

RESEARCH ARTICLE

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Anisotropy of coherent phonon in Bismuth crystal

Davide Boschetto 

Laboratoire d'Optique Appliquée, ENSTA Paris, CNRS, Ecole Polytechnique, Institut Polytechnique de Paris, 91761 Palaiseau, France

Received 6 September 2024 / Accepted 11 October 2024

Abstract. In this article, we investigate the coherent A_{1g} phonon mode in bismuth crystal using transient reflectivity measurements, focusing on two distinct crystallographic orientations: one with the principal axis ((1 1 1)-direction in the trigonal cell representation) perpendicular to the sample surface, and the other with the principal axis parallel to the surface. Our results demonstrate significant variations in the amplitude, frequency, and lifetime of the coherent phonon mode between these two orientations, even when identical pumping and probing conditions are applied. We attribute these differences to the anisotropy of the electron effective mass, which influences electron mobility and, in turn, affects the phonon dynamics in bismuth.

Keywords: Coherent phonon, Pump/probe experiment, Ultrafast transient reflectivity, Bismuth, Anisotropy, Phonon dynamics.

1 Introduction

The coherent control of atomic vibrations offers a powerful tool to manipulate the properties of matter at the microscopic level [1]. In crystalline solids, these coherent vibrations correspond to specific phonon modes that can be excited by ultrafast laser pulses [2]. When the photon energy of the laser matches an electronic transition that destabilizes the crystal lattice, it induces a coherent atomic motion, setting up one or more phonon modes [3]. Coherent optical phonons enable the study of selective electron-phonon coupling, offering insights into phenomena of significant interest, particularly in strongly correlated materials. Coherent optical phonons are also important in driving or modulating phase transitions, as their interaction with electronic states can help stabilize or enhance specific phases of a material [4]. To investigate these processes, a wide range of experimental configurations have been employed, primarily using the pump-probe technique with sub-100 fs time resolution [5]. Early studies focused on all-optical configurations at a wavelength of 800 nm, but these have since expanded to cover broader spectral ranges for both pump and probe pulses, including advanced methods such as high-order harmonics generation [6] and time-resolved electron diffraction [7].

Bismuth has often been the prototypical material for coherent optical phonon experiments [5–9] due to its relatively simple crystal structure, in which two Raman-active

phonon modes are present: the A_{1g} mode with a frequency centered at 2.92 THz, also known as the breathing mode, and the E_g mode with a frequency centered at 2.22 THz [10]. The A_{1g} mode involves symmetric oscillation of the two Bi atoms against each other along the (1 1 1)-direction, preserving all the symmetry operations of the unit cell. In contrast, the E_g mode corresponds to atomic oscillations in the plane orthogonal to the (1 1 1)-direction, making it degenerate within that plane. Among these, the breathing mode (A_{1g}) is more efficiently excited in pump-probe experiments because it maintains the full symmetry of the crystal unit cell [10]. As a result, the A_{1g} mode has become one of the most extensively studied coherent phonon modes, examined across a wide range of experimental setups. However, nearly all optical studies to date have focused on bismuth samples with the principal axis oriented perpendicular to the sample surface ((1 1 1)-oriented). One previous study has reported the behavior of the reflectivity in two different crystallographic orientations [11]. However, that study primarily focused on the sign change of the reflectivity at the plateau, which was interpreted within the framework of the two-temperature model, and did not address the critical comparison of the coherent phonon mode dynamics between the two types of crystallographic orientations.

In this study, we extend the investigation of the coherent A_{1g} phonon mode in bismuth crystals to two distinct crystallographic orientations: one with the principal axis ((1 1 1)-direction) perpendicular to the sample surface and another with the principal axis parallel to the surface. Despite the preserved symmetry of the breathing mode,

* Corresponding author: davide.boschetto@ensta.fr

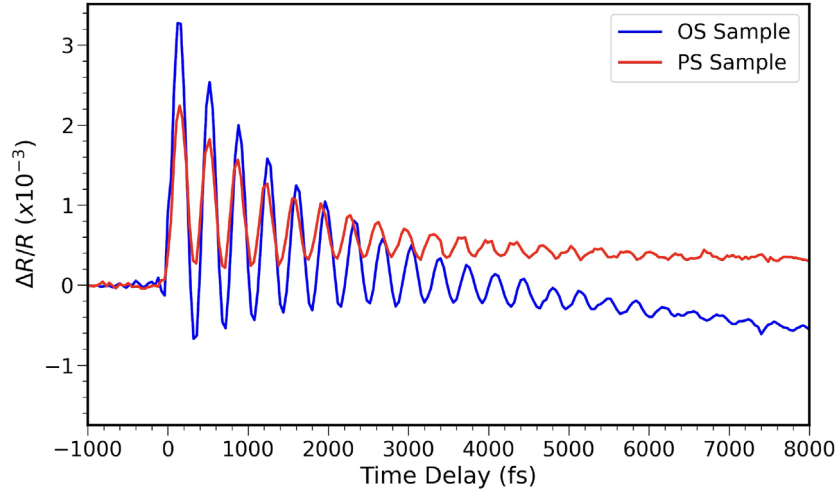


Fig. 1. Transient reflectivity measurements for both crystallographic orientations: OS (blue) and PS (red).

our experimental results show clear differences in the phonon dynamics between these two configurations. We attribute these differences to the anisotropy of the electron effective mass, which affects electron mobility and, consequently, the behavior of the coherent phonon mode.

2 Results and discussion

Experiments have been carried out in a pump-probe configuration [12] with a custom-built laser system, delivering a 50 fs laser pulse at a wavelength of 800 nm and at repetition rate of 1 kHz. The pump and probe pulses are orthogonally polarized, and are focused on around 130 μm and 40 μm , respectively, in order to probe a homogeneously excited surface. The pump fluence was kept at 15 mJ/cm^2 , while the probe fluence was kept at 0.1 mJ/cm^2 .

Figure 1 presents the experimental results of the transient reflectivity measurements for both crystallographic orientations: OS (where the principal axis is orthogonal to the surface) and PS (where the principal axis is parallel to the surface). In both cases, we observe a damped coherent phonon mode superimposed on a slowly varying background. This background is attributed to the competition between electron and lattice temperatures, as described by the two-temperature model [11]. The behavior of the OS sample is consistent with previously reported results [5, 8, 11]. Several key differences can be identified from Figure 1. Firstly, the amplitude of the coherent phonon oscillations is more pronounced in the OS sample, and it exhibits a slightly longer lifetime compared to the PS sample. Secondly, despite the same pump fluence being used for both samples, the phonon frequencies differ between the two orientations.

To isolate the coherent oscillations from the slower thermal dynamics, we calculated the temporal derivative of the signals, as shown in Figure 2. This approach allows us to fit the oscillatory behavior more accurately without the influence of thermal effects. The fits of the temporal derivative of the signal were performed using a damped cosine

function: $\frac{d}{dt} \left(\frac{\Delta R}{R} \right) = A \cdot e^{-\gamma t} \cdot \cos(2\pi\omega t + \phi) + c_0$, where

t is the pump-probe time delay, A is the amplitude, γ is the phonon damping rate, ω is the frequency, ϕ is the phase, and c_0 accounts for any baseline shift. Overall, the fits show good agreement with the experimental data, although a slight discrepancy is observed at longer time delays (beyond approximately 4 ps), which could indicate a minor change in the phonon frequency over time, as suggested by previous studies [5]. For simplicity, we have modeled the frequency as constant in our analysis, as this assumption does not significantly impact the main trends and conclusions of our study. Three parameters of particular interest here are the phonon amplitude, frequency and damping rate. For the OS sample, the best fit yields $A_{\text{OS}} = 3.3 \times 10^{-5}$, $\omega_{\text{OS}} = 2.77$ THz and $\gamma_{\text{OS}} = 5.6 \times 10^{-4} \text{ fs}^{-1}$. In contrast, the PS sample shows $A_{\text{PS}} = 2 \times 10^{-5}$, $\omega_{\text{PS}} = 2.85$ THz and $\gamma_{\text{PS}} = 6.3 \times 10^{-4} \text{ fs}^{-1}$.

The observed differences in both the amplitude and frequency of the coherent phonon mode between the two samples could be attributed to anisotropy in their optical properties, particularly the real and imaginary parts of the dielectric function. At a wavelength of 800 nm, while the real part of the dielectric function remains nearly constant, the imaginary part shows a significant difference: -16.25 for the OS sample and -20 for the PS sample [8, 13]. This indicates that the PS sample has a stronger absorption, which would typically suggest a higher number of excited electrons and a more efficient driving of the coherent phonon mode. Consequently, one might expect the PS sample to exhibit a larger phonon amplitude and a lower phonon frequency due to a phenomenon known as mode softening [5], where a higher pump fluence generally leads to an increased phonon amplitude and a decrease in phonon frequency. However, the experimental results show the opposite trend: the amplitude is greater in the OS sample, which also exhibits a slightly lower phonon frequency. This contradicts the expectation based on the stronger absorption of the PS sample, suggesting that the underlying mechanism is more complex than initially assumed.

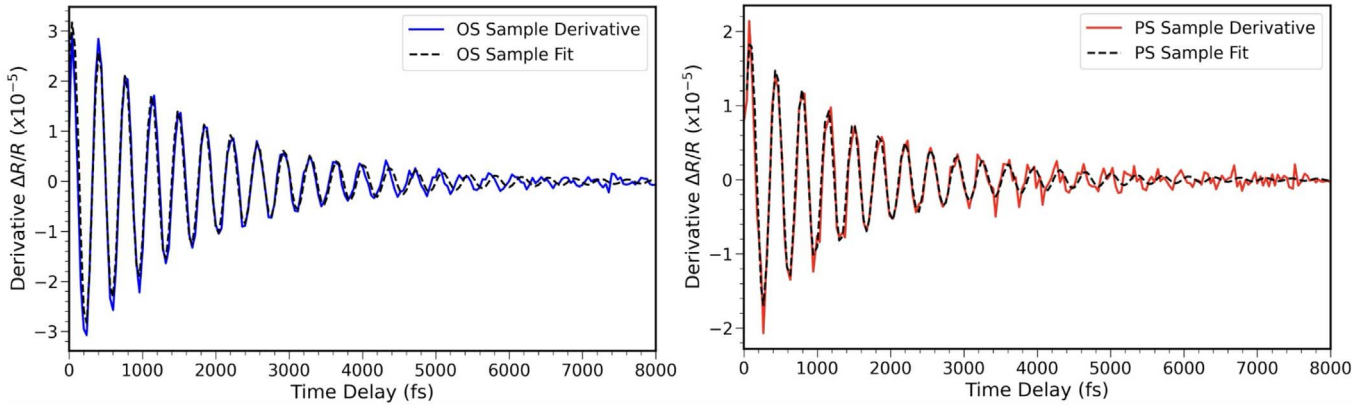


FIG. 2

Fig. 2. Derivative of the experimental results with fitted curves for both OS (left panel) and PS (right panel) samples.

To explain the observed change in frequency, we refer to the model explained in [5], for which $\omega^2 = \omega_0^2(1 - T_e/\epsilon_b)$, where $\omega_0 = 2.92$ THz is the equilibrium Raman frequency, T_e is the electron temperature in eV, and $\epsilon_b = 2.16$ eV is the electron binding energy in bismuth. According to this model, the frequency depends on the electron temperature established shortly after excitation. The higher frequency observed in the PS sample suggests that the electron temperature in this configuration is actually lower than in the OS sample. Indeed, previous studies have shown that electron diffusion plays a crucial role in the early stages of dynamics in bismuth [9]. The strong gradient induced by pump absorption causes high-energy electrons to migrate away from the heated region, leading to a lower electron temperature in the probed skin depth. Therefore, our results suggest that electron mobility and diffusivity are higher in the PS sample than in the OS sample. To verify this hypothesis, we must examine the electron mobility and diffusivity in both cases. The electron mobility μ is given by $\mu = e\tau/m^*$, where e is the electron charge, τ is the collision time, and m^* is the electron effective mass. The electron diffusivity D is related to mobility by $D = \mu k_B T/e$, where k_B is the Boltzmann constant and T is the temperature. Bismuth exhibits strong anisotropy in its electron effective mass, with a difference of about an order of magnitude between the two crystallographic directions: $m_{OS}^* = 0.612$ and $m_{PS}^* = 0.0675$ [14]. Since electron mobility and diffusivity are inversely proportional to the effective mass, it is reasonable to conclude that electron transport in the PS sample is more efficient, leading to faster diffusion out of the pumped region, a lower electron temperature, and consequently, a higher phonon frequency. These results support the validity of the model proposed in [5] and highlight the significant role of electron mobility in the photo-excited dynamics of bismuth.

However, electron diffusion is not the only possible mechanism to explain the observed changes in frequency. Other possible explanations involve nonlinear optical effects and laser-induced structural changes. For example, the increased absorption in the PS sample suggests a higher likelihood of multi-photon absorption. This process can promote electrons to higher energy states, where they may couple less efficiently with the A_{1g} mode, leading to a lower

amplitude of the coherent phonon oscillations and, consequently, a higher frequency. To evaluate these hypotheses, it is worth noting that investigations using double-pump experiments [8] have shown that the amplitude, frequency, and damping time of the coherent phonon excited by the first pump pulse are nearly identical to those excited by a second pulse arriving 25 ps later after the first phonon mode has vanished. This observation suggests that the vibrational parameters of the coherent phonon mode are primarily determined by the electron temperature immediately after photoexcitation – which is quasi-instantaneously modified by each pump pulse – and are not significantly affected by the increased lattice temperature or residual excited carriers. On the other hand, if laser-induced structural phase transitions were occurring under our experimental conditions, we would expect significant changes in the phonon parameters between the first and second pump pulses due to altered electronic or structural states of the sample. Therefore, the consistency of the phonon parameters indicates that no structural phase transition took place. This supports the scenario that the coherent phonon dynamics are governed by the initial photoexcited electron population resulting from linear absorption processes, and that any process altering the local electron temperature, such as electron diffusion, can significantly influence the vibrational parameters of the coherent phonon. It is also worth mentioning that in insulators and semiconductors, two-photon absorption becomes relevant for pulse intensities in the range from 10^9 up to 10^{12} W/cm² [15]. However, in metals and semimetals like bismuth, one-photon absorption remains dominant even within this intensity range due to the high free-electron density, which ensures the availability of carriers for one-photon transitions. In conclusion, if significant multi-photon absorption or laser-induced structural changes were occurring at our experimental fluence, we would expect to observe notable differences in the phonon parameters, which is not the case based on our double-pump experiments. Therefore, while additional experiments and theoretical calculations are needed to clearly distinguish between the proposed mechanisms, multi-photon absorption and laser-induced structural changes are less likely to play dominant roles at the experimental fluence used here. In contrast, the explanation attributing the

observations to the anisotropy of the effective electron mass and electron diffusion is more consistent with existing measurements [9, 14]. However, additional experimental and theoretical efforts are needed to further confirm the proposed mechanism responsible for the differences in the coherent phonon parameters between the two crystallographic orientations.

An interesting and unexpected observation in our study is the higher phonon damping rate in the PS sample compared to the OS sample, despite the larger amplitude of atomic motion in the latter. This result seems counterintuitive if one assumes that a larger atomic displacement would naturally lead to a higher damping rate due to increased phonon-phonon interactions. However, in this case, other mechanisms may contribute to the observed behavior. One plausible explanation is that in the PS orientation, the pump pulse perturbs more efficiently other phonon modes, for example the E_g mode or acoustical modes, which subsequently couple to the A_{1g} mode. This additional coupling can provide a more efficient pathway for energy transfer, enhancing the overall damping rate of the breathing mode. Such mode coupling could lead to a faster redistribution of energy from the coherent A_{1g} mode to other modes, thereby increasing the damping rate observed in the PS sample. Further studies are required to explore this hypothesis, potentially through techniques that can selectively probe different phonon modes or their interactions, such as time-resolved electron diffraction [16].

3 Conclusions

In conclusion, we investigated the A_{1g} coherent phonon in bismuth crystals with two different crystallographic orientations, showing anisotropic behavior. These differences can be attributed to the anisotropy in the electron effective mass in bismuth, which influences the electron mobility and subsequently the phonon behavior. However, additional experiments and theoretical calculations are needed to further elucidate the suggested mechanisms. Our results underscore the importance of considering crystallographic orientation in the study of coherent phonon dynamics and suggest that further investigation into mode coupling effects and their dependence on sample orientation could provide deeper insights into the fundamental mechanisms governing phonon behavior in anisotropic materials.

Acknowledgments

The author acknowledges the support from the French Department of Defense (DGA).

Funding

This research received no external funding.

Conflicts of interest

The author declares no conflict of interest.

Data availability statement

Data obtained in this work are not publicly available but may be obtained from the authors upon reasonable request.

References

- 1 Cavalleri A, Photo-induced superconductivity, *Contemp. Phys.* **59**, 31 (2018). <https://doi.org/10.1080/00107514.2017.1406623>.
- 2 Weis M, Lejman M, Faure J, Phuoc VT, Cario L, Boschetto D, Coherent phonons in incommensurate LaVS3 crystal, *Appl. Phys. Lett.* **125**, 011903 (2024). <https://doi.org/10.1063/5.0211057>.
- 3 Servol M, Moisan N, Collet E, Cailleau H, Kaszub W, Toupet L, Boschetto D, Ishikawa T, Moréac A, Koshihara S, Maesato M, Uruichi M, Shao X, Nakano Y, Yamochi H, Saito G, Lorenc M, Local response to light excitation in the charge-ordered phase of (EDO-TTF)₂SbF₆, *Phys. Rev. B* **92**, 024304 (2015). <https://doi.org/10.1103/PhysRevB.92.024304>.
- 4 Stojchevska L, Vaskivskiy I, Mertelj T, Kusar P, Svetin D, Brazovskii S, Mihailovic D, Ultrafast switching to a stable hidden quantum state in an electronic crystal, *Science* **344**, 177 (2014). <https://doi.org/10.1126/science.1241591>.
- 5 Garl T, Gamaly EG, Boschetto D, Rode AV, Luther-Davies B, Rousse A, Birth and decay of coherent optical phonons in femtosecond-laser-excited bismuth, *Phys. Rev. B* **78**, 134302 (2008). <https://doi.org/10.1103/PhysRevB.78.134302>.
- 6 Papalazarou E, Boschetto D, Gautier J, Garl T, Valentin C, Rey G, Zeitoun P, Rousse A, Balcou P, Marsi M, Probing coherently excited optical phonons by extreme ultraviolet radiation with femtosecond time resolution, *Appl. Phys. Lett.* **93**, 041114 (2008). <https://doi.org/10.1063/1.2966180>.
- 7 Bugayev A, Esmail A, Abdel-Fattah M, Elsayed-Ali HE, Coherent phonons in bismuth film observed by ultrafast electron diffraction. *AIP Adv.* **1**, 012117 (2011). <https://doi.org/10.1063/1.3574888>.
- 8 Boschetto D, Garl T, Rousse A, Ultrafast dielectric function dynamics in bismuth, *J. Mod. Opt.* **57**, 953 (2010). <https://doi.org/10.1080/09500341003632670>.
- 9 Jnawali G, Boschetto D, Malard LM, Heinz TF, Sciaini G, Thiemann F, Payer T, Kremeyer L, Meyer zu Heringdorf FJ, Horn-von Hoegen M, Hot carrier transport limits the displacive excitation of coherent phonons in bismuth, *Appl. Phys. Lett.* **119**, 091601 (2021). <https://doi.org/10.1063/5.0056813>.
- 10 Ishioka K, Kitajima M, Misochko OV, Temperature dependence of coherent A_{1g} and E_g phonons of bismuth, *J. Appl. Phys.* **100**, 093501 (2006). <https://doi.org/10.1063/1.2363746>.
- 11 Olivier C, Moisan N, Boschetto D, Anisotropy of ultrafast transient reflectivity during electron-phonon thermalization in bismuth crystal, *J. Intense Pulsed Lasers Appl. Adv. Phys.* **3**, 11 (2013).
- 12 Khalili A, Weis M, Mizrahi SG, Chu A, Dang TH, Abadie C, Greboval C, Dabard C, Prado Y, Xu XZ, Péronne E, Livache C, Ithurria S, Patriarche G, Ramade J, Vincent G, Boschetto D, Lhuillier E, Guided-mode resonator coupled with nanocrystal intraband absorption, *ACS Photon.* **9**, 985 (2022). <https://doi.org/10.1021/acsp Photonics.1c01847>.
- 13 Lenham AP, Treherne DM, Metcalfe RJ, Optical properties of antimony, bismuth crystals, *J. Opt. Soc. Am.* **55**, 1072 (1965). <https://doi.org/10.1364/JOSA.55.001072>.
- 14 Liu Y, Allen RE, Electronic structure of the semimetals Bi and Sb. *Phys. Rev. B* **52**, 1566 (1995). <https://doi.org/10.1103/PhysRevB.52.1566>.
- 15 Boyd RW, in *Nonlinear Optics*, edited by Academic Press, 3rd edn. (Academic Press, 2008). <https://doi.org/10.1016/B978-0-12-369470-6.00020-4>.

- 16 Gonzalez Vallejo I, Gallé G, Arnaud B, Scott SA, Lagally MG, Boschetto D, Coulon PE, Rizza G, Houdellier F, Le Bollo  ch D, Faure J, Observation of large multiple scattering effects in ultrafast electron diffraction on monocrystalline silicon, *Phys. Rev. B* **97**, 054302 (2018). <https://doi.org/10.1103/PhysRevB.97.054302>.