I. INTRODUCTION

Terahertz spectroscopy has emerged as a powerful probe of non-equilibrium dynamics in quantum materials [1]. More recently, the generation of intense terahertz (THz) high-field pulses has enabled nonlinear drive of the low energy electrodynamics, offering new insights into the many-body response while also providing a route for on-demand control of emergent properties [2]. Superconductors are particularly amenable to high-field interrogation and manipulation of the condensate with terahertz pulses. This includes the Higgs amplitude mode in conventional superconductors where light couples nonlinearly to the condensate, driving oscillations of the order parameter amplitude at twice the pump frequency, leading to harmonic generation [6,11]. Higgs mode spectroscopy has been extended to cuprate superconductors with novel mode dynamics associated with the d-wave gap symmetry and to iron pnictides where multiband effects have been observed [12,14].

In the high-$T_c$ cuprates the phase mode response (Josephson plasma mode – JPM) manifests at THz frequencies [15,16]. Briefly, the copper-oxygen planes are weakly interacting and Josephson coupling dictates c-axis Cooper pair tunneling based on the interlayer phase difference of the superconducting order parameter between adjacent planes. This results in a plasma edge in the c-axis reflectivity at the Josephson plasma frequency $\omega_p$. For single layer cuprates, $\omega_p$ typically manifests at THz frequencies with $\omega_p^2$ proportional to the condensate density $n_s$ (e.g., see Fig.1 discussed in more detail below). As such, the JPM serves as a reporter of the condensate response which includes nonlinearities such as field-induced renormalization of $\omega_p$ and harmonic generation [18,21].

We investigate the nonlinear spectral response of c-axis La$_{1.85}$Sr$_{0.15}$CuO$_4$ (LSCO) using high field THz-TDS as a function of field strength and temperature. A redshift of $\omega_p$ with increasing field (2.4 kV/cm up to 80 kV/cm) arises from the Josephson effect. With increasing temperature the maximum redshift increases from $\sim$110 GHz at 10 K to $\sim$220 GHz at 32 K. This temperature dependent frequency shift cannot be explained solely using the Josephson equations which predict a high-field shift of the JPM is a constant fraction of the equilibrium JPM at each temperature. This is the opposite of the observed behavior, and could be related to increased quasiparticle damping at higher temperatures. Commenurate with this is broadband third harmonic generation above the plasma edge which exhibits a slight increase with decreasing temperature below $T_c$, dropping off in the normal state. The temperature dependence is compared with calculations based on the theory in Reference [21]. The qualitative agreement between calculations and experiment suggests that the temperature dependence is related to the competing factors of Josephson coupling strength, the resonance of the pump with the JPM, thermal population of excited plasmon states, and quasiparticle damping. For our broadband drive, we estimate a power conversion efficiency of $\sim 6 \times 10^{-5}$.

II. METHODS

THz radiation is generated via optical rectification using a Ti:sapphire regenerative amplifier (1 KHz, 800 nm, 100 fs, 3 mJ) using tilted pulse front generation in a MgLiNbO$_3$(LNO) crystal [22,23]. The THz output from the LNO crystal surface is collimated with a lens ($f = 120$ mm) and focused onto the sample with an angle of incidence of 15° and a beam diameter of $\sim$2.3 mm FWHM (pulse energy $\sim$2 $\mu$J). Before reaching the sample, the THz light passes through a pair of wire grid polarizers which are used to attenuate the THz pulse, covering the range from 2 - 80 kV/cm. The reflected beam from the sample surface is collected and focused onto a 300 $\mu$m thick (110) GaP crystal for EO sampling. The GaP crys-
III. RESULTS

We first measured the temperature dependent c-axis response at the lowest available electric field to characterize the linear response. The c-axis reflectivity is plotted in Fig. 1(a) for several temperatures above and below $T_c = 38$ K, and shows a clear plasma edge emerge and sharpen with decreasing temperature from 32 K to 10 K, coinciding with an increase in superconducting condensate. The low temperature (10K) plasma edge $\omega_p$ is at $\sim 1.7$ THz is in agreement with previous c-axis measurements for $x = 0.15$ doping [25]. Figure 2(b) shows the plasma frequency $\omega_p(T)$ normalized by the low temperature measurement $\omega_p(10$ K) and scales with BCS-like order parameter temperature dependence, as $\omega_p^2 \propto \tanh(2.6 \sqrt{T_c/T-1})$. The inset of Fig. 1(b) displays the normalized loss function $-\text{Im}(1/\epsilon)$ at each temperature.

For frequencies below $\omega_p$ the reflectivity is $\sim$90%, whereas near-unity reflection is expected as $\omega \rightarrow 0$. This deviation is attributed to imperfectly focusing since the sample size and beam diameter are comparable. This effect is more pronounced at lower frequencies as the focused THz beam diameter is frequency dependent. However, the low temperature $\omega_p(T)$ (and associated temperature dependence) is consistent with previous studies for $x = 0.15$ doping, indicative of a high-quality crystal. The reflectivity presented in Fig. 1 and 2 are normalized to characterize the linear response. The c-axis reflectivity is plotted in Fig. 1(a) for several temperatures above and below $T_c = 38$ K, and shows a clear plasma edge emerge and sharpen with decreasing temperature from 32 K to 10 K, coinciding with an increase in superconducting condensate. The low temperature (10K) plasma edge $\omega_p$ is at $\sim 1.7$ THz is in agreement with previous c-axis measurements for $x = 0.15$ doping [25]. Figure 2(b) shows the plasma frequency $\omega_p(T)$ normalized by the low temperature measurement $\omega_p(10$ K) and scales with BCS-like order parameter temperature dependence, as $\omega_p^2 \propto \tanh(2.6 \sqrt{T_c/T-1})$. The inset of Fig. 1(b) displays the normalized loss function $-\text{Im}(1/\epsilon)$ at each temperature.

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The nonlinear terahertz reflectivity results are shown in Fig. 2b-f. As shown in Fig. 2b (base temperature 10 K), two pronounced effects occur: There is a redshift of the plasma edge with increasing field and, above the plasma edge, there is an increase in the reflectivity corresponding to third harmonic generation (as described in greater detail below). When increasing temperature, there is a decrease in the condensate density, but there is still a clear redshift in the plasma edge and enhanced reflectivity. At 32 K (Fig. 2e), the plasma edge shift as a function of field is $\sim 220$ GHz, larger than the $\sim 110$ GHz shift at 10 K, but the reflectivity increase is relatively small. Above $T_c$ (Fig. 2f), there is no longer a superconducting response and the nonlinear increase in reflectivity is minimal to nonexistent. The nonlinear reflectivity data in Figure 2 is informative as it reveals both the JPM redshift and the increase in reflectivity above $\omega_p$. However, the increase in reflectivity requires a more careful analysis as we now discuss.

Figure 3a plots the spectral amplitude of the electric fields reflected from the LSCO at 10K, comparing the reflectivity of the nonlinear (NL) and linear (L) response. The red curve is $E_{NL}^{\omega}(T)$ at the highest field (80kV/cm). The black curve is $E_L^{\omega}$ at the lowest field, appropriately normalized to enable quantitative comparison with the spectral changes that arise in the nonlinear regime [29].

FIG. 1. (a) Low field c-axis reflectivity of La$_{1.85}$Sr$_{0.15}$CuO$_4$ at several temperatures. At 10K, $\omega_p$ is $\sim 1.7$ THz. (b) Temperature dependence of $\omega_p$ below $T_c$ normalized to the low temperature measurement $\omega_p(T = 10$ K). The dashed line is a fit to a BCS-like order parameter temperature dependence, as described further in the text. The inset shows the (normalized) loss function, $-\text{Im}(1/\epsilon)$, using the same legend in panel (a).
FIG. 2. La$_{1.85}$Sr$_{0.15}$CuO$_4$ c-axis THz reflectivity. (a) Schematic of experimental setup. Panels (b)-(f) show the reflectivity taken at temperatures 10 K, 20 K, 27 K, 32 K, and 45 K respectively. At each temperature, the reflectivity was measured for fields ranging from 2.4 – 80 kV/cm as indicated in the legend.

As with the reflectivity data in Figure 2, the redshift of the plasma edge is evident when comparing $E^*_L(\omega)$ and $E_{NL}(\omega)$ in Fig. 3a. Moreover, the increase in the spectral amplitude above the plasma edge is also evident (blue shaded region). The peak spectral amplitude of the terahertz pulses is at $\sim$0.65 THz. The second peak in $E_{NL}(\omega)$ is at $\sim$1.9 THz, consistent with third harmonic generation. The data in Fig. 3a reveals that the nonlinear signal is relatively small in comparison to the peak amplitude of the incident pulse (i.e.,$E^*_L(\omega)$) at 0.65 THz, but considerably larger than the spectral spectral amplitude of $E^*_L(\omega)$ between 2 - 3 THz. Nonetheless, the dynamic range is sufficient to enable a determination of the field dependence of the integrated spectral amplitude above the plasma edge (Fig. 3b), which further verifies that the enhanced signal arises from third harmonic generation (THG).

The THG response in Fig. 3(b) is quantified by integrating

$$E_{3\omega} \equiv \int \left[ E_{NL}(\omega) - E^*_L(\omega) \right] d\omega$$  \hspace{1cm} (1)

where $E_{NL}(\omega)$ and $E^*_L(\omega)$ are the reflected signals from the sample as defined above. To avoid integrating over the Josephson plasma edge, the integration is taken from 1.8 THz to 2.4 THz. Figure 3(b) displays the magnitude of the third harmonic $E_{3\omega}$ as a function of field strength at 10 K, along with a cubic polynomial fit (red line, $R$-squared value of 0.99). This further confirms the reflectivity/spectral amplitude increase arises from third harmonic generation in the superconducting phase. The lowest field strengths have more third harmonic intensity than the cubic fit, which may be attributed to the fit over-favoring the highest fields.

IV. DISCUSSION

The experimental observations can be further understood by examining the higher order terms in the phase dynamics of layered superconductors described by the Josephson equations [18, 30].

In a layered superconductor, the interlayer phase difference $\theta(t)$ changes with time according to the second Josephson equation

$$\frac{d\theta(t)}{dt} = \frac{2e}{\hbar} E(t)$$  \hspace{1cm} (2)

where $2e$ is the cooper pair charge, $d$ is the interlayer spacing (\sim1 nm), $\hbar$ is Planck’s constant divided by $2\pi$, and $E(t) = E_0\sin(\omega_{pump}t)$ is an electric field along the c-axis with $E_0$ the field strength which oscillates at frequency $\omega_{pump}$. Solving equation 2 yields the relation $\theta(t) = (2eE_0/\hbar)\cos(\omega_{pump}t)$. Since the c-axis superfluid density $\rho_c$ scales as the order parameter phase difference, $\rho_c \propto \cos\theta$ and $\rho_c \propto \omega_p^2$ as shown in Fig. 3(b), the plasma frequency renormalizes according to $\omega_{NL}^2 = \omega_p^2\cos\theta(t)$ where $\omega_{NL}$ is the new Josephson plasma frequency under intense field strengths. By inserting $\theta(t)$ and expanding the $\omega_{NL}$ we arrive at
$$\omega_{JPM}^2 = \omega_{JPM0}^2 \cos(\theta) = \omega_{JPM0}^2 \cos \left[ \theta_0 \cos(\omega_{pump} t) \right]$$

$$\approx \omega_{JPM0}^2 \left[ 1 - \frac{\theta_0^2}{4} \cos(2\omega_{pump} t) + \ldots \right]$$

(3)

where $\theta_0 = 2e\phi_0/\hbar$. From this expansion we can see that the next leading order term is subtracting, resulting in a redshift in the plasma frequency. This is what is observed below $T_c$ for high fields as shown in Fig. 2.

The tunneling interlayer current depends on the phase difference as $I(t) = I_0 \sin[\theta(t)]$, and solving for $I(t)$ gives

$$I(t) = I_0 \sin \left[ \theta_0 \cos(\omega_{pump} t) \right]$$

$$\approx I_0 \left[ \theta_0 \cos(\omega_{pump} t) - \frac{\theta_0^3}{6} \cos^3(\omega_{pump} t) + \ldots \right]$$

(4)

where the leading higher order in the expansion is cubic. This expanded term leads to driving the current at the third harmonic and is observed as THz emission at $3\omega$, which manifests as a reflectivity increase above the plasma edge as shown in Fig. 2(a)-(d).

The above equations predict the third harmonic signal to scale with the superfluid density, as observed in previous work on LBCO [20]. The temperature dependence of the third harmonic emission for our LSCO studies is shown in Fig. 3 (black dots). Clearly, the signal does not solely scale with the superfluid density (which is directly proportional to the square of the JPM frequency), but instead decreases slightly for temperatures lower than 27K. Recent work has shown that detailed calculations are necessary to understand the temperature dependence of the third harmonic signal. Calculations based on this theory are plotted as red dots in Fig. 4[31]. The third harmonic signal is calculated from the nonlinear optical kernel of the Josephson phase, and its overlap with the spectral amplitude of the pump pulse, as shown in equation [5]

$$I_{NL}^n(\omega) = \int d(\omega') A(\omega - \omega') K(\omega') A^2(\omega')$$

$$K \propto \frac{\omega_J^2 \coth(\beta\omega_J/2)}{4\omega_J^2 - (\omega + i\gamma(T))^2}$$

(5)

$A$ is the spectral amplitude of the electric field profile and $K$ is the nonlinear optical kernel. This kernel does have an overall scaling with the superfluid density as $\omega_J^2$. However, there is also a factor in the kernel, $\coth(\beta\omega_J/2)$, that comes from the thermal excitation of plasmon modes, which causes third harmonic emission to increase with temperature [21]. The kernel also has a resonance at the Josephson plasma frequency. For our experiment, the pump pulse is centered at a frequency lower than the Josephson plasma frequency for all measured temperatures. However, with increasing temperature this process is closer to being on resonance since the condensate density (and hence $\omega_p$) is reduced. Finally, quasiparticle damping increases with temperature, causing third harmonic emission to decrease. Thus, there are four competing factors that determine the overall temperature dependence of third harmonic emission due to Josephson plasma waves. These calculations capture the qualitative features of the data including a maximum in third harmonic emission at 27K, a decrease as the temperature is decreased, and a sharp decline in third harmonic emission in the vicinity of $T_C$.

The work in [21] and the results shown here motivate looking at the temperature dependence of third harmonic emission from other c-axis cuprates since the non-monotonic temperature dependence goes beyond basic Josephson-equations predictions. To our knowledge, third harmonic emission from c-axis cuprates has only been previously reported in La$_{2-x}$Ba$_x$CuO$_{4}$ [21] and shares some similarities with our results. More detailed

**FIG. 3.** Third harmonic generation from c-axis LSCO at 10K. (a) Linear (black) and nonlinear (red) spectral amplitude of the THz pulses reflected from the sample. The nonlinear spectrum is at the maximum field strength of ~80 kV/cm, and the linear spectrum is at the minimum field strength (renormalized as explained in the text). The shaded region in blue is the spectral content attributed to third harmonic generation. The inset contains a plot of the spectral amplitudes with a linear y-axis. (b) Third harmonic generation as a function of incident THz field strength at 10K. Each data point is from integrating Eq. 1 over the third harmonic region. The red line is a cubic polynomial fit, and the shaded area is bounded by cubic fits of the data including the upper and lower bounds of the data including the error bars.
studies of third harmonic generation and THz nonlinearities have been performed in many superconductors, including cuprates, focusing on light polarized in the ab-plane. The interpretation of the data has been in terms of the Higgs mode and quasiparticle contributions.

FIG. 4. Magnitude of c-axis THG from LSCO versus temperature. All data points were taken with maximum field strengths of 80 kV/cm. The black circles are experimental data and the red circles are calculations as described in the text. The experimental data and calculations are normalized to the maximum value, which occurs at 27 K in both experiment and simulation.

V. CONCLUSION

We have explored the nonlinear c-axis response of LSCO and have observed THz third-harmonic generation arising from the Josephson plasma mode. The emission from the sample under intense THz radiation displays cubic behaviour indicative of third harmonic generation, which has been shown to be consistent with phase dynamics between the copper-oxygen planes in LSCO. An interesting future direction for the cuprates would be to investigate the relationship between the phase mode and amplitude mode and their potentially coupled contributions to the nonlinear terahertz response.

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We note that there is a prediction of contribution of plasma waves to the third harmonic generation for light polarized in the ab-plane [21]. The nonlinear THz response of cuprates can also be studied with pump-probe protocols, with [21] giving predictions for the response using the nonlinear optical kernel formalism. Experimentally, this pump-probe protocol has been used to study LBCO, where both amplification of Josephson Plasma Waves [14] and long-lived oscillations in the THz pump-probe signal [34] were observed.

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The linear spectral amplitude is scaled using the reflection coefficient at the minimum field strength. Specifically, $E_L(\omega) = E_L(\omega)\eta$, where $E_L(\omega)$ is the spectral amplitude reflected from the LSCO at the lowest incident field. $\eta = E_{NL}(\omega)/E_{L}(\omega)$ where $E_{NL}(\omega)$ and $E_{L}(\omega)$ are reference pulses reflected off a gold surface at the nonlinear and minimum field strengths, respectively.
