Two Ising-like magnetic excitations in a single-layer cuprate superconductor

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There exists increasing evidence that the phase diagram of the high-transition temperature (Tc) cuprate superconductors is controlled by a quantum critical point. According to one distinct theoretical proposal, on decreasing the hole-carrier concentration a transition occurs to an ordered state with two circulating orbital currents per CuO2 square. Below the ‘pseudogap’ temperature T*(T* > Tc), the theory predicts a discrete order parameter and two weakly-dispersive magnetic excitations in structurally simple compounds which should be measurable by neutron scattering. Indeed, novel magnetic order and one such excitation were recently observed. Here, we demonstrate for tetragonal HgBa2CuO4+δ the existence of a second excitation with local character, consistent with the theory. The excitations mix with conventional antiferromagnetic fluctuations, which points towards a unifying picture of magnetism in the cuprates that will probably require a multi-band description.

It is widely agreed that attaining a thorough understanding of the peculiar electronic and magnetic properties in the pseudogap regime of the cuprates would constitute a major leap towards solving the high-Tc problem. A pivotal and intensely debated question has been whether this regime is a genuine new phase of matter and, if so, what symmetries are broken at the pseudogap temperature T* (refs 1–4). There is mounting evidence that T* indeed marks a transition into a novel electronic phase in which time-reversal symmetry is broken1–10 and, in compounds with relatively high maximal transition temperatures (Tc(max) > 90 K) at the optimal hole concentration popt ≈ 16% per planar Cu atom), translational symmetry is preserved11–13.

Neutron scattering is a powerful probe of magnetic correlations and has shed much light on the high-Tc problem. In the superconducting doping regime, magnetic neutron scattering experiments have been carried out mostly near the two-dimensional (2D) wave vector qAF that characterizes the antiferromagnetic order of the undoped Mott-insulating parent compounds12–20. A spin-1 ‘resonance’ excitation13,15–17,21 is observed at qAF in the superconducting state, between nearly temperature-independent spin fluctuations at higher energy and a magnetic gap at lower energy. This phenomenon has been regarded as indicative of a magnetic-fluctuation-driven superconducting mechanism12,22. On the other hand, recent measurements of the Tc(max) > 90 K compounds YBa2Cu3O6.64 (YBCO; ref. 6) and HgBa2CuO4+δ (Hg1201; refs 6, 7,8) revealed a novel kind of magnetic order (broken time-reversal symmetry) below T* that is characterized by the wave vector q = 0 (preserved lattice translational symmetry). The measurements were motivated by the distinct theoretical proposal that magnetism due to orbital charge currents (rather than local spin moments) lies at the heart of the cuprate phase diagram1. The subsequent discovery of a prominent magnetic excitation in Hg1201, that also appears below T* and is centred at q = 0, seems to be the first dynamic fingerprint of this pseudogap magnetism11. However, it has remained largely elusive if and how the antiferromagnetism and the pseudogap magnetism are related. Here we use inelastic neutron scattering to further determine the excitation spectrum associated with the latter. Our new results for Hg1201 reveal a second weakly dispersive magnetic excitation branch, as predicted theoretically12,23, as well as an intriguing mixing with the antiferromagnetic fluctuations near qAF that is not yet explained theoretically.

Hg1201 has a simple tetragonal crystal structure, exhibits the highest value of Tc(max)(≈96 K) of all single-layer cuprates (one CuO2 layer per primitive cell), and is thought to be relatively free of disorder effects15,24,25. Sizeable crystals of Hg1201 have become available only in recent years25,26 and enabled initial neutron scattering experiments16,24,30,31. Our underdoped (TD = 65 K, T* ≈ 330 K, mass = 1.8 g; denoted UD65) and nearly optimally doped (Te = 95 K, T* ≈ 210 K, mass = 2.0 g; denoted OP95) samples24 were measured with both spin-polarized and unpolarized neutrons. Scattering wave vectors are quoted as q = Ha* + Kba* + Lc* = (H, K, L) in units of the reciprocal lattice vectors (r.l.u.), with typical room-temperature values a* = b* = 1.614 Å−1 and c* = 0.657 Å−1. Further experimental details are provided in the Supplementary Information.

We first provide evidence for magnetic excitations below T* from measurements with unpolarized neutrons. Figure 1a–c shows energy scans at various locations in the first 2D Brillouin zone. As both nuclear and magnetic scattering contribute to the intensity, we use the intensity difference between the lowest temperature and the gap magnetism are related. Here we use inelastic neutron scattering to further determine the excitation spectrum associated with the latter. Our new results for Hg1201 reveal a second weakly dispersive magnetic excitation branch, as predicted theoretically12,23, as well as an intriguing mixing with the antiferromagnetic fluctuations near qAF that is not yet explained theoretically.

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a high temperature (close to $T^*$) to extract magnetic signals, on the basis of the expectation that phonon intensity decreases on cooling, whereas magnetic intensity increases. In particular, for UD65, this method clearly reveals the presence of two weakly dispersive excitation branches throughout the entire Brillouin zone, with approximate energies of 38 and 54 meV (Fig. 1b). The branch near 54 meV was the subject of our previous study, and its magnetic origin was verified with spin-polarized neutrons.\(^{24}\) Although the presence of a low-energy excitation is not as evident for OP95 as for UD65, there is a clear difference between the data in Figs 1b and 1c: unlike for UD65, for OP95 there is no peak at $\sim 38$ meV, but instead a ‘shoulder’ near 31 meV. This is best seen in Fig. 2a by comparing the ‘4K–330 K’ intensity difference for both samples, measured at (0, 0, 4.6) under nearly identical experimental conditions. Given the rather small difference in oxygen concentration between OP95 and UD65 ($\Delta \delta \sim 0.03$, assuming each oxygen dopes two holes), the difference in the data is rather unlikely to be due to phonons and more naturally explained by a shift of the excitation from $\sim 38$ meV in UD65 to $\sim 31$ meV in OP95, reflecting a doping dependence of the underlying magnetism.
The presence of a magnetic signal at $\sim 31$ meV in OP95 is further supported by the data in Fig. 2c, which reveal that the intensities of the two excitations depend on the momentum transfer direction in a peculiar, opposite fashion. It was previously found that the high-energy excitation becomes indiscernible when $Q$ is parallel to the CuO$_2$ planes (Supplementary Fig. S4 of ref. 24), which is confirmed in Fig. 2c. Conversely, although non-zero intensity is observed for the low-energy excitation for $Q \parallel c$, higher intensity is observed for $Q \parallel ab$ with both unpolarized (Fig. 2c) and polarized neutrons (Fig. 4b,c). The low-energy features at both $Q$ positions are more clearly observed from the ‘4 K–110 K’ intensity difference (Fig. 2b), because the lower reference temperature keeps the variation in phonon scattering to a minimum. The opposite momentum dependence of the intensities implies that the two excitation branches are associated with fluctuations in perpendicular directions, either purely in the magnetic degrees of freedom, or in conjunction with lattice vibrations. However, without an extensive study of the neutron spin-polarization dependence of the signal beyond the present work (especially of the low-energy branch with $Q \parallel ab$), which would allow for a differentiation between magnetic fluctuations parallel and perpendicular to the copper–oxygen planes) a conclusive explanation of this phenomenon is unreachable. Here we simply regard it as empirical evidence that the two branches have the same physical origin. This is further evinced by the fact that the excitations exhibit similar intensity amplitudes (Figs 1b,c and 2a) and temperature dependences (Fig. 3), with an onset temperature consistent with $T^*$ determined from resistivity and neutron diffraction$^{21}$. No well-defined magnetic signal is observed in the raw data above $T^*$ (Fig. 1a) or in the intensity difference for temperatures above $T^*$ (Fig. 2d). Together with the fact that the excitations emanate from $q = (0, 0, 4.6)$ because the baseline due to phonons is less negative at smaller $Q$, and therefore the difference is not necessarily a low-energy magnetic signal. Error bars represent statistical uncertainty (1 s.d.).

We used spin-polarized neutrons (see Supplementary Information for a detailed description of the method) to further verify the magnetic origin of the low-energy excitation branch. Such measurements are extremely difficult, not only because of the much reduced neutron flux, but also because a large part of the background intensity arises from incoherent scattering and cannot be suppressed further in spin-flip measurements. Moreover, imperfect shielding leads to an additional (small) background intensity which is not negligible compared to the weak signal strength in the polarized measurements. Altogether, this results in a much reduced signal, but not necessarily an improved signal-to-background ratio compared to unpolarized measurements, hence extremely long counting times are required (see Supplementary Fig. S4 for a comparison between polarized and unpolarized measurements).

In Fig. 4a–c, the intensity difference between low and high temperatures for OP95, measured in the spin-flip scattering geometry, shows a peak at $\sim 31$ meV near the 2D zone centre (Fig. 4b) and also for $L = 0$ (Fig. 4c), consistent with the unpolarized results (Figs 1c, 2a,c, 3b,c). As no prominent nuclear scattering feature is observed in the non-spin-flip geometry (Fig. 4d,e), the experiment’s flipping
Our results provide valuable insight into the fundamental properties of the pseudogap magnetism. The very weak dispersion of about 5% (Fig. 1d) and the absence of a Goldstone mode dispersing to zero energy at the ordering wave vector \( q = 0 \) imply that the order parameter has discrete symmetry. The dispersion is even weaker than that of the classic local-moment Ising-like antiferromagnet \( \text{Rh}_2\text{CoO}_4 \), in which the spin excitations disperse by about 20% (ref. 32). Contrary to this model magnet, we observe two excitation branches rather than one. Together, these results suggest the presence of multiple scattering centres per CuO\(_2\) square (or CuO\(_x\) octahedron) and the need for a multi-band rather than a single-band theoretical description. The orbital–current theory, which is based on a multi-band Hamiltonian and makes the non-trivial prediction of two magnetic collective excitations in a single-layer system measurable via neutron scattering, seems to be able to explain our findings.\(^{25,26,33}\) This superposition has also been proposed to account for the peculiar experimental result that the magnetic moment direction is neither perpendicular nor parallel to the CuO\(_2\) layers\(^{6,8,34}\). On general grounds, mode softening is expected at high temperature and on approaching the quantum critical point. The former is not observed in our experiment and would require high-statistics energy scans at temperatures just below \( T^* \). However, with increasing doping, we observe a clear softening of the low-energy branch.
Our results are consistent with the orbital–current theory. We note, however, that a distinctly different possibility consistent with the very weak dispersion is that the excitations are related to intrinsic inhomogeneity in the local electronic environment\textsuperscript{35,36}. It has been proposed that such inhomogeneity can give rise to local ‘edge modes’ that are partially magnetic\textsuperscript{35}.

Our data reveal an intriguing connection between the pseudogap excitations and the conventional antiferromagnetic fluctuations at $q_{AF}$. Initial evidence comes from the prior observation for OP95 (ref. 24) that the resonance occurs at an energy which is indistinguishable from that of the high-energy pseudogap excitation, which is confirmed with improved precision in Supplementary Figs S1a and S2. A local intensity maximum at $q_{AF}$ is also found for the low-energy excitation in OP95 (Supplementary Fig S1b), but the relatively weak signal does not allow a detailed study. Even though there exists no clear resonance (distinct intensity change) across $T_c$ in UD65, we observe an enhanced response at $q_{AF}$ at 39 meV, the energy of the pseudogap excitation (Fig. 5a). Figure 5b provides a detailed view of the response near $q_{AF}$ along $a^*$. For YBCO, this momentum direction is optimal for observing the ‘hourglass’ dispersion of the antiferromagnetic fluctuations in the superconducting state\textsuperscript{37}. Indeed, we find initial evidence for a similar concave dispersion near $q_{AF}$ in Hg1201, with a maximum energy that is indistinguishable from that of the lower pseudogap excitation. The signal amplitudes of the antiferromagnetic fluctuations, determined from momentum scans (which are insensitive to the pseudogap excitations because of the weak dispersion), are comparable to those of the pseudogap excitations in Hg1201, and to those of antiferromagnetic fluctuations in other cuprates (for example, YBCO). Moreover, the signal that peaks at $q_{AF}$ exhibits maxima at approximately the same energies as the pseudogap excitations.

Figure 4 | Magnetic origin verified by spin-polarized measurements. a, Spin-flip spectra at $Q=(0.05, 0.05, 4.4)$ for OP95. Filled symbols are measured with the initial neutron spin polarization (S) parallel to $Q$, a geometry in which all magnetic fluctuations are probed. Open symbols are the average of intensities measured with S in the horizontal scattering plane but perpendicular to $Q$ ($S \perp Q$) and with S vertical ($S \parallel Z$), which measures only half of the total magnetic signal (Supplementary Fig. S5, shows that $I_{S \perp Q}$ and $I_{S \parallel Z}$ are the same within the error, consistent with the system’s tetragonal symmetry). b, Intensity difference between 4 K and 250 K for OP95 measured in the $S \parallel Q$ spin-flip geometry at $Q=(0.05, 0.05, 4.4)$ and (1.3, 1.3, 0), respectively. Solid lines are Gaussian fits assuming a common width and baseline. c, Non-spin-flip intensity at 4 K for sample OP95 at $Q=(0.05, 0.05, 4.4)$ and (1.3, 1.3, 0). Dotted lines illustrate the size of the non-spin-flip nuclear (phonon) signal that would be required to produce the peaks in a. d, Spin-flip data at $Q=(0, 0, 4)$ for UD65. e, Magnetic signal extracted from polarization analysis of the 4 K data in a and f. Solid blue line is the best Gaussian fit to the data for UD65 assuming zero offset. Solid and dashed green lines are best Gaussian and constant fits which allow for a non-zero offset. Red line is adapted from the fit in b without the linear baseline. A statistical analysis of the data is presented in the Supplementary Information. h, Unpolarized neutron data for UD65 adapted from Fig. 1b to directly demonstrate that the magnetic signal in g occurs at the peak position of the unpolarized result for closely similar values of $Q$. Error bars represent statistical uncertainty (1 s.d.).
Excitations. In fact, the size of the superconducting gap ($\Delta$) seems to be defined already at $T^*$: the magnetic resonance energy in unconventional superconductors has been shown to be universally proportional to $\Delta$ (ref. 21) and, in the model compound Hg$_{1201}$, the resonance occurs at the same energy as the high-energy pseudogap excitation.

Bearing in mind that the pseudogap excitations and the antiferromagnetic fluctuations in Hg$_{1201}$ occur at the same energy, we note that there might exist a correspondence between the magnetic energy scales of single-layer Hg$_{1201}$ and double-layer YBCO, two cuprates with similar values of $T_c$ and $\Delta$, and with well-defined resonances at $q_{\text{AF}}$ near optimal doping$^{13,15-17,30}$. In YBCO, the presence of two resonances in the 30–60 meV range has been interpreted as due to the interaction between the two adjacent CuO$_2$ layers in the same primitive cell$^{12}$. Surprisingly, we find that the energies of the pseudogap excitations in UD65 Hg$_{1201}$ (39 ± 2 meV and 56 ± 2 meV at $q_{\text{AF}}$) are equal within the error to those of the odd ($\approx 37$ meV) and even ($\approx 55$ meV) parity resonances in YBCO with a similar $T_c$ ($\approx 63$ K; ref. 43). This observation also holds for the high-energy mode of OP95 Hg$_{1201}$ (55 ± 2 meV at $q_{\text{AF}}$), but not for the corresponding low-energy mode (32 ± 3 meV at $q_{\text{AF}}$): in nearly optimally-doped YBCO ($T_c \approx 89$ K), the two resonance energies are about 53 and 41 meV (ref. 42).
The pseudogap excitations should be most easily discernable in compounds in which the $q = 0$ order is prominent, and so far they have been reported only for Hg1201. The well-studied single-layer materials (La, Nd, Sr, Ba)$_2$CuO$_4$ possess a relatively low $T_{c\text{,max}}$ of about 40 K and have long been known to exhibit an instability towards broken translational symmetry (spin/charge 'stripe' order) well below $T^*$ (ref. 18). The lack of evidence of pseudogap excitations in these compounds probably results from a competition between the two types of order$^{19}$.

On the other hand, it should be possible to observe the pseudogap excitations in YBCO ($T_{c\text{,max}} \approx 93$ K). At low doping, near the onset of superconductivity, neutron diffraction measurements have revealed a quasi-elastic signal consistent with a transition to long-range density-wave order $\propto q_{\text{onset}} = 0$ (ref. 20). Superconductivity and $q = 0$ orders are associated with very different wave vectors and seem to compete in the deeply underdoped regime ($p < 0.09$; ref. 44), whereas the $q = 0$ order is found to dominate at higher doping$^6$, where the pseudogap excitations are most likely to be found. Material-specific differences, such as the more complicated double-layer structure of YBCO, can be expected to cause variations in the number of pseudogap excitations and in their strength relative to antiferromagnetic fluctuations. Analogous to the situation for single-layer LSCO and Hg1201, the pseudogap magnetism in the double-layer compounds might eventually be most clearly revealed in HgBa$_2$CuO$_{4+d}$ ($T_{c\text{,max}} \approx 124$ K (ref. 45), the highest value for all double-layer compounds) once sizeable single crystals become available.

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