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Spectrally filtered time domain study of coherent phonons in semimetals

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Abstract

We have investigated the spectrally resolved coherent phonon oscillation in semimetals of Sb and Bi. The oscillation initial phase is π-shifted for the high- and low-frequency components of the probe pulse, indicating that not only the integrated intensity, but also the spectral content of the probe, are a function of time delay. This means that the coherent phonon, corresponding to nuclear motion, is a wavepacket localized in different regions of the phase space. Furthermore, the spectral filtering results in the appearance of the signal for negative delay time with the simultaneous disappearance of the coherent artefact. We conjecture that all these findings are the indication of the non-classical nature of coherent phonons that has been earlier inferred from squeezing and revivals of the lattice mode in semimetals.

1. Introduction

Following recent developments in femtosecond laser technology, there has been considerable interest in the properties of coherent lattice fields. The ultrafast lasers have created the possibility of exploring lattice dynamics in real time which has been realized in a variety of solids by the observation of coherent phonons [1–3] manifested in the oscillations of transient reflectivity (or transmission) at the frequency corresponding to an optical phonon. Although in most situations involving phonons a *classical* description is adequate [4], at low enough temperatures, or at sufficient short timescales *quantum* fluctuations become dominant [3]. Such quantum (as opposite to classical) behaviour has been successfully demonstrated by the observation of squeezed coherent phonons [5, 6, 13, 7, 8] and of their collapse and revival [9]. These phenomena, having no classical analogue, necessitate a clarification of the generation mechanism for coherent phonons. Assuming that off-diagonal density matrix elements (lattice coherences) can be representing by the amplitude of a harmonic oscillator, and further taking this amplitude as a real displacement, the question of coherent phonon generation can be reduced to the determination of either the potential or kinetic energy of the oscillator being

changed to initiate the oscillation. In the former case, the excitation goes through a displacive mechanism in which the driving force is imaginary, whereas in the latter case the driving force is real. Mathematically, for the displacive mechanism, the driving force in the time domain is given by the Heaviside step function $F(t) = \frac{1}{2}[1 + \mathrm{sgn}(t)]$, whose Fourier transform has no real component $F(\omega) = \frac{1}{2}\delta(\omega) - \mathrm{i}/\pi\omega$. For the impulsive mechanism, the driving force is represented by the Dirac delta function, whose Fourier transform, $F(\omega) = 1$, contains all possible frequencies.

Optical photons cannot be coupled to lattice excitation due to a large energy mismatch. Their interaction is always 'effective', taking one or another form of electron–phonon coupling. In transparent materials, the mechanism for coherent phonon generation was ascribed to impulsive stimulated Raman scattering [1, 3]. However, there is no consensus on the mechanism for opaque materials where linear absorption is substantial [1–3]. The difficulty arises from the fact that coherence in this case can be created in the electronically excited as well as in the ground state. Up to now, the main candidates for the mechanism in opaque materials are displacive excitation of coherent phonons (DECP) [10] and transient stimulated Raman scattering (TSRS) [1]. Quite often, the generation mechanism is identified by means of measuring the initial phase of oscillation. This phase is equal to $\pi/2$ (cosine-like oscillation) for a displacive mechanism, whereas the phase is zero (sine-like oscillation) for a pure impulsive mechanism. However, for TSRS the initial phase depends on the resonance conditions, changing from sine to cosine for the non-resonant and resonance cases, respectively [1]. Some insight into the generation mechanism can be gained by considering a simple picture to single out the limitations set by each of the models. Let us assume that the pump pulse excites the lattice, inducing a nuclear motion (that is, a coherent wavepacket) and the probe pulse interrogates this motion [11]. For the case of DECP, the instantaneous electronic excitation leads to a sudden change in equilibrium position of the lattice, which responds to it by moving towards a new equilibrium. Here the initial phase of oscillation is uniquely defined by the shifted potential minimum and the oscillation starts either from their maximum or minimum, depending on which side of the potential the wavepacket is to be created. In this case, all Fourier components of the probe pulse see saturated absorption and the intensity of the probe is modulated by beating between split levels of the excited state. For the case of TSRS, the coherence is achieved through a scattering process and the probe pulse, apart from the saturated absorption, will demonstrate a change of its spectral content [11].

In this paper we make an attempt to clarify the generation mechanism of coherent phonons by employing frequency-dispersed time-resolved pump–probe spectroscopy. The simultaneous measurement of the time and frequency resolved signals should be most helpful for the disentangling of complex lattice dynamics and for the separation of impulsive and displacive contributions. By spectrally analysing the transient reflectivity signal, we are able to ascertain that not only the integrated intensity but also the spectral content of the probe pulse are modulated at phonon frequency and, in addition, there is a signal for negative time delay. We suggest that these results are evidence for a scattering process to be dominant in coherent phonon generation and, furthermore, they imply that the phonon state created by the ultrashort pulse is essentially a non-classical one.

2. Experiment

The samples used in this study are single crystals of antimony and bismuth with cleaved surfaces perpendicular to the trigonal axis. The choice of samples was dictated by the fact that the coherent oscillations in the semimetals are most pronounced, while their generation

mechanism is still controversial [12–15]. The time domain experiments are performed using a Ti:sapphire mode-locked laser producing 40 fs pulses at 800 nm with the repetition rate of 80 MHz. These pulses are divided into high-intensity pump and low-intensity probe pulses (with the ratio 20:1) polarized perpendicular to each other. Both the pump and probe beams were kept close to normal incidence and focused to a spot diameter of 70 μm by a single 5 cm lens. The typical fluence of the pump does not exceed 0.5 μJ cm^{-2}. Temporal overlap is determined by the cross-correlation between the pump and probe in a nonlinear crystal. For 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. Spectral filtering is achieved by placing a narrow-band interference filter in front of the detector. All experiments were carried out at room temperature.

3. Results and discussion

For a spectrally integrated signal [3, 14], the transient reflectivity in antimony and bismuth consists of non-oscillatory and oscillatory parts and can be modelled as

$$\frac{\Delta R}{R_0} = A_e \exp(-t/\tau_e) + A_p \exp(-t/\tau_p) \sin(\Omega t + \varphi) \tag{1}$$

where A_p and τ_p are the coherent phonon amplitude and the decay time, A_e and τ_e are the amplitude and the decay time for non-oscillatory component and φ is the initial phase with respect to time zero. Figure 1(a) shows transient reflectivity in Bi for four different Fourier components of the probe pulse. In these experiments, an interference filter with $\Delta\lambda = 10$ nm is placed in front of the detector and the transients are recorded for the different wavelengths within the spectral width of the probe pulse (the response of the photodetector is flat for that frequency range). Quite similar transients are observed for Sb, see figure 1(c). Inspection of figure 1 shows that the initial phase of the oscillation depends on the wavelength of the probe light in such a way that the oscillation on high and low frequency sides (with respect to the central frequency of the probe pulse) are shifted, see figure 2. This shift means that not only is the integrated intensity of light modulated by lattice reaction, but also that its spectral content is time-dependent, oscillating with time at the phonon frequency. The full lines in the middle and bottom panels of figure 2 are the fits (shown only for short time delays) to the oscillating part of the signal calculated on the basis of equation (1). By fitting the transient reflectivity data in the time domain (as well as analysing it in the frequency domain by Fourier transform), we found that neither the oscillation frequency nor the decay time depend on the central frequency of the interference filter, see figure 3. The coherent amplitude magnitude taken as $A_p = [\Delta R(t = 0)/R_0]_{osc}$ is also independent of the filter band-pass, while the sum of the frequency resolved scans approximately equals the spectrally integrated signal. The magnitude of ΔR (not normalized) behaves as expected, that is, it becomes larger for the central frequency and lower for the wing frequency. Spectral filtering results in the disappearance of the coherent artefact, clearly seen in the integrated signal, and the appearance of the noise most pronounced for short time delays, see figure 4. The noise is decaying quite fast, significantly faster than the oscillation itself and, in fact, it exists for only half of the oscillation period. The intriguing feature is the noise existence even for negative time delays, where the temporal overlap between the pump and probe is absent. The only difference between bismuth and antimony is that the coherent phonon amplitudes for the former come out equal on both Stokes and anti-Stokes sides, whereas for the latter they appear different, see figures 1 and 3.

We will discuss the creation of coherent phonons by the pump beam in terms of DECP and TSRS, each imparting a different phase to the oscillation. However, regardless of how

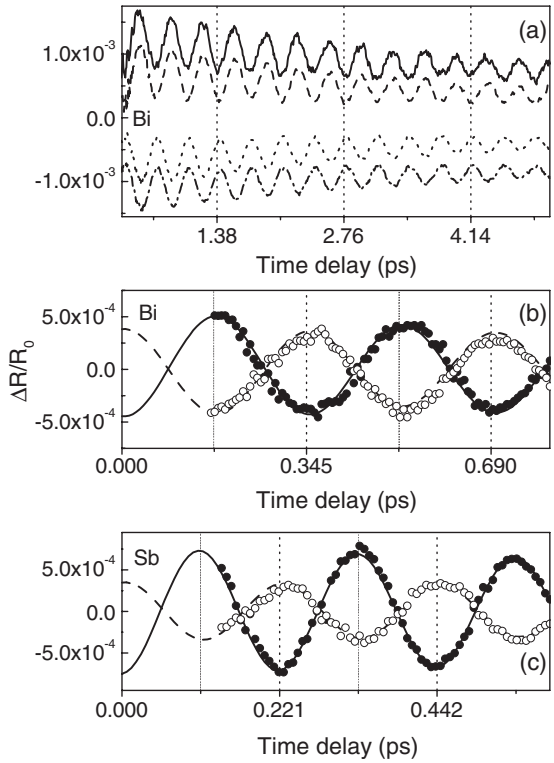

Figure 1. The transient differential reflectivity R/R_0 in Bi as a function of the time delay is shown in (a) for the wavelengths of 780 nm (full curve), 790 nm (broken curve), 810 nm (chain curve) and 820 nm (dotted curve), whereas the corresponding oscillating part for 790 and 810 nm together with the fits are given in (b). Panel (c) shows the same transients as panel (b) but for Sb.

the phonons were created, there exist two 'other' distinct processes by which the coherent phonon interacts with the probe: a Raman scattering mechanism and a coupling of the reflectivity to the transient refractive index. Our first task is to select one of them. To explain the observed facts let us consider the detection process. In a pump–probe experiment, the photodiode measures the full energy of the probe pulse without regard to its spectral content. $R(\omega) \backsim \pi \int h\omega n(\omega)\,\mathrm{d}\omega$, where $R(t)$ is the detected signal, ω is an optical frequency and $n(\omega)$ is the number of photons with that frequency. For displacive excitation of coherent phonons, $n(\omega)$ is modulated by the reflection which changes the number of photons at all frequencies uniformly. Thus $\int n(\omega)\,\mathrm{d}\omega$, and thereby $R(t)$, is modulated. For transient stimulated Raman scattering, the signal is additionally modulated by scattering the photons into modes with different frequencies. This means that, although $n(\omega)$ is not changed, the total signal $R(t)$ is, nevertheless, modulated because the distribution of photons between the photon modes changes. Therefore, the observed spectral modulation of transient reflectivity suggests that the detection mechanism is somehow related to the scattering process. Since the phase should be a smooth function of the spectral filtering, the transient reflectivity contains both displacive and impulsive components (we expect that, at certain combinations of frequency and band-pass of the interference filter, the initial phase should be zero). The strong prevalence of displacive components deduced from the initial phase value tells us that coherence is predominantly created in the excited electronic state. However, we should note that the frequency of light

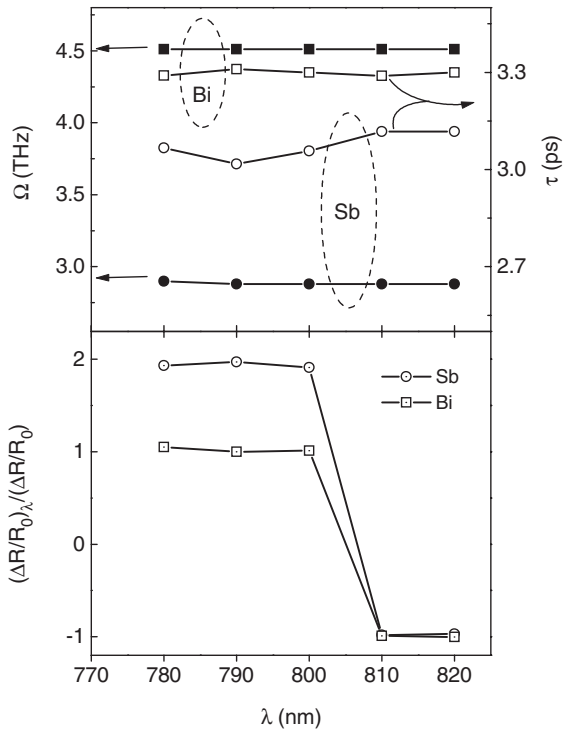

Figure 2. The upper panel shows the frequency (full symbols) and decay time (open symbols), while the bottom panel displays the normalized coherent amplitude as a function of the detection wavelength for Bi (squares) and Sb (circles). The bottom panel shows the normalized coherent amplitude for Bi (squares) and Sb (circles).

used in the study is far away from either the one-photon absorption band or from the maximum for a spontaneous Raman resonance profile [16]. To sum up this part, the observed phase shift indicates that the detection is a scattering process. Assuming the identical character of the interaction for the pump and probe, we can conjecture that the generation mechanism is TSRS as well.

It should be mentioned that a similar phase shift has been observed for the coherent oscillation in transparent materials [1], where it was considered as evidence for stimulated Raman scattering being the main excitation mechanism for coherent phonons. The explanation of the shift was as follows: the probe pulse contains many pairs of Fourier components with a difference in frequency equal to the phonon frequency. If the delay time of the probe is an integer number of the phonon period, the probe will enhance the lattice oscillation, losing energy from the Fourier components of high frequency to those of low frequency. When the delay is an odd integer of the half phonon period, the energy is shifted back from the lattice to the probe in an anti-Stokes scattering. It is clear that this explanation cannot be straightforwardly used for opaque materials where the driving force is imaginary and the interaction length is limited by the penetration depth of light. Instead, the π-shift may be interpreted as the oscillator representing the coherent phonon being localized in the different regions of phase space (or, alternatively, the wavepacket being formed on different slopes of the potential). This delocalized structure of the wavepacket may be considered as a signature of non-classical nature for coherent phonons. Given the fact that the state we measure consists of a macroscopical

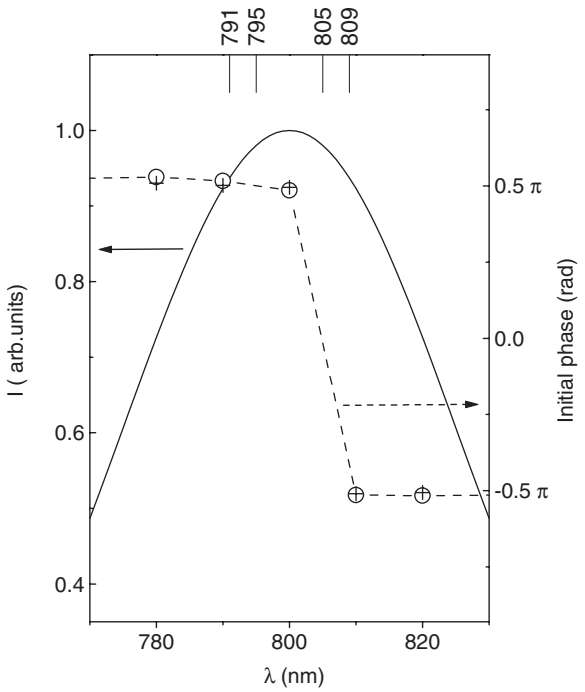

Figure 3. Measured initial phase as a function of the central wavelength of the interference filter. Open symbols—Bi, crossed symbols—Sb. The full curve shows the spectrum of the pump pulse.

number of phonons ($\sim 10^{12}$ in the interaction volume) [17, 18], such a situation resembles the long-lived entanglement observed for two macroscopical ensembles of caesium atoms [19], even though our 'entanglement' occurs in k space. This nonlocality is asking us to revise completely our ideas about coherent phonons as we can no longer consider the phonons as independently existing entities that can be localized in well-defined regions of phase space. It appears that every wavepacket responsible for the coherent phonons consists of subway packets running in different directions in k space. The phonons appear to be interconnected in a way not even conceivable using ideas from classical physics [18]. This initial phase dependence and comparison of the integrated and spectrally resolved oscillation give additional evidence for the non-classical behaviour of the coherent phonon state in semimetals as it had previously been observed in the form of squeezing[3] and revivals[4] for coherent lattice fields [8, 18, 9]. The ions responsible for these nuclear motions are the heaviest 'particles' which have ever demonstrated their wave character in experiments. Hopefully, the observed phase shift and negative time noise in spectrally filtered experiments will help single out a correct theoretical model for the nature and generation mechanism of the coherent phonon. Understanding the exact form of the non-classical lattice state in semimetals remains a challenge and is a good direction for future research.

[3] It should be noted that this observation of vacuum squeezing has been questioned by a number of authors, see, for example, [4]. The authors of [4] suggested that although "The answer to the question: 'Can phonons be squeezed like photons?' is yes on theoretical grounds, the experimental proof still lies in the future."

[4] The situation with revivals is completely opposite to that with squeezing. Here the experimental evidence is absolutely clear since there is no classical counterpart for the effect. However, the theoretical explanation is still lacking.

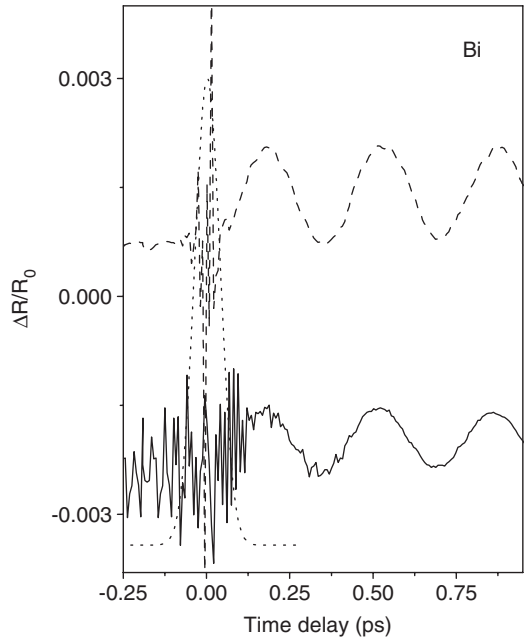

Figure 4. The transient differential reflectivity R/R_0 in Bi for the filtered (full curve) and unfiltered (broken curve) cases. The transients are offset along the vertical axis for clarity. The dotted curve is the cross-correlation of the pump and probe, shown for reference.

A further interesting feature of the filtered probe signal is provided by the comparison of integrated and spectrally resolved transients. As already mentioned, the spectral filtering leads to the appearance of the signal at negative time delays, while the coherent artefact, clearly seen in the integrated signal, disappears, see figure 4. The coherent artefact in the integrated signal is due to four-wave mixing scattering the pump into the probe. It exists only for the time span where the pump and probe overlap. So its disappearance cannot be related to the appearance of the noise at negative time delay, where there is no temporal overlap between the two pulses. It should be remarked that very similar phenomena (signals at negative time delay) have been observed for the electronic response in semiconductors [20, 21]. Most probably this noise needs not to be linked to the coherent phonon dynamics. Nevertheless, the spectrally resolved pump–probe experiments demonstrate the richness in the optical response of semimetals and its fundamental and profound differences from atoms. In particular, the ultrafast response of semimetals (as well as that of the electronic degrees of freedom in semiconductor [22]) cannot be understood in terms of the non-interacting two-level model that has worked so well for dilute atomic systems. For a non-interacting two-level system, the time-domain signal appears as an interaction between the electric field of the probe pulse with the polarization created by the pump pulse and thus does not exist when they do not overlap. In our case, the effective Rabi frequency (describing effective phonon–photon coupling) and the energy of the phonons are renormalized by polarization and population, respectively. It is the renormalization of the Rabi frequency that allows interaction between the polarizations created by the two pulses. As polarizations persist for times of the order of the dephasing time after the exciting electric field, they overlap, regardless of the pulse sequence, to produce the negative time signal [22]. This means that spectrally resolved pump–probe experiments do not represent a real time measurement [23]. Indeed, in conventional (spectrally integrated) pump–probe experiments,

the time resolution is determined by the probe duration, while the spectral width of the probe defines the frequency window of the spectrum. Thus, time and frequency resolutions are Fourier-limited. By adding frequency resolution to the experiment, we lose time resolution due to the Heisenberg uncertainty principle $\Delta\Omega\Delta t \succeq 1$. Hence an observable such as the position of a wavepacket cannot be precisely detected. However, the very fact that the object (coherent phonon) obeys the uncertainty principle indicates its quantum (non-classical) nature. It is on such a short timescale that the non-classical evolution begins to surface and the phonon state created by ultrashort pulses does not act as a classical oscillator since the effect of coherence is significant.

4. Conclusions

We have shown that the excitation of coherent phonons in antimony and bismuth results not only in intensity modulation, but also in modification of the spectral content of the probe pulse. The present experimental results show that the initial phase of the coherent phonon is a function of the detection wavelength, indicating the involvement of a scattering process for the generation and detection of coherent phonons in these narrow-gap materials.

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