Asymmetry of collective excitations in electron and hole doped cuprate superconductors

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High-temperature superconductivity (HTSC) emerges upon doping holes¹ or electrons² into antiferromagnetic (AFM) copper oxides. The large energy scale of magnetic excitations, e.g. compared to phonon energies, is thought to drive superconductivity with high transition temperatures (T_c)³⁻⁵. Comparing high-energy magnetic excitations of hole- and electron-doped superconductors provides an opportunity to test this hypothesis⁶⁻⁹. Here, we use resonant inelastic x-ray scattering (RIXS) at the Cu L_3 -edge^{10,11} to reveal collective excitations in the electron-doped cuprate $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ ². Surprisingly, magnetic excitations harden significantly across the AFM-HTSC phase boundary despite short-ranged AFM correlations¹², in contrast to the hole-doped cuprates^{6,7}. Furthermore, we find an unexpected branch of collective modes in superconducting compounds, absent in hole-doped cuprates. These modes emanate from zone center and possess a higher temperature scale than T_c , signaling a distinct quantum phase. Despite their differences, the persistence of magnetic excitations and the existence of a distinct quantum phase appear to be universal in both hole- and electron-doped cuprates.

Hole-doped cuprates display compelling evidence for the surprising persistence of magnetic excitations beyond the AFM phase boundary^{6,7}, as well as the existence of symmetry-broken phases, such as charge density waves^{13,14,15} and orbital loop currents¹⁶, distinct from superconductivity. Whether these are universal and exist on the other side of the cuprate phase diagram, i.e. with electron-doping, remains an important open question. To address this issue, collective excitations in antiferromagnetic ($x = 0.04$) and superconducting ($x = 0.147$ and 0.166) $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ (NCCO) compounds are investigated via RIXS, uncovering unexpected behaviors.

We first discuss the types of 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 (centered at zero energy transfer) at zone center (the Γ point). It disperses toward higher energy with increasing momentum (denoted as $q_{\parallel}$, see Supplementary Information for the scattering geometry), and reaches a maximum along high-symmetry directions at the AFM zone boundary $(\pi, 0)$ and $(\pi/2, \pi/2)$. The geometry of our experiment (σ -polarization-grazing-incidence branch, $q_{\parallel} > 0$; π -polarization-grazing-exit branch, $q_{\parallel} < 0$) allows us to identify this peak with single-magnon excitations, similar to those found in undoped AFM insulating compounds^{17,18}. 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 fit by linear spin waves of the two-dimensional nearest-neighbor Heisenberg model $\omega_m = \frac{\sqrt{2}}{a} c_s \sqrt{1 - \left(\frac{\cos q_x + \cos q_y}{2}\right)^2}$ (dashed line in Fig. 1c), where a and c_s are the lattice constant and spin-wave velocity, respectively. The band width of magnetic excitations (~ 300 meV) and the extracted value of $c_s = 830 \pm 9$ meV $\cdot\text{\AA}$ are consistent with those found in other AFM cuprates^{17,18,19}.

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. Since AFM correlations become short-ranged at this doping level¹², these excitations are not magnons, but rather paramagnons with a short lifetime, as indicated by broad spectral widths comparable to their energies (See 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 finer momentum steps (Fig. 2b), these excitations are strongest at 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 $|q_{\parallel}| > 0.3\pi$. 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.*²⁰ using inelastic neutron scattering on the $\text{Pr}_{1-x}\text{LaCe}_x\text{CuO}_4$ 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.*²¹, who did not observe any 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 behavior differs from that exhibited by hole-doped cuprates, for which the magnetic excitation spectrum slightly softens with doping^{6, 7}. Naïvely, one would expect magnetic excitations to significantly soften upon either hole or electron doping away from the parent compounds, since the doped carriers suppress long-range AFM order in both cases. In addition, since the in-plane lattice constants change by less than 0.5% from undoped to optimally-doped compounds⁸, 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 in the single-band Hubbard model, as shown by our determinant quantum Monte Carlo simulations (see Ref. 22 and Supplementary Theory) summarized in Fig. 3b. In addition, the simulations²² reveal a softening of the two-magnon

excitations which has been observed in Raman scattering⁸ 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 zone center in the superconducting compounds (blue markers in Fig. 2d). The dispersion of these modes in the $x = 0.147$ compound can be fit with a standard form for charge collective modes $\omega_x = \sqrt{(E_F)^2 + (v_x \cdot q_{//})^2}$ (blue dashed curve in Fig. 2d) with an extracted zone center energy $E_F = 300 \pm 30$ meV, and velocity $v_x \sim 3.0$ eV·Å/π, comparable to the Fermi velocity²³ $v_F \sim 2.0$ (eV·Å/π). Although $v_x \sim v_F$ suggests that the modes may have charge character, a conclusive determination to distinguish between charge or magnetic excitations requires a polarization analysis of the spectra¹⁰, 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, E_F of the $x = 0.166$ compound appears to shift toward lower energies which cannot be resolved due to insufficient instrument resolution. Nevertheless, our results unambiguously demonstrate the existence of these modes, which are absent in heavily underdoped NCCO (i.e. $x = 0.04$ compounds shown in Fig. 1) and in any of the hole-doped superconducting cuprates^{6,7,17}.

What is the origin of these collective modes? Their dispersion is reminiscent of plasmons; however, optical measurements²⁴ do not detect any plasmonic features at the energy scale comparable with E_F . Neither do these modes originate from bi-magnon nor higher-order magnetic excitations, since 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, since the

superconducting gap⁸, (~ 5 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 Γ point does suggest that they might be associated with a symmetry-broken state other than superconductivity. As shown in Fig. 4c and d, collective modes near the Γ point weaken with increasing temperature in a doping dependent manner. While the modes in the $x = 0.166$ compound vanish at temperatures higher than $T_F \sim 240$ K, the zone center mode of the $x = 0.147$ compound persists even to room temperature, indicating that T_F increases with underdoping. A doping-dependent T_F cannot be explained by thermal broadening; rather, it likely is 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 $x = 0.166$ also is consistent with the mass of a collective mode changing near a quantum critical point (QCP) associated with a symmetry-broken state. Notably, T_F appears to be higher than characteristic temperatures deduced from other measurements^{8,25,26}; however, this is reminiscent of the existence of multiple temperature scales¹⁴ 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^{13,14,15}, or more exotic ordered state, such as a d -density wave²⁷ or intra-unit-cell orbital currents^{16,28}, 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, upon hole-doping, the bandwidth of magnetic

excitations (as determined by the AFM zone boundary energy) slightly softens, and a spin incommensurability plus a spin gap near (π, π) emerges at low energies⁹. This contrasts with the magnetic excitations observed in the optimally electron-doped superconducting compound^{8,9}, where the magnetic bandwidth hardens significantly and no spin incommensurability develops near (π, π) ⁸. In addition, the rapidly dispersive collective modes near zone center 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^{29,30}. 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^{3,4,5}, 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 (π, π) , the underlying Fermi-surface topology, or additional 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 $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ were grown by traveling-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 EDS/SEM (see Supplementary Method). The lattice constants for the NCCO crystals are $a = b = 3.9 \text{ \AA}$, and $c = 12.1 \text{ \AA}$. The data shown in Fig. 1, Fig. 2, and Fig. 3 were taken at the ADRESS beamline, Swiss Light Source (SLS, Switzerland); some of the data shown in Fig. 4 were taken at beamline BL05A1, National Synchrotron Radiation Research Center (NSRRC, Taiwan) using the newly constructed AGM-AGS spectrometer³¹. All the data were taken with an energy resolution of approximately 130 meV, and with the scattering angle set at 130 degrees. The sample (001) surface was prepared by *in-situ* cleaving. The RIXS spectra shown in Fig. 1, Fig. 2, and Fig. 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, due to noticeable photon flux fluctuation at 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) (Fig. S1a). The scattering geometry is sketched in Supplementary Figure 1. Measurements along the two high symmetry directions $(0,0)$ - $(\pi,0)$ and $(0,0)$ - (π,π) were performed on different crystals at the same doping levels and synthesized in the same batch. The crystallographic orientation was aligned using Laue diffraction prior to our RIXS measurements. For the measurements along $(0,0)$ - $(\pi,0)$, the (100) direction is aligned in the scattering plane; and for the measurements along $(0,0) - (\pi, \pi)$, the (110) direction is aligned in the scattering plane. As the electronic structures in NCCO can be regarded as quasi-two-dimensional, the RIXS spectra presented here were plotted as a function of in-plane momentum only ($q_{\parallel}$ shown in Supplementary Figure 1).

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Figure 1 Magnons in antiferromagnetic NCCO ($x = 0.04$). **a**, Energy-momentum intensity maps (upper) and waterfall plots (lower) of representative RIXS spectra along $(0, 0) - (\pi, 0)$ and $(0, 0) - (\pi, \pi)$, respectively. Here momenta are expressed in units of the reciprocal lattice spacing ($1/a$). Red ticks indicate the maxima of the spectra, which are dominated by single magnon excitations. The data were taken with σ polarization. **b**, Representative spectra taken with π and σ incident x-ray polarizations at symmetric $q_{\parallel}$ positions. Thick black curves are from the sum of

Gaussian fits to the elastic scattering peak as well as phonon (two thin black curves), a single magnon peak (red shaded region) and a constant background (black dashed line). The residual spectral weight after subtracting this fit is shown by the blue curves. The fitted magnon peak positions have been superimposed on the color maps in **a** (red markers) and further summarized in **c**. **c**, Magnon dispersion along $(0, 0) - (|\pi|, 0)$ and $(0, 0) - (\pi, \pi)$ deduced from RIXS spectra. The dashed curves show a linear-spin-wave theory dispersion for a two dimensional antiferromagnetic Heisenberg model fitted to the data with $c_s = 830 \pm 9 \text{ meV} \cdot \text{\AA}$. Error bars are estimated by the uncertainty in determining the energy loss reference point.

Figure 2 Paramagnons and unexpected collective modes in superconducting NCCO ($x = 0.147$). **a**, Energy-momentum intensity maps (upper) and waterfall plots (lower) of RIXS spectra along $(0, 0) - (\pi, 0)$ and $(0, 0) - (\pi, \pi)$, respectively. Red (blue) ticks indicate the peak positions for paramagnons (unexpected collective modes). The data were taken with 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 polarization at symmetric $q_{\parallel}$ 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 $(0, 0) - (|\pi|, 0)$ and $(0, 0) - (\pi, \pi)$ directions deduced from RIXS spectra. The paramagnon dispersion deviates from simple linear-spin-wave theory (as a guide-to-eye, black dashed curve, with $c_s = 1240 \text{ meV}$). 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.

Figure 3 Magnetic excitations hardening. **a**, RIXS 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 (upper) and hole-doping (lower). Red ticks indicate the positions of maximum intensity of $S(q, \omega)$.

Figure 4 Doping and temperature dependence of the collective modes. **a**, 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 with σ polarization. **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 indicated the energy-momentum region that was not resolvable due 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 Γ point for $x = 0.147$ (upper) and $x = 0.166$ (lower) 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 $x = 0.166$ compound, the background is assumed to be energy independent 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 also superimposed in the phase diagram (right panel) via color intensity stripes to demonstrate the dramatic change in temperature dependence within a small doping window.

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 $(\pi, \pi)-(0, \pi)$ near (π, π) obtained via inelastic neutron scattering are sketched on the images. The spin gap (Δ_S) and spin incommensurability (ϵ) 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 (labeled as “other order”) on both sides of the phase diagram. While 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.

Figure 1

Figure 2

a **b**

Figure 3

Figure 4

Figure 5