

## HIGH-TEMPERATURE SUPERCONDUCTIVITY

## To pair or not to pair?

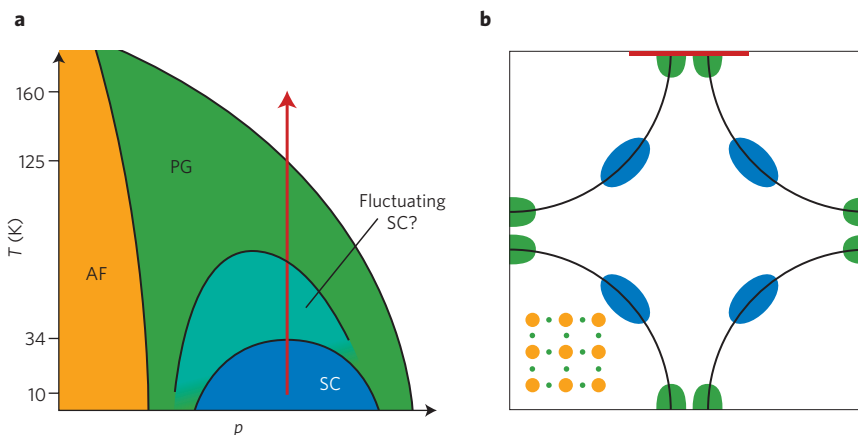
Is the mysterious pseudogap in the copper oxide superconductors a signature of preformed pairs or a competing ordered state? Measurements of broken symmetries suggest that the pseudogap cannot originate from superconductivity alone.

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Superconductivity — the flow of charge without resistance below some temperature  $T_c$  — was discovered in mercury in 1911, but theoretical understanding followed slowly. A pivotal clue was the observation in 1954 of the low-temperature exponential dependence of specific heat in superconducting vanadium, indicating a gap in the electronic density of states<sup>1</sup>. The gap was interpreted as a signature of paired electrons, which finally led to the highly successful Bardeen–Cooper–Schrieffer theory of superconductivity in 1957. Ironically, in high- $T_c$  cuprate superconductors, the appearance of a gap brings more confusion than clarity to the situation, as the gap is seen to open at a temperature  $T^*$  far above the transition to zero resistivity. What is the nature of this precocious gap, and how does it relate to the superconductivity? As reported in *Nature Physics*, Makoto Hashimoto and co-workers<sup>2</sup> provide evidence that this gap originates from a state other than simple superconductivity.

The pseudogap, as this very real but definitely not resistanceless gap is known, dominates the phase diagram of underdoped cuprates, as shown in Fig. 1a. Early tunnelling experiments<sup>3</sup> implied that the pseudogap evolved smoothly into the superconducting gap at  $T_c$ . The detection of an anomalous Nernst effect<sup>4</sup>, suggesting the existence of superconducting vortices above  $T_c$ , furthered the idea that the pseudogap was in fact the very same superconducting gap, signifying the pairing of electrons at a temperature too high for the phase coherence that is also needed for superconductivity<sup>5</sup>. However, other experiments showed evidence for distinct pseudogap phases, such as a charge density wave<sup>6</sup> or an electronic glass<sup>7</sup>. Some experiments suggest that two distinct gaps coexist but compete in momentum space, as shown in Fig. 1b: the  $d$ -wave superconducting gap opens up with nodes along the diagonals of the Cu–O square lattice, whereas the pseudogap dominates the so-called antinodal regions along the square lattice axes<sup>8</sup>.

The origin of the pseudogap — either preformed pairs or competing order — has become the most contentious debate in



**Figure 1** | Experiment coverage in phase space and momentum space. **a**, Sketch of the temperature–doping ( $T$ – $p$ ) phase diagram of Bi2201, showing antiferromagnetism (AF; orange), superconductivity (SC; blue), pseudogap (PG; green) and a possible region of fluctuating superconductivity (turquoise). The experiment of Hashimoto *et al.* covers the red arrow from 10 K to 160 K. **b**, Brillouin zone of Bi2201, with the Fermi surface shown in black. Below  $T_c$ , it is not controversial that superconductivity opens up a pairing gap near the nodes (shaded blue), causing back-bending at the Fermi momentum  $k_F$ . Between  $T_c$  and  $T^*$ , it is not controversial that the pseudogap (be it preformed pairs or alternative order) dominates the antinodal region (shaded green). However, it is less clear whether superconductivity extends to the antinodes even below  $T_c$ , or whether the pseudogap extends to the nodes between  $T_c$  and  $T^*$ . Hashimoto and co-workers’ experiment covers the red line at the antinode. Inset is a representation of the Cu–O lattice, with the Cu and O atoms shown in orange and green, respectively.

the contentious field of high-temperature superconductivity. Why is it so challenging to resolve? The experiments most commonly used to detect pairing just look for the energy gap caused by those pairs. But in this case we know there’s a gap so the question is reversed: does this gap signify pairing?

Although a gap can originate from many causes other than pairing, a superconducting pairing gap does have a notable marker that is not required of any other known electronic-order-induced gap. A superconducting pairing gap must be particle–hole symmetric, tied to the Fermi momentum  $k_F$ . Tests for such symmetry would seem to be limited to experiments that measure both filled and empty states. The most stringent test of symmetry would compare the filled and empty states momentum by momentum, and would focus on the antinode, where any purported competing pseudogap phase would be expected to dominate.

Angle-resolved photoemission spectroscopy (ARPES), which uses conservation of momentum and energy for photoejected electrons to reconstruct the band structure of the electrons in the material, would be perfect for the job — if only it could detect empty states. One recent ARPES experiment did just this, using the fact that at higher temperatures, states above the Fermi level will be partially occupied. By dividing out the Fermi occupation function from the ARPES-detected band structure of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  (Bi2212), Yang *et al.*<sup>9</sup> reported particle–hole symmetry near (but not at) the antinode in the pseudogap state above  $T_c$ . Kanigel *et al.* used a different strategy to check for particle–hole symmetry, relying on the momenta of filled states instead of the amplitudes of partially occupied states<sup>10</sup>. Many gapping scenarios cause the filled band to bend backwards at the momentum where the gap opens, but only

superconductivity requires that this occur at  $k_F$ . Kanigel and co-workers observed that the back-bending above  $T_c$  occurs at the same  $k$  as below  $T_c$ . But at the antinode, their claim of particle-hole symmetry is not strong because  $k_F$  is uncertain: even below  $T_c$  the pseudogap state may alter the antinodal back-bending momentum from the  $k_F$  that would be expected for pure superconductivity. Their experiment doesn't go above  $T^*$  for an independent measure of  $k_F$  in the normal state.

Hashimoto and co-workers provide a more thorough glimpse into the pseudogap state — choosing the lower  $T_c$  compound  $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_{6+\delta}$  (Bi2201) to allow measurements from below  $T_c = 34$  K up through  $T^* = 125$  K. The authors found that below  $T^*$ , at the antinode, the back-bending momentum is not  $k_F$ . This particle-hole symmetry breaking implies that something other than simple superconducting pairing is responsible for the pseudogap at the antinode. Furthermore, a dramatic broadening of the spectra exactly as the temperature drops through  $T^*$  confirms

that one of the short-range ordered states imaged at lower  $T$  by scanning tunnelling microscopy<sup>6,7</sup> is probably the pseudogap state.

It is important to emphasize that all of the experiments mentioned here are indirect tests of pairing. The existence of a gap could signify any ordered state. The symmetry of the gap is more telling — a superconducting state is the only one known to produce a particle-hole symmetric gap tied to the Fermi momentum. But just because the gap is not symmetric at the antinode (the only region measured in the experiment of Hashimoto *et al.*) doesn't rule out pairs at lower energies nearer the nodes. A number of experiments such as measurements of the Nernst effect<sup>4</sup>, diamagnetism<sup>11</sup>, tunnelling<sup>12</sup>, and quasiparticle interference<sup>13</sup> do suggest incoherent pairs in some range above  $T_c$  (although none all the way up to  $T^*$ ). ARPES experiments such as this one<sup>2</sup> should be repeated in momentum space approaching the node, to detect the boundary between pairing and non-pairing behaviour. Ultimately, we should hold out hope for an

experiment that directly measures the charge of a carrier above the superconducting dome all the way up to the pseudogap line — is it  $e$  or  $2e$ ? □

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