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Coherent phonon generation mechanism in solids

Ahmed I. Lobad* and Antoinette J. Taylor†
Condensed Matter and Thermal Physics Group, Los Alamos National Laboratory, MS K764, Los Alamos, New Mexico 87545
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We investigate the driving force for coherent phonons by employing a nonlinear two-pump/probe technique. In accordance with the displacive excitation mechanism we demonstrate that the electronic excitation is the driving force for the coherent phonons in semimetals. This is accomplished by analyzing the relation between the nonlinearities in the electronic and phononic contributions. On the other hand, no dependence of the coherent phonon dynamics on the electronic excitation was observed in high temperature superconductors (HTSC), although displacive excitation has been invoked for these materials. We discuss the possible implications of this observation on the microscopic nature of the coherent phonons in the HTSC.

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Advances in the generation and application of femtosecond laser pulses, with multiterahertz spectral bandwidth, lead to the possibility of the excitation of coherent phonon states. They are manifested in transient measurements $\gamma_o(t)$ as a modulation of the optical dielectric function at a frequency Ω corresponding to a lattice phonon. A theoretical description of displacive excitation of coherent phonon theory (DECP) was proposed to explain the generation of coherent phonons in absorbing condensed matter.[1] Realization of this displacive mechanism requires a strong dependence of the equilibrium nuclear coordinates on the electronic excitation. This coupling to the electronic system leads to the excitation of fully symmetric breathing modes of the lattice. In DECP, the *instantaneous* electronic excitation leads to a sudden change in the free energy of the lattice, which responds to the new electronic state by moving δQ toward a new equilibrium displacement. The inertia of the lattice causes electrons to oscillate around the new position in a $\cos(\Omega t)$ fashion with amplitude proportional to δQ, where $t=0$ corresponds to the arrival of the excitation pulse. Conversely, purely impulsive excitation in nonabsorbing materials leads to a strict $\sin(\Omega t)$ motion indicating oscillations around nonshifted ionic equilibrium positions. DECP was later shown to be a special case of the more general impulsive stimulated Raman scattering (ISRS) mechanism.[2]

In the past, the phase of the phonon oscillation served as the means to identify the generation mechanism. In this work we attempt to investigate the link between the electronic excitation component $\gamma_{o(e)}(t)$ and the phononic component $\gamma_{o(ph)}(t)$ of the measured transient $\gamma_o(t)$ in materials where DECP was identified as the generating mechanism. Specifically, in semimetals we are able to ascertain that the electronic excitation is the coherent generation force by comparing the nonlinearity in the electronic and phononic response in semimetals. We employed a nonlinear two-pump/probe technique. In this technique, two pump pulses are chopped at two different frequencies f_1 and f_2. Through various carrier-carrier interactions and scattering mechanisms, the dynamics of the carriers injected by one pump are influenced by those injected by the second pump and vice versa. This nonlinearity in the electronic response, $\gamma_{o(e)}(t)$, will result in the detection of an electronic related signal at the sum frequency (f_1+f_2) in the probe beam, $\gamma_{sf(e)}(t)$. (A variation of this technique has been applied in the past to investigate carrier-carrier interactions through the intrinsic nonlinearities of the luminescence process.[3]) Below, we demonstrate that for impulsive excitation no phononic sum frequency component would be generated. On the other hand, if the electronic density drives the phonons, as in DECP, then a sum frequency phononic component $\gamma_{sf(ph)}(t)$ of a certain magnitude and sign, in relation to $\gamma_{o(ph)}(t)$, should be detectable. Absence of a phononic sum frequency contribution, despite the presence of a strong electronic nonlinearity, suggests that coherent phonon generation is independent of the electronic excitation.

The coherent phonon field is given by

$$\frac{\partial^2 Q}{\partial t^2}+\Omega^2 Q=F(t), \tag{1}$$

where the driving force $F(t)$ is a function of the pump pulse intensity for impulsive excitation or of the pump-generated electronic distribution $\gamma_{o(e)}(t)$ for displacive excitation. The measured dielectric modulation is assumed to be proportional to the amplitude of the phonon field Q. In a purely impulsive excitation the driving force is given by $F(t) \propto(\partial\chi/\partial Q)|E(t)|^2$, where χ is the electronic susceptibility and E is the magnitude of the pump electric field. In the presence of two pump pulses separated by $\Delta\tau$ and modulated at different frequencies (f_1 and f_2) the phonon driving force is

$$F(t)=(\partial\chi/\partial Q)\{|E_1(t)|^2 f_1+|E_2(t-\Delta\tau)|^2 f_2\}, \tag{2}$$

the modulation frequencies f_1 and f_2 are of the order of 1 KHz. Since Eq. (1) is a linear differential equation, no component at the sum frequency will be generated. In what follows we show that in the semimetal alloy $Bi_{0.97}Sb_{0.03}$, the injected carrier density is the driving force of the coherent phonons. This is accomplished by analyzing the relation between the electronic and phononic sum frequency signals for pump pulses separated by $\Delta\tau=0.5\,\Omega^{-1}$ and Ω^{-1}. We also investigated the coherent phonons in a high temperature superconductor where DECP was invoked. In the latter, no phononic sum frequency component was detected, despite the presence of a large electronic sum frequency signal. We discuss the possible implication of this observation on the

identification of the phonon driving force and the microscopic nature of the phonon oscillations.

The samples used in this investigation are a 300 nm thick *c*-axis oriented $YBa_2Cu_3O_{7-\delta}$ (YBCO) twinned film sputtered on an MgO substrate[4] and a $Bi_{0.97}Sb_{0.03}$ (BiSb) bulk alloy. The superconducting transition in the YBCO film occurs at $T_C = 87\,\mathrm{K}$, with a transition width of 1.5 K. The experiments are performed using a Ti:Sapphire oscillator producing 25 fs pulses at 1.5 eV. The pump beam polarization is orthogonal to that of the probe. All measurements are performed at a fluence of 100 μJ/cm^2 corresponding to a photoexcited carrier density of $5\times10^{18}\,\mathrm{cm}^{-3}$. Measurements on the YBCO were conducted at $T = 40\,\mathrm{K} < T_C$, revealing a 120 cm^{-1} Ba mode and a 150 cm^{-1} Cu(2) mode. The BiSb sample has a dominant phonon oscillation at 2.7 THz with $\Omega^{-1} = 360$ fs. Vidal *et al.* investigated the coherent phonon generation in the $Bi_{1-x}Sb_x$ alloy system as a function of x.[5] With increasing x, this system exhibits a semiconductor-semimetal transition at $x = 0.05$ and then a semimetal-semiconductor transition at $x = 0.22$. A Stanford Research Systems chopper SR540 was used to modulate the two pumps. The chopper blade is divided into two concentric circles with a different number of holes and is therefore capable of simultaneously modulating the two pump beams at two different frequencies, inner (f_{in}) and outer (f_{out}) frequencies. The ratio of $f_{\mathrm{in}}/f_{\mathrm{out}} = 5/6$ is determined by the number of holes in each circle. The two pump beams are parallel but separated by ~1 cm, enabling the modulation Pu1 and Pu2 at f_{out} and f_{in}, respectively. By assuming that $\gamma_o(t)$ has both a linear and a quadratic dependence on the injected carrier density, it can be shown that the sum frequency component is effectively given by

$$\gamma_{\mathrm{sf}}(t) = \Theta(t-\Delta\tau)\{\gamma_o(t)|_{\mathrm{pu1\ \&\ pu2}} - [\gamma_o(t)|_{\mathrm{pu1}} + \gamma_o(t)|_{\mathrm{pu2}}]\}, \tag{3}$$

where $\Theta(t)$ is the unit step function, $\Delta\tau$ is the separation between the two pump pulses, and $\gamma_o(t)|_{\mathrm{pu1\ \&\ pu2}}$ indicate the response for two pump excitations rather than only one or the other. Clearly, $\gamma_{\mathrm{sf}}(t)$ would be zero in a purely linear system.

Figure 1 shows the transient reflectivity in BiSb for a single pump (Pu1) response at f_1 and the sum frequency response at f_1+f_2 for a pump separation of $\Delta\tau = 0.5\,\Omega^{-1}$ (solid line) and Ω^{-1} (dashed line). The vertical dashed line represents the position of Pu1, while the arrows represent the position of the Pu2 as a solid arrow for $0.5\ \Omega^{-1}$ and dashed one for the Ω^{-1} case. As expected, the sum frequency signal starts after the arrival of the second pulse. Just as the single pump response, the sum frequency signal consists of an electronic and a phononic contribution. The negative electronic contribution to the sum frequency signal $\gamma_{\mathrm{sf(e)}}(t)$ indicates that the electronic response $\gamma_{\mathrm{o(e)}}(t)$ (at f_1) increases sublinearly with the increase of excitations, i.e., saturates. The sum frequency signal is a measure of the nonlinearity of the single pump response since this nonlinearity is what couples the two chopping frequencies. As shown in the figure, the sum frequency signal is ~16% that of the single pump response. We note that in the above we measure the dielectric

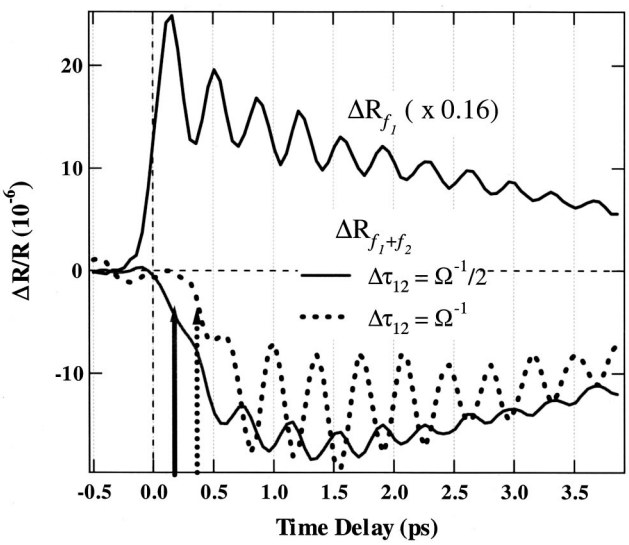

FIG. 1. Single pump response and the nonlinear sum frequency response in BiSb for $\Delta\tau = 0.5\,\Omega^{-1}$ (solid) and $\Delta\tau = \Omega^{-1}$ (dashed). The vertical dashed line indicates the position of Pu1. The position of Pu2 is indicated by the vertical arrows, solid for $\Delta\tau = 0.5\,\Omega^{-1}$, and dashed for $\Delta\tau = \Omega^{-1}$.

properties through the reflection transient which itself is a nonlinear function of the dielectric constants. This implies that, in principle, a sum frequency reflectivity-transient could be measured even for a purely linear response for the dielectric properties. However, it can be shown that this functional nonlinearity is at least an order of magnitude too small to account for the measured nonlinearity. In addition, no measurable nonlinearity in the detector could account for the measured sum frequency signal. The phase of the phononic sum frequency component for $\Delta\tau = 0.5\,\Omega^{-1}$ is opposite to that $\Delta\tau = \Omega^{-1}$ and is in phase with the phonon oscillations in the single pump response. We show below that these phases can be accounted for using the DECP theory by assuming that the electronic response is the driving force for the coherent phonons.

In DECP the driving force in Eq. (1) is the excited electronic density, $\gamma_{\mathrm{o(e)}}(t)$, and the coherent phonon amplitude is given by

$$\gamma_{\mathrm{o(ph)}}(t) \propto [1 - \Gamma_{\mathrm{o(e)}}(\Omega)\cos(\Omega t)], \tag{4}$$

where $\Gamma_{\mathrm{o(e)}}(\Omega)$ is the Fourier component of $\gamma_{\mathrm{o(e)}}(t)$ at Ω.[6] To test whether the electronic density is the driving force of the coherent phonons, the correct phase of the oscillations in the phononic sum frequency component for both $\Delta\tau = 0.5\,\Omega^{-1}$ and Ω^{-1} should come out from Eq. (1) using the corresponding electronic sum frequency component $\gamma_{\mathrm{sf(e)}}(t)$ as the driving force. Similar to Eq. (4) the sum frequency phononic component is given by $\gamma_{\mathrm{sf(ph)}}(t) \propto [1 - \Gamma_{\mathrm{sf(e)}}(\Omega)\cos(\Omega t)]$. In order to determine the oscillation phase of $\gamma_{\mathrm{sf(ph)}}(t)$ in relation to $\gamma_{\mathrm{o(ph)}}(t)$ we need to express $\Gamma_{\mathrm{sf(e)}}(\Omega)$ in terms of $\Gamma_{\mathrm{o(e)}}(\Omega)$. The sum frequency electronic component $\gamma_{\mathrm{sf(e)}}(t)$ in Fig. 1 is roughly a scaled, inverted,

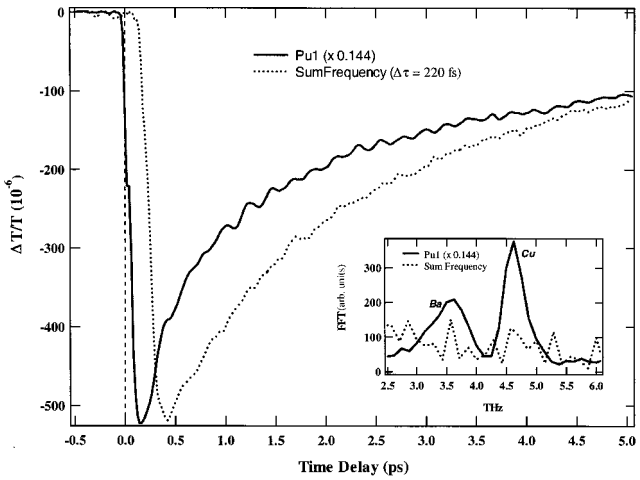

FIG. 2. Single pump and sum frequency response in YBCO at 40 K for $\Delta\tau = 220$ fs. The inset shows the FFT spectrum. The single pump response is scaled ($\times 0.144$) to the electronic sum frequency amplitude.

and time shifted replica of the linear component $\gamma_{o(e)}(t)$, such that $\gamma_{sf(e)}(t)|_{\Delta\tau} \propto -0.16\gamma_{o(e)}(t-\Delta\tau)$. Therefore, $\Gamma_{sf(e)}(\Omega)$ is given by

$$\Gamma_{sf(e)}(\Omega)|_{\Delta\tau} \propto -0.16\Gamma_{o(e)}(\Omega)\exp(-i2\pi\Omega\Delta\tau). \quad (5)$$

This suggests that the phononic sum frequency component $\gamma_{sf(ph)}(t)$ for $\Delta\tau = 0.5\,\Omega^{-1}$ is opposite to that for $\Delta\tau = \Omega^{-1}$ and is in phase with the linear phonon oscillation $\gamma_{o(ph)}(t)$, in agreement with the result of Fig. 1. The same result can be reached by solving Eq. (1) with the driving force given by $\gamma_{o(e)}(t)|_{Pu1} + \gamma_{o(e)}(t-\Delta\tau)|_{Pu2/1}$ and using Eq. (3) to calculate $\gamma_{sf(ph)}(t)$. The $\gamma_{o(e)}(t-\Delta\tau)|_{Pu2/1}$ term is the electronic response due to Pu2 in the presence of Pu1 which is smaller than the electronic response due to Pu2 in the absence of Pu1 as a result of the saturating nonlinearity in the electronic response. The ability to directly measure $\gamma_{sf}(t)$ through sum frequency detection is highly superior to using Eq. (3). Typically, the magnitude of the measured sum frequency signal is $\sim$10% that of $\gamma_o(t)|_{pu1\ \&\ pu2}$ and the inherent uncertainty in each separately measured term of Eq. (3) is several percent. Therefore, attempting to extract $\gamma_{sf}(t)$ through Eq. (3) would result in more than 50% error.

Hase *et al.* used two pump pulses to investigate the optical control of coherent phonons in Bi as a function of the time delay between the two pulses.[7] They observed an anomalous phase dependence around pump-pump separations that are expected to result in total destructive phonon interference. The authors conjectured that this phase deviation arose from a phonon-phonon coupling. In their modeling they assumed a linear phonon dependence, i.e., the left-hand side of Eq. (3) is always zero. We believe that the phononic nonlinearity investigated in this work is the origin of this perceived phase deviation.

Figure 2 shows the transmission transient for a single pump and the sum frequency response for $\Delta\tau = 220$ fs for YBCO at $T = 40$ K. After fitting and subtracting the electronic part, the fast Fourier transforms (FFT) of the remaining (phononic) signals were calculated and plotted in the inset. The single pump response and its FFT were scaled to that of the sum frequency amplitude. The single pump response has strong phononic components for the Cu and Ba modes. Yet no phononic components in the sum frequency is observed in the FFT spectrum. Therefore, the electronic sum frequency component does not generate a corresponding Cu or Ba phononic component. Due to signal to noise levels, we can say this with more certainty for the Cu rather than the Ba mode. The expected sum frequency Cu phononic component is about $\sim 4\times$ the noise level, while the expected Ba phononic component is only $\sim 1.5\times$ the noise level.

Below the superconducting transition it was shown that the transient electronic response together with the amplitude of the Ba mode scale with the density of Cooper pairs and *qualitatively* exhibits a BCS-like temperature dependence.[8] Thus, Kutt *et al.* proposed that the breakup of Cooper pairs is the driving force below the critical temperature.[9] This observation was used to suggest that lattice deformations (phonons) are involved in the pairing mechanism and superconductivity in high temperature superconductors (HTSC).[10] DECP comes in naturally since the ionic equilibrium positions in the superconducting state should be different from that in the normal state depending on the presence or absence of the pairing energy. The sudden breakup of Cooper pairs and disappearance of the pairing energy should cause the lattice to oscillate around a shifted ionic position. DECP was also invoked by Mazin et al. to explain the enhancement of the phononic dynamics below T_C corresponding to the enhancement in the electronic response.[11]

The absence of a phononic component in the sum frequency signal seems to argue against the DECP being the generation mechanism in superconducting YBCO. On the other hand, this observation could potentially expose the microscopic nature of the coherent oscillations in HTSC. It is generally assumed that the observed oscillations result from a single macroscopic phonon field Q. A large number of independent microscopic oscillators q each excited by a single photon from a short pulse can, in principle, induce the same dielectric oscillations. The latter case could be applicable to the HTSC and other mixed-valence perovskites[12] where the phonon spatial extent is limited by disorder and more importantly where localized polaronic effects are well established. In this case, increasing the pump intensity would lead to the excitation of more oscillators rather than an increase in the amplitude of the macroscopic oscillator. It is then more appropriate to talk about localized lattice oscillations resulting from the liberation of a localized polaron by a single photon. A second photon cannot interact with this already excited (*liberated*) oscillator, therefore no phononic sum frequency signal could be generated in this case.

In conclusion, we have employed a nonlinear technique to investigate the driving force for coherent phonons in solids. We have furnished the strongest evidence so far for the applicability of DECP in semimetals. This is accomplished by relating the phononic nonlinearities to those of the injected electronic distribution. On the other hand, no such relation

was observed in HTSC although DECP was invoked for these materials. This result either contradicts DECP as the generation mechanism or requires the presence of localized lattice oscillations resulting from the single photon liberation of a localized polaron in HTSC's.

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*Present address: DELS, Kirtland Air Force Base, Albuquerque, NM 87117.

†Corresponding author. Email address: ttaylor@lanl.gov

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