Time-Resolved Optical Reflectivity of the Electron-Doped $Nd_{2-x}Ce_xCuO_{4+\delta}$ Cuprate Superconductor: Evidence for an Interplay between Competing Orders

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We use pump-probe spectroscopy to measure the photoinduced reflectivity ΔR of the electron-doped cuprate superconductor $Nd_{2-x}Ce_xCuO_{4+\delta}$ at a value of x near optimal doping, as a function of time, temperature, and laser fluence. We observe the onset of a negative ΔR signal at $T^* \approx 75$ K, above the superconducting transition temperature, T_c, of 23 K. The relatively slow decay of ΔR, compared to the analogous signal in hole doped compounds, allows us to resolve time-temperature scaling consistent with critical fluctuations. A positive ΔR signal onsets at T_c that we associate with superconducting order. We find that the two signals are strongly coupled below T_c, in a manner that suggests a repulsive interaction between superconductivity and another fluctuating order.

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Historically, research on high-transition temperature superconductors has pursued two goals: uncovering their diverse properties, while at the same time identifying those that are essential to superconductivity. The latter path leads naturally to searching for those features that are common to the electron and hole-doped cuprates, as well as iron-pnictide superconductors. Certainly, the most discussed of these features, aside from superconductivity itself, are the pseudogap (PG) phenomena. However, in contrast with their prominence in hole-doped systems, PG phenomena in the electron-doped cuprates [1] and iron-based superconductors are less well explored. In hole-doped cuprates, time resolved optical spectroscopy has proven to be a powerful method for tracking the onsets of both PG and superconducting (SC) order with a single technique [2–7]. Here we report time-resolved reflection (TRR) experiments on the electron-doped superconductor $Nd_{2-x}Ce_xCuO_{4+\delta}$ (NCCO), in which we measure the change in reflectivity induced by an ultrashort optical pulse as a function of time after excitation. While the amplitude of the TRR signal shows features reminiscent of hole-doped cuprates, the decay of ΔR with time, t, is very different. $\Delta R(t)$ decays much more slowly and, in the normal state, displays scaling behavior indicative of approach to $T = 0$ order. In further contrast to hole-doped cuprates, we observe that very low fluence (≈ 2 $\mu J/cm^2$) per laser pulse, is sufficient to vaporize the SC condensate in NCCO. We use this effect to measure the temperature dependence of the PG signal below T_c as the strength of the SC order is tuned by photoexcitation, revealing a repulsive interaction between SC and PG order.

Crystals of NCCO were grown in a traveling-solvent floating-zone furnace in an oxygen atmosphere of 5 bar. To remove the excess oxygen and achieve superconductivity, the crystals were annealed for 10 h in flowing argon at 970 °C, followed by 20 h in flowing oxygen at 500 °C [8]. The Ce concentration was measured by atomic emission spectrometry. In this Letter, we study samples near optimal doping, for which $x = 0.156$ and $T_c = 23$ K. Our measurements were performed using a mode-locked Ti:Sapphire oscillator generating pulses of 800 nm wavelength light of duration of 150 fs and repetition rate 80 MHz. A pulse picker was employed in order to lower the repetition rate and control average laser heating effects.

Figure 1(a) shows the transient reflectivity as a function of probe delay and temperature as a false color image, and Fig. 1(b) shows the maximum amplitude of the transient reflectivity, $\Delta R/R$, induced at low fluence (0.6 $\mu J/cm^2$). We observe two distinct signals of opposite sign, similar to observations in the hole-doped single-layer cuprate $Pb_{0.55}Bi_{1.5}Sr_{1.6}La_{0.4}CuO_{6+\delta}$ [2] and double-layer $Bi_2Sr_2CaCu_2O_{8+\delta}$ [5,6]. We associate the positive signal that appears at T_c with superconductivity and the negative signal with the PG, as its onset at 75 K lies on an extrapolation of the pseudogap temperature $T^*(x)$ determined from the appearance of gaps in optical conductivity [9,10] and photoemission spectra [11,12].

We focus first on the temperature dependence of the PG signal in the normal state. In Fig. 2(a), we plot $\Delta R(t)$ for several temperatures in the range $T_c < T < T^*$. The time-resolved data show that the increase in amplitude of the transient reflectivity with decreasing T is accompanied by a slowing of response time. We find that $\Delta R(t, T)$ scales such that its rise and decay time are described with a single parameter, τ_{PG}. Figure 2(b) shows that the data in Fig. 2(a) collapse to a single curve of the form, $\Delta R(t, T) = A(T)te^{-t/\tau_{PG}}$. $A(T)$ increases rapidly with decreasing temperature near T^* and levels off below 50 K. Figure 2(c)

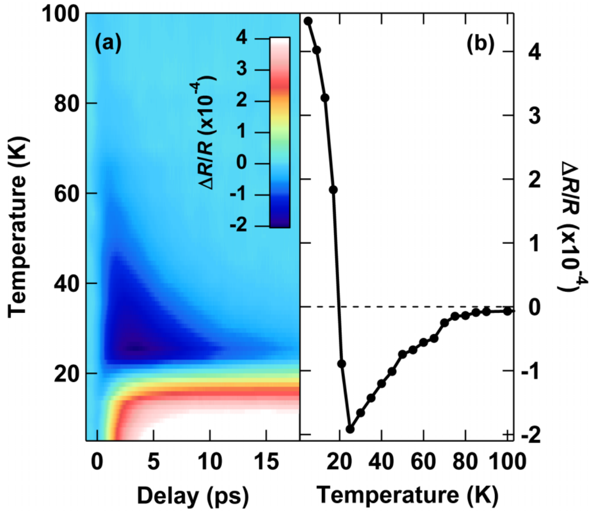

FIG. 1 (color online). $\Delta R(t)/R$ measured at a pump fluence of 0.6 μJ/cm^2 over a range of temperatures. (a) Dependence on temperature and time delay displayed as a false color image. (b) Temperature dependence of the peak value of $\Delta R(t)/R$. Note the onset of the negative PG signal at $T^* \approx 75$ K and the onset of the positive SC signal at $T_c = 23$ K.

shows that τ_{PG} grows approximately in proportion to $1/T$ in the normal state, providing strong evidence that TRR is probing critical fluctuations of $T = 0$ PG order.

We next address the question of how the critical fluctuations shown in Fig. 2, which are a property of the equilibrium state, arise in a pump-probe measurement. When considering the physical origin of the TRR signal, it is useful to divide photoexcitation by the pump beam into two classes. In one, photoexcitation generates a nonequilibrium population of single-particle excitations, which eventually decay as the system returns to equilibrium. In the cuprates, the SC signal is of this type; pump photons break Cooper pairs into superconducting quasiparticles which ultimately recombine pairwise to produce phonons, a process that can be described by the phenomenological Rothwarf-Taylor equations [13–16]. For such processes, the excitation and recombination steps are decoupled, and the rise and fall of the amplitude is not expected to obey the one parameter scaling that we observe.

The other class of photoexcitation involves coupling to a collective mode through the Raman interaction, described by a Hamiltonian of the form [17],

$$H_R = \frac{1}{2}\frac{\partial \epsilon_{ij}}{\partial \hat{Q}}\delta\hat{Q}E_iE_j, \tag{1}$$

where ϵ is the dielectric tensor, E_i are components of the electric field of the light, and for simplicity of notation, we take $\hat{Q}$ to be a scalar collective mode coordinate such as electron density, a component of spin density, or local Néel order $S_m \cdot S_n$. A linearly polarized pump electric field $E_i(t) = f(t)\cos(\omega t)$ exerts a force on $\hat{Q}$ given by,

$$\mathcal{F}(t) = \frac{1}{4}\frac{\partial \epsilon_{ii}}{\partial \hat{Q}} f^2(t)[1 + \cos(2\omega t)], \tag{2}$$

where ω is the radiation frequency and $f(t)$ is the pulse profile. The response of the mode coordinate to this force is

$$\langle \delta\hat{Q}(t)\rangle = \int \chi_Q(t - t')\mathcal{F}(t')dt', \tag{3}$$

where $\chi_Q(t)$ is the impulse response function. In the limit that the pulse is short compared to the typical response time, Eq. (3) simplifies to $\langle \delta\hat{Q}(t)\rangle = I\chi_Q(t)$, where

$$I = \frac{1}{4}\frac{\partial \epsilon_{ii}}{\partial \hat{Q}} \int f^2(t)dt. \tag{4}$$

The same Raman interaction causes the mode displacement driven by the pump beam to modulate the reflectivity of a time-delayed probe, a process known as impulsive stimulated Raman scattering (ISRS) [18]. The mode displacement induces a change in ϵ given by

$$\langle \delta\epsilon_{ij}(t)\rangle = \frac{\partial \epsilon_{ij}}{\partial \hat{Q}} I\chi_Q(t), \tag{5}$$

which, in turn, generates a corresponding change in the reflection amplitude, that is, $\Delta r \propto \langle \delta\epsilon_{ii}(t)\rangle$. Thus, ISRS provides a mechanism by which the equilibrium time-domain response function, $\chi_Q(t)$, can be observed in TRR measurements.

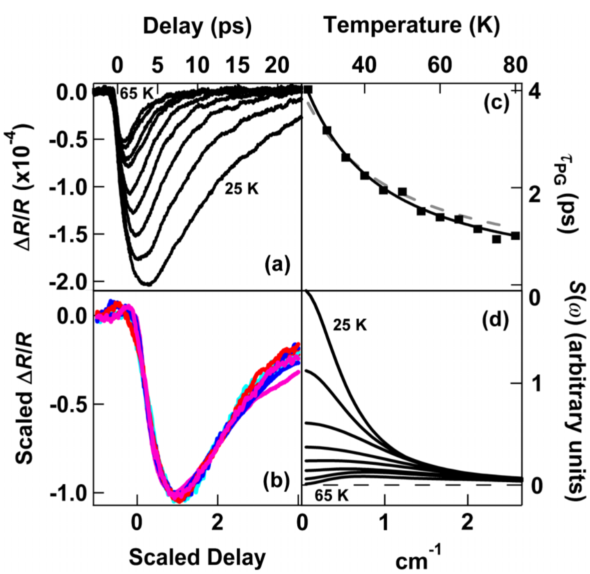

FIG. 2 (color online). (a) $\Delta R(t)/R$ shown for normal state temperatures between 25 and 65 K. (b) Same data collapsed onto a single curve according to the scaling relation described in the text. (c) τ_{PG} extracted from this collapse plotted vs temperature. The grey dashed line is proportional to $1/T$, and the solid line is a fit to $T^{-\alpha}$, with $\alpha = 1.18$. (d) Spontaneous Raman intensity obtained by Fourier transforming the PG data as described in the text.

For a collective mode $\hat{Q}$ that obeys damped oscillator dynamics, the impulse response function in the overdamped regime is given by,

$$\chi_Q(t) \propto \frac{e^{-\gamma_{+t}} - e^{-\gamma_{-}t}}{\gamma_{+} - \gamma_{-}}, \qquad (6)$$

where ω_0 and γ are the resonant frequency and damping parameter of the mode, respectively, and $\gamma_{\pm} = \gamma \pm (\gamma^2 - 4\omega_0^2)^{1/2}$. At critical damping, $\gamma = 2\omega_0$, the impulse response function is proportional to $te^{-\gamma t}$, which is the scaling form for TRR that we measure.

Based on the analysis presented above we conclude that fluctuations of a collective mode first become visible to our probe at T^*, and with further decrease of T, these fluctuations slow in a manner that is characteristic of the approach to $T = 0$ PG order. It is possible that the same scenario is responsible for the TRR signal that onsets near T^* in the hole-doped cuprates. However, the characteristic relaxation times of TRR in the normal state of the hole-doped cuprates are at least a factor of 10 shorter than what we have observed in NCCO and, therefore, the simple time-temperature scaling may be obscured by insufficient temporal resolution.

If the interpretation in terms of ISRS given above is correct, there should be a direct relationship between the TRR signal and spontaneous Raman scattering in the normal state. The connection between the two measurements is through the fluctuation-dissipation theorem, which gives for the scattered intensity,

$$S(\omega) \propto \frac{2k_B T}{\omega} \mathrm{Im}[\chi_Q(\omega)], \qquad (7)$$

where $\chi_Q(\omega)$ is the Fourier transform of $\chi_Q(t)$. In Fig. 2(d), we plot the spontaneous Raman spectra corresponding to the TRR transients shown in Fig. 2(a). To compare with frequency-domain Raman data, we note that TRR performed with linear polarized light corresponds to the xx or yy scattering geometries, which selects modes of A_{1g} symmetry. Previously measured Raman spectra of electron-doped cuprates are consistent with our results, in that they show increased intensity with decreasing frequency in the A_{1g} channel [19], down to the low-frequency limit of the measurement, ≈ 20 cm^{-1}. Measuring χ_Q in the time rather than frequency domain enables us to follow the quantum critical scaling of the dynamics to significantly lower frequency.

Possessing an understanding of the response in the normal state allows us to examine the interplay of the PG and SC signals below T_c as a function the laser fluence, Φ. Figures 3(a)–3(c) show plots of $\Delta R(t)/R$ at several temperatures spanning T_c for pulse fluencies of 2, 4, and 8 μJ/cm^2, respectively. In recording these data, the pulse repetition rate was varied in inverse proportion to the energy per pulse, such that the average optical power delivered to the sample remained the same. Thus, the average temperature rise, estimated at less than 1 K based on the observed shifts in T_c, is the same for all the data shown in Fig. 3. Below T_c, and at the lowest fluence, the positive SC signal dominates the response and the PG signal is not clearly discernible. As Φ is increased, the relative strength of the two signals reverses, with $\Delta R/R$ approaching a single component PG response at high fluence.

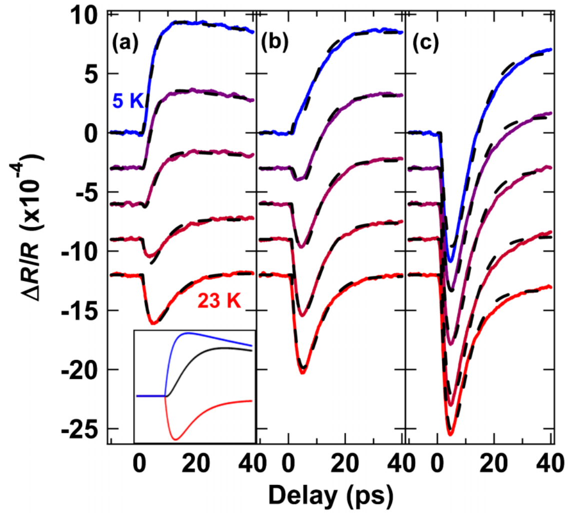

FIG. 3 (color online). Time delay and temperature dependence of $\Delta R/R$ for laser fluences (a) 2 μJ/cm^2, (b) 4 μJ/cm^2, and (c) 8 μJ/cm^2. Dashed line fits were obtained using the procedure described in text. The inset to (a) shows the decomposition of the signal measured at 5 K and 4 μJ/cm^2 (black) into negative PG (red) and positive SC (blue) components.

To determine the relationship between PG and SC responses, we resolve $\Delta R/R$ into its components, $\Delta R(t) = \Delta R_{\mathrm{PG}}(t) + \Delta R_{\mathrm{SC}}(t)$. In performing this decomposition, we assume that $\Delta R_{\mathrm{PG}}(t, T)$ obeys the same scaling form as in the normal state. A further assumption is that the rise and decay of $\Delta R_{\mathrm{SC}}(t)$ can be described by exponential functions, that is, $\Delta R_{\mathrm{SC}}(t) = A_{\mathrm{SC}}(1 - e^{-t/\tau_r})e^{-t/\tau_d}$. Given these forms for the PG and SC components, we then vary the parameters τ_d, τ_{PG}, and A_{SC} to achieve the best fit to $\Delta R(t, T)$ [12]. The dashed lines in Fig. 3 illustrate the high quality of the fits obtained by the superposition of PG and SC responses described above (an example of the decomposition is shown in the Fig. 3(a) inset). In Figs. 4(a) and 4(b), we plot the peak values $\Delta R_{\mathrm{PG}}(T, \Phi)$ and $\Delta R_{\mathrm{SC}}(T, \Phi)$ as determined by the fitting procedure described above. Figure 4(a) shows ΔR_{PG} and ΔR_{SC} as functions of Φ, for a representative temperature above T_c (26 K) and one below T_c (5 K). While above T_c, ΔR_{PG} is linear in laser fluence, both components of ΔR are nonlinear functions of Φ in the superconducting state. The SC signal plateaus at a rather low saturation fluence, $\Phi \approx 1.5$ μJ/cm^2, a value that is much smaller than that found in the higher-T_c materials $Bi_2Sr_2CaCu_2O_{8+\delta}$ and $YBa_2Cu_3O_{7-\delta}$, but is consistent with the scaling

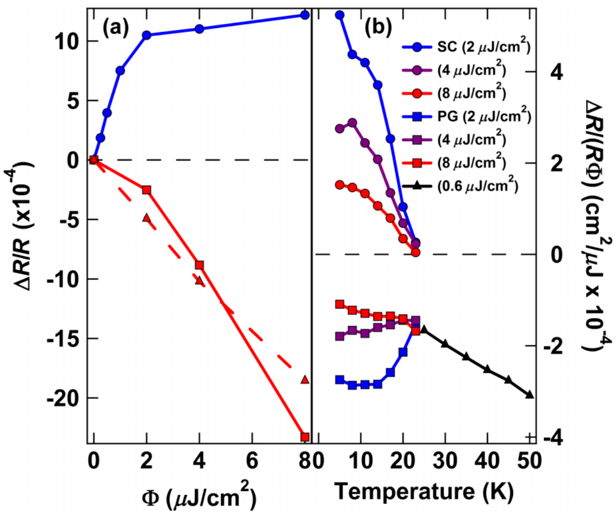

FIG. 4 (color online). (a) The PG (red squares) and SC (blue circles) components of the transient reflectivity as a function of laser fluence at 5 K, compared with the normal state signal (red triangles) as measured at 23 K. In the normal state, the transient reflectivity is linear in fluence. Below T_c, the SC component saturates while the PG component exhibits a superlinear dependence on fluence. (b) The fluence-normalized SC (upper circles) and PG (lower squares) components as a function of temperature. At the lowest fluence, 2 μJ/cm^2, the PG component is suppressed at the onset of superconductivity. The extent of this suppression becomes smaller as increased laser fluence causes a weakening of superconducting order.

$\Phi_S \propto T_c^2$ recently reported in hole-doped cuprates and pnictide superconductors [20]. This saturation phenomenon is generally associated with photoinduced vaporization of the SC condensate. In contrast, ΔR_{PG} at 5 K grows superlinearly in the same fluence regime where ΔR_{SC} is sublinear. The clear implication is that with increasing fluence, the PG correlations strengthen as SC order weakens, suggestive of a repulsive interaction between two order parameters.

Evidence for repulsive interaction is seen as well in Fig. 4(b), which is a plot of the fluence-normalized components, $\Delta R_{\mathrm{PG}}/(R\Phi)$ and $\Delta R_{\mathrm{SC}}/(R\Phi)$, as functions of T, for the same three values of Φ as in Fig. 3. Above T_c, $\Delta R_{\mathrm{PG}}/(R\Phi)$ is independent of fluence, indicating that $\Delta R_{\mathrm{PG}}/R$ is linear in Φ throughout the normal state. However, at 23 K the normalized amplitudes for PG and SC diverge, demonstrating that nonlinearity appears abruptly at T_c. Specifically, at low fluence the pump pulse does not appreciably weaken superconductivity, and the PG signal is maximally suppressed. At high fluences the SC signal saturates, indicating evaporation of the superconducting condensate, and the suppression of the PG signal is lifted. Based on our hypothesis relating ΔR_{PG} to the impulsive response of a Raman active collective mode, we would tend to associate the suppression of the PG signal that begins at T_c with a decrease in the correlation time of PG fluctuations in the presence of superconductivity.

While our TRR measurements reveal a critically fluctuating order which competes with superconductivity, we emphasize that we cannot directly distinguish between charge order, spin order, or a combination of the two. Previous work on NCCO has linked the formation of the pseudogap to the onset of fluctuating antiferromagnetic order [1,9,21,22]. Probing incipient antiferromagnetic order through ISRS is a plausible scenario for describing our data, and is consistent with theoretical calculations showing a repulsive interaction between superconductivity and antiferromagnetism [23]. However, this scenario is notably inconsistent with inelastic neutron scattering results [24], which reveal that the magnetic correlation length is roughly constant over the doping and temperature range where our TRR measurements indicate diverging correlations. On the other hand, the suppression of the PG response below T_c bears a striking resemblance to the T dependence of recently reported fluctuating charge density wave order in $YBa_2Cu_3O_{7-\delta}$ measured using resonant soft [25] and hard [26] x-ray scattering. It is possible that our TRR measurement in NCCO probes as yet undiscovered charge fluctuations that onset near T^* in the electron doped cuprates. Yet another candidate for the fluctuating order are orbital currents [27], whose existence in hole doped cuprates is inferred from spin-flip neutron scattering measurements [28].

To conclude, we have measured the photoinduced reflectivity ΔR as a function of time delay, temperature, and laser fluence in $Nd_{2-x}Ce_xCuO_{4+\delta}$. We observed the onset of a ΔR in the normal state near 75 K, with a response time that grows as approximately T^{-1} with decreasing temperature. We proposed that $\Delta R(t)$ directly measures the Raman susceptibility in the time domain, exhibiting a form of time-temperature scaling consistent with critical fluctuations. At T_c, we observed the onset of a second component of ΔR that is clearly associated with superconductivity. The SC and PG components of the transient reflectivity were found to be strongly coupled below T_c, indicating a repulsive interaction between superconductivity and some other order; further study of the doping and magnetic field dependencies is needed to reveal the nature of the competing order.

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