Physics Letters A 375 (2011) 2017–2022

Contents lists available at ScienceDirect

Physics Letters A

www.elsevier.com/locate/pla

Generation of coherent phonons in bismuth by ultrashort laser pulses in the visible and NIR: Displacive versus impulsive excitation mechanism

A.A. Melnikov [a,b,*], O.V. Misochko [c], S.V. Chekalin [a]

[a] Institute of Spectroscopy, Russian Academy of Sciences, 142190 Troitsk, Moscow region, Russia
[b] Moscow Institute of Physics and Technology, 141700 Dolgoprudny, Moscow region, Russia
[c] Institute of Solid State Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow region, Russia

ARTICLE INFO

Article history:
Received 17 March 2011
Accepted 31 March 2011
Available online 6 April 2011
Communicated by V.M. Agranovich

ABSTRACT

We have applied femtosecond pump-probe technique with variable pump wavelength to study coherent lattice dynamics in Bi single crystal. Comparison of the coherent amplitude as a function of pump photon energy for two different in symmetry E_g and A_{1g} phonon modes with respective spontaneous resonance Raman profiles reveals that their generation mechanisms are quite distinct. We show that displacive excitation, which is the main mechanism for the generation of coherent A_{1g} phonons, cannot be reduced to the Raman scattering responsible for the generation of lower symmetry coherent lattice modes.

1. Introduction

When ultrashort laser pulses interact with solids they can excite lattice vibrations showing high degree of temporal and spatial coherence [1–3]. These coherent phonons reveal themselves as damped oscillations of a certain optical parameter (e.g. reflectivity or transmittance) in the time domain. To create coherence one needs to establish fixed phase relations either among different q modes of the same phonon branch [4], or between vacuum and excited states of a single $q \approx 0$ phonon mode [5]. Coupling of these lattice states can be achieved in two distinct ways. First, owing to the large spectral bandwidth of an ultrashort laser pulse, it can generate nonstationary phonon states in a crystal through impulsive stimulated Raman scattering, providing a kick to the atoms of the crystal [6,7]. In this case, which we will further refer to as Raman mechanism (RM), the coherence is "field driven", with the driving force responsible for both the energy and coherence transfer from electromagnetic field to lattice. Apart from the "field driven" coherence directly prepared by laser radiation, lattice coherence can also be driven by rapid nonradiative processes. For opaque crystals that have long-lived excited states, the excited state coherence is usually dominant [1–3]. To describe the creation of coherence in this case the displacive excitation of coherent phonons (DECP) model was introduced [8]. In contrast to RM, for DECP the lattice coherence is "relaxation-driven" with no momentum imparted to the atoms from the pump pulse. Additionally, DECP can generate only fully symmetric coherent phonons, whereas RM is capable to create coherent phonons of full and lower symmetry, provided the latter belong to even (gerade) representations of a space group. The primary difference is that in DECP selection rules for the pump play no role and coherent amplitude is determined by the absorption coefficient alone, while in RM the selection rules are controlled by the symmetry of Raman tensor. Thus, DECP is controlled by first order (in electromagnetic field) process, but RM is governed by a second order process.

In an attempt to describe the creation of lattice coherence within a unified approach it was suggested that DECP is not a distinct mechanism, but a particular case of RM [9,10]. Specifically, the off-resonance excitation by laser light pulses at wavelengths lying in the transparency region of a crystal was predicted to impose impulsive driving force on atoms resulting in sine-like coherent oscillations. On the other hand, when the pump radiation falls into resonance with electronic transitions the excitation should be displacive and the atomic motion is then characterized by a cosine-like phase. Each of the two limiting cases is described by a component of a Raman tensor introduced in [10].

However, in many crystals an intermediate initial phase of coherent phonons is observed and therefore, to bring this Raman-based model into agreement with experimental data, its further elaboration included the effects of finite lifetime of excited charge density on the phase and amplitude of coherent phonons [11]. The concept is based on the fact that the decay time of charge carrier density defines the duration of driving force acting on atoms. Provided the decay is rather fast (as compared to the oscillation period), the excitation of coherent phonons acquires impulsive features even in the resonant case. Thus, in time domain the DECP model loses its distinctive features and seemingly should be replaced by a unified RM [11].

* Corresponding author at: Department of Laser Spectroscopy, Institute of Spectroscopy RAS, Fizicheskaya Street 5, Troitsk, Moscow region, 142190, Russia. Tel.: +7 (496) 751 0237; fax: +7 (496) 751 0886.
E-mail address: melnikov@isan.troitsk.ru (A.A. Melnikov).

0375-9601/$ – see front matter
doi:10.1016/j.physleta.2011.03.057

One straightforward way to check the validity of the generalized Raman model is to measure the initial phase of oscillations in the photoinduced response. However, this approach has at least two disadvantages. The first is that for a number of semimetals (Te, Bi, and Sb) DECP and RM give nearly identical predictions for the initial phase of fully symmetric phonon modes [11]. The second results from the difficulty in a precise phase determination. The latter procedure deals with a signal at the moment of the pump and probe pulses overlap and thus it is usually ambiguous.

In the present study an alternative approach is used. We have measured the dependence of coherent phonon amplitude of fully symmetric A_{1g} and doubly degenerate E_g phonon modes in bismuth on excitation wavelength in visible and near infrared ranges. According to the unified Raman model, the coherent phonon amplitudes should be proportional to the corresponding Raman cross sections. Moreover, at any given wavelength the relative intensities of excited phonon modes obtained from the frequency- and time-domain data should be identical. Yet, a comparison of our pump-probe results with spontaneous Raman measurements obviously contradicts the predictions of the unified Raman theory, showing that DECP cannot be reduced to RM.

2. Experimental details

In our experiments all measurements were done at room temperature with a typical ultrafast pump-probe setup. Amplified pulses of a Ti:Sapphire laser operating at $\lambda = 800$ nm were divided into two parts. The first was attenuated to be used to probe the sample — a single crystal of bismuth oriented in such a way that its surface was perpendicular to the trigonal axis. The second part of the beam was used to seed a parametric amplifier to provide pump pulses of 70 fs duration with a tunable central wavelength. The pump and probe beams were incident nearly perpendicular to the surface of the crystal. We detected a component of the probe beam reflected from the crystal and polarized parallel to the pump polarization, while the probe pulses were polarized at 45° relative to the pump. Energy of this component was measured with opened and closed pump beam and the relative change in reflectivity $\Delta R/R_0$ was recorded at a given time delay between the pump and probe pulses. The size of the probe beam spot was about 50 μm in all experiments. The size of the pump beam had a minimum value of about 120 μm for 400 nm pulses and increased at longer pump wavelengths (e.g. for 1300 nm the spot size was as large as 400 μm).

3. Results

Fig. 1 shows the transient reflectivity obtained with pump wavelengths of $\lambda = 400$ and $\lambda = 1300$ nm. Ultrafast excitation at $t = 0$ is followed by a monotonic decay on which pronounced oscillations are superimposed. Since the dominant oscillation frequency almost matches that of A_{1g} phonon mode, these oscillations are the result of fully symmetric A_{1g} coherent atomic motion induced by the laser pulse. It should be emphasized that we did not define zero time delay and therefore, the initial phase of coherent oscillations remains unknown. Nevertheless, in the previous time-domain studies [8,12] the phase of A_{1g} mode was measured for 600 and 800 nm excitation wavelengths and we use this result here, assuming A_{1g} oscillations to be cosine ones, at least in the visible excitation range.

Taking into account the above, the transient reflectivity excited by the $\lambda = 400$ nm pump pulses can be well fitted at positive time delays by the sum of a damped cosine with varying frequency and a monotonic term:

$$\Delta R/R_0 = A(A_{1g}) \exp(-\gamma_1 t) \cos\big(\nu_1(t)t\big) + B(t) \tag{1}$$

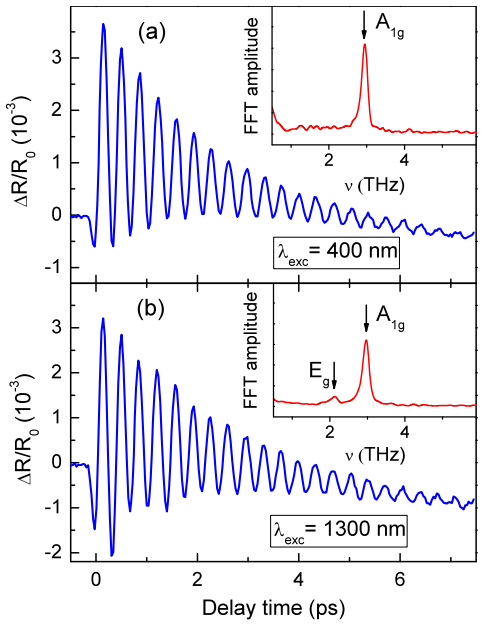

Fig. 1. (a) Transient reflectivity of bismuth excited at $\lambda = 400$ nm as a function of time delay. The inset shows normalized Fourier spectrum for the oscillatory part of the signal. (b) The same curves for the case of $\lambda = 1300$ nm excitation. Note that in the inset apart from the A_{1g} mode, the E_g mode is clearly visible.

where $A(A_{1g})$ is the amplitude and γ_1 is the decay rate of coherent A_{1g} oscillations. The exact form of $B(t)$ term is of no importance in the present study; however, we note that the term has a multi-exponential character. The temporal dependence of frequency ν_1 reflects the effect of so-called frequency or bond softening [13]. Briefly, the instantaneous frequency of A_{1g} coherent phonons in bismuth is not constant due to the presence of excited charge carriers. Its decrease is the most appreciable during few initial cycles of vibrations and then the frequency gradually returns to the unperturbed value of 2.93 THz. It is reasonable in our case to treat the relaxation of the frequency shift as exponential with decay time of ~ 1 ps, while the minimal value of ν_1 attained near zero time delay is ~ 2.8 THz. The photoinduced response described by Eq. (1) is typical for bismuth and it has been observed in numerous previous experiments [8,12,13].

As far as the photoinduced response measured with 1300 nm pump pulses is concerned, it shows a considerable deviation from that excited by the shorter wavelength pulses, especially during the first few picoseconds. Its Fourier spectrum shown in the inset indicates that the main difference is due to the presence of strongly damped oscillations at ~ 2.1 THz, which can be naturally ascribed to the coherent phonons of E_g symmetry [14,15]. By including E_g oscillations into analysis it is possible to fit the measured decay traces. The additional term is a damped harmonic oscillatory function at frequency of 2.1 THz and the only parameter to be addressed specially is its phase. As it has been already noted, we did not measure the absolute initial phase, and in the case of A_{1g} mode just relied on the data available. For E_g mode in bismuth the coherent oscillations reported to have sine-like pattern, with the initial phase being independent on temperature [16]. In our measurements, due to significant difference of A_{1g} and E_g frequencies the *relative* phase may be defined with a satisfactory precision. Therefore, we represented the overall time resolved signal in the following form:

$$\Delta R/R_0 = A(A_{1g}) \exp(-\gamma_1 t) \cos\big(\nu_1(t)t\big) + A(E_g) \exp(-\gamma_2 t) \sin(\nu_2 t + \phi) + B(t) \tag{2}$$