Fluctuating charge-density waves in a cuprate superconductor


I. Film synthesis & characterization

The films were synthesized using atomic-layer-by-layer molecular beam epitaxy (ALL-MBE)\textsuperscript{1-4}. We used single-crystal LaSrAlO\textsubscript{4} substrates polished to epitaxial smoothness, with the (001) axis perpendicular to the surface. During the film growth the substrates were kept at the nominal temperature $T_s \approx 630$ °C, (as per pyrometer reading), in atmosphere of essentially pure ozone at the pressure of $p \approx 10^{-5}$ Torr. The growth kinetics were controlled by pneumatically actuated source shuttering. The growth rate was kept very low, at about ~0.05 Å/sec. The atomic fluxes were monitored in real time using an Atomic Absorption Spectroscopy system. The absolute deposition rates were checked before each growth using a quartz crystal balance, which was in turn calibrated against the results of a range of \textit{ex-situ} measurements (Rutherford backscattering, grazing-angle X-ray reflectance oscillations, X-ray diffraction finite-thickness fringes, and the film thickness measurements by Atomic Force Microscopy and by a mechanical profilometer).

The film growth was monitored in real time by Reflection High Energy Electron Diffraction (RHEED). In Fig. S1, we show the RHEED pattern obtained from the La\textsubscript{1.9}Sr\textsubscript{0.1}CuO\textsubscript{4} film surface. In Fig. S2, we show RHEED oscillations – the intensity integrated over a small area around the specular reflection spot and plotted as a function of time – as recorded during the synthesis of the same film. The graph shows pronounced oscillations; the maxima are reached each time when a molecular layer, 6.6 Å thick, is completed and the surface becomes atomically flat. Similar RHEED patterns have been observed and recorded during growth of all the other La\textsubscript{2-x}Sr\textsubscript{x}CuO\textsubscript{4} films studied in this work as control samples.

After growth, the La\textsubscript{1.9}Sr\textsubscript{0.1}CuO\textsubscript{4} film was cooled in ozone down to $T_s = 300$ °C; the ozone supply was then closed and the film annealed for 30 minutes in high vacuum to remove any interstitial oxygen, and then cooled down to the room temperature. In the case of La\textsubscript{1.86}Sr\textsubscript{0.16}CuO\textsubscript{4}, where no
significant interstitial oxygen occupation has been found so far, the film was cooled in ozone down to $T_s = 250$ °C at which point the ozone was shut off and the film cooled down to room temperature in high vacuum.

![RHEED pattern](image)

**Figure S1**: (a) RHEED pattern recorded during growth of a La$_{1.9}$Sr$_{0.1}$CuO$_4$ film on a single-crystal LaSrAlO$_4$ substrate. The electron beam is impinging along the (100) direction. The distance between the main streaks corresponds to the inverse of the in-plane lattice constant ($a_0 = 3.8$ Å) of La$_{1.9}$Sr$_{0.1}$CuO$_4$. The four weaker sidebands indicate some surface reconstruction, with 5 times larger superstructure period. (b) The oscillations in the intensity of the specular reflection as a function of time recorded during growth of the same film. The RHEED oscillations originate from periodic roughening and smoothening of the surface; the intensity reaches a maximum after each molecular layer is completed and the surface gets atomically smooth.

The films’ quality was double-checked after the growth (*ex situ*) by Atomic Force Microscopy (AFM), X-ray diffraction (XRD) crystallography, and mutual-inductance measurements. No secondary-phase precipitates, grains, or grain boundaries were seen by AFM, and the measured rms surface roughness was less than 0.4 nm, significantly less than the unit cell height (1.32 nm). Excellent film crystallinity and absence of any unwanted phases was also confirmed by X-ray diffraction crystallography.

Mutual inductance measurements were done in the transmission geometry, i.e., the cuprate film was situated between the drive and pick-up coils. The data were acquired at the frequency $\nu = 10$ kHz. The drive coil current excitation was $I_{dr} = 5 \mu A$; given the geometry of the coil assembly this corresponds to the screening current density in the film of $j_f \approx 10^3$ A/cm$^2$ at the peak value. The data displayed in Fig. S3 indicate $T_c \approx 26$ K in La$_{1.9}$Sr$_{0.1}$CuO$_4$ and $T_c \approx 38.5$ K in La$_{1.84}$Sr$_{0.16}$CuO$_4$. (We have verified in numerous previous experiments that the temperature at which the inductive screening response onset coincides with the temperature at which the sample resistance has dropped to zero.)
II. Pump-probe & transient grating: detailed experimental methods

Pump-probe (PP) results were obtained using a standard optical pump-probe (PP) technique.$^{59,510}$ A single, spatially Gaussian “pump” beam excites the sample uniformly and the resulting dynamical response is monitored by the normalized change in the reflectivity ($\Delta R(t)/R$) of a separate “probe” beam as a function of time delay $t$ between the pump and probe. Transient grating (TG) results were obtained by using a heterodyne box-car detection scheme.$^{511}$ Two pump beams are combined at the surface of the sample at an angle $\theta$ between them to produce an interference pattern of wavelength $\Lambda = \lambda/(2\sin(\theta/2))$ which in turn produces a sinusoidal varying transient photo-excitation density. If the photo-excitations affect the refractive index of the sample, the interfering pump beams generate a transient diffraction grating at the sample surface. To study the time evolution of this grating, and thus the time evolution of the corresponding photo-excitations, a third beam, “the probe”, is impinged upon the sample and is both specularly reflected and diffracted from the grating. The reflected probe beam encodes information about the average excitation while the diffracted beam encodes information of the $q = 2\pi/\Lambda$ sinusoidal excitation.

In order to detect the diffracted beam, we utilize a box-car geometry$^{511}$ that arranges the two pump beams and the probe beam parallel to each other such that the laser spots from each beam lie at three corners of a rectangle in a plane perpendicular to their path. A lens is then used to focus the three beams onto the sample. The resulting diffracted probe beam passes through the

Figure S2. (a) The real (reactive) part of the mutual inductance in La$_{1.9}$Sr$_{0.1}$CuO$_4$ showing diamagnetic screening below $T_c \approx 26$ K. (b) The same, for La$_{1.84}$Sr$_{0.16}$CuO$_4$ with $T_c \approx 38.5$ K.
fourth corner of the rectangle. In this way, the direction of the weak diffracted beam is conveniently determined due to phase matching. However, the diffracted signal can be difficult to measure accurately using standard methods of intensity detection. In order to enhance the measurement sensitivity, we employ heterodyne detection in which a fourth beam, the local oscillator (LO), is sent along the fourth corner of the rectangle in the box-car geometry. The diffracted probe signal is then collinear with the reflected LO. As shown below, the measured signal is dependent on the phase between the probe beam and the LO. To calibrate the phase we utilize the symmetry between the LO and the probe beam since they are interchangeable in the box-car geometry. We refer to these beams as P1 and P2.

![Figure S3](image-url)

**Figure S3.** Experimental setup for transient grating. The pump and probe beams are focused onto the phase mask (PM) which splits each beam into two. The beams are then collimated using lens L1. Each of the probe beams passes through a thin cover slip (CS). One cover slip is held fixed while the other can be rotated by angle $\theta$ to alter the phase between the two probe arms. Lens L2 is then used to focus the four beams onto the sample.

A schematic of the experimental setup is shown in Fig S3. The pump and the probe beams are focused onto a transmission grating (phase mask) which splits each beam into two. If we block the reflected probe arm P2, the signal at the detector ($I_s$) is the sum of the reflected P1 and the diffracted P2:

$$I_s \propto |E_{P1}r_0|^2 + 2|E_{P1}|^2|r_0||R_{PP}|\cos(\phi) + |R_{TG}|\cos(\phi - \theta)$$

where $E_{P1}$ is the electric field of P1 which is equal to the electric field of P2 ($E_{P2}$), $r_0$ is the equilibrium reflection coefficient, $R_{PP}$ is the change in the reflection coefficient for uniform excitation (i.e., at $q = 0$), $R_{TG}$ is the change in the reflection coefficient for sinusoidal excitation (i.e., at
\( q = 2\pi/\Lambda \), \( \phi \) is the phase of \( R_{PP} \) relative to that of \( r_0 \) and \( \theta \) is the phase of \( E_{P1} \) relative to that of \( E_{P2} \). If the reflected probe \( P1 \) is now blocked, the sign of \( \theta \) is changed:

\[
I_s \propto |E_{P1}|^2 + 2|E_{P1}|^2 |r_0| (|R_{PP}| \cos(\phi) + |R_{TG}| \cos(\phi + \theta))
\]  

(2)

We isolate the second term in each equation by modulating the pump beam using a photo-elastic modulator (PEM) at a frequency of \( \sim 100 \text{ kHz} \). Standard lock-in techniques are then used to isolate the second terms. To determine \( \theta \), we place cover slips (CS in Fig. S3) in the path of each probe arm. One cover slip is fixed while the other is rotated to vary the phase \( \theta \) between the two probe arms.

**Figure S4.** Calibration of the phase. The cover slip is rotated in steps of 1° and transients are recorded at each value of the angle for each probe arm. The initial maximum value is plotted with the cover slip angle and fitted to sinusoidal fits (shown above). From the intersection points between the two curves we obtain the cover slip angles corresponding to \( \theta = 0, \pi/2 \) and \( \pi \).

To calibrate this phase, we obtain time-resolved traces at various values of \( \theta \) for each probe arm. We then plot (Fig. S4) the initial peak value for each trace with the cover slip angle to obtain cover slip angles that correspond to \( \theta = 0, \pi/2 \) and \( \pi \). Performing measurements at these values of \( \theta \) gives us the following transient signals from which we can solve for both \( R_{PP} \) and \( R_{TG} \):

\[
|R_{PP}| \cos(\phi) + |R_{TG}| \cos(\phi)
\]  

(3)

\[
|R_{PP}| \cos(\phi) + |R_{TG}| \sin(\phi)
\]  

(4)

\[
|R_{PP}| \cos(\phi) - |R_{TG}| \cos(\phi)
\]  

(5)
We refer to \( R_{PP} \) as PP and to \( R_{TG} \) as TG in the Main Text. The procedure used to calibrate \( \theta \) is only dependent upon alignment and not upon the properties of the sample. Thus, the calibration was carried out once per data run. Tests of the calibration’s stability were conducted independently of the acquisition for this experiment, and it was found that the drift in calibration over long times resulted in error that was smaller than the noise floor of the experiment. This indicated that the data acquisition was robust over the entire acquisition period.

**III. Data extraction & fitting procedures**

To extract information about the lifetime and frequency of the AM mode, we fit the data in the pump-probe (PP) geometry to the DECP functional form:

\[
A e^{-t/\tau_A} \sin(2\pi f_A t) + B (1 - e^{-t/\tau_A} \cos(2\pi f_A t)) + C/|t/\tau_{th}| + D \delta(t) + E \tag{6}
\]

This function was convolved with the Gaussian shape of the laser pulse: \( y = e^{-(t-t_0)/\tau_{st}} \). The first term in eq. (6) represents the response of the AM mode with \( A \) as its amplitude, \( \tau_A \) as its lifetime and \( f_A \) as its frequency. In our fits \( B = 0 \) and we only use the term in \( A \) in the main text. The third term is used to model the electronic decay above and below \( T_c \). The fourth term is used to isolate the initial fast spike we observe in our data at all temperatures. The last term is a constant used to model any long-lived change in reflectivity.

This fitting equation ensures that we can separate out the amplitudon response from the electronic decay. All of our analysis of the AM is based on the first term in eq. (6); the term in \( C \) is used only as a phenomenological function to eliminate the background so that we could isolate the oscillating component. We found that the term \( \propto C \) provides a better fit to our data than an exponential function. The choice of this function does not affect the measured amplitudon lifetime and frequency as their time scales are different.

To extract information about the phason, we first fit the PP response for 100 K using the phenomenological fit in the second term in eq. (6). The resulting fit was then subtracted from the raw TG data (Main text, Fig. 4a) so we could study the TG response independent of the unchanging normal component observed by the PP transients. The resulting TG – PP response is then the response from the overdamped phason and is fitted to a single exponential \( P e^{-(t)/\tau_P} \).
IV. TG data at different grating wave-vectors

In order to further rule out intrinsic damping as the only source of the phason lifetime, we acquired TG data at both $\Lambda = 6 \, \mu m$ and at $\Lambda = 2.5 \, \mu m$. If the lifetime of the phason were to depend on intrinsic damping only then it should also depend on the wave-vector of the phason since the damping rate for an overdamped mode is dependent on the wave-vector of that mode. To study this, we carried out the experiment in the transient grating geometry at $\Lambda = 2.5 \, \mu m$ and found that the TG data matched with the TG data at $\Lambda = 6 \, \mu m$ (Fig. S5). Thus, the lifetime of the phason does not change with changing wave-vector. This is an additional indication that the lifetime is not determined by intrinsic damping but rather by the lifetime of the CDW fluctuation.

![Graph showing TG data at different wave-vectors](image)

**Figure S5.** TG data at $\Lambda = 6 \, \mu m$ and at $\Lambda = 2.5 \, \mu m$ at 5 K. Changing the wave-vector of the grating does not change the TG signal, indicating that the phason lifetime is independent of the phason wave-vector and is thus determined by the CDW fluctuation lifetime.

V. Data from the LSAO substrate

The thickness of the LSCO thin films is about 50 nm which is about half the optical penetration depth in LSCO (~ 100 nm). In order to rule out any possible signal from the underlying LSAO substrate, we took data on a half-etched sample (half of the LSCO thin-film was etched away from the LSAO substrate). We first found pump-probe signal from the LSCO thin film and then translated the sample such that the pump and the probe overlapped at the LSAO substrate. The results are shown in Fig. S6. As shown, there is no evident signal from the LSAO substrate.
Concerning the possible role of the LSAO-LSCO interface, we note that the optical penetration depth of the LSCO films is ~100 nm, while the thickness of LSCO-LSAO interface layer is ~1 nm (see refs S14 and S15). Furthermore, this interfacial layer is disordered and insulating, and it is buried under a 50 nm thick metallic LSCO film. So, the contribution of the interface layer to the measured reflectance is quite small.

To further rule out the LSAO substrate or the interface between LSAO and LSCO as a possible origin for the amplitudon or phason, we note that our observed modes clearly disappear for the optimally and overdoped samples and show a small kink in their temperature dependence near T_c (Main Text). However, this should not be the case if the mode originated from the substrate or the interface.

Taken together, the above observations rule out the possibility that the observed modes in our data could possibly originate from the LSAO substrate, or from the LCSO-LSAO interface.

References


