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Can high-T_c superconductivity in cuprates be explained by the conventional BCS theory?

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For overdoped cuprates, it is believed that the normal state behaves as an ordinary Fermi liquid while the superconducting state conforms to the BCS theory. We have put these beliefs to the test by a comprehensive experiment in which over two thousand cuprate films were synthesized by molecular beam epitaxy and studied in great detail and precision. Here, we compare our key experimental results to various proposed explanations based on BCS theory extended to dirty *d*-wave superconductors, including the cases of strong (unitary) and weak (Born) scattering on impurities. The discrepancies seem insurmountable, and point to the need to develop the theory further, likely beyond the canonical BCS paradigm.

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74.62.En Effects of disorder.

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1. Introduction

The understanding of high-temperature superconductivity (HTS) in cuprates has been the central problem in condensed matter physics for three decades. The most basic dichotomy is between Bardeen–Cooper–Schrieffer (BCS) theory, formulated under the assumption that the pairing interaction is relatively weak, and Bose–Einstein condensation (BEC), which is expected if the electrons are strongly bound in small pairs. While for underdoped cuprates it has been hotly debated which of these pictures is appropriate, it has been commonly believed that on the overdoped side the strongly-correlated fermion physics evolves smoothly into the conventional BCS behavior [1–3].

To test this dogma we have performed an extensive experiment that incorporated many technical advances, included synthesis and study of over two thousand cuprate films, and took 12 years to complete. To our surprise, the main findings turned out not to conform to BCS predictions anywhere in the phase diagram. Rather, evidence points to small, preformed pairs, suggesting that the critical temperature T_c is high primarily because of strong pairing and unusual kinematics.

Given that much of the dispute has been semantic, it seems prudent to first clarify what we mean by saying that BCS theory may be insufficient.

1.1. BCS theory

The original BCS theory [4] assumed that electrons, which in the normal state behave as a standard Fermi liquid, experience a pairing potential V that is weak compared to the Fermi energy E_F. Upon cooling, at some critical temperature T_c Cooper pairs form and condense; they are large and overlap densely. On warming up to T_c, the gap closes, the critical fields vanish, and the coherence length ξ diverges. The value of T_c depends on V, the density of states $D(E_F)$, and on some "typical" phonon frequency $<\omega>$. In the more elaborate Eliashberg theory [5] the entire detailed phonon spectrum is taken into account, but the physical picture remains essentially the same.

The BCS theory has been also extended to include, as perturbations, the effect of impurities and structural defects. A BCS superconductor is commonly called "clean" if the mean-free-path l_0 is larger than the coherence length ξ_0, and "dirty" if $l_0 < \xi_0$. Non-magnetic impurities have little effect [6] on T_c and on the superfluid density N_S. In contrast, as shown in a pioneering paper by A.A. Abrikosov and L.P. Gor'kov [7], magnetic impurities can break Cooper pairs and, since the BCS gap is a collective property, can cause both T_c and N_S to decrease.

The BCS paradigm also includes "unconventional superconductors" with an order parameter of nontrivial

symmetry (such as *p*- or *d*-wave). While still having all the above characteristics, they differ in some details, including how T_c and N_s are affected by impurities [8–10].

1.2. Non-BCS theories

Some theories of superconductivity, however, go substantially beyond BCS in various directions. If any of the following: the pairing interaction, the electron-electron correlations, the pair breaking, or superconducting fluctuations, are very strong, a qualitatively different physical picture can emerge.

A. Strong pairing interaction. As the pairing interaction strength is increased the theory (typically at the mean-field level and using the same BCS variational trial wavefunction) indicates a smooth crossover from BCS to BEC [11–16]. The two limits show much of the same physics: superconductivity, Meissner effect, flux quantization with $\phi_0 = h/2e$, Josephson effects, etc., since all of these follow just from the same broken (gauge) symmetry [17]. Note that the same is true [18] of the Caroli–de Gennes–Matricon bound states [19] that occur within the vortex core so their observation [20] is *not* a proof of BCS physics. Experimentally, in ultra-cold trapped gases of *fermionic* atoms, BCS behavior is observed for weak pairing; as the interaction is boosted up the pair size shrinks until local pairs (i.e., diatomic molecules) are formed, and a crossover to BEC occurs [21,22].

Nevertheless, there are also profound differences between BCS and BEC that actually matter here. In a Fermi liquid, Pauli exclusion keeps most electrons frozen inside the Fermi sphere, while only a small fraction (in the narrow Debye shell, about k_BT/E_F wide) is perturbed by thermal agitation. In contrast, in BEC a large fraction of bosons — essentially all for $T\to 0$ and a weak interaction — can occupy the same state. So they all contribute to condensation, which is largely driven by a reduction in the kinetic energy; everything else being the same, this results in a much higher T_c. Thus, in bosonic ^{4}He superfluidity persists up to $T_c = 2.17$ K, two orders of magnitude higher than in fermionic ^{3}He ($T_c \approx 30$ mK). One distinctive feature of BEC superconductivity is the existence of preformed pairs well above T_c. Another is that T_c is controlled by the pair density rather than the dynamics of electrons and bosons, and their coupling.

Apart from the strength of the pairing interaction, dimensionality also differentiates between BCS and BEC. In a three-dimensional (3D) potential well, bound states do not form unless the well is deep enough, while in 2D they form in arbitrarily shallow wells; thus, 3D favors BCS while 2D favors BEC. Indeed, a dimensional crossover from BCS to BEC can be triggered just by making the cold-atom cloud thinner [23]. Note that in a (quasi) 2D Bose gas N_s is indeed predicted [24–28] to decrease linearly with T.

Thus, (a) the strong pairing, (b) the high T_c, and (c) the 2D nature of superconductivity in cuprates, *a priori* all point to BEC rather than to BCS. Accordingly, BEC has been invoked in numerous theories of HTS in cuprates.

B. Strong electron–electron interaction. In Eliashberg theory, which is based on Migdal approximation [29], the electron–electron interaction is neglected. However, it can be strong in transition-metal oxides, so cuprates are frequently modeled as doped Mott insulators [2,24,25,30]. Note that the "plain-vanilla" rendition of the Resonant Valence Bond (RVB) theory also relies on the BCS trial wave function, except Gutzwiler-projected [25]. Nevertheless, the RVB physics is "exotic" and, except from the common broken gauge symmetry, quite different from BCS.

C. Strong pair breaking. One way to account for dynamic coexistence of small pairs and free fermions is to postulate massive pair breaking that depletes the superfluid condensate and creates unpaired electrons. At a phenomenological level, this idea has been just patched onto the BCS picture by using the Dynes substitution, $E\to E - i\Gamma_{pb}$, where Γ_{pb} is the pair-breaking rate [31–35]. Note that this Γ_{pb} is different from and unrelated to the rates of elastic scattering of free fermions, Γ_f, and of free (uncondensed) pairs, Γ_p, on impurities, defects, phonons, etc. While Γ_f and Γ_p determine the transport properties such as electric resistivity, Γ_{pb} controls the relative abundance of pairs and unpaired fermions. Since this "Dynes superconductor" model implies unorthodox (dissipative) quantum mechanics with complex eigenvalues and non-normalizable (Gamow) states, one would consider this also as stepping outside the original BCS paradigm.

D. Strong superconducting fluctuations. Yet another direction for generalization is to include strong thermal and/or quantum superconducting phase fluctuations. In standard BCS superconductors, the phase stiffness $\rho_{s0} >> T_c$; the Ginzburg parameter is small, and the fluctuation region narrow, typically on the scale of 1 μK to 1 mK. Hence, fluctuations can generally be ignored, except very near T_c. However, in superconductors with a very low superfluid density and/or reduced dimensionality, this may not be true [36,37]. As shown in the next section, in cuprates the superfluid stiffness, i.e., the characteristic temperature scale at which thermal phase fluctuations destroy long-range superconductivity, is in fact comparable to T_c. This may call for going beyond any mean field theory, BCS included.

2. Experimental

We have used atomic-layer-by-layer molecular beam epitaxy (ALL–MBE, see Fig. 1) to synthesize films of $La_{2-x}Sr_xCuO_4$ (LSCO) [38–49]. To isolate the HTS layers of exactly known thickness, some of these films were engineered at the atomic level as illustrated in Fig. 2. We characterized these samples in great detail and studied how the key parameters of the normal and superconducting states depend on doping, temperature, and external fields [48,49]. The main purpose of this paper is to discuss the implications for the theory of HTS of several simple but striking obser-

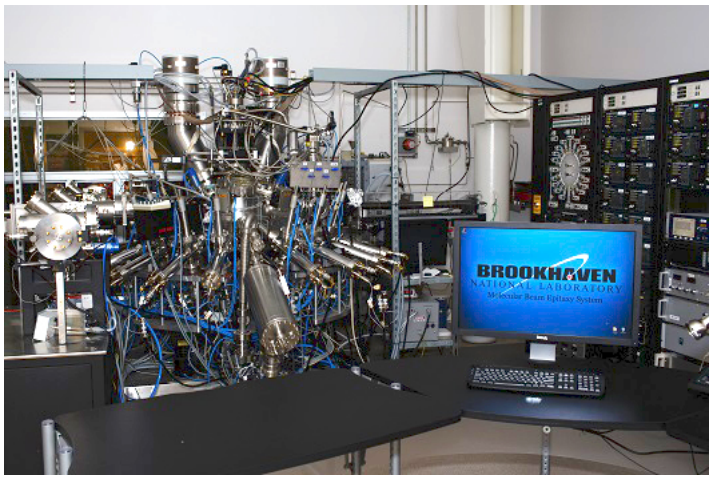

Fig. 1. Atomic-layer-by-layer molecular beam epitaxy (ALL-MBE) system at Brookhaven National Laboratory. Using this system, we have synthesized over 2,200 LSCO films in 2005–2017.

vations reported in Ref. 48 and listed below as (i)–(v). For rigor, in Ref. 48 we used only the quantities that we measure directly, such as T_c and the superfluid phase stiffness ρ_s. To facilitate communication, here we use instead a closely related but more familiar quantity, the dimensionless superfluid density N_s (the number of supercarriers per Cu atom). This introduces some uncertainty because the conversion of stiffness to N_s requires the knowledge of the effective mass of mobile holes, but this subtlety will not affect the present discussion.

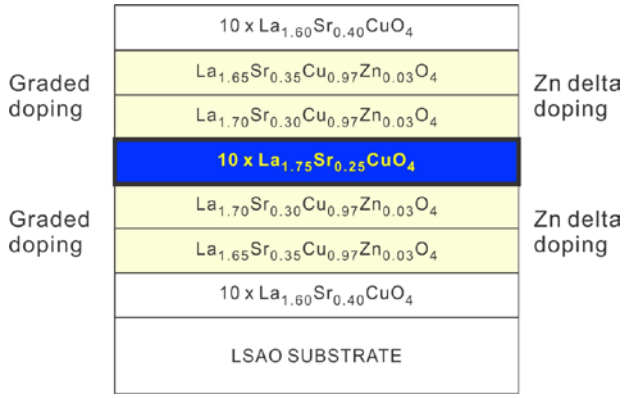

Fig. 2. An example of atomic-layer-by-layer engineering of LSCO films used in this experiment. The goal here is to fabricate a sample in which the thickness of the HTS layer is known exactly, since this is critical to get the accurate absolute value of penetration depth using the mutual inductance technique in the transmission geometry. Metallic but non-superconducting $La_{1.60}Sr_{0.40}CuO_4$ is used for the buffer and the cover layers to protect the HTS layer from interactions with the substrate and the atmosphere and consequent formation of "dead" layers. However, the mismatch of the chemical potentials can generate depletion and accumulation of mobile carriers across the interface and engender spurious interface superconductivity. This is eliminated by graded doping to make the gradient of carrier density less steep, and then by δ-doping with Zn that greatly diminishes the local superfluid density in these particular layers.

(i) All the films considered here were quite homogeneous; variations in the critical temperature (T_c) within a single LSCO film are very small (<< 1 K), see Fig. 3.

(ii) The $N_s(T)$ curves are for the most part linear, $N_s(T) = N_{s0} - AT$ with A = const (Fig. 4).

(iii) When $p \to p_{c2}$, both $T_c \to 0$ and $N_{s0} \to 0$.

(iv) The $T_c(N_{s0})$ dependence is linear but with a clear offset, except very close to the origin where it changes to $T_c \propto \sqrt{N_{s0}}$ (Fig. 5).

N_{s0} is very small for every doping, so that ρ_s is comparable to T_c. For comparison, in overdoped LSCO with the same T_c as in Nb, N_{s0} is three orders of magnitude smaller.

A decrease of N_{s0} with overdoping has been observed previously [50,51] in Y- and Tl-based cuprates, so it is likely a generic property of overdoped cuprates.

3. Difficulties with the clean-*d*-wave-BCS description

The coherence length in cuprates is generally very small, typically in the 1–2 nm range. Hence, $l_0 > \xi_0$ in every cuprate sample of a reasonably good quality, and in some $l_0 >> \xi_0$, so we should be in the clean limit. The *d*-wave-BCS theory in the clean limit is indeed compatible with our experimental observations (i) and (ii). The later has in fact been interpreted as one of its signatures: the depletion of N_s with T is ascribed to excitation of nodal quasi-particles, and the T-linear dependence to a V-shaped gap in the density of states. However, in the clean *d*-wave-BCS theory N_{s0} should be equal to the total charge carrier density N, so this scenario is totally incompatible with (iii) and (iv). We are unaware of anyone having questioned this statement so far.

4. Difficulties with the dirty-*d*-wave-BCS description

Naturally one turns to the BCS theory in the dirty limit [7–9]. The basic premise here is that the demise of N_{s0} with overdoping is primarily due to increasing disorder, usually attributed to the increased density of dopant

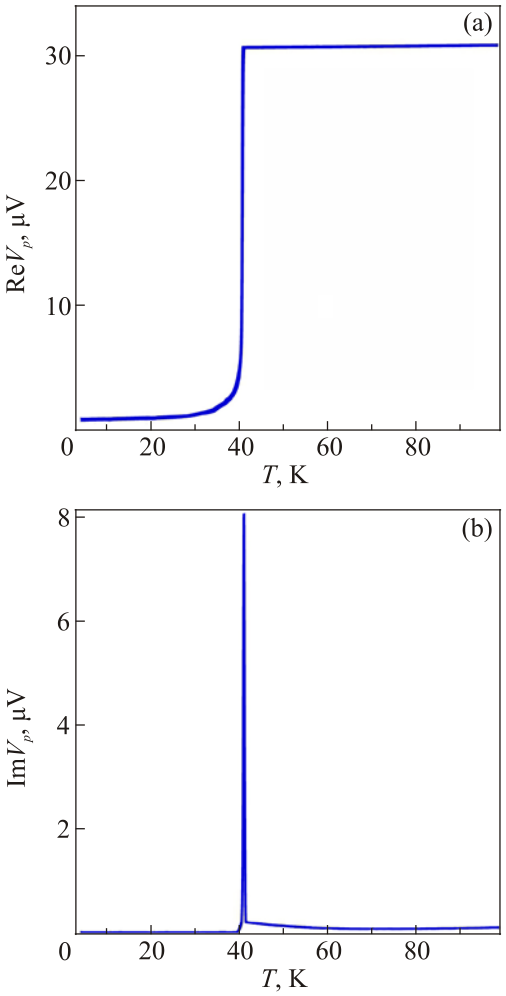

Fig. 3. Inductance data for an optimally doped (p = 0.16) LSCO film, of 100 mm^2 area, showing that T_c is uniform to within ± 0.1 K. (a) The in-phase component of V_p, the voltage across the pickup coil (proportional to the mutual inductance). It shows diamagnetic screening (the Meissner effect) below T_c. (b) The imaginary part of V_p in the same film.

ions. An argument frequently raised is that if the superconducting gap decreases with doping so that $\Delta_0 \to 0$ when $p \to p_{c2}$ then at some point we must have $\Delta_0 < \Gamma_n$ and hence $l_0 < \xi_0$, thus entering the "dirty" regime. This would indeed be true ***if*** *d*-wave-BCS theory applied and ***if*** ξ diverged at T_c. But this is not what we observe in experiments.

4.1. Some general comments

A. Disorder and inhomogeneity in films are easily detected in mutual inductance experiments. In inhomogeneous LSCO films, Im$M(T)$ shows a broad peak or even multiple peaks, and $N_s(T)$ is not linear but parabolic, or even shows kinks. To account for (i) by BCS–Abrikosov–Gor'kov theory or its generalizations, one would need to postulate the presence of a huge density of paramagnetic pair-breaking defects or impurities, of the order of one per several unit cells. Disorder at that level would be overwhelmingly apparent in reflection high-energy electron diffraction, *x*-ray diffraction, transmission electron microscopy, etc. — but we see essentially none. Moreover, if pair-breaking impurities were spaced about 3–4 $a_0 \approx$ 1.0–1.5 nm apart, the mean free path would be about two orders of magnitude smaller than what is observed, the corresponding resistivity would be that much larger, and the slope of $\rho(T)$ would be negative (semiconductor-like) — contrary to our experimental observations.

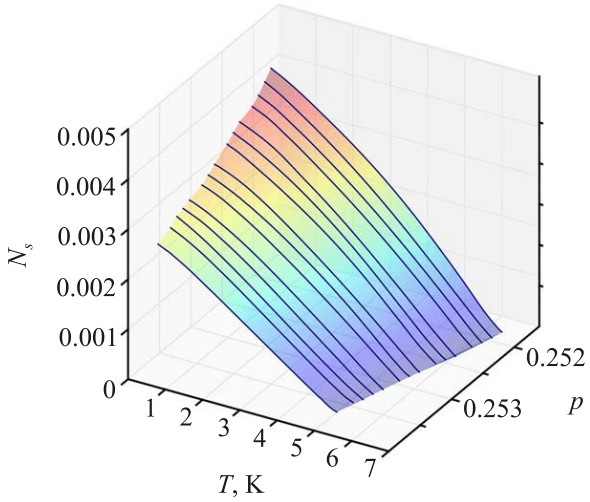

Fig. 4. (Color online) Blue solid lines: the temperature dependence of superfluid density measured down to T = 300 mK in 15 strongly overdoped LSCO films. (After Ref. 48.)

B. The inequality $l_0 < \xi_0$ defining "dirty" BCS superconductors is not satisfied in our LSCO films at any doping level. For example, from the resistivity data shown in Fig. 6 for a set of typical LSCO films, one infers l_0 in the range 20–100 nm, significantly larger than ξ_0 = 2.5–5 nm, implying a "clean" superconductor. Note that the residual resistivity from scattering on impurities and defects is an extrinsic property and sometimes can be reduced much further; an example is shown in Fig. 7 of a more recent LSCO film in which $\rho_0 \approx 0$ within the error bar. In some Y-, Tl- and Hg-based cuprate crystals de Haas–van Alphen and Shubnikov–de Haas oscillations are seen [52,53]. Such pronounced quantum oscillations are typical of clean metals; indeed, in some of these crystals the inferred l_0 is two orders of magnitude larger than ξ_0, so they should be considered ultraclean. Nevertheless, in heavily overdoped Tl-2201, with T_c = 7 K, N_{s0} is less than 1% of the total carrier density. Moreover, note that $l(T_c)$ grossly underestimates l_0, since the inelastic electron–electron scattering rate Γ collapses as the gap opens. For example, Hosseini *et al.* [54] inferred $l_0 > 4$ μm — 250 times larger than $l(T_c)$.

C. If T_c and N_{s0} vanished at $p = p_{c2}$ because of increasing disorder, we would observe a superconductor-to-insulator transition there — but we don't. To make this quantitative, note that for a dirty-BCS superconductor, the

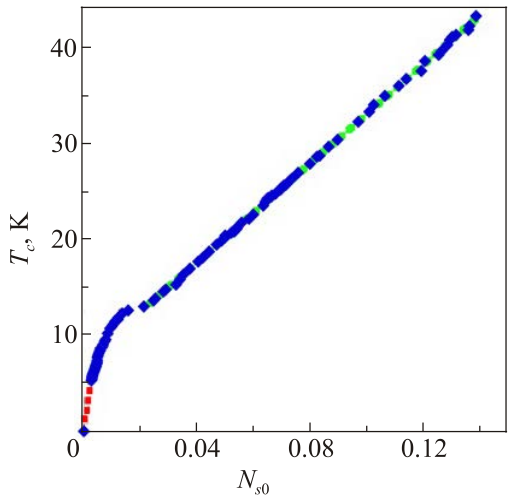

Fig. 5. (Color online) The relation between T_c and $N_{s0} \equiv N_s(T \to 0)$ (experimental data: solid blue diamonds). For $N_{s0} > 0.03$, the dependence is linear but with a clear offset, $T_c = T_0 + \alpha N_{s0}$, where $T_0 = (7 \pm 0.1)$ K, and $\alpha = (2.5 \pm 0.1) \cdot 10^2$ K, (fit: green dashed line). In the narrow region near the origin (for $N_{s0} < 0.02$), the curve fits well to $T_c = \beta\sqrt{N_{s0}}$, with $\beta = (1.1 \pm 0.1) \cdot 10^2$ K (fit: red dashed line).

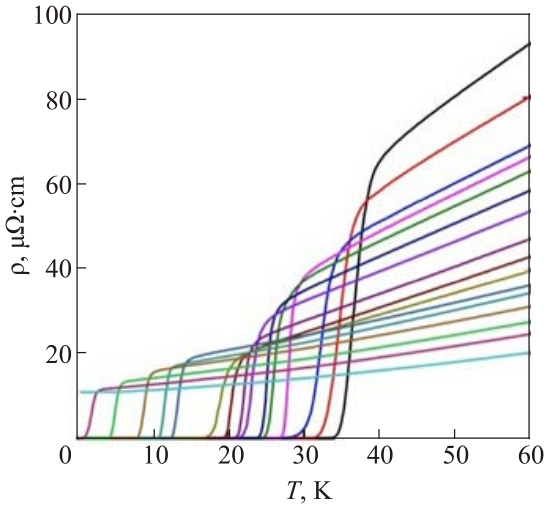

Fig. 6. Resistivity as a function of temperature in LSCO films with different doping level, top to down: $p = 0.203$, 0.208, 0.218, 0.220, 0.224, 0.225, 0.229, 0.230, 0.241, 0.244, 0.246, 0.250, 0.254, 0.258, 0.275 (nominal values). As the doping level is increased to $p_{c2} = 0.26$ and beyond, the normal-state resistivity keeps decreasing monotonically. This rules out the divergence of m^* when $p \to p_{c2} = 0.26$. Moreover, the low resistivity just above T_c indicates a relatively long mean-free path ($l_0 = 20$–100 nm), significantly larger than the coherence length ($\xi_0 = 2.5$–5 nm). In BCS theory, a superconductor is called "clean" if $\xi_0 < l_0$.

Ferrell–Glover–Tinkham sum rule [55] implies the so-called Homes' Law, $N_{s0} \propto \sigma_n T_c$, where N_{s0} is the superfluid density in the $T \to 0$ limit, and σ_n denotes the dc conductivity just above T_c [56–61]. Now, insert the scaling $T_c \propto \sqrt{N_{s0}}$ that we observe experimentally near p_{c2}; we get $\sigma_n \propto \sqrt{N_{s0}}$, and hence $\sigma_n \to 0$ when $p \to p_{c2}$. Experimentally, however, LSCO in fact becomes smoothly more metallic, see Fig. 8. By the way, this argument also rules out the (unlikely) possibility that m^* diverges when $p \to p_{c2}$.

D. The measured values of the key parameters violate the constraints imposed by the dirty-BCS theory. In particular, within this model the penetration depth λ_{dirty} is related to that of the clean parent material as follows [55]: $\lambda_{\text{dirty}} \approx \lambda_{\text{clean}} * \sqrt{(\xi_0 / l_0)}$. If one inserts the measured ξ_0, l_0 and λ values for an LSCO film with $p = 0.25$, and use for λ_{clean} the value measured in optimally doped LSCO ($\lambda \approx 200$ nm), one gets $l_0 < 1$ Å, in violation of the Mott–Ioffe–Regel limit. Likewise, using the Smith–Ambegaokar relation $N_{s0}^{\text{dirty}}/N \approx \pi\Delta_0/\hbar\Gamma_0$ [62], for $p = 0.25$ one gets $\hbar\Gamma_0 > 200\Delta_0$ — clearly unphysical.

Let us now discuss several theoretical studies that explored different concrete models for the nature and origin of impurity scattering.

4.2. Strong scattering

In a clean *d*-wave BCS superconductor $N_s(T)$ is predicted [8,9] to be linear up to about 0.3 T_c or so. If some strong (unitary) scattering defects are present, $N_s(T)$ should turn quadratic below some characteristic temperature $T^{**} = 0.83(\hbar\Gamma_n^2\Delta_0)^{0.5}/k_B$. Inserting the parameters for a heavily overdoped ($p = 0.25$) LSCO film, one infers that $\Gamma_n \lesssim 5 \cdot 10^{10}$ s^{-1} and from this $l_0 \gtrsim 4$ μm, which ***if true*** would make it ultra-clean rather than dirty.

Experimentally, we tested this possibility by replacing just 0.5% Cu by Zn — one in 200 atoms. This causes a small (< 10%) reduction in T_c. However, the change in the $N_s(T)$ dependence is spectacular — it turns parabolic below 20–25 K, see Fig. 9. Hence, one cannot explain in this way the reduction of T_c by an order of magnitude simultaneously with $N_s(T)$ staying linear.

4.3. Weak scattering

In a recent study [10] of *d*-wave BCS superconductors with weak (Born) scattering impurities, it is claimed that $N_s(T)$ can be linear down to a low temperature, even for a very high density of defects. The authors insist that for proper fit to the data of Ref. 48, it is critical to take into account the shape and doping dependence of the specific band structure exactly, as they do. This is a new insight, reported after Ref. 48 was published. It is important insofar that, if true, it implies that (ii) alone is not sufficient to rule out a dirty-BCS-scenario. Thus this model warrants a more detailed scrutiny.

At a closer look, the calculated $N_s(T)$ curves shown in Ref. 10 Fig. 3(b) show some curvature at low temperature; this is not a major problem for higher T_c but it becomes more serious for higher doping. In Fig. 10 we compare their calculated $N_s(T)$ dependence for $T_c = 5$ K with the one we measure experimentally. They differ qualitatively

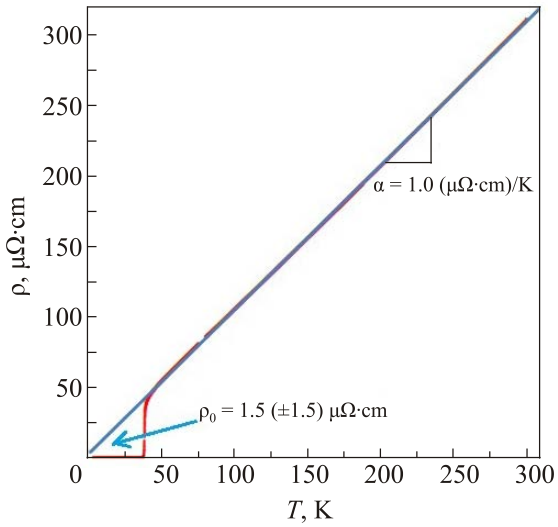

Fig. 7. Resistivity data for a moderately overdoped ($p = 0.19$) LSCO film, showing a very small extrapolated residual resistance. This alone brings into the question a description of the normal state as an ordinary Fermi liquid — which, however, is a basic premise of the BCS theory.

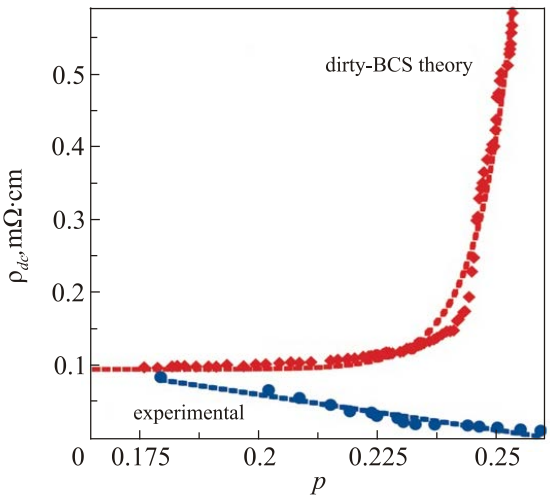

Fig. 8. (Color online) Red solid diamonds: resistivity ρ_{dc} just above T_c calculated from Homes' Law, $N_{s0} \propto \sigma_{dc} T_c$ (which in dirty-BCS theory follows from the Ferrell–Glover–Tinkham sum rule) and inserting our measured values of T_c and N_{s0}. Clearly, if $T_c \propto \sqrt{N_{s0}}$, then $\rho_{dc} \propto 1/\sqrt{N_{s0}}$ and hence it would diverge (red dotted line) when $N_s \to 0$. Blue solid dots: ρ_{dc} measured experimentally in our LSCO samples. The discrepancy is quite dramatic.

and quantitatively; note that we measure the absolute value of the penetration depth to the accuracy of ± 1%. This is a sharp litmus test for this, and any other theoretical model: how to explain the data for extreme overdoping where N_{s0} drops to 1% of the total carrier density, while the Meissner transition stays sharp, $N_s(T)$ stays linear, and $l_0 >> \xi_0$.

Next, there seems to be some numerical errors in Ref. 10; the plot in Fig. 5(a) there is presumably calculated from the formula (15), but it seems to be off by > 300% at $p = 0.26$. Given the claimed sensitivity to details and numbers, this error might affect at least some of their results and statements.

Moreover, in this study a number of additional assumptions are made. The band structure is approximated by tight-binding fits to the ARPES data. This is used to determine the plasma frequency ω_p and from it $N_{s0} = N$ for a hypothetical clean sample. Then, impurity scattering is introduced assuming two additive contributions to the scattering rate, $\Gamma_{\text{Born}} = 17$ K and $\Gamma_{\text{unitary}} = 1$ K. Then, the corrections and renormalizations are calculated using the Eliashberg formalism, while the theory is further simplified assuming a separable potential and self-consistent T-matrix approximation. While each of these assumptions can be questioned, we will only point to one: experimentally, there is a dramatic mismatch between the ω_p inferred from the measured ARPES Fermi surface and carrier density and ω_p measured by optics or by electron-energy loss spectroscopy; in the optimally doped LSCO the later is in fact twice *lower*. [We are indeed referring here to the *bare* plasma frequency; the measured *screened* plasma frequency is lower by another factor of two.] While this "paradox" begs for a theoretical explanation, the experimental fact stays and invalidates inferring $N_{s0}^{\text{clean}} = N$ from the theoretical ω_p. This seems critical, as the authors insist that the exact shape and doping dependence of the band structure are crucial.

Turning this around, this may be the strongest argument against this proposed explanation. For all we know so far, the observations (i)–(v) are not specific to LSCO. In fact, an almost identical $T_c(N_{s0})$ dependence has been observed by Broun *et al.* [63]. in microwave experiments on extremely *underdoped* YBCO crystals, see Fig. 11. However, many details of the YBCO band structure (planes and chains, bonding/antibonding bilayer band splitting, band filling) are rather different from those of LSCO. And hardly anyone believes that in underdoped cuprates the physics is weak-coupling BCS and that $\Delta_0 \to 0$ as $p \to p_{c1} \approx 0.06$ from above; for all we know Δ_0 keeps growing as the doping is reduced. Then one would be forced to postulate that the physics on two sides is completely disparate, and yet somehow producing the exact same $T_c(N_{s0})$ dependence; such a strange coincidence seems unlikely.

Note also that while this argument alone seems sufficient, it is by no means the only one. The above objections 4.1 *A*–*D* all apply to this variant of the dirty-BCS scenario as well. Moreover, our additional experiments on the same huge sample set, that we cannot detail here for the lack of space – the measurements of resistivity, Hall Effect, THz conductivity, magnetoresistance in field up to 90 T, etc. — all show that the basic assumptions of the BCS theory are not fulfilled: the gap has a different T-dependence, it does

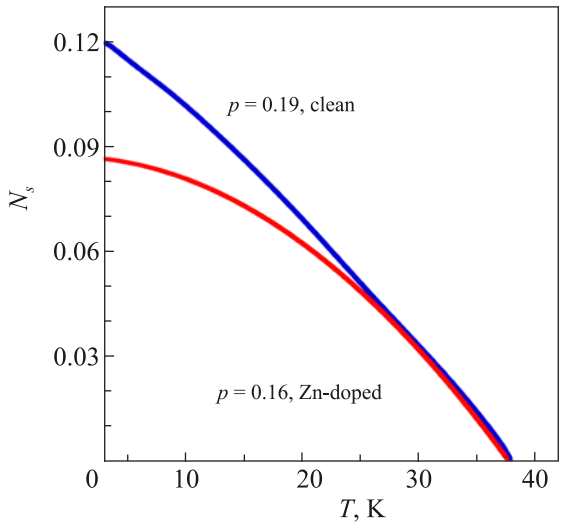

Fig. 9. A comparison of the temperature dependence of superfluid density in an optimally Sr-doped $La_{1.84}Sr_{0.16}Zn_{0.005}Cu_{0.995}O_4$ film but with 0.5% of Cu substituted by Zn, with that in a clean $La_{1.81}Sr_{0.19}CuO_4$ film, slightly overdoped to have the matching $T_c \approx 38$ K. In the clean film the $N_s(T)$ dependence is essentially linear, while in the "dirty" one pair breaking makes it parabolic below about 25 K. This shows that even a tiny density of pair-breakers (1 per 200 Cu atoms) is sufficient to turn the $N_s(T)$ dependence parabolic and that they are easily detected experimentally if present in our films.

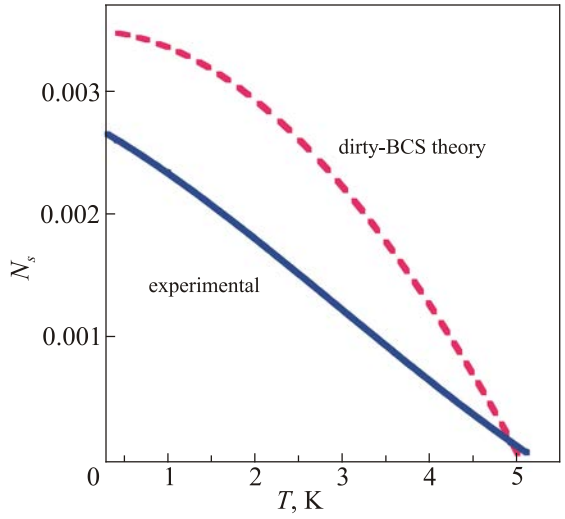

Fig. 10. (Color online) Red dashed line: the temperature dependence of superfluid density $N_s(T)$ calculated for an LSCO film with $T_c \approx 5$ K using BCS-Eliashberg theory and assuming a large density of weak (Born) scatterers (after Ref. 10). Blue solid line: $N_s(T)$ measured experimentally down to $T = 300$ mK in a strongly overdoped LSCO film with comparable T_c (after Ref. 48). The discrepancy is quite substantial. Note that the accuracy of our measurements of the absolute value of the penetration depth is ±1%, and that this constrains the theory quite tightly.

not close at T_c, it in fact fills rather than closes, and ξ diverges neither at $T = T_c$ nor at $p = p_{c2}$. Nor does the normal state behave as a canonical Fermi liquid — as seen clearly from the $\rho(T)$ data shown in Fig. 5, the observation of electronic nematicity [49], etc. — which, however, is a key premise of BCS theory.

5. Difficulties with phase-separation models

Another natural idea is the possibility of phase separation, where one phase is superconducting and the other insulating or metallic but not superconducting [50,64]. To explain (iii) and (iv), one needs to postulate that the size and density of superconducting islands shrink with doping in a very specific way, so that the relative abundance of superconducting phase decreases from maximal (perhaps 100%) at optimum doping to zero at $p_{c2} = 0.26$. In principle, the two phases can differ chemically, structurally or just electronically.

These scenarios also face several problems.

5.1. In our LSCO films superconductivity appears very uniform

Phase separation that breaks superfluid into islands would be easily detectable in our measurements of penetration depth by mutual inductance. A sample in which superconducting islands are weakly (Josephson) coupled would be very sensitive to a magnetic field — the effect we looked for but have not observed in experiments where we measured mutual inductance while applying an additional static magnetic field up to 9 T.

5.2. We see no other phase(s) experimentally

Many competing phases —charge-, spin- and *d*-density waves, spin glass, charge cluster glass, etc. — have been observed in cuprates on the underdoped side. The point is, if any of these phases is present, it can be detected with the techniques readily available. However, none of these has been observed so far in overdoped LSCO. We have also looked for hypothetical competing ferromagnetic order [64] but observed none [65]. (The same experiment also ruled out the presence of a large density of magnetic impurities.)

5.3. No other phases are expected theoretically

In view of the argument 4.1.C above, the other competing phase would have to be metallic. Conductivity increases with doping, and beyond $p \approx 0.28$ we indeed see a purely Fermi liquid behavior in resistivity ($\rho \propto T^2$), in magnetoresistance, etc. This constrains the theory, which needs to explain what that second metallic phase is, why is it not superconducting down to 0.3 K (our lowest measured T), why does it grow with doping in the precise manner required to fit the experiments, and why does it separate from the other metallic phase that goes superconducting (at $T_c = 42$ K) like

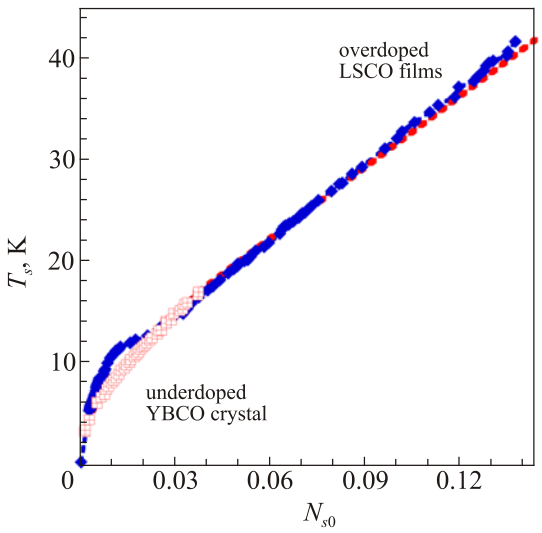

Fig. 11. (Color online) Open red squares: the $T_c(N_{s0})$ data measured by microwave absorption in underdoped YBCO bulk crystal subject to a series of successive annealing to change the oxygen content (after Ref. 9). Dashed red line: extrapolation to match the measured λ_0 = 140 nm in optimally doped YBCO with T_c = 92 K, assuming that m^* is the same. Solid blue diamonds: the $T_c(N_{s0})$ data for overdoped LSCO films grown by ALL-MBE, as in Fig. 6.

oil from vinegar. None of these is expected from a Fermi liquid with a simple cylindrical Fermi surface, as seen by APRES [66,67], STM, and AMRO. In this model, we are aware of only one known instability, namely BCS superconductivity, and it should affect the entire electron fluid.

5.4. We do not see a percolation transition

In a phase-separation model, one would expect a percolation transition at some critical island density. In 2D, the percolation threshold should be at about 50%. However, we have measured N_{s0} as low as 1% of that at optimal doping, while still showing a sharp transition, linear $N_s(T)$ dependence, etc. Another experimental fact to have in mind is that all the parameters of both the normal and the superconducting states — ρ, the Hall coefficient, magnetoresistance, T_c, λ, ξ, etc. — evolve smoothly with doping, T, and magnetic field. In contrast, when phase separation is indeed present, as is the case in oxygen-doped $La_2CuO_{4+\delta}$ in which the extra oxygen orders in stages, T_c shows clear jumps between a few discrete preferred values.

6. Conclusions

As of January 2018, we are unaware of any plausible explanation of our key observations (i)–(v) within the standard BCS framework (as defined in Sec. 1.2 above) that is consistent with all the key experimental data. We cannot rule out that one will not be produced in the future. But we consider it unlikely, for the following reasons.

6.1. All the data point to HTS being in the strong-coupling regime

In the BCS–BEC crossover phase diagram [16], that would correspond to the right-hand, unitary-BEC side. Preformed pairs exist well above T_c, as well as to the left and right of the superconducting dome [32,33,41,68–78]. The relation between the superconducting gap Δ_0 and T_c is not the one expected for weak-coupling. On the underdoped side Δ_0 increases as T_c decreases and the Δ_0/T_c ratio diverges, and yet the T_c (N_{s0}) dependence seems to be the same as on the overdoped side.

6.2. Electron correlations seem to be at least moderately strong, in particular on the extreme underdoped side

We would like here to draw the attention to the fact that spontaneous breaking of the rotational symmetry in the electron fluid, the so-called "electronic nematicity", has been observed directly and unambiguously in LSCO for every doping $p < 0.26$ [49]. The microscopic origin of this extraordinary phenomenon is not yet fully understood, but certainly it is not expected in a standard, simple Fermi liquid. One possibility is that this electronic symmetry breaking is due to a Pomeranchuk instability [69]; if this is indeed the case, that would imply that electron-electron interaction is strong. Another strong piece of experimental evidence is the $\rho(T)$ dependence that stays linear up to 1,000 K and in a strong magnetic field, down to mK scale.

6.3. Extensive pair-breaking has been clearly observed in ARPES, STM and our own THz data, pointing to "Dynes-superconductor" physics [31–35]

But this pair breaking does not originate from magnetic impurities [65], as it does in BCS–Abrikosov–Gorkov theory. In fact the origin of the strong residual ($T\to0$) fermionic Drude response is likely the central mystery in overdoped cuprates.

6.4. Strong thermal phase fluctuations must be present simply because $N_{s0} \approx T_c$

Experimental evidence for this is overwhelming; in cuprates T_c and H_{c2} are smeared into broad crossovers because of vortex flow; trace superconductivity is seen well above and outside the $T_c(p)$ dome by ARPES, microwave and THz spectroscopy, and many other probes [68–78].

In summary, we believe that the new experimental results presented here and in Refs. 48 and 49 provide strong new constraints on the theory of HTS in cuprates, and point to the need to its further development beyond the confines of the canonical BCS framework.

Note added

After this paper was submitted for publication, two related preprints have been posted: F. Mahmoud *et al.*, Locating the missing superconducting electrons in overdoped

cuprates, arXiv:1802.02101v1, and Lee-Hone *et al.*, Optical conductivity of overdoped cuprate superconductors: application to LSCO, arXiv:1802.10198v2.

The first, a study of overdoped LSCO by THz spectroscopy, reports the absence of the gap expected in dirty-BCS theory. Rather, a gradual decrease of spectral weight starts at much higher energy (well above $10\, k_B\, T_c$ for the sample with $T_c = 7$ K), while a large residual Drude-like absorption remains down to zero energy and even as $T \to 0$, growing as N_{s0} decreases with doping.

The second paper interprets the above findings using the model of Ref. 10, and concludes that "exotic physics beyond Fermi liquid and Eliashberg theory is probably not required to understand the data". However, for a reasonable fit they had to introduce an arbitrary "fudge factor" to compensate for a large (over 300%) discrepancy in the plasma frequency, which they attribute to many-body effects, not included in their model. We agree with the later but have a semantic objection: the original Migdal–Elisahberg theory explicitly hinges on the assumption that electron-electron interactions can be neglected. So we would rather infer that a substantial (and as yet unknown) generalization or modification of this theory appears to be necessary.

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