Direct observation of bulk charge modulations in optimally-doped Bi$_{1.5}$Pb$_{0.5}$Sr$_{1.54}$CaCu$_2$O$_{8+\delta}$

M. Hashimoto, G. Ghiringhelli, W.-S. Lee, G. Dellea, A. Amorese, C. Mazzoli, K. Kummer, N. B. Brookes, B. Moritz, Y. Yoshida, H. Eisaki, Z. Hussain, T. P. Devereaux, Z.-X. Shen, and L. Braicovich

1 Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, 2575, Sand Hill Road, Menlo Park, California 94025, USA
2 CNR-SPIN, CNISM and Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci 32, I-20133 Milano, Italy
3 Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, CA 94025, USA
4 European Synchrotron Radiation Facility (ESRF), BP 220, F-38043 Grenoble Cedex, France
5 Nanoelectronics Research Institute, AIST, Ibaraki 305-8568, Japan
6 Advanced Light Source, Lawrence Berkeley National Lab, Berkeley, CA 94720, USA
7 Geballe Laboratory for Advanced Materials, Departments of Physics and Applied Physics, Stanford University, CA 94305, USA

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Charge density modulations, recently observed in underdoped high critical-temperature ($T_c$) cuprate superconductors, coexist with the so-called pseudogap [1]. Surface sensitive techniques have suggested that bulk charge modulations could be present also around the summit of the superconducting dome (optimal doping). Using energy-resolved resonant x-ray scattering we have found evidence for such bulk charge modulations, or soft collective charge modes (soft CCMs), in optimally-doped Bi$_{1.5}$Pb$_{0.5}$Sr$_{1.54}$CaCu$_2$O$_{8+\delta}$ (Pb-B2212) around momentum transfer $q_\parallel \sim 0.28$ r.l.u. along the Cu-O bond direction. The signal is stronger at $T \sim T_c$ than at lower temperatures, thereby confirming a competition between charge modulations and superconductivity. These results demonstrate that soft CCMs are not constrained to the underdoped regime but extend at least up to optimal doping.

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A much studied property of high critical-temperature ($T_c$) cuprate superconductors is the opening, below the temperature $T^*$ ($> T_c$), of the so-called pseudogap [1]. The pseudogap is pronounced at low hole-doping, its width and the value of $T^*$ decrease at higher doping, and it vanishes in the overdoped regime. Recent experiments have suggested that the pseudogap is accompanied by a special broken electronic symmetry, often indicated as a modulation of the charge density residing in the CuO$_2$ planes [2–30]. These charge modulations can be seen as soft charge collective modes (soft CCMs), comprising both static charge density waves with no energy loss, and dynamical charge modes having finite mass. If the pseudogap was connected to a broken symmetry, the soft CCMs would be truly static.

Soft CCMs in bulk states have been observed only in a narrow interval of hole doping content; and, even in those cases, no causality link has been verified convincingly with the opening of the pseudogap. Their properties, how they shape the Fermi surface, and how strongly they couple to the phonon dispersion are very active matters of experimental activity. Further, revealing how the soft CCMs change from the static charge order to dynamical charge modes may provide crucial insights about the quantum critical point in the cuprate phase diagram, which has been one of the central questions in the field for many years.

Evidence for soft CCMs in the bulk states around $p = 1/8$ hole doping was provided first indirectly by inelastic neutron scattering (INS), as a magnetic incommensurate peak near the antiferromagnetic points (0.5± ~ 0.125,0.5,L) and (0.5,0.5± ~ 0.125,L) in La$_{1.6-x}$Nd$_{0.4}$Sr$_x$CuO$_4$ (LNSCO) and La$_{0.8}$Sr$_x$CuO$_4$ (LBCO) [2, 3], compounds belonging to the “214” family. Later, the corresponding charge peak was observed by x-ray scattering at the incommensurate wavevector $q_\parallel \sim 0.25$ along the Cu-O bond direction in LBCO, LNSCO [4–8] and La$_{1.8-x}$Eu$_x$Sr$_2$CuO$_4$ (LESCO) [9]. More recently, soft CCMs with incommensurate wavevector $q_\parallel \sim 0.3$ r.l.u. have been observed around $p = 1/8$ in the “123” family and Bi-based cuprates, in YBa$_2$Cu$_3$O$_{6+\delta}$ (YBCO) and NdBa$_2$Cu$_3$O$_{6+\delta}$ (NBCO) [8, 10–14], and in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (B2212) [15] and Bi$_{1.5}$Pb$_{0.5}$Sr$_{1.5}$La$_{0.5}$CuO$_{6+\delta}$ (Bi2201) [16], respectively. Particularly, in YBCO and Bi2212, the temperature dependence of charge modulations strongly indicates that soft CCMs are in competition with superconductivity.

Although soft CCMs have not been observed around optimal doping, evidence for translational symmetry-breaking has been accumulating indirectly from measurements via other techniques. Quantum oscillation studies have revealed evidence for Fermi surface reconstruction under magnetic fields in YBCO [17, 18]. Scanning tunneling microscopy (STM) has shown complex charge modulations of the surface electronic states in Bi2201, Bi2212 and Ca$_{1.88}$Na$_{0.12}$Cu$_2$Cl$_2$ (CNOC) [15, 16, 19–
Angle-resolved photoemission study also has suggested that the dispersion in the antinodal region is consistent with translational symmetry-breaking [26, 28]. These charge modulations have been observed in a wide doping range and the doping dependence follows that of the pseudogap, but questions arise about the correspondence of bulk electronic states with those studied at the surface of samples.

In this Letter, we have studied optimally-doped Bi$_{1.5}$Pb$_{0.6}$Sr$_{1.54}$CaCu$_2$O$_{6+δ}$ (Pb-Bi2212) by high resolution resonant inelastic x-ray scattering (RIXS), focusing on the quasi-elastic spectral component that is sensitive to charge modulations [10]. We have found a peak at $q_{∥} \approx 0.28$ r.l.u. along the Cu-O bond direction, indicating the presence of bulk, incommensurate, soft CCMs in the pseudogap state. The associated peak is weaker at low temperatures, in the superconducting state, than at $T_c = 98$K. The direct observation of soft CCMs in an optimally-doped compound expands very significantly towards the high doping regime the coexistence of superconductivity, the pseudogap, and the tendency towards charge ordering.

The high quality optimally-doped Pb-Bi2212 single crystal was grown by the floating zone method. The hole concentration was optimized by annealing the samples in $N_2$ flow. The RIXS measurements were performed with the AXES spectrometer at the beamline ID08 of the European Synchrotron Radiation Facility (ESRF) [31]. We used the incident photon energy of $~931$ eV, at the maximum of the Cu $L_3$ absorption peak ($2p_{3/2} \rightarrow 3d$ transition). The combined energy resolution was $~0.26$ eV, and the illuminated area on the sample surface was $7 \mu m \times 60 \mu m$. The sample size was approximately $2 \times 2 \times 0.5$ mm$^3$. The sample was measured twice, and for each experimental run it was cleaved in air some minutes before installation inside the ultra-high vacuum measurement chamber ($\sim 3 \times 10^{-9}$ mbar). The sample temperature was varied between $20$K and $95$K. In Bi2212 an incommensurate structural modulation of the BiO planes along the pseudo-tetragonal (110) direction is common, but can be suppressed by Pb doping [26, 28]. We have observed it with RIXS and checked that it does not affect the results along (100), i.e., the Cu-O bond direction.

We show in Fig. 1(a) the experimental geometry. The scattering angle between the incident and outgoing photons was fixed at $130$ deg. The in-plane momentum transfer along the Cu-O bond direction was scanned by rotating the sample. We used both $\pi$ and $\sigma$ polarizations, which are parallel and perpendicular to the scattering plane, respectively. A typical RIXS spectrum, shown in Fig. 1(b) for $q_{∥}=0.25$ r.l.u., consists of $d$-$d$ and charge transfer (CT) excitations at higher energy, magnetic and phonon excitations and the elastic peak at low energies [32]. We show in Figs. 1(c) and 1(d) the intensity maps at $50$ K ($< T_c$) for $q_{∥} \geq 0$ r.l.u. along the Cu-O bond direction, with $\pi$ and $\sigma$ polarizations, respectively. All spectra in all figures are normalized to the total intensity (integrated over the $-3.5$ eV and $1.0$ eV energy loss interval).

The RIXS spectra of Fig. 1(c), measured with $\pi$ polarization, are dominated by single spin-flip excitations, particularly at large $q_{∥}$ values [33, 34]. The dashed line highlights the dispersion of a broad spectral feature that reaches the maximum energy of $~350$ meV at the zone boundary. These are paramagnon excitations, already observed by RIXS in LSCO, YBCO, B2212 [35–38] and in the Fe-based superconductors [39]. On the other hand, the map of Fig. 1(d), measured with $\sigma$ polarization, is composed of non-spin-flip and double spin-flip processes (elastic scattering, charge excitations, phonons and bi-magnons)[33, 34]. In this work, we focus on the low-energy excitations with $\sigma$ polarization, particularly around $q_{∥} ~0.25$ r.l.u., where the quasi-elastic signal reaches a maximum intensity. This type of signal, although weak, is similar to the charge density wave signature detected in RIXS spectra of YBCO by Ghiringhelli et al. [10].
We show in Figs. 2(a) and 2(b) the color intensity maps of the RIXS spectra at $T = 95 K \ (\sim T_c)$ and $T = 20 K \ (\ll T_c)$, respectively. At both temperatures the low energy part of the spectra is stronger at $q_{\parallel} \simeq 0.28$ r.l.u., but the peak appears more intense at $T \simeq T_c$, as made evident by the map of Fig. 2(c) obtained by subtracting the low-$T$ from the high-$T$ data sets. In the difference map the peak at $q_{\parallel} \simeq 0.28$ r.l.u. is very close to the zero energy loss position. However, it is not possible to conclude whether the peak is exactly at zero energy loss due to experimental energy resolution.

To evaluate this temperature dependence more quantitatively, we show in Fig. 3(a) the $q$ dependence of the RIXS spectra at low energies at $T \sim T_c$ (red) and $T \ll T_c$ (blue). Differences between the two temperatures are highlighted by green shading. This representation confirms the effect close to zero energy loss at $q_{\parallel} \simeq 0.28$ r.l.u. This is seen more clearly in the constant-energy cuts of Fig. 3(b), obtained by integrating the intensity over a 200 meV band centered at zero energy loss at 20K and 95K in red circles and blue squares, respectively. We can thus evaluate the full width at half maximum (FWHM) of the peak at $q_{\parallel} \simeq 0.28$ r.l.u. to be $>0.05$ r.l.u. at $T_c$. This peak becomes significantly weaker and possibly broader at lower temperatures but remains visible down to 20K. Also in this representation, the difference between 96K and 20K [open green triangles in Fig. 3(b)] highlights the peak at $q_{\parallel} \sim 0.28$ r.l.u. As a reference, we report in Fig. 3(c) the corresponding -0.4±0.1 eV constant-energy cuts. At this energy spectra are dominated by the multi-magnon excitations and the result shows an almost negligible momentum and temperature dependence. We note that the quasi-elastic intensities at 50K from experiment 2 [black triangles in Fig. 3(b)] are weaker than those for experiment 1, although the enhancement of the quasi-elastic signal at $q_{\parallel} \simeq 0.28$ r.l.u. is observed consistently. This is probably due to differences in surface quality. To better compare the intensity profiles along $q_{\parallel}$ the intensity at 50K from experiment 2 is multiplied by a factor of 1.25.

The peak of the quasi-elastic signal at $q_{\parallel} \simeq 0.28$ r.l.u. suggests the existence of soft CCMs with a periodicity of $\sim 3.57$ lattice units in the bulk state of optimally-doped Bi2212. The result is very similar to previous scattering reports from underdoped samples. The only previous observation of soft CCMs in an optimally-doped sample is on LBCO, which however undergoes a structural transition not present for other cuprates. There the stabilization of static charge order is abrupt across the orthorhombic-tetragonal transition at 56K [5], although the soft CCM signal was detected with RIXS up to 85K [7]. Therefore, these previous results (see table I) cannot conclusively establish whether soft CCMs exist in a wider doping range including optimal doping ($\sim$16%).

On the other hand, it has been reported by STM that Bi2212 [19–23] and CNCCOC [22] show a short range chequerboard or stripe-like order. The characteristic wave vector is $q_{\parallel} \simeq 0.25$ r.l.u. along the Cu-O bond direction [19–23]. Further, the dispersion in the pseudogap state, determined by ARPES, is consistent with short correlation-length charge modulations [26, 28]. However, STM and ARPES are surface sensitive probes, and cannot confirm the bulk electronic states. Our RIXS results on Bi2212 demonstrate that bulk charge modulations ex-
The correlation length as deduced from the full width at half maximum is the correlation length as deduced from the full width at half maximum $w$ of the scattering peak, $\xi = a/(\pi \times w)$.

| Sample  | $p$  | $T_c$ (r.l.u.) | $q_0$ (r.l.u.) | $\xi$ (Å) | refs. |
|---------|------|----------------|---------------|----------|------|
| B2201  | 0.115| 15             | 0.265         | 26       | [16] |
| B2201  | 0.130| 22             | 0.257         | 23       | [16] |
| B2201  | 0.145| 30             | 0.243         | 21       | [16] |
| Bi2212 | 0.09 | 45             | 0.30          | 24       | [15] |
| Bi2212 | 0.160| 98             | 0.28          | <24 (at $T_c$) this work |
| YBCO   | 0.115| 61             | 0.32          | $\sim$60 (at $T_c$) [8, 10] |
| LBCO   | 0.125| 2.5            | 0.236         | $\sim$200 [4, 6–8] |
| LBCO   | 0.155| 30             | 0.244         | $\sim$240 (15–25 K) [4, 6–8] |

The drastic decrease of the $q_0$ of $\sim 0.28$ r.l.u. peak below $T_c$ [Fig. 3(b)] shows that soft CCMs are suppressed by superconductivity due to competition between these two order parameters, in analogy to what has been observed in YBCO, where the soft CCM peak weakens and broadens below $T_c$ but is restored by an external magnetic field [8, 10, 11, 13]. We note that at $T_c$ the soft CCM peak is broader in Bi2212 than in YBCO, and that the incommensurate wave vector is slightly different. Data summarized in Table I we can deduce that the soft CCM wave-vector is strongly dependent on the material within the 0.24–0.31 r.l.u. range, and the intensity and width of the soft CCM peak is influenced by the compositional disorder, which may be stronger in Bi2201 and Bi2212, and by the possible coupling with lattice structure (e.g. in LBCO). To detect broader and weaker modulation of the quasi-elastic signal in Bi2212, the energy resolution of RIXS plays a crucial role. With conventional elastic scattering measurements that inevitably integrate over the whole inelastic spectrum shown in Fig. 1(a), the tiny quasi-elastic signal would be easily lost, buried under the large inelastic signal [10]. It is also noteworthy that ARPES has suggested a competition between the pseudogap and superconducting order parameters in Bi2212 [40], establishing an important connection to the competition between soft CCMs and superconducting order parameters encountered in the present study. Further, such a phase competition could results in the recently proposed phase diagram [41] where the phase boundary for the competing order bends back in the superconducting dome.

Charge modulations are often driven by Fermi surface nesting, as it has been discussed also for the cuprates. The Fermi momentum at the Brillouin zone boundary (antinode) for optimally-doped Bi2212 is $\sim 0.1 \pi/a$ for the antibonding band and $\sim 0.2 \pi/a$ for the bonding band, where $a$ is the in-plane lattice constant [40]. Neither of the two nesting vectors appear close to $q_0 \sim 0.28$ r.l.u., which has been observed here by RIXS, indicating that a soft CCM gap would lie above the Fermi level. This suggests that soft CCMs are not driven by the Fermi surface nesting between the antinodes, also in agreement with the non-trivial doping and material dependences of the wave vector (Table I) and the recent study by de Silva Neto et al. in Ref. 15. Our RIXS results cannot either be connected with the Fermi surface reconstruction observed by quantum oscillations [17, 18]. Further systematic studies are required to understand the different $q_0$’s in different materials (Table I).

Having firmly established the existence of soft CCM at optimal doping, it is worth considering the future implications of this result. The soft CCMs not being related with a Fermi surface nesting vector should not stop the search for a link between the pseudogap and the soft CCMs in superconducting cuprates up to optimal doping and even in the overdoped regime. In fact the two phenomena evidently coexist. These facts suggest that an incipient charge density instability is inherent to the pseudogap regime. Although our result cannot conclude whether the soft CCMs are fluctuating or static, i.e., whether they have finite mass or not, the short correlation length in the optimally-doped sample may be consistent with the tendency towards dynamical charge modes as the doping level increases. The observation of the soft CCM peak gaining mass, decreasing in intensity, and increasing in width as the phase boundary is crossed would be a compelling evidence for an underlying quantum critical point and the competition with superconductivity, which bears further study with more sensitive and selective x-ray probes in the future.

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