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Probing emergent excitations with middle-energy electron energy loss spectroscopy

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Abstract – Probing the emergent excitations in a range of 1–50 eV is fundamentally important to understand a variety of emergent phenomena in quantum materials, however, the characterization techniques of which are very limited at present. Here, we take high-temperature superconducting $YBa_2Cu_3O_{7-\delta}$ films ($T_C \sim 90$ K) as an archetype to demonstrate the powerful capabilities of middle-energy electron energy loss spectroscopy (EELS) in determining the emergent excitations. Three dominative features (2.9, 12.9, and 25 eV) are observed in the EELS spectra, one of which is a newly observed peak near 2.9 eV resulting from excitations between the Zhang-Rice state and the upper Hubbard band. Moreover, incident energy-dependent EELS spectra indicate that the signals of these three features are strongly dependent on the energy of incident electrons. Our work provides a route to probe emergent excitations in the energy range 1–50 eV with utilizing high-resolution two-dimensional energy and momentum mapping.

Introduction. – Emergent excitations (such as phonons, magnons, plasmons, spinons, *d-d* excitations to name a few), a broad concept beyond elementary excitations (quasiparticles and collective excitations), are attracting a great amount of interest recently [1–8]. Investigating emergent excitations is fundamentally important to understand the novel phenomena in quantum materials, *e.g.*, the roles of phonons and plasmons in the formation of cooper pairs in high-temperature superconductors [3,4,8]. One of the main experimental objectives of characterizing emergent excitations is to determine their energy-momentum relations, which is the key to analysing the entanglements of charge, spin, orbital, and lattice in quantum many-body systems. Experimentally, in contrast to the rapid progress of tools for probing electron quasiparticles, *e.g.*, modern angle-resolved photoemission spectroscopy (ARPES, a technique of photon-in and electron-out) [9,10], the techniques for detecting collective excitations are not so popular. Generally, the techniques designed for collective excitations are developed based on inelastic scattering of probing particles, including Raman spectroscopy [11], inelastic neutron scattering [12], high-resolution inelastic X-ray scattering (IXS) [13], resonant inelastic X-ray scattering (RIXS) [14], and high-resolution electron energy loss spectroscopy (HREELS) [15,16]. However, none of the above techniques are specially designed for probing a wide range of excitation energy (1–50 eV). Therefore, developing a specific tool, such as middle-energy electron energy loss spectroscopy (EELS) with a reasonable incident energy of electron beam (such as 200–2000 eV) to characterize the emergent excitations, is very essential to furnish present techniques [17].

In analogy to RIXS (a photon-in and photon-out spectroscopy) [14,18–20], EELS is an electron-in and electron-out technique [21–26]. Both of RIXS and EELS

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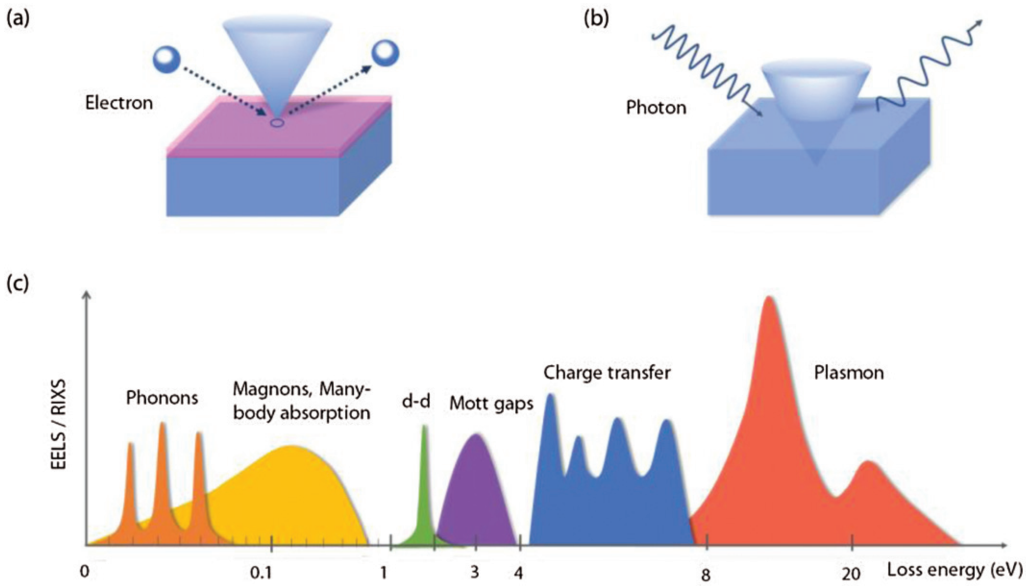

Fig. 1: Experimental setup of (a) EELS and (b) RIXS, respectively. The EELS measurement is an electron-in and electron-out technique (surface sensitive), whereas the RIXS is a photon-in and photon-out spectroscopy (bulk sensitive). (c) Emergent excitations probed by EELS and RIXS.

are powerful to probe variable collective excitations like phonons, magnons, plasmons and also other emergent excitations, *e.g.*, many-body absorptions, electron excitations (*d-d* excitations, charge transfer), the energy scale of which could range from meV to a few eV [14,27–31]. As shown in fig. 1, reflection EELS is a surface-sensitive technique, whereas RIXS is a bulk-sensitive probe. With the application of hemispherical angle-resolved electron analyser, modern HREELS has been able to collect the data with a way of two-dimensional energy-momentum mapping with high momentum and energy resolution ($0.002\,\text{Å}^{-1}$ and 0.7 meV, respectively) [15,16]. Therefore, for low-dimensional quantum materials such as thin films and van der Waals materials, EELS would be a potent supplement to RIXS. However, most reported EELS are either low-energy HREELS with low incident electron energy 2–200 eV or high-energy EELS in transmission electron microscopy (TEM) with high incident electron energy >60 keV, and the study of middle-energy EELS with incident electron energy in 200–2000 eV is limited to probe exotic excitations. Moreover, due to the charging effect for insulating materials, the HREELS does not work very well on insulating samples.

In this letter, we investigated emergent excitations of YBCO films using *in situ* middle-energy EELS with incident electron energy in 200–2000 eV. The high superconductive YBCO films were synthesized in a layer-by-layer way using pulsed laser deposition (PLD). Temperature-dependent electrical transport was carried out to determine the superconducting critical temperature (∼90 K). Three dominative features were observed in the EELS spectra, one of which is a new peak near 2.9 eV, resulting from the excitation between the Zhang-Rice state (ZRS) and the upper Hubbard band (UHB). Moreover, incident energy-dependent EELS spectra indicate that the signal of these three features strongly depends on the energy of incident electrons, demonstrating the importance of applying middle-energy electrons. Our work provides a route to probe emergent excitations in the energy range of 1–50 eV.

Experiment. – The high-quality YBCO films (∼35 unit cells) were synthesized on $5 \times 5\,\text{mm}^2$ $SrTiO_3$ (001) single crystal substrates with a layer-by-layer way by PLD [32,33]. The temperature-dependent electrical transport was measured by using the van der Pauw geometry. The EELS was *in situ* performed utilizing the STAIB double-pass cylindrical mirror analyser. The incident electron energy of electron beams was continuously tunable from 100 eV to 2000 eV. The schematic of one-unit cell of YBCO is shown in fig. 2(a). As seen, YBCO has an orthorhombic structure (space group *Pmmm*) with lattice parameters $a = 3.828\,\text{Å}$, $b = 3.888\,\text{Å}$, and $c = 11.65\,\text{Å}$), which match well with the lattice parameter ($a = 3.905\,\text{Å}$) of cubic STO (see fig. 2(b)) for film epitaxy [10,33,34]. The temperature-dependent sheet resistances of YBCO films show a standard superconducting behaviour with a critical temperature near 90 K (see fig. 2(c)), further confirming the high quality of films.

Results and discussion. – Figure 3 shows the incident energy-dependent EELS spectra of YBCO films. As seen in fig. 3(a), three dominative peaks (near 2.9, 12.9, and 25 eV) are observed, which correspond to three excitations generally. Based on the understanding of RIXS and XAS spectra [5,32,34–38], the first peak A (∼2.9 eV) can be assigned to the excitation from ZRS to UHB, being consistent with the excitation ∼2.6 eV observed in

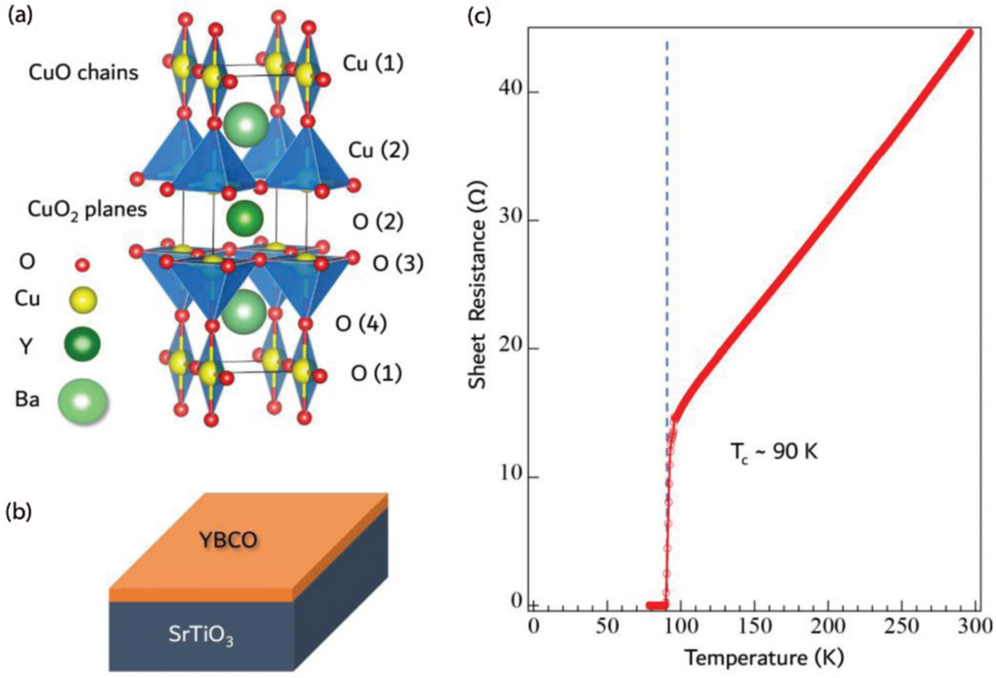

Fig. 2: (a) Schematic of the orthorhombic unit cell of $YBa_2Cu_3O_{7-\delta}$. (b) Sketch of the YBCO thin films grown on an STO single crystal substrate. (c) The temperature-dependent sheet resistance of YBCO films with a critical temperature near 90 K.

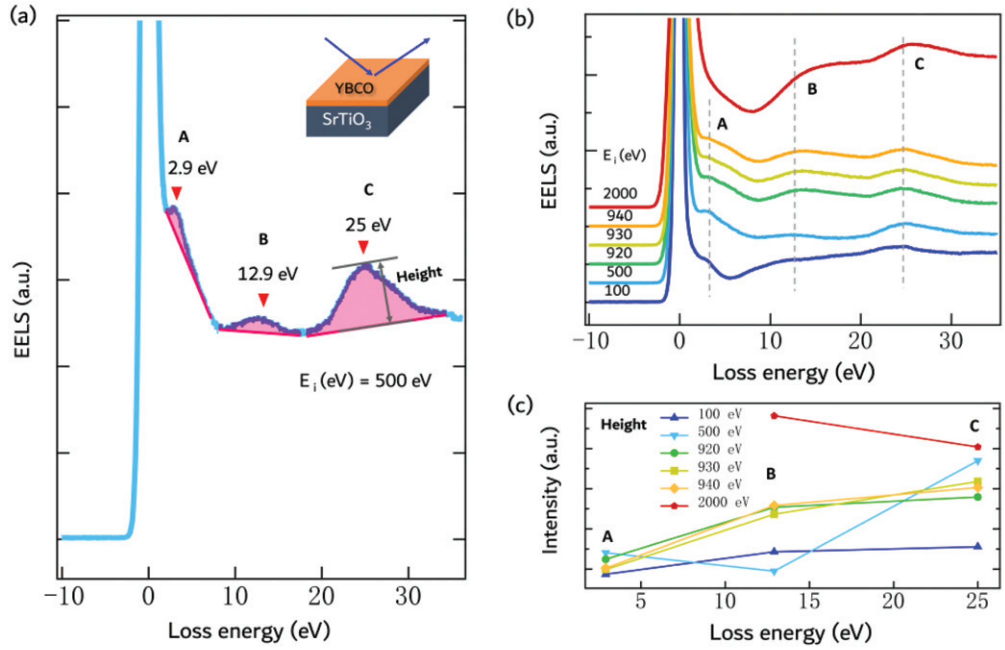

Fig. 3: (a) EELS measurement on YBCO films with incident energy fixed at 500 eV. The three red triangles label the three dominative emergent excitations (A $\sim$ 2.9 eV, B $\sim$ 12.9 eV, and C $\sim$ 25 eV). Inset indicates the experimental setup of EELS. (b) Incident energy-dependent EELS spectra. Three dashed lines indicate the peak positions labeled in (a). (c) Incident energy-dependent signal intensities of the three peaks, which are estimated by the height of the three peaks after substrating a linear background.

optical spectroscopy [39]. The second peak B ($\sim$12.9 eV) can result from a $3p$ to $3d$ excitation, Cu $3p^6 3d^9 \rightarrow$ Cu $3p^5 3d^{10}$ [5,40], which also has been observed in the resonant photoemission spectroscopy [41–43]. The third peak C ($\sim$25 eV) corresponds to the surface plasmon of conduction electrons in YBCO films [43]. To further understand the properties of these three features, we investigate incident energy-dependent EELS spectra. As seen in fig. 3(b),

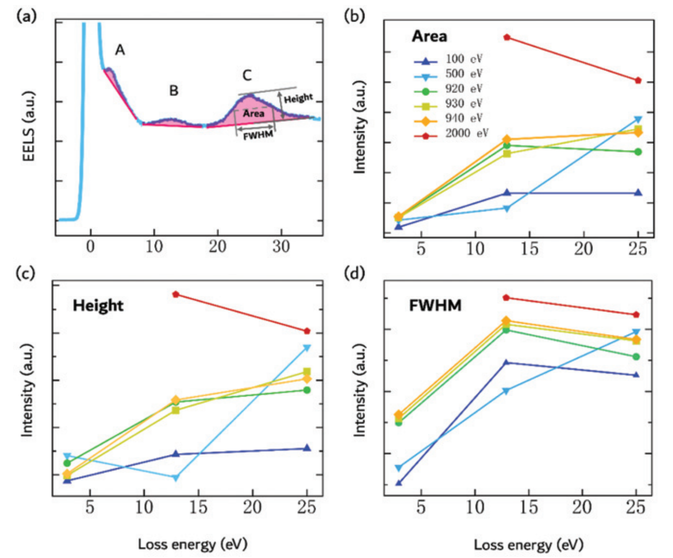

Fig. 4: (a) The estimation of the area, height, and FWHM of the three features. Incident energy-dependent area (b), height (c), and (d) FWHM for YBCO films.

the signals of A, B, and C intensity strongly depend on the incident energy of electron beams. When the incident energy is fixed at 100 eV, the signals of all these three peaks are weak. This behaviour can be due to the fact that the scattering cross sections of these three features are too small for the incident electron beam with energy 100 eV. When increasing the incident energy to 500 eV, the features (A, B, and C) are more distinct, emphasizing the importance of middle-energy EELS on uncovering emergent excitations. However, the signal of feature A becomes too weak to distinguish after further increasing the incident energy to 2000 eV. Considering the FWHM of the elastic peak is much larger for the electron beam with 2000 eV incident energy, the signal of feature A can be buried into the tail of elastic peaks and absent. To reveal the details, we extracted the area, height, and FWHM of A, B, and C (see fig. 3(c) and fig. 4). As seen, the area of peak A has maximum only for the electron beam with 500 eV incident energy, whereas its height almost keeps constant for 500–940 eV. In contrast, the height of peak B is minimum for 500 eV incident energy and it strongly depends on the scale of incident energy.

Next, we discuss the origin of feature A (~2.9 eV), which plays a key role to fully understand the band structure of YBCO near Fermi surface. As seen in fig. 5(a), the picture of the band structure of YBCO is very complex and unclear yet. Generally, the occupied states are composed of ZRS, non-bonding band (NB), Zhang-Rice triplet (T), and lower Hubbard band (LHB) away from the Fermi surface [44–47], whereas the empty state is UHB. To show the occupied and empty states experimentally, we carried out *ex situ* XPS and XAS, respectively. On the one hand, due to the limited energy resolution of XPS, the band structure of occupied state is continuous (see fig. 5(b)).

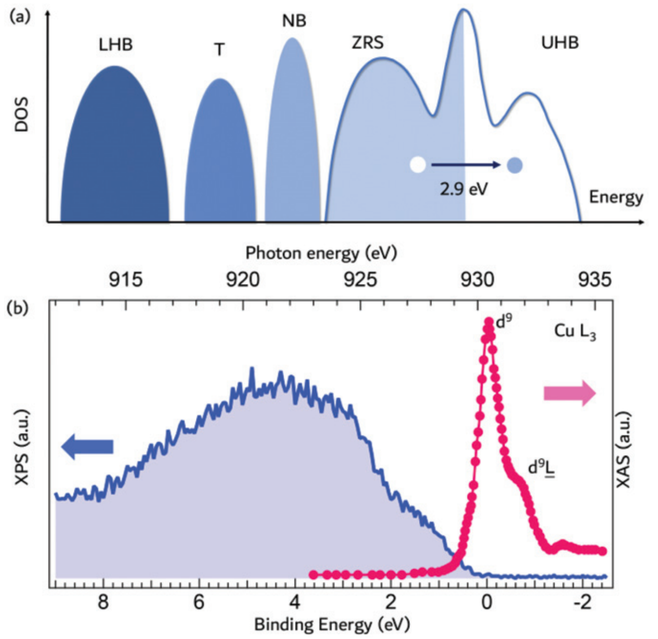

Fig. 5: (a) Sketch of the energy bands of YBCO films. (b) Occupied (blue shadow) and empty states characterized by XPS and XAS, respectively. The XAS data was adapted from ref. [47].

In the XAS spectra, the empty state formed by Cu d^9 (~930.5 eV, near Fermi surface) and $d^9\underline{L}$ (~932 eV) states is clearly shown, indicating the UHB in YBCO films is close to the Fermi surface and its energy range is ~2 eV. Therefore, the excitation A at 2.9 eV in EELS spectra can be a Mott excitation from occupied ZRS to empty UHB states.

In conclusion, we synthesized high-quality YBCO films by PLD and characterized their electronic properties with temperature-dependent electrical transport, XPS, and incident energy-dependent EELS. Three dominative features near 2.9, 12.9, and 25 eV were observed in the EELS spectra, in which the excitation at 2.9 eV could result from the excitation between Zhang-Rice state and upper Hubbard band. Moreover, incident energy-dependent EELS indicate the signals of these three features are strongly dependent on the energy of incident electrons, demonstrating the importance of carrying out middle-energy EELS. Our work provides a route to probe a variety of emergent excitations.

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