Asymmetry of collective excitations in electron- and hole-doped cuprate superconductors

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High-temperature superconductivity emerges on doping holes or electrons into antiferromagnetic copper oxides. The large energy scale of magnetic excitations, for example, compared with phonon energies, is thought to drive superconductivity with high transition temperatures (Tc). Comparing high-energy magnetic excitations of hole- and electron-doped superconductors provides an opportunity to test this hypothesis. Here, we use resonant inelastic X-ray scattering at the Cu L3-edge to reveal collective excitations in the electron-doped cuprate Nd2−xCeCuO4. Surprisingly, magnetic excitations harden significantly across the antiferromagnetic high-temperature superconductivity phase boundary despite short-ranged antiferromagnetic correlations, in contrast to the hole-doped cuprates. Furthermore, we find an unexpected branch of collective modes in superconducting compounds, absent in hole-doped cuprates. These modes emanate from the zone centre and possess a higher temperature scale than Tc, signalling a distinct quantum phase. Despite their differences, the persistence of magnetic excitations and the existence of a distinct quantum phase are apparently universal in both hole- and electron-doped cuprates.

Determining universal aspects of the cuprate phase diagram and the evolution of collective excitations away from the antiferromagnetic (AFM) parent compounds has important implications for unraveling the mechanism of high temperature superconductivity (HTSC). In hole-doped cuprates' compelling evidence now exists for symmetry-broken phases, such as charge density waves and orbital loop currents, distinct from superconductivity. In addition, recent resonant inelastic X-ray scattering (RIXS) at the Cu L3-edge revealed the persistence of high energy magnetic excitations well beyond the AFM phase boundary. Whether these features of hole-doped compounds also exist on the other side of the cuprate phase diagram—that is, with electron doping, and how they evolve remain important open questions. To address these issues, collective excitations in antiferromagnetic (x = 0.04) and superconducting (x = 0.147 and 0.166) Nd2−xCeCuO4 (NCCO) compounds are investigated via RIXS, uncovering unexpected behaviours.

We first discuss low-energy excitations seen in high-resolution RIXS in antiferromagnetic NCCO (x = 0.04). As shown in Fig. 1a, a distinct feature emerges from the elastic peak (centred at zero energy transfer) at zone centre (the Γ point). It disperses towards higher energy with increasing momentum (denoted as qz), see Supplementary Information for the scattering geometry), and reaches a maximum along the high-symmetry directions at the AFM zone boundary (π, 0) and (π/2, π/2). The geometry of our experiment (o-polarization-grazing-incidence branch, qz > 0; π-polarization-grazing-exit branch, qz < 0) allows us to identify this peak with single-magnon excitations, similar to those found in undoped AFM insulating compounds. The peak position of magnon excitations can be determined by fitting the spectra to Gaussians, as depicted in Fig. 1b, and extracting their energy–momentum dispersion, as shown in Fig. 1c. The dispersion is well fitted by linear spin waves of the two-dimensional nearest-neighbour Heisenberg model (dashed line in Fig. 1c), where a and c are the lattice constant and spin-wave velocity, respectively. The bandwidth of magnetic excitations (~300 meV) and the extracted value of c = 830 ± 9 meV Å are consistent with those found in other AFM cuprates.

Figure 2a presents an overview of the RIXS spectra in superconducting NCCO (x = 0.147). We again observe a dispersive feature (red markers) which reaches a maximum at the AFM zone boundary. Because AFM correlations become short-ranged at this doping level, these excitations are not magnons, but rather paramagnons with a short lifetime, as indicated by broad spectral widths comparable to their energies (Supplementary Data). Unexpectedly, in addition to the paramagnon excitations, another excitation branch (blue ticks) is clearly resolved near the Γ point. As shown in the energy–momentum spectral intensity map with

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finer momentum steps (Fig. 2b), these excitations are pronounced near the Γ point, where the paramagnon structure factor is zero. Moving away from the Γ point, the modes disperse to higher energies and weaken, becoming undetectable for |q| > 0.3π. The energy positions of the paramagnons and the additional excitation branch can be determined by fitting the spectra with Gaussians (Fig. 2c) to extract their energy–momentum dispersions, as shown in Fig. 2d.

One key discovery from this work is the finding that the paramagnon dispersion extends to much higher energies in the superconducting compound than in the AFM compound, as indicated in Fig. 2d. The AFM zone boundary energy of these paramagnons is approximately 450 meV for x = 0.147, a hardening of approximately 50% with respect to that of x = 0.04, also evident directly from the raw RIXS spectra (Fig. 3a). The hardening of the magnetic excitations was reported previously by Wilson et al., using inelastic neutron scattering on the Pr1−xLaCe2Cu3O7 family of electron-doped cuprates, where an increase of spin-wave velocity near (π, π) was found upon doping. However, this result was challenged by Fujita et al., who observed no spin-wave-like dispersion up to 180 meV. Our result, which covers a wide range of the Brillouin zone away from (π, π), crucially confirms the hardening of magnetic excitations in the electron-doped cuprates. Notably, this behaviour differs from that exhibited by hole-doped cuprates, for which the magnetic excitation spectrum softens slightly with doping. Naively, one would expect magnetic excitations to soften significantly on either hole or electron doping away from the parent compounds, because the doped carriers suppress long-range AFM order in both cases. In addition, because the in-plane lattice constants change by less than 0.5% from undoped to optimally doped compounds, the pronounced magnetic excitation hardening cannot be attributed to structural modifications. We note that this surprising disparity with respect to electron and hole doping is inherent to the single-band Hubbard model, as shown by our determinant quantum Monte Carlo simulations (see ref. 19 and Supplementary Theory) summarized in Fig. 3b. In addition, the simulations reveal a softening of the two-magnon excitations which has been observed in Raman scattering and coincides with the single-paramagnon hardening observed in this work.

The other important discovery of our work is the observation of additional, distinct collective modes emanating from the zone centre in the superconducting compounds (blue markers in Fig. 2d). The dispersion of these modes in the x = 0.147 compound can be fitted with a standard form for charge collective modes, ωc = √(Eα)2 + (vαq)2 (blue dashed curve in Fig. 2d), with an extracted zone centre energy Eα = 300 ± 30 meV and velocity vα ≈ 3.0 eV a/π, comparable to the Fermi velocity vF ≈ 2.0 eV a/π. Although vα ≈ vF suggests that the modes may have charge character, a conclusive determination to distinguish between charge or magnetic excitations requires a polarization analysis of the spectra, which is presently unavailable with comparable resolution. The existence of these collective modes is further confirmed by their observation in a slightly overdoped superconducting compound (x = 0.166, Fig. 4a). As demonstrated in Fig. 4b, the velocity is similar to that found in the x = 0.147 compound; however, Eα of the x = 0.166 compound seems to shift towards lower energies which cannot be resolved owing to insufficient instrument resolution. Nevertheless, our results unambiguously demonstrate the existence of these modes, which are absent in heavily underdoped NCCO (that is, x = 0.04 compounds shown in Fig. 1) and in any of the hole-doped superconducting cuprates.

What is the origin of these collective modes? Their dispersion is reminiscent of plasmons; however, optical measurements detect no plasmonic features at the energy scale comparable to Eα.
Figure 2 | Paramagnons and unexpected collective modes in superconducting NCCO (x = 0.147). a, Energy–momentum intensity maps (top) and waterfall plots (bottom) of resonant inelastic X-ray scattering (RIXS) spectra along (0, 0)–(π, 0) and (0, 0)–(π, π), respectively. Red (blue) ticks indicate the peak positions for paramagnons (unexpected collective modes). The data were taken with the σ polarization. b, Spectra near the Γ point with finer momentum steps to highlight the dispersion of the unexpected collective modes. c, RIXS spectra taken with π and σ incident X-ray polarizations at symmetric q̂ points. The red and blue shaded areas are Gaussian fits to the paramagnons and the collective modes, respectively. The thick black curve is a fit to the data. The thin black and dashed black curves are a Gaussian fit to the elastic scattering signal and the background as determined from the dd and charge-transfer excitations at higher energy loss. d, Paramagnon and collective mode dispersions along (0, 0)–(π, 0) and (0, 0)–(π, π) directions deduced from RIXS spectra. The paramagnon dispersion deviates from simple linear-spin-wave theory (as a guide-to-eye, black dashed curve, with c_s = 1.240 meV Å). Superimposed for comparison is the magnon dispersion in the x = 0.04 compound. The blue dashed line is a fit to the collective mode dispersion in the form of generic collective charge excitations, as described in the text. Error bars are estimated by the uncertainty in determining the energy loss reference point.
Neither do these modes originate from bi-magnon nor higher-order magnetic excitations, as they are absent in the AFM $x = 0.04$ compound. Furthermore, it is unlikely that the new modes are directly associated with the superconducting state, because the superconducting gap ($\sim 5\text{ meV}$) is much smaller than $E_F$ and the modes persist well above the superconducting transition temperature (Fig. 4c).

The temperature and doping dependence of the collective modes near the $\Gamma$ point does suggest that they might be associated with a symmetry-broken state other than superconductivity. As shown in Fig. 4c,d, collective modes near the $\Gamma$ point weaken with increasing temperature in a doping-dependent manner. Whereas the modes in the $x = 0.166$ compound vanish at temperatures higher than $T_T \sim 240\text{ K}$, the zone centre mode of the $x = 0.147$ compound persists even to room temperature, indicating that $T_T$ increases with underdoping. A doping-dependent $T_T$ cannot be explained by thermal broadening; rather, it is possibly associated with the emergence of a doping-induced symmetry-broken state, which vanishes or may become fluctuating at high temperatures. Furthermore, the considerable decrease of $E_F$ with doping from $x = 0.147$ to $x = 0.166$ is also consistent with the mass of a collective mode changing near a quantum critical point (QCP) associated with a symmetry-broken state. Notably, $T_T$ appears to be higher than characteristic temperatures deduced from other measurements; however, this is reminiscent of the existence of multiple temperature scales and the well-known discrepancy of the ‘pseudogap’ temperature $T^*$ in the literature for hole-doped cuprates. This suggests that a similarly complicated phenomenon may be at play in electron-doped compounds. Whether the putative symmetry-broken state in NCCO is a charge/spin density wave or more exotic ordered state, such as a $d$-density wave or intra-unit-cell orbital currents, remains an open question requiring further investigation.

Our results crucially complement existing knowledge, allowing us to draw a more complete picture regarding the doping evolution of collective modes in doped cuprates on both sides of the phase diagram. As sketched in Fig. 5, on hole doping, the bandwidth of magnetic excitations (as determined by the AFM zone boundary energy) softens slightly, and a spin incommensurability plus a spin gap near $(\pi, \pi)$ emerges at low energies. This contrasts with the magnetic excitations observed in the optimally electron-doped superconducting compound, where the magnetic bandwidth hardens significantly and no spin incommensurability develops near $(\pi, \pi)$ (ref. 12). In addition, the rapidly dispersive collective modes near zone centre in electron-doped superconducting NCCO are absent in hole-doped compounds, but imply the existence of a quantum critical point beyond the AFM–SC phase boundary reminiscent of those discussed for their hole-doped counterparts. This suggests that a QCP located in proximity to the HTSC phase may be generic in both electron- and hole-doped cuprates.

Despite the common belief that magnetic excitations are crucial to HTSC (refs 29–31), the significantly larger magnetic bandwidth in the superconducting electron-doped compounds does not correspond to a higher superconducting transition temperature ($T_c$). The spectral weight of the paramagnon remains significant in the superconducting compounds (see Fig. 3a and Supplementary Data), indicating that this is not the reason for the lower $T_c$. Thus, it is important to identify which factors—the magnetic excitations near $(\pi, \pi)$, the underlying Fermi-surface topology, or additional

Figure 3 | Hardening of magnetic excitations. a, Resonant inelastic X-ray scattering spectra of $x = 0.04$ and 0.147 compounds at two representative in-plane momentum points, as indicated by the red markers in the insets. Red ticks indicate the positions of the magnon and paramagnon. b, Quantum Monte Carlo simulation of the dynamical spin structure factor $S(q, \omega)$ at $(\pi/2, \pi/2)$ in the single-band Hubbard model for both electron (top) and hole doping (bottom). Red ticks indicate the positions of maximum intensity of $S(q, \omega)$.
Figure 4 | Doping and temperature dependence of the collective modes. a, Resonant inelastic X-ray scattering (RIXS) spectra of the $x=0.166$ compound along the $(0, 0)$–$(\pi, 0)$ direction. Red (blue) ticks indicate the peak positions for paramagnons (unexpected collective modes). The data were taken at 80 K and using the $\sigma$ polarization scattering geometry. b, Energy-momentum dispersion of the collective modes in superconducting compounds $x=0.147$ (open symbol) and $x=0.166$ (closed symbol). The shaded area indicates the energy-momentum region that was not resolvable owing to finite resolution of the instrument. Error bars are estimated by the uncertainty in determining the energy loss reference point. c, Temperature-dependent RIXS spectra taken at a momentum position near the $\Gamma$ point for $x=0.147$ (top) and $x=0.166$ (bottom) compounds. d, The temperature-dependent spectral weight of the collective modes, shown in c, is calculated by integrating the background-subtracted spectra between 0.2 and 0.4 eV. As motivated by the $T=270$ K spectra of the $x=0.366$ compound, the background is assumed to be independent of energy, with the value of the spectral intensity at 1 eV. The temperature-dependent spectral weight is normalized to that of the lowest temperature. The error bars are estimated by the noise level of the spectra. The temperature-dependent spectral weight is also superimposed in the phase diagram (right panel) via colour intensity stripes to demonstrate the pronounced change in temperature dependence within a small doping window.
effects—are not optimized in the electron-doped cuprates for the purpose of achieving a higher $T_c$. Finally, whether the observed collective modes near the Γ point are beneficial or detrimental to the formation of superconducting pairs remains an important open question.

Methods

Single-crystals of Nd$_{1−x}$Ce$_x$CuO$_4$ were grown by travelling-solvent floating-zone (TSFZ) methods. Antiferromagnetic ($x = 0.04$), near-optimally doped superconducting crystals $x = 0.147$ and $x = 0.166$ were selected for our measurements. The superconducting transition temperatures of $x = 0.147$ and $0.166$ compounds are 25 K. The doping levels of the superconducting samples were further characterized by energy dispersive spectroscopy along with a scanning electron microscope (Supplementary Method). The lattice constants for the NCCO crystals are $a = b = 3.9$ Å and $c = 12.1$ Å. The data of $x = 0.04$ and 0.147 were taken at the ADRESS beamline of the Swiss Light Source at the Paul Scherrer Institut (PSI, Switzerland); the data of $x = 0.166$ were taken at beamline BL05A1, National Synchrotron Radiation Research Center (NSRRC, Taiwan) using the newly constructed AGM-AGS spectrometer$^{17}$. All the data were taken with an energy resolution of approximately 130 meV (full width half maximum), and with the scattering angle set at 130°. The sample (001) surface was prepared by in situ cleaving. The RIXS spectra shown in Figs 1–3 were normalized by the incident photon flux; the BL05A1 data shown in Fig. 4 were normalized by the spectral weight of the $dd$ excitations, owing to noticeable photon flux fluctuation at the BL05A1 during measurements.

Unless specified, all RIXS spectra presented in the main text were taken at a temperature of 10 K with the photon energy of incident X-rays tuned to the maximum of the absorption curve near the Cu L$_3$-edge ($2p–3d$ transition) (Supplementary Fig. 1a). The scattering geometry is sketched in Supplementary Fig. 1. Measurements along the two high-symmetry directions $(0, 0)–(\pi, 0)$ and $(0, 0)–(\pi, \pi)$ were performed on different crystals at the same doping levels and synthesized in the same batch. The crystallographic orientation was aligned using Laue diffraction before our RIXS measurements. For the measurements along $(0, 0)–(\pi, 0)$, the (100) direction is aligned in the scattering plane; for the measurements along $(0, 0)–(\pi, \pi)$, the (110) direction is aligned in the scattering plane.

Figure 5 | Distinct doping evolution of the collective excitations in electron- and hole-doped cuprates. Sketches of the collective excitation spectra in energy–momentum space for electron-doped (e-SC, NCCO), lightly doped antiferromagnetic (AFM) and hole-doped (h-SC) superconducting cuprates. Representative data points shown in Figs 1 and 2 have been superimposed on the panels for e-SC. The bandwidth of magnetic excitations is marked on the energy axis. The low-energy magnetic excitations along $(\pi, \pi)$–(0, 0) near $(\pi, \pi)$ obtained via inelastic neutron scattering are sketched on the images. The spin gap ($\Delta_s$) and spin incommensurability ($x$) are not drawn to scale. The lowest panel is a sketch of the cuprate phase diagram. The dots represent quantum critical points associated with symmetry-broken states (labelled as ‘other order’) on both sides of the phase diagram. Although the existence of such a quantum critical point on the electron-doped side of phase diagram is suggested by our results, its exact position remains an open question.

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**Author contributions**

W.S.L. conceived and designed the experiments with suggestions from Z.X.S., M.G., T.P.D. and T.S.; W.S.L., J.L.L., W.T., S.G., S.W.H., Y.B.H., V.N.S. and T.S. performed the measurement at the SLS; W.S.L., H.Y.H., R.P.W., W.B.W., C.T.C. and D.J.H. performed the measurement at the NSRRC. E.M.M., G.Y. and M.G. synthesized and prepared the single-crystals used for the measurements. E.A.N., B.M. and T.P.D. performed the theoretical calculations. W.S.L. wrote the manuscript with contributions from all authors.

**Additional information**

Supplementary information is available in the online version of this paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to W.S.L., Z.X.S. or T.P.D.

**Competing financial interests**

The authors declare no competing financial interests.