log $T$ behavior at $T \gtrsim \xi^{-2}/\gamma$. Assuming that the largest contribution to $\gamma$ comes from the approximate nesting of small and large Fermi-surfaces, we get $\gamma^{-1} \sim a_0 v_{F1}$, so

$$T \gtrsim \frac{a_0 v_{F1}^2}{\xi} = \frac{v_{F1}^2}{a_0} \left( \frac{a_0}{\xi} \right)^2$$

(38)

the factor $v_{F1}/a_0$ can be estimated to be of the order of effective hopping $t_1 \approx 1000K$. Hence, the correlation length of order of 10 lattice spacings can bring the log $T$ behavior to the range of several Kelvins.

The calculation can be easily repeated if one assumes that lattice effects produce a significant lifting of degeneracy of the kinetic term for spin fluctuations. E.g. let us replace $(\sqrt{q_x^2 + q_y^2} - k_{F1})^2 \to (q_x^2 - k_{F1}^2 + q_y^2)$, then the integration in eq.(36) gives logarithmic behavior of $C/T$ in the same range $T > \xi^{-2}/\gamma$. In the main text we used the approximate theoretical formula $C(T)/T \propto \log T$ to fit the experimental data.

**F. Fits of $C(T)/T$ to $\gamma_1 + \gamma_3 T^2$ in temperature intervals centered at different $T$.**

As emphasized in the main text, the $T$-dependence of the experimental $C(T)/T$ around $x = 0.62$ is stronger than $T^2$, as evidenced by the fact that the fits of the data on $C(T)/T$ to $\gamma_1 + \gamma_3 T^2$ behavior in finite intervals around different $T$ yield larger $\gamma_3$ with decreasing $T$. We show the fits in two temperature intervals centered at different $T$ in Fig. 6.

---

We used the same dispersion as in Ref. 32 with the nearest-neighbor hopping in XY plane $t_1 \approx 0.1 \text{eV}$, the second neighbor hopping $t_2 = -0.35 t_1$, the third neighbor hopping $t_3 = -0.07 t_1$, and the nearest-neighbor hopping along z-direction $t_z = -0.15 t_1$.

NMR experiments observed a rapid change of relevant momenta of spin fluctuations at $x \approx 0.6$. We interpret these results as a transition from predominantly $q \approx 2k_F$ fluctuations before fermions near $\Gamma$ point become soft to $q \approx k_F$ fluctuations near the onset of the pocket.

The data show that from the increase of interplane distance with doping and is rather small.

We interpret these results as a transition from predominantly $q \approx 2k_F$ fluctuations before fermions near $\Gamma$ point become soft to $q \approx k_F$ fluctuations near the onset of the pocket.