Bounding the pseudogap with a line of phase transitions in $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$

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Close to optimal doping, the copper oxide superconductors show 'strange metal' behaviour1–3, suggestive of strong fluctuations associated with a quantum critical point4–6. Such a critical point requires a line of classical phase transitions terminating at zero temperature near optimal doping inside the superconducting 'dome'. The underdoped region of the temperature–doping phase diagram from which superconductivity emerges is referred to as the 'pseudogap'7–13 because evidence exists for partial gapping of the conduction electrons, but so far there is no compelling thermodynamic evidence as to whether the pseudogap is a distinct phase or a continuous evolution of physical properties on cooling. Here we report that the pseudogap in $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ is a distinct phase, bounded by a line of phase transitions. The doping dependence of this line is such that it terminates at zero temperature inside the superconducting dome. From this we conclude that quantum criticality drives the strange metallic behaviour and therefore superconductivity in the copper oxide superconductors.

Resonant ultrasound spectroscopy (RUS) measures the frequencies $\nu_0$ and widths $\Gamma_0$ of the vibrational normal modes of a crystal acting as a free mechanical resonator. The frequencies of the normal modes are determined by the density and geometry of the crystal as well as by its elastic properties. The elastic component of the temperature evolution of these frequencies, $\Delta\nu_0(T)$, depends on a linear combination of all elastic moduli and reflects changes in the thermodynamic state of the system such as those associated with a phase transition. The width of a resonance, $\Gamma_0(T)$, is proportional to the energy dissipation caused by time-dependent (dynamic) fluctuations in the system. Measuring many resonances provides access to elastic properties and fluctuations with different symmetries14–17. Recent advances in the quality of single crystal $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ (YBCO) have pushed the boundary of possible measurements, as demonstrated by the observation of quantum oscillations18. Advances in resonant ultrasound enable the determination of the thermodynamics of these submillimetre crystals to an accuracy of parts per million.

The narrow temperature range over which the resonances evolve across the superconducting transition illustrates the quality of the crystals and the accuracy of the measurement19 (Fig. 1). For the underdoped crystal, $\text{YBa}_2\text{Cu}_3\text{O}_{6.60}$, we observe a sharp (0.5 K wide) discontinuity in the resonance frequency, $\Delta\nu/\nu \approx 10^{-4}$, at the superconducting transition (Fig. 1). A sharper discontinuity is observed in the overdoped crystal, $\text{YBa}_2\text{Cu}_3\text{O}_{6.98}$, a possible consequence of the decrease in oxygen disorder near optimal doping. The step discontinuity in resonance frequency and the accompanying discontinuous change (break) in slope are thermodynamic signatures of the superconducting transition (Supplementary Information).

RUS measurements across the temperature range encompassing the pseudogap in the two YBCO crystals are shown in Fig. 2. The temperature dependence of the resonance frequencies in underdoped $\text{YBa}_2\text{Cu}_3\text{O}_{6.60}$ reveals a break in slope at the pseudogap boundary $T^* = 245\text{K}$—in itself a standard thermodynamic marker for a phase transition (Fig. 2a, c). It differs from the signature of the superconducting transition in that there is no resolvable discontinuity in the frequency itself. This temperature is the same as the onset temperature of magnetic order observed by neutron scattering measurements of YBCO specimens of similar composition (Fig. 3)20. In the overdoped crystal, $\text{YBa}_2\text{Cu}_3\text{O}_{6.98}$, the break in slope of the temperature dependence is observed at $T^* = 68\text{K}$ (Fig. 2b). To emphasize the break in slope in these data, we use the redundant information contained in all observed resonances to extract the different contributions to their temperature dependences (Fig. 4c). This process reduces the temperature dependence of all 15 normal modes measured to three dominant

Figure 1 | The temperature evolution of resonances in underdoped and overdoped YBCO crystals: superconductivity. a, A typical resonance frequency scan (normalized at room temperature) from room temperature to 10 K for underdoped $\text{YBa}_2\text{Cu}_3\text{O}_{6.60}$ (blue) with $T_c = 61.6\text{K}$, and overdoped $\text{YBa}_2\text{Cu}_3\text{O}_{6.98}$ (red) with $T_c = 88\text{K}$. The scan for the overdoped crystal is offset vertically for clarity. The smooth increase in frequency, which saturates at low temperature, is driven by the anharmonicity of the lattice and is typical of most solids20. b, c, Superconducting transition in the underdoped (b) and overdoped (c) crystals. Measurements were made at roughly 70 mK steps. The elastic moduli decrease discontinuously at the transition. The discontinuity is roughly 1 part in $10^{-4}$ in the underdoped crystal, and 5 parts in $10^{-4}$ in the overdoped crystal. The form of the smooth monotonic background subtracted to obtain b and c was chosen only to emphasize the discontinuity20. d, e, Resonance width for underdoped (d) and overdoped (e) YBCO. In the underdoped crystal no feature at the superconducting transition can be resolved. A broad maximum in resonance width well below $T_c$ in the overdoped crystal is an effect of the pseudogap (see the text).

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components (see Supplementary Information). The blue and red curves in Fig. 4c capture the effects of superconductivity and of fluctuations in the vicinity of the pseudogap, respectively. The green curve, which has a break in slope at \( T^* \approx 68 \text{ K} \), corresponds to the thermodynamic effects at the pseudogap, revealing that the pseudogap occurs by means of a phase transition.

The ‘strange metal’ behaviour that copper oxide superconductors show universally at higher temperature breaks down in the pseudogap region of the temperature–doping phase diagram, where measurements indicate the presence of magnetic order (Fig. 3). The break in slope that we observe in both underdoped and overdoped YBCO establishes the pseudogap as a thermodynamic phase that moves to lower temperature with increased doping. Observation of the pseudogap boundary below the superconducting transition temperature in overdoped YBCO indicates that the superconducting dome surrounds the zero-temperature end point of the pseudogap phase boundary.

At both dopings the pseudogap is accompanied by a large (up to 100-fold in the overdoped crystal) increase in the width of the resonances at temperatures above the pseudogap phase boundary (Fig. 2c, d). The widths of the resonances are determined by the ultrasonic energy absorption (attenuation), revealing strong fluctuations in the dynamics of the metallic state as it approaches \( T^* \). From the width of the resonances we estimate the thermodynamic effects accompanying the pseudogap phase transition to be \( t/f \approx 5 \times 10^{-3} \), about 50-fold the relative modulus shift across the superconducting phase transition for both dopings. Energy absorption is highest when the measurement frequency matches the characteristic relaxation time of the system: \( 2\pi f = 1 \). The characteristic time \( t \) diverges as the phase transition temperature is approached (critical slowing down); the maximum in ultrasonic energy absorption is therefore closer to the pseudogap phase boundary for resonances of lower frequency. For the underdoped crystal, the width of the maximum and the contribution of the large phonon background at 245 K obscures this effect. The overdoped crystal, with its narrower maxima and smoother background, shows this effect clearly: \( 1/t(T) \) extrapolated from resonances at different frequencies vanishes at the pseudogap phase boundary (Fig. 4a, b). Causality requires that the maxima in energy absorption be accompanied by elastic stiffening over the same temperature range. This stiffening is observed in addition to the distinct break in slope at \( T^* \) (Fig. 2b).

The potential for RUS to determine the broken symmetry in the pseudogap phase was limited in this study by the precision with which crystal shape could be controlled, an issue that may be resolvable as sample preparation techniques improve. The pseudogap phase transition

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**Figure 2** The temperature evolution of resonances across the pseudogap phase boundary. **a**, **b**, At both dopings a discontinuous change in slope of the temperature dependence of the frequency reveals a phase transition: underdoped (**a**) at \( T^* = 245 \text{ K} \), and overdoped (**b**) at \( T^* = 68 \text{ K} \). **c**, **d**, At both dopings the resonance width has a broad maximum above \( T^* \) (underdoped (**c**) and overdoped (**d**)). The break in slope is 5 K wide in the underdoped crystal, and 3 K wide in the overdoped crystal. The increase in scatter of points near the break in slope in **b** is a result of a strong increase in resonance width at this temperature (**d**).
is located by our RUS measurements with ±3 K uncertainty, improving on the ±30 K uncertainty in onset of neutron spin-flip scattering. This clearly separates the onset of magnetic order\textsuperscript{14,15,17} at T* from the onset T\textsubscript{e} of the Kerr rotation signal\textsuperscript{27} and charge order\textsuperscript{28} at lower temperature (Fig. 3). In our measurements we observe an increase in energy absorption over a broad region near T\textsubscript{e} (Fig. 2c); however, we do not observe an accompanying thermodynamic signature there. Our observed evolution of the pseudogap phase boundary from underdoped to overdoped establishes the presence of a quantum critical point inside the superconducting dome, suggesting a quantum-critical origin for both the strange metallic behaviour and the mechanism of superconducting pairing.

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Supplementary Information is available in the online version of the paper.