Observation of an Amplitude Collapse and Revival of Chirped Coherent Phonons in Bismuth

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We have studied the A_{1g} coherent phonons in bismuth generated by high fluence ultrashort laser pulses. We observed that the nonlinear regime, where the phonons' oscillation parameters depend on fluence, consists of subregimes with distinct dynamics. Just after entering the nonlinear regime, the phonons become chirped. Increasing the fluence further leads to the emergence of a collapse and revival, which next turns into multiple collapses and revivals. This is explained by the dynamics of a wave packet in an anharmonic potential, where the packet periodically breaks up and reconstitutes in its original form, giving convincing evidence that the phonons are in a quantum state, with no classical analog.

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Coherent excitation of optical phonons is a general phenomenon occurring whenever an ultrashort laser pulse interacts with crystalline solids [1]. The necessary condition to realize the coherent excitation is the availability of Raman active phonons with frequencies smaller than the inverse of a laser pulse duration. For semimetals, the generation mechanism of coherent phonons was initially identified as a displacive one. However, it was later shown that the displacive mechanism is not a distinct process, but a particular case of stimulated Raman scattering [2]. Although many studies have dealt with time-resolved lattice dynamics, experiments performed with the use of high-energy laser pulses are still rare [3–7]. These high fluence studies revealed a specific feature of coherent oscillations: Above a well-defined threshold, the coherent oscillations are not linear with optical excitation, so that their parameters (including frequency) are a function of fluence. Even though in most situations involving phonons a *classical* description is adequate, at low enough temperatures or at sufficiently short time scales, *quantum* fluctuations become dominant [8]. This quantum behavior has been successfully demonstrated by the observation of squeezed coherent phonons [9,10]. Motivated by these recent developments, we have made a thorough study of coherent oscillations in a wide temperature and laser fluence range. Note that until now there were not any high fluence experiments performed at low temperatures. We report in this Letter that in the nonlinear regime the coherent A_{1g} phonons in Bi are chirped and, moreover, above a critical fluence they exhibit a collapse and revival phenomenon, testifying to nonclassical dynamics.

In this study, we used a single crystal of bismuth ($10 \times 10 \times 1$ mm^3) with the cleaved surface perpendicular to the trigonal axis. The crystal was mounted into a closed-cycle cryostat and our experiment was performed in a conventional degenerate pump-probe scheme. The experimental setup is similar to previous experiments [6,7] except the detection: We employed a phase-sensitive scheme modulating the pump beam at 2 kHz with a chopper and recording the signal by a lock-in amplifier. A Ti:sapphire mode-locked laser oscillator at 800 nm was amplified using a regenerative 100 kHz amplifier. The final amplified and compressed laser pulse had the duration of 130 or 140 fs (at the sample position). The amplified output was divided into pump and probe beams polarized perpendicular to each other. Both the pump and probe beams were kept close to normal incidence, and focused to a spot diameter of 300 μm by a single 10 cm lens. From the linear absorption coefficient $\sim 6 \times 10^5$ cm^{-1} at 800 nm [6], we estimated that the absorption depth was around 17 nm, whereas the photoexcited carrier density at the maximum pump fluence of ~ 15 mJ/cm^2 was $\simeq 6 \times 10^{21}$ cm^{-3}, which comprised $\simeq 4\%$ of all the valence electrons. We observed permanent damage of the crystal only above a threshold $F \simeq 22$ mJ/cm^2. Consequently, all of our experiments were performed at fluences lower than the damage threshold. The high intensity laser pulses can excite coherent acoustic phonons and also transient temperature changes; however, none of them were detected in our experiments.

Figure 1(a) shows the transient reflectivity data demonstrating the high-amplitude coherent oscillations generated by a high fluence laser pulse at room temperature. The signal consists of nonoscillatory and oscillatory parts. Attempts to model the transient signal as

$$\frac{\Delta R}{R_0} = A_e \exp\left(-\frac{t}{\tau_e}\right) + A_p \exp\left(-\frac{t}{\tau_p}\right) \sin(2\pi\nu t + \varphi), \tag{1}$$

where A_e and τ_e are the amplitude and the decay time for nonoscillatory component, A_p, ν, and τ_p are the coherent phonon amplitude, the frequency, and the oscillation decay time, φ is the initial phase with respect to time zero, were unsatisfactory. It was impossible to obtain a good fit for all time intervals where the oscillations exist, since the frequency providing a good fit for short time delays does not match that at longer time delays (see the inset of

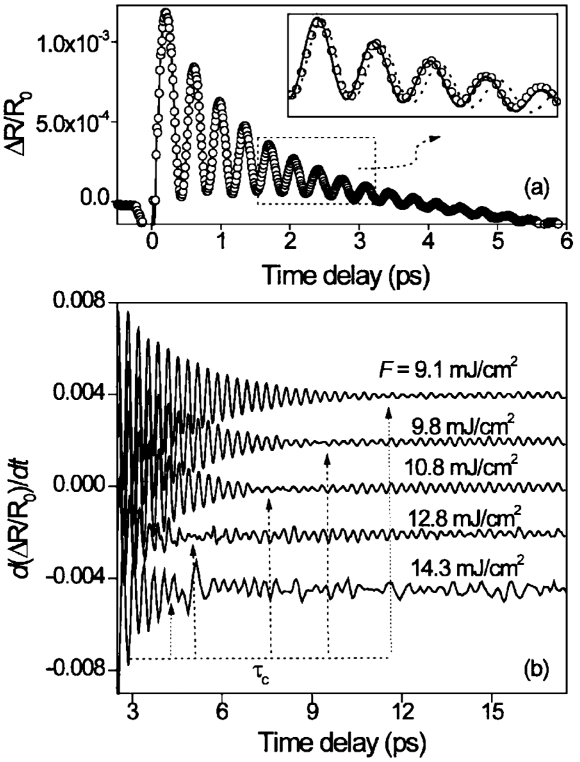

FIG. 1. (a) Transient reflectivity $\Delta R/R_0$ taken with $F = 4.8\ \mathrm{mJ/cm^2}$ at room temperature: open symbols. The inset shows the enlarged part for the selected delays: Dotted line, fit to Eq. (1) with $\nu = 2.68$ THz; solid line, fit to Eq. (2) with $\nu = 2.72$ THz and $\alpha = 0.05$. (b) Time derivative of R/R_0 as a function of the time delay demonstrating the collapse and revival in Bi at $T = 10$ K for different laser fluences with $\Delta_t = 130$ fs (the transients are offset along the y axis and labeled with the fluence value).

Fig. 1). Therefore, we tried to make the fit using the following formula:

$$\frac{\Delta R}{R_0} = A_e \exp\left(-\frac{t}{\tau_e}\right) + A_p \exp\left(-\frac{t}{\tau_p}\right)\sin\{(2\pi\nu + \alpha t)t + \varphi\}, \quad (2)$$

where α is the chirp. Equation (2) gives a satisfactory fit for the whole time interval where the signal-to-noise ratio for the oscillatory part is large. For low fluences, the chirp is almost zero. The higher the fluence, the larger positive chirp [7], amplitude, and inverse frequency [3–7] (see Fig. 2). Further, in the nonlinear regime there is a kink at $F \simeq 9\ \mathrm{mJ/cm^2}$ for low temperature (at $F \simeq 5\ \mathrm{mJ/cm^2}$ for room temperature) for almost all the oscillation parameters, signaling the entrance into a new subregime. At fluences greater than this threshold value, the oscillation pattern changes spectacularly: Now the oscillations die out up to a characteristic time τ_c as they did below the threshold. However, at some time later τ_r the oscillations revive, as seen in Fig. 3(a) [11]. For an even higher fluence, the oscillations die out again only to revive again. This collapse and revival scheme continues until the two

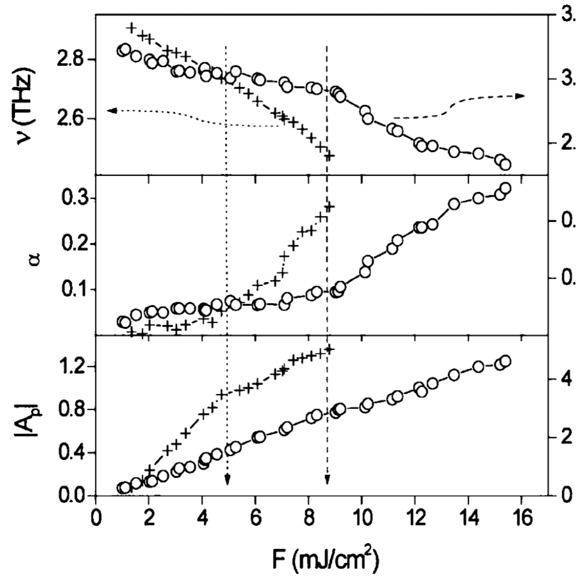

FIG. 2. The parameters of oscillatory part as a function of fluence. These parameters were obtained by fitting the data in real time until the first collapse. Crosses, room temperature; solid circles, $T = 10$ K (note that the two sets of data refer to different y axes). Dotted and dashed vertical lines denote the threshold fluence for room and helium temperature, respectively.

effects flow together, setting the lattice into a quasirandom motion, as shown in Fig. 1(b). Similar revivals have been extensively studied theoretically and experimentally for Rydberg atoms, optical parametric oscillators, molecular vibrations, the Jaynes-Cummings model [12], as well as for atom Bose-Einstein condensation [13]. Our revival has more similarity to the Bose-condensate case since it occurs for a collective mode (phonon) and not for single particle excitation as in the case of Rydberg atoms. The collapse and revival for coherent phonons prove the nonclassical nature of the crystal lattice state created by ultrashort laser pulses because this effect belongs to a class of quantum phenomena with no classical analog [12]. The collapse is due merely to the relative dephasing of the various elements of the phonon field, whereas the revival is entirely due to the grainy nature of the phonon field [7]. Even though the collapse and revival is a purely quantum phenomenon, one could try to explain the observed effect as a classical beating between *two* different sets of oscillators. Since there is only one naturally occurring isotope for Bi, the beating between the local and crystal modes for an isotopically disordered crystal is not possible. One potential candidate for the second oscillator might be the E_g mode. However, given its frequency $\simeq$2 THz, the beating would occur at a different time scale [7]. The next option is to consider two distributions of the oscillators with slightly different frequencies arising due to imperfect pump-probe overlap. However, it is important to note that, if two classical oscillators are coupled, then their lifetime remains unaffected. By contrast, as will be shown later, we observed an *increase* for the

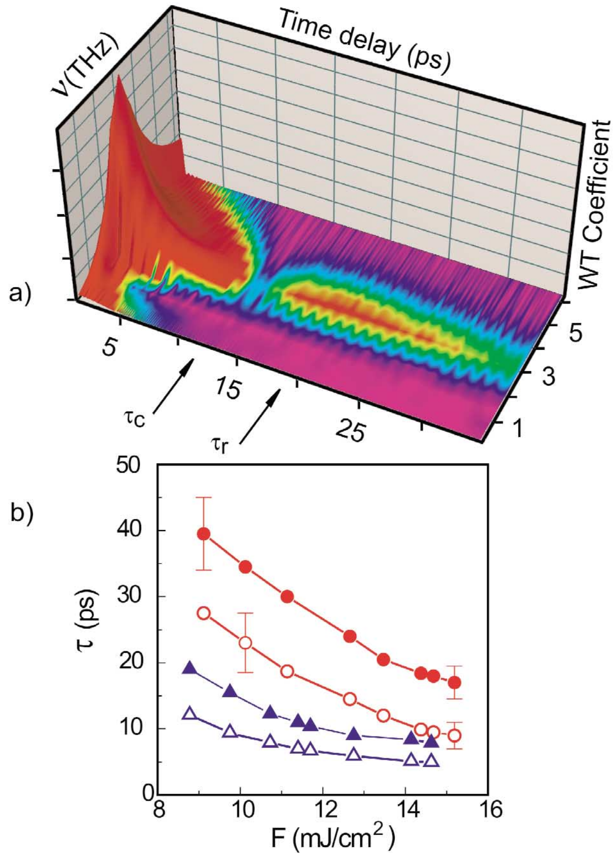

FIG. 3 (color). (a) Time-scale spectrum of the signal obtained by the wavelet transformation. The experiment parameters: $F = 14.2\ \mathrm{mJ/cm^2}$ and $\Delta_t = 130$ fs. (b) Measured τ_c (open symbols) and τ_r (closed symbols) as a function of fluence. The pulse duration $\Delta_t = 140$ fs (circles) and 130 fs (triangles).

coherent phonon lifetime after the revival, therefore excluding the possibility of beating between the classical oscillators. In some sense, the collapse and revival is the beating, albeit among different number states, that occurs only for quantum oscillators. More exactly, the collapse and revival phenomenon is just a manifestation of a universal scenario for long-term evolution of a wave packet consisting of highly excited states of a quantum system. In the terminology of Averbukh and Perelman, the first revival is in fact a half revival [12]. Indeed, if we fit the oscillation from the zero delay until the collapse time with a harmonic function, and expand this function to longer delays, then we observe that, between τ_c and τ_r, the fitting function and signal are π phase shifted. This indicates that the revival is inverted in time relative to collapse. We detected a decrease in the collapse time and an increase in the revival amplitude when the pump fluence is increased. The data shown in Fig. 3(b) suggests that the collapse and revival times decrease approximately linearly with fluence. Additionally, we observed a significant increase of τ_c and τ_r when the pulse duration was increased by only $\sim$10%. These experimental findings confirm that the collapse and revival is controlled by the anharmonicity parameter [12], which grows for higher fluences and higher intensities.

We gain a deeper insight into the physics of collapse and revival when we consider Fourier transforms made for different time spans. To this end, we introduce a spectrogram, which is a sliding-window Fourier transform. In the following, we choose the window size to be equal to $[0 - \tau_c]$, $[\tau_c - \tau_r]$, and $[\tau_r - 100\ \mathrm{ps}]$. The results of Fourier transform for temporally sliced oscillations are shown in Fig. 4(a), together with the time dependence of the instantaneous frequency. For short delay times, between 0 and τ_c, the phonon line shape is broad, redshifted [14], and strongly asymmetric. Between τ_c and τ_r, the phonon line is progressively less redshifted and more narrow. Finally, for $t > \tau_r$, the line shape is extremely narrow having a frequency in between the two above-mentioned cases. After the revival, the lifetime is longer than that of thermal phonons observed by spontaneous Raman scattering. Further, not only the chirp magnitude but also the chirp sign are different for the time delays when the oscillations grow and fade out. We interpret these findings as follows: The positive chirp arises when the wave packet, in the course of its evolution, loses the components representing the highly excited stationary states with the large quantum numbers. The negative chirp can be thought of as resulting from the opposite process: The very same components that ran away during the collapse now start catching up with the wave packet and, as a result, the frequency becomes smaller. The explanation of the alternating chirp is supported by the emergence of multiphonon states shown in Fig. 4(b), which presents the Fourier transform power spectrum of the whole time scan. This spectrum includes frequencies around ν, ν_2, and other higher harmonics. The observation of ν_2 is indicative of a quarter revival, whereas the occurrence of higher harmonics is suggestive of higher-order revivals seen in the nonclassical region of time evolution [12]. Note that the higher harmonics observation is a justification of the prediction made in Ref. [15], where it was suggested that the coherence in the phonon subsystem realized in pump-probe experiments is the result of simultaneously occurring *multiphonon* processes within the same phonon mode. It should be remarked that there are two peculiarities of the Fourier spectrum. First, the intensity of the higher harmonics with $n > 2$ does not appear to depend on the quantum number. Second, the lifetime of the highest harmonic significantly exceeds that of the other harmonics (including the principal one).

When asking whether the observed phenomenon is an "essentially quantum effect," one must first lay down criteria for categorizing an effect as quantum mechanical. In theory, there are at least four such sufficient criteria: wave-particle duality, entanglement (or nonlocality), quantum condensation involving indistinguishable particles, and revivals. Hence, the observation of a collapse and revival pattern provides irrefutable evidence

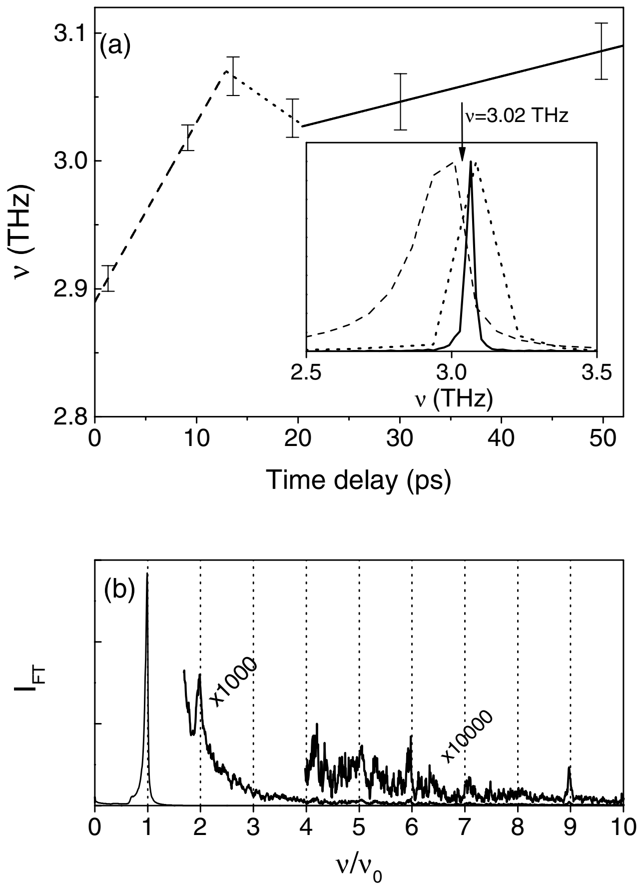

FIG. 4. (a) Frequency as a function of time for the transient obtained with $F = 12.8$ mJ/cm^2 and $\Delta_t = 130$ fs at $T = 10$ K. The inset shows the Fourier transforms for $0 < t < \tau_c$ (dashed line), $\tau_c < t < \tau_r$ (dotted line), and $t > \tau_r$ (solid line), while the arrows denote the frequency of thermal phonon obtained by Raman scattering [14]. (b) The power Fourier transform for the oscillations, taken with fluence $F = 14.6$ mJ/cm^2.

of a nonclassical state for crystal lattice. The revivals are universal features of the long-time behavior of weakly anharmonic wave packets [12]. They occur if the spectrum is nearly quadratic, and if the classical frequency is significantly larger than the anharmonicity. This means that the short-time behavior of the lattice is harmonic: It oscillates back and forth, while the quadratic anharmonic effects govern the long-time evolution.

Being a proof for an essentially quantum nature of phonon states, the collapse and revival phenomenon also provides the explanation why, in most femtosecond pump-probe experiments, a classical description is sufficient. Indeed, the revival time is given by $\tau_r = \frac{2}{\nu}(h|\frac{\partial \nu}{\partial E}|)^{-1}$, where E is the oscillator energy and h is the Plank constant [12]. Thus, for the measurements with unamplified pulses, the revival occurs for a time span inaccessible in experiments since the anharmonicity is too small. In this time interval (not exceeding collapse time), the system evolution obeys, according to the correspondence principle, classical Newtonian equations. Indeed, the wave packet in quantum mechanics is often viewed as the most "nearly classical" state and is known to display many classical properties. However, its inherent quantum nature (discrete spectrum) also causes the wave packet to exhibit many quantum mechanical features, and the collapse and revival is one of them. The phenomenon is just a manifestation of the fact that, in the course of its evolution, the wave packet periodically breaks up and reconstitutes its original form, whereas at intermediate times the wave packet gathers into a series of subsidiary wave packets [12].

In conclusion, our measurements have revealed that the nonlinear regime of coherent phonon generation can be divided into a few subregimes. Just after entering the nonlinear regime, the optical coherent phonons become chirped with their instantaneous frequency being a function of oscillation amplitude. Increasing the laser fluence further, we enter the region of collapse and revival that is adjacent to the region of multiple collapses and revivals. The collapse and revival of a collective lattice mode provides convincing evidence for the nonclassical state created by ultrafast pulses.

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