Electron-Phonon Coupling in High-Temperature Cuprate Superconductors Determined from Electron Relaxation Rates

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We determined electronic relaxation times via pump-probe optical spectroscopy using sub-15 fs pulses for the normal state of two different cuprate superconductors. We show that the primary relaxation process is the electron-phonon interaction and extract a measure of its strength, the second moment of the Eliashberg function $\lambda\langle\omega^2\rangle = 800 \pm 200$ meV^2 for $La_{1.85}Sr_{0.15}CuO_4$ and $\lambda\langle\omega^2\rangle = 400 \pm 100$ meV^2 for $YBa_2Cu_3O_{6.5}$. These values suggest a possible fundamental role of the electron-phonon interaction in the superconducting pairing mechanism.

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The electron-phonon interaction (EPI) is decisive for determining the functional properties of materials. It is the main scattering process governing electronic conductivity and is crucial for the formation of ordered electronic states such as charge-density waves and often the superconducting state. The determination of its strength—usually defined as the second moment $\lambda\langle\omega^2\rangle = 2\int_0^\infty \alpha^2F(\omega)\omega d\omega$ of the Eliashberg spectral function $\alpha^2F(\omega)$ [1]—is thus of fundamental importance. Standard methods for determining $\lambda\langle\omega^2\rangle$ experimentally from phonon linewidths in Raman or neutron scattering are often biased by selection rules and inhomogeneous broadening, and have given controversial results in the past. Since scattering from phonons is one of the main relaxation processes for electrons, $\lambda\langle\omega^2\rangle$ can be accurately extracted from the electron-phonon relaxation time $\tau_{e\text{-ph}}$, provided that: (i) the experiment affords adequate time resolution to determine $\tau_{e\text{-ph}}$, and (ii) an appropriate model connecting $\lambda\langle\omega^2\rangle$ and $\tau_{e\text{-ph}}$ is used. We will show in this paper that for materials with strong EPI, to satisfy both conditions, we need to go beyond current approaches. Here, by using optical spectroscopy with ultrahigh time-resolution (< 20 fs instrument response) and a new, more appropriate model, we obtain $\lambda\langle\omega^2\rangle$ values for two high-critical temperature (T_c) cuprate superconductors, which allows us to assess the role of the EPI in the superconducting mechanism in these materials. Ultrahigh time-resolution is important to detect fast processes in strongly interacting systems, and to correctly identify the EPI relaxation in cases where the data contain the dynamics of several processes. Since for strong EPI $\tau_{e\text{-ph}}$ can be well below 100 fs, we need a better resolution than the usual 50–80 fs used so far [2–5]. Therefore we use state-of-the art ultrashort laser pulses from two synchronized noncollinear optical parametric amplifiers [6].

In femtosecond optical pump-probe spectroscopy the sample is excited with a short pump laser pulse, and the reflectivity is measured with a (weaker) probe pulse at a variable delay. The pump beam is periodically modulated and the photoinduced signal is expressed as a relative change of the reflected light intensity $\frac{\Delta R}{R} = \frac{R_{\text{pump}} - R_0}{R_0}$, where R_{pump} and R_0 are the reflected intensities with and without pump pulse, respectively. The temporal evolution of $\frac{\Delta R}{R}$, which—for small perturbations—is related to the temporal evolution of the dielectric constant $\Delta\epsilon/\epsilon$, is a direct signature of the energy relaxation processes in the sample. We used 15-fs pump pulses centered at 530 nm and broad band sub-10-fs probe pulses with a spectrum ranging from 500 to 700 nm (a detailed scheme is found in the supplementary information [7]). This nondegenerate pump-probe configuration eliminates coherent interference artefacts. Single crystals of $YBa_2Cu_3O_{6.5}$ (YBCO, $T_c = 60$ K) and $La_{1.85}Sr_{0.15}CuO_4$ (LSCO, $T_c = 38$ K) were prepared as in Ref. [8,9]. To avoid any competing relaxation processes from emergent low temperature states (e.g., superconducting, pseudogap, antiferromagnetic, or stripe order), we performed all experiments at room temperature.

Until recently, a theoretical framework expressing $\tau_{e\text{-ph}}$ in terms of $\lambda\langle\omega^2\rangle$ has been provided by the so-called two-temperature model (TTM) [10,11]. It is based on the assumption that the relaxation time due to electron-electron (e-e) collisions $\tau_{e\text{-}e}$ is much shorter than $\tau_{e\text{-ph}}$. The e-e scattering is assumed to establish a thermal distribution of electrons with a temperature $T_e > T_l$ (T_l being the lattice temperature) on a time scale typically faster than the experimental time resolution. The relaxation

time $\tau_{e\text{-ph}}$ of subsequent electron cooling via EPI is related to $\lambda\langle\omega^2\rangle$:

$$\lambda\langle\omega^2\rangle = \frac{\pi}{3}\frac{k_B T_e}{\hbar\tau_{e\text{-ph}}} \quad (1)$$

This expression has been used in the analysis of transient optical experiments [2–4], and recently also time-resolved angle-resolved photoemission spectroscopy (ARPES) [5]. For the typical laser fluences used in these experiments T_e is in the range 400–800 K. This gives an estimate for $\tau_{e\text{-}e} = 350$ fs to 1.4 ps, depending on the fluence (see supplementary information [7]). From Eq. (1), $\tau_{e\text{-ph}}$ is expected to be proportional to T_e and thus vary significantly over the range of fluences used in the experiment.

Outside the TTM regime, the relaxation behavior can be described via the kinetic Boltzmann equation using e-e and e-ph collision integrals, where the electrons and phonons are both out of equilibrium. This has been done both numerically [12] and recently also analytically [13,14]. The calculated electron distribution based on the analytical solution of this nonequilibrium model (NEM) [14] departs from the equilibrium Fermi-function particularly for high energies. (A comparison with published time-resolved ARPES data is shown in the supplement [7].) The analytical treatment yields a relation:

$$\lambda\langle\omega^2\rangle = \frac{2\pi}{3}\frac{k_B T_l}{\hbar\tau_{e\text{-ph}}}. \quad (2)$$

which is applicable also when $\tau_{e\text{-}e} > \tau_{e\text{-ph}}$. Besides the factor 2, a notable difference compared to the TTM formula [Eq. (1)] is that $\tau_{e\text{-ph}}$ is predicted to be linearly dependent on T_l (not T_e). Since the heat capacity of the lattice is much higher than that of electrons, in our experiments T_l is close to room temperature for all fluences, so we expect that $\tau_{e\text{-ph}}$ should be independent of fluence. This provides a critical test of the model's applicability.

The experimental data for LSCO [Figs. 1(a) and 1(b)] and YBCO [Fig. 1(c)] show a fast initial decay followed by a slower dynamics, all of which are independent of laser fluence. We fit the transient response of both cases [see Figs. 1(b) and 1(c)] with two exponential decays with time constants τ_a and τ_b respectively, and a long-lived plateau, using the pump-probe cross-correlation as the generation term. For each sample, the same τ_a and τ_b are obtained at different probe wavelengths. YBCO also contains an oscillatory response due to impulsively excited coherent phonons. This coherent phonon contribution can be removed almost entirely by fitting the oscillatory response of the known Raman-active modes and subtracting it from the data [see Fig. 1(c)]. The fact that in YBCO at 520 nm the two signal components have opposite sign nicely confirms that we are actually observing two processes and not at a nonexponential process which could accidentally be fitted with two exponentials. The fit yields $\tau_a = 45 \pm 8$ fs and $\tau_b = 600 \pm 100$ fs for LSCO and $\tau_a = 100 \pm 20$ fs and $\tau_b = 450 \pm 100$ fs for YBCO, respectively. This behavior is systematically observed over the whole spectral range of our probe pulse between 500 and 700 nm (see supplementary information [7]).

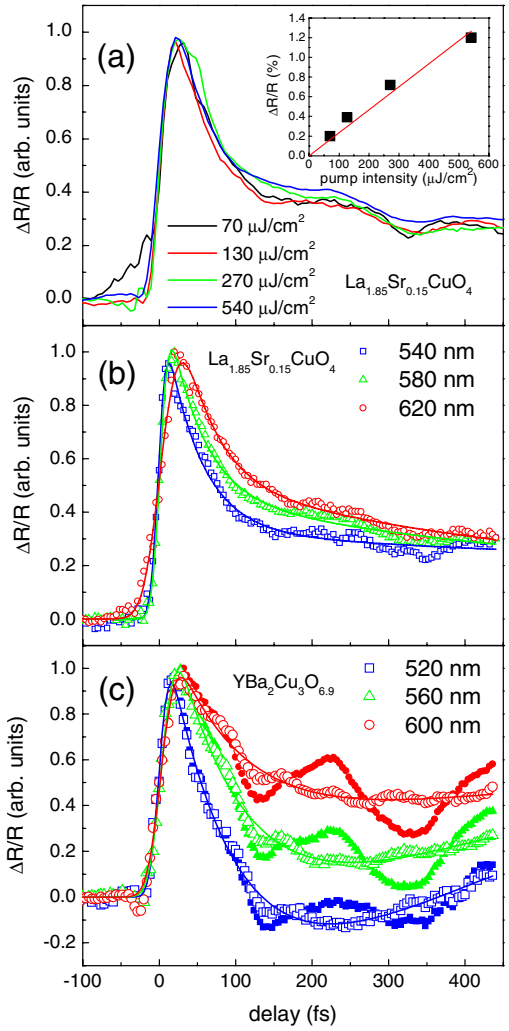

FIG. 1 (color online). (a) Normalized photoinduced reflectivity change in $La_{1.85}Sr_{0.15}CuO_4$ at 590 nm for different pump intensities. The inset shows the signal magnitude as a function of pump intensity. (b) $\Delta R/R$ of $La_{1.85}Sr_{0.15}CuO_4$ at different probe wavelengths (symbols) and double-exponential fits (lines). (c) $\Delta R/R$ of $YBa_2Cu_3O_{6.5}$ at different probe wavelengths and double-exponential fits. Small full symbols show the original data, large open symbols show the data after subtraction of three oscillating modes at 115, 145, and 169 cm^{-1}. These oscillations arise from a modulation of the reflectivity by phonons coherently excited in the sample by the pump pulse, whose duration is much shorter than the oscillation period [44,45]. The three modes are known from Raman spectroscopy [46,47].

Since the observed dynamics is fluence independent [see Fig. 1(a)], neither of the two fast relaxation processes can be attributed to e-e scattering. Following previous studies [4,5], we assign τ_a to relaxation via the EPI mechanism. The origin of the longer relaxation time τ_b has been

discussed in detail previously [4,5,9,15] and is of no further interest here.

The choice of model (TTM or NEM) for determining $\lambda\langle\omega^2\rangle$ from $\tau_{e\text{-ph}}$ is based on the relatively stringent requirement regarding the fluence dependence of $\tau_{e\text{-ph}}$. A fluence-dependent $\tau_{e\text{-ph}}$ is clearly not observed here, and to the best of our knowledge has never been observed in cuprates. We thus conclude that the TTM is not applicable, while the data are consistent with the NEM solution without the assumption that $\tau_{e\text{-}e} \ll \tau_{e\text{-ph}}$. Calculating the EPI strength, Eq. (2) yields $\lambda\langle\omega^2\rangle = 800 \pm 200$ meV^2 for LSCO and $\lambda\langle\omega^2\rangle = 400 \pm 100$ meV^2 for YBCO. As additional confirmation regarding the choice of model, we note that a dependence of $\tau_{e\text{-ph}}$ on the sample temperature, as predicted by the NEM *has* actually been observed in cuprates [16] and superconducting iron pnictides [17] above the pseudogap temperature, where it is expected to apply. No such dependence is predicted by the TTM.

To assess the consequences of using the NEM rather than the traditional TTM, in the supplementary information [7] we compare $\lambda\langle\omega^2\rangle$ values obtained with the two models both for our data and for several metals from the literature. The TTM assumption $\tau_{e\text{-}e} \ll \tau_{e\text{-ph}}$ is generally not valid. The discrepancy in $\lambda\langle\omega^2\rangle$ calculated with the two models can be up to a factor of 2. If different fluences are used, as in our data, the variation of T_e introduces an additional uncertainty if we use the TTM estimate.

To obtain an estimate of λ from the data, we express the second moment of the Eliashberg function as the product of a dimensionless electron-phonon coupling constant λ and the square of a characteristic phonon frequency ω_0: $\lambda\langle\omega^2\rangle = \lambda\omega_0^2$. The estimate of ω_0 and consequently λ requires a detailed knowledge of the Eliashberg spectral function. This can be extracted from other experiments such as optical absorption [18,19], neutron scattering [20–22], ARPES [23,24], and tunneling [25–30]. Based on these references the best estimate of ω_0 is about 40 meV, which gives $\lambda \gtrsim 0.5$ for LSCO and $\lambda \gtrsim 0.25$ for YBCO. Remarkably, these values agree very well with *ab initio* calculations that predict 0.27 for YBCO [31] and 0.4 for LSCO [32,33].

To assess the possible contribution of EPI to the superconductive pairing mechanism in the cuprates, we briefly discuss the observations in terms of existing theories based on phonon mediated pairing—most notably BCS theory and polaronic pairing [34–37]. BCS theory predicts that $k_B T_c = \hbar\omega_0 \exp[-(1+\lambda)/\lambda]$ (if any repulsive Coulomb pseudopotential is neglected). At maximum ($\lambda = 2$, $\omega_0 = \sqrt{\lambda\langle\omega^2\rangle/2}$, see the supplementary information [7]) the BCS critical temperature can be $T_c^{\max} = 52$ K for LSCO and only $T_c^{\max} = 37$ K for YBCO. Remarkably—contrary to the experiment—it predicts a *higher* T_c for LSCO than for YBCO.

Polaronic pairing within the band picture, on the other hand, yields a maximum $T_c(\lambda)$ that is significantly higher than for BCS and is obtained at a lower λ value. Polaronic band-narrowing due to phonon "dressing" of carriers strongly enhances the density of states in a narrow polaron band and consequently also the critical temperature of polaronic superconductors [34]. With further increase of the EPI strength carriers form real-space (bipolaronic) pairs and the critical temperature, which is now the Bose-Einstein condensation temperature, drops since the effective mass of these composed bosons increases [35]. The highest $T_c(\lambda)$ exceeding the BCS value by several times is hence found in the intermediate crossover region of the EPI strength from the weak-coupling BCS to the strong-coupling polaronic superconductivity. Strong e-e correlations increase the effective mass of carriers (or decrease the bare bandwidth), and heavier carriers form lattice polarons at a smaller value of λ [38,39] ($\lambda_c \approx 0.9$ for uncorrelated 2D polarons [40], while $\lambda_c \lesssim 0.4$ in the Holstein t-J model [39]). The observed EPI strengths are therefore consistent with polaronic pairing in the presence of strong electron correlations, whereby YBCO lies in the crossover region close to the maximum T_c, while LSCO would appear to be on the strong-coupling side of this region ($\lambda > \lambda_c$). Alternatively, within local bipolaron pairing models [36], the limits of T_c are set by (dynamic or static) phase coherence percolation [41], where the interplay of the EPI and the Coulomb repulsion between doped carriers V_c determine the pair density and detailed real-space texture [37]. These models give a charge-ordered regime when Coulomb repulsion dominates ($\lambda/N_0 \ll V_c$, with N_0 being the density of states at the Fermi energy) and a fully phase separated state when EPI is dominant ($\lambda/N_0 \gg V_c$). In the crossover region between these two regimes, a textured state favoring pair (bipolaron) formation exists, leading to superconductivity with a distinct maximum T_c.

Our results reinforce the other compelling experimental evidence for a strong role for the EPI in cuprates obtained from isotope effects [30], high resolution ARPES [23,24], optical [18,19], neutron scattering [20–22], and tunneling [28,29,42] spectroscopies. However, our data on two materials can only demonstrate the realistic feasibility of the polaronic pairing mechanism, and cannot rule out any nonphononic contribution to the pairing. Indeed part of the glue function has been identified with an energy well above the upper limit of the phonon frequencies in the cuprates (100 meV) [43]. While this could be a signature of multiphonon dressing of carriers, spin and/or electron density fluctuations might be alternative mechanisms of the high-energy glue. By using the appropriate theory and adequate time resolution, as we have shown, one can now collect accurate data for further cuprate high-T_c materials to decide whether the agreement with the polaronic mechanism is coincidental or systematic. Similar work will be of fundamental significance for other effects where EPI is

important, such as high T_c superconductivity in noncuprate materials (notably iron-pnictides [17]), colossal magnetoresistance, the formation of orbitally-ordered states and charge-density waves.

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