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Observation of Second Sound in Graphite over 200 K

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Abstract

Second sound refers to the phenomenon of heat propagation as temperature waves in the phonon hydrodynamic transport regime. We directly observe second sound in graphite at temperatures of over 200 K using a sub-picosecond transient grating technique. The experimentally determined dispersion relation of the thermal-wave velocity increases with decreasing grating period, consistent with first-principles-based solution of the Peierls-Boltzmann transport equation. Through simulation, we reveal this increase as a result of thermal zero sound—the thermal waves due to ballistic phonons. Our experimental findings are well explained with the interplay among three groups of phonons: ballistic, diffusive, and hydrodynamic phonons. Our ab initio calculations further predict a large isotope effect on the properties of thermal waves and the existence of second sound at room temperature in isotopically pure graphite.

Introduction

Thermal transport in dielectrics and semiconductors is often mediated by the random-walk behavior of phonons and follows Fourier's law of heat diffusion. However, Fourier's law breaks down at sufficiently small length scales or low temperatures, where unusual regimes of ballistic and hydrodynamic phonon transport are observed. In the ballistic regime, phonons can travel a distance longer than the conduction length scale without scattering, leading to an effective thermal conductivity value that diminishes as the length scale is reduced. This regime has been studied extensively owing to its importance in applications such as electronics thermal management and thermoelectric energy conversion¹⁻⁴. The hydrodynamic regime takes place when momentum-conserving normal scattering (N-scattering) is stronger than momentum-destroying resistive scattering (R-scattering), leading to a collective drift motion of phonons under a temperature gradient. This strongly correlated collective motion of phonons leads to peculiar thermal transport phenomena such as second sound⁵⁻¹¹, phonon Poiseuille flow^{6,12,13} and Knudsen minimum^{12,14}, parallel to the hydrodynamic regime of strongly correlated electrons¹⁵⁻¹⁸. For over half a century, phonon hydrodynamic transport was deemed exotic and mattered only at extremely low temperatures. However, phonon hydrodynamics at substantially higher temperatures in low-dimensional and van der Waals materials has recently been theoretically predicted and experimentally observed, stimulating renewed interest, especially in second sound^{12,13,19-25}.

Second sound is the wavelike propagation of heat²⁶. First observed by Peshkov in 1944 in superfluid ³He at 1.4~1.6 K²⁷ and explained with Landau's two-fluid model²⁸, it was later predicted to exist also in solids when phonon-phonon N-scattering dominates over R-scattering⁸. Experimentally, second sound in solids was initially observed via heat-pulse methods near liquid-helium temperatures, for example, at 1.2~4.0 K in Bi²⁹ and 10~18 K in NaF³⁰. Some of us recently reported observation of second sound above 100 K in graphite using the transient thermal grating (TTG) technique²¹ in which the thermal transport length scale is imposed by the use of crossed excitation laser pulses that produce an optical interference pattern of alternating peaks and nulls at the sample, resulting in a sinusoidally varying temperature "grating" profile. The observation of second sound in graphite is further confirmed via the transient hydrodynamic lattice cooling by picosecond laser irradiation of graphite³¹. The kinetics of transport from the heated transient

grating peaks to the unheated nulls are measured through time-resolved diffraction of probe laser light from the surface modulation caused by thermal expansion at the heated grating peaks. Transport by second sound was expected to be observable at even higher temperatures for TTG spatial periods smaller than those used in our previous study as suggested by the theoretical calculations^{21,32}. However, the temporal resolution of our continuous-wave-laser-probed TTG system (~ 0.5 ns) imposed a lower limit of the grating period of about 6 μm , below which the kinetics could not be resolved.

Theoretically, phonon-mediated second sound is described as damped temperature waves derived either from the phonon Peierls-Boltzmann transport equation (PBTE)^{5,6,9,10} or equilibrium correlation functions^{11,33}. In particular, the dispersion of second sound has been analyzed by applying a temperature perturbation to the PBTE⁹ and analytically solving it for the quasi-momentum auto-correlation function¹¹. However, all these efforts focus on the frequency windows within which we can observe second sound, while the wavevector dependence of the second-sound velocity, i.e., the dispersion of the velocity, has not been discussed.

While second sound originates from phonons in local thermal equilibrium caused by strong normal scattering (a drifting equilibrium)⁶, ballistic phonons can also generate a wavelike heat flow, as was evident in past experiments on NaF and Bi^{29,30}, in which heat pulses due to ballistic longitudinal and transverse phonons reached the detectors before the arrival of second sound. These thermally excited phonons were mistakenly attributed to first sound, but it was shown³⁴ that heat-pulse excitation used in the earlier experiments cannot excite a mechanical wave of large amplitude. Mechanically excited first sound can be damped by phonons in local equilibrium via the Landau-Rumer³⁵ and Akhiezer mechanisms³⁶, because the wavelength of the first sound is much longer than the phonon thermalization length, i.e. the phonon mean free path (MFP). If the MFP is longer than the wavelength of the first sound, it was called zero sound, in analogy to the propagation of zero-sound waves across a Fermi liquid in the ballistic limit³⁷⁻⁴⁰. In analogy to the zero sound for mechanical sound waves, we call the ballistic thermal wave “thermal zero sound.” In heat-pulse experiments^{29,30}, phonons are excited in all directions by the heater, but only those propagating within a small solid angle subtended by the detector are recorded, leading to thermal zero-sound velocities close to those of the longitudinal and transverse phonons. Oscillations due

to thermal zero sound were also calculated theoretically by solving the PBTE under the constant MFP approximation for the TTG experimental geometry⁴¹.

In this work, we report the observation of second sound at record-high temperatures of over 200 K via pulsed-laser-probed TTG measurements at grating periods of around 2 μm . The thermal transport that is measured also includes contributions from thermal zero sound due to ballistic phonons. We show that the transport can be viewed as a mixture of three groups of phonons: hydrodynamic phonons experiencing strong normal scattering, contributing to second sound; ballistic phonons contributing to thermal zero sound; and resistive phonons contributing to diffusion along the temperature gradient. Using exact solutions of the PBTE, we demonstrate increasing contributions of thermal zero sound to the TTG signal with decreasing grating period. We also predict a large isotope effect on second sound. Notably, room-temperature second sound is expected in isotopically enriched graphite. What is reported here is the “drifting” second sound as discussed by Hardy⁵ where collective drift motion of phonons due to strong N-scattering is essential. This “drifting” second sound is distinguished from “driftless” second sound suggested by a recent report on measurements in a rapidly varying temperature field⁴².

Results

Observation of second sound in graphite above 200 K

As discussed in Ref. 21, second sound has recently been observed in graphite at around 100 K via transient thermal grating (TTG) measurement with a continuous-wave (CW) probe laser. However, with a CW probe and the measurement bandwidth of Ref. 21, the time resolution was limited to ~ 0.5 ns which prevented measurements at smaller grating period where second sound is expected at much higher temperatures. In this work, we replaced the CW laser with a femtosecond pulsed laser and used the standard ultrafast measurement technique in which the pump-probe delay time is varied to acquire time-dependent signals^{43,44}. The experimental details can be found in Material and methods and the Supplementary Materials (SM1). Following the Green function approach developed by Chiloyan et al.⁴⁵, we also theoretically simulate the TTG response using first-principle calculations with no fitting parameters (SM2).

As demonstrated in the simulated TTG signal (Fig. 1a), second sound is characterized by a sign reversal in the heterodyned TTG signal²¹. Shortly after TTG excitation, the diffracted signal field from the modulated surface profile in which thermal expansion has occurred at the grating peaks is superposed constructively with a reference field, yielding a positive heterodyned signal. Second sound moves heat away from the peaks and into the nulls in wavelike fashion, not merely equalizing the temperature as in ordinary thermal transport but raising the temperature at the nulls above that of the peaks. Thermal expansion becomes more pronounced at the nulls than at the peaks, reversing the surface modulation profile and therefore reversing the phase of the diffracted signal field. The resulting destructive superposition with the reference field yields a negative heterodyned TTG signal, a clear signature of wavelike transport. The strength of the wavelike feature can be measured expediently by the ratio of the negative dip depth to the initial signal peak height. Figure 1b summarizes experimental results recorded at different grating periods and temperatures, using the normalized dip depth as the metric for the wavelike contribution to transport. The calculated temperature windows for second sound at each grating period are also indicated. A normalized depth of 0.05 marks the experimental limit below which we cannot clearly observe second sound. TTG signals often contain oscillations due to acoustic vibrations, which have much lower damping rates. We found that the acoustic signal could be suppressed by maximizing the peak height through adjustment of the reference field phase as discussed in SM1. At 250 K (Fig. 1c), any sign flip in the signal is obscured by the acoustic signal at the experimental signal-to-noise ratio. But the clear hallmark of second sound is observed at 200 K (Fig. 1d) and 225 K (Fig. S3a). The calculated temperature windows (Fig. 1b) indicate that second sound can persist for longer thermal transport length scales at lower temperatures, which is consistent with the present and previous [21] experimental observations at 100 K (Fig. 1e). A larger discrepancy between experiment and simulation is observed at 100 K (Fig. 1e) than 200 K (Fig. 1d), which might result from the increasing importance of phonon-impurity scattering at lower temperatures compared to phonon-phonon scattering. At 100 K (Fig. 1f), about 0.02% vacancy density could explain the discrepancy between simulation and experiment, while the simulated response at 200 K showed a much smaller effect at the same level of defect (Fig. S4).

Dispersion of measured thermal wave

Based on the TTG signal, the velocity v_p and propagation length l_p of the thermal waves can be estimated from the dip position t_d and normalized depth ΔT_d as (Fig. 1a):

$$v_p = \frac{l}{2t_d} \quad (1a)$$

$$l_p = \frac{l}{-2 \ln(-\Delta T_d)} \quad (1b)$$

where l is the grating period. Equation (1a) follows from the definition of the dip position as the time duration it takes for the thermal wave to travel from a high-temperature region to an adjacent low-temperature region, that is, half the grating period; Eq. (1b) arises from the fact that the amplitude of an exponentially decaying wave drops to $\exp(-l/2l_p)$ over a distance of $l/2$. Using Eq. (1), we determined the thermal-wave velocity and propagation length at different temperatures and grating periods, from both experimental and simulated TTG signals. As shown in Figs. 2a and 2b, there is a qualitative agreement between the simulations and experiment. The quantitative discrepancy is attributed to defects in our graphite samples.

Refs. [5–8] used Callaway model⁴⁸ to study second sound. The Callaway model splits the scattering term in the PBTE into two different relaxation terms: resistive scattering and normal scattering that drive the phonon distribution to the local equilibrium Bose-Einstein distribution and displaced Bose-Einstein distribution respectively. From the energy and momentum conservation equations, the second-sound velocity v_{ss} and propagation length l_{ss} in the x -direction can be written as⁴⁷:

$$v_{ss}^2 = \frac{\langle \frac{c_q q_x v_x}{\omega_q} \rangle_2}{\langle \frac{c_q q_x^2}{\omega_q^2} \rangle \langle c_q \rangle} \quad (2a)$$

$$l_{ss} = \frac{2v_{ss} \langle \frac{c_q q_x^2}{\omega_q^2} \rangle}{\langle \frac{c_q q_x^2}{\omega_q^2 \tau_{qR}} \rangle} \quad (2b)$$

Where C_q , q_x , v_x , ω_q , and τ_{qR}^{-1} are the mode-specific heat capacity, wavevector, group velocity, frequency, and R-scattering rate, respectively, and $\langle \rangle$ means summation over all the phonon modes i.e. $\langle C_q \rangle = \sum_q C_q$. We refer to the second-sound velocity and propagation length obtained from Eq. (2) as the intrinsic limits (Fig. 2a, b, d). To further understand the dispersion of the measured wave velocity, we also simulated the TTG temperature response at the ballistic limit, where phonons propagate without interactions. Wavelike behavior due to thermal zero sound is also seen in the calculated response in the investigated temperature range in the ballistic regime (Fig. 2c and Fig. S5), although the wave contains multiple frequencies from different polarizations. A similar wave propagation velocity could be defined based on the position of the first dip and is referred to as thermal zero sound velocity. The thermal zero sound is faster than the intrinsic second-sound speed at all the investigated temperatures (Fig. 2d) as expected, because second sound involves mixing and scattering of different phonons to approach a local thermal equilibrium^{5,6}. We can also consider longitudinal and transverse waves separately as these waves do not interact in the ballistic limit, as plotted in Fig. 2c. At 100 K, the flexural mode dominates the signal and its superposition with longitudinal and transverse waves leads to higher thermal zero sound velocity. Both the second sound velocity obtained from Eq. (2a) and the thermal zero sound velocity increase from 100 K to 125 K first, then start to decrease upon further rise in temperature (Fig. 2d). However, the group velocity of the measured thermal wave, which includes both second sound and thermal zero sound, decreases monotonically with increasing temperature at a fixed grating period (Fig. 2a and Fig. S6a). As the grating period decreases, the measured wave propagation speed increases from the intrinsic second sound velocity to the thermal zero sound velocity (Fig. 2a) since a greater portion of the phonon MFPs exceed the grating spacing. On the other hand, the measured wave propagation length increases at longer grating periods (Fig. 2b) because of the reduced contributions of ballistic phonons with effective propagation lengths limited by the grating period.

The measured grating-period-dependent wave propagation speed yields a convex dispersion relation, which is consistent with the calculated dispersion (Fig. 2e, also Material and methods and SM4). In addition, the gap between the real and imaginary parts of the frequency is maximized at mid-wavevector, which is consistent with the trend of the second-sound strength metric (i.e. normalized dip depth) we defined (Fig. 2f).

Three groups of phonons

Phonons participating in thermal transport are a mixture of those experiencing no scattering, those experiencing both N- and R-scattering, and those experiencing R-scattering only⁴⁹. The observed thermal wave is formed by a superposition of ballistic, diffusive and hydrodynamic phonons. The dispersion and temperature-dependence of the measured thermal waves can be understood with three groups of phonons, i.e., ballistic phonons, diffusive phonons and hydrodynamic phonons. Such a picture could also explain the heat-pulse experimental observations as detailed in SM5. To qualitatively describe how much the ballistic/diffusive component is contributing to the measured thermal waves, we estimate the fraction of the initially excited phonons with traveling distance shorter/longer than the corresponding mean free path as:

$$f_b = \frac{\langle c_q v_x^2 f_b^q(\Lambda_o/d) \rangle}{\langle c_q v_x^2 \rangle} \quad (4a)$$

$$f_d = \frac{\langle c_q v_x^2 f_d^q(\Lambda_R/d) \rangle}{\langle c_q v_x^2 \rangle} \quad (4b)$$

where d is the traveling distance, Λ_o is the total MFP, considering all scattering processes, and Λ_R is MFP considering only resistive scattering processes. Here $f_{b/d}$ is the fractions of ballistic and diffusive contribution to the transport. The fraction of hydrodynamic contribution f_h could be approximated as: $1 - f_b - f_d$. $f_{b/d}^q$ is the ballistic/diffusive contribution function for phonon mode q . Details on the definition of traveling distance d and function $f_{b/d}^q$ are provided in SM6. Figures 3 shows the approximated fractions of ballistic, hydrodynamic and diffusive phonons defined at different grating periods and temperatures.

As the grating period decreases, more phonons have MFPs exceeding the period and therefore contribute to ballistic transport (Fig. 3a), hence the wave propagation velocity increases from the bulk second sound velocity to the thermal zero sound velocity (Fig. 2a). For the same reason, the second sound propagation length increases with longer grating period (Fig. 2b), as more phonons participate in the second sound wave type of propagation rather than ballistic transport (Fig. 3a). The velocity of the wavelike mode at fixed grating period monotonically decreases with increasing temperature (Fig. 2a and Fig. S6a), as less phonons participate in ballistic transport at

higher temperature due to increasing phonon scattering rates (Fig. 3a). The second-sound strength, as measured by the normalized dip depth, is greatest at an intermediate grating spacing (Fig. 2f). This can be understood as follows. When the spacing is large, R-scattering dominates. The increased diffusive transport leads to a smaller dip depth. When the spacing is small, ballistic phonons, which do not dip much below zero due to superposition of three different polarizations, mix with second sound waves and diminish the measured normalized dip depth. The thermal wave we observed on 200 K mainly comes from second sound, which is supported by the large difference between the experimental signals and the ballistic limit in Fig. 1d and the mean free path analysis as in SM 7.

Strong isotope effect

Large enhancement in the thermal conductivity via isotope enrichment has been reported in high-thermal-conductivity materials⁵⁰. Isotope scattering is a R-scattering process and can significantly influence second sound. Figures 4a and 4b compare simulated wave propagation speed and propagation length in isotopically-enriched graphite with natural graphite. In isotopically enriched graphite, the propagation speed is more than 15% higher than in natural graphite across all grating periods at 125 K, and larger enhancements in the propagation length are observed. Moreover, in isotopically pure samples, our simulations indicate that we could observe second sound even at room temperature at the grating periods of 1.0 μm and 1.5 μm (Fig. 4c, d). The smaller measured wave propagation speed (Fig. 4a) in natural graphite than in isotopically enriched graphite can be understood as arising from the increased contribution of diffusive phonons.

Discussion

The picture of three groups of phonons reduces to Fourier diffusion when diffusive phonons dominate. In the TTG experiment, thermal transport can be observed in the form of second sound when hydrodynamic phonons are dominant and thermal zero sound when ballistic phonons are dominant. When the three groups of phonons co-exist, the wave propagation velocity increases with decreasing grating period because (1) the thermal zero sound contributes more at shorter grating period, and (2) the thermal zero sound velocity is higher than the intrinsic second sound velocity. The latter is guaranteed because second sound involves mixing of phonons via normal scattering processes. For example, for a Debye material with sound velocity v , the velocity of the

thermal zero sound should be around $0.7 v$, while that of the intrinsic second sound is $v/\sqrt{3}$. (See SM8 for details.)

We directly observe second sound in graphite above 200 K through TTG experiments. The measured TTG signal also includes contributions from thermal zero sound, i.e. the propagation of ballistic phonon thermal waves. The experimental results can be explained by the coexistence of ballistic, diffusive, and hydrodynamic phonons. The measured wave propagation velocity increases with decreasing grating period due to the increased influence of the thermal zero sound. The experimental results in thermal wave dispersion and strength are in qualitative agreement with first-principles simulations. In isotopically pure graphite, we predict that second sound can be observed even at room temperature, and with higher propagation speed and longer propagation length than seen in our measurements to date. A sign reversal in the thermal response due to non-local thermal conductivity is also reported in a recent theoretical study⁴⁶, however, the nontrivial relation between non-local thermal transport and second sound is beyond the scope of our present study.

Methods

Sample

The natural graphite samples used in this work were obtained from Naturally Graphite©. Based on Atomic force microscopy (AFM) images, the average area of grain is estimated as $382 \pm 270 \mu\text{m}^2$ with the grain size larger than $20 \mu\text{m}$. More details are provided in SM9.

Thermal transient grating measurements

To capture the fast dynamics of second sound at micrometer transport lengths, we employ femtosecond laser pump-probe spectroscopy. A schematic illustration of our femtosecond laser thermal transient grating experimental setup is shown in Fig. S1. Ultrafast laser pulses with 290 fs pulse width and with 515 nm and 532 nm wavelengths are produced by a second harmonic generator from the 1030-nm amplified laser output and by an optical parametric amplifier, respectively. The repetition rate of the laser pulses is 25 KHz. The 515 nm pulse is used as the pump and the 532 nm pulse is used as the probe. The pump pulse is modulated by an optical chopper at a frequency of around 2 KHz and directed into a delay stage, which can introduce up to 16 ns time delay between the pump and probe pulses. The pump and probe laser beams cross vertically at a phase mask, which diffracts them into horizontally separated +1 and -1 orders which are recombined at the sample after passing through a 2-lens imaging system. The crossed pump diffraction orders generate the excitation interference pattern at the sample. The +1-probe diffraction order is taken as a reference beam, and its intensity is reduced by an attenuator made of a 100 nm Au film coated on a $170 \mu\text{m}$ -thick glass slide. The -1 diffraction order is taken as the probe beam. An uncoated $170 \mu\text{m}$ thick glass slide mounted on a rotation stage is used to adjust the heterodyne phase shift between the probe and the reference fields. All the beams are focused onto the surface of a natural graphite sample mounted in a cryostat chamber, with pump and probe/reference spot sizes ($1/e^2$ diameters) of $120 \mu\text{m}$ and $105 \mu\text{m}$ respectively. The diffracted probe pulse spatially and temporally overlaps with the reflected reference pulse. After passing through Lens 2, the diffracted probe pulse and reflected reference are redirected by a mirror and collected by a photodetector as the heterodyned transient thermal grating diffraction signal. The output of the photodetector is analyzed by a lock-in amplifier which is synchronized with the optical chopper. The pump and probe pulse energies are set at 70 nJ and 52 nJ respectively. The surface temperature rise due to the pulses is estimated to be less than 3 K.

Computational details

All the first-principle calculations are performed by Vienna Ab Initio Package (VASP)^{51–53} with projector-augmented-wave (PAW) pseudopotentials and local density approximation for the exchange-correlation energy functional. To include the nonlocal vdW interactions, we use an explicit nonlocal density functional named optB88 functional.^{54,55} The geometrical optimization of the unit cell was performed with a $24 \times 24 \times 10$ grid of k-point sampling. The second-order (third-order) force constants were calculated using a real space supercell approach with a $5 \times 5 \times 2$ ($4 \times 4 \times 2$) supercell and $6 \times 6 \times 6$ ($8 \times 8 \times 6$) k-grid. The Phonopy package⁵⁶ was used to obtain the second-order force constants. The thirdorder.py and ShengBTE packages⁵⁷ were used to obtain the third-order force constants and the phonon scattering matrix on a $16 \times 16 \times 8$ wavevector mesh.

Temperature response calculation

The calculation is based on the temperature response with an arbitrary heating profile derived earlier.⁴⁵ An expression for the temperature response function for a general heating profile is given as:

$$\Delta\tilde{T}(\Omega, \mathbf{k}) = \tilde{Q}(\Omega, \mathbf{k}) \frac{\text{sum}[\mathbf{A}^{-1}\vec{p}]}{\text{sum}[i\mathbf{A}^{-1}D\vec{c}]} \quad (5)$$

where Ω and \mathbf{k} are the frequency and wavevector from the Fourier transform. We define the sum operation of a vector to add up the values of its elements, i.e. $\text{sum}[\mathbf{a}] = \sum_{\mu} a_{\mu}$. The details of Eq. (5) can be found in SM2.

To obtain the temperature response in a TTG measurement with grating period l , we need to substitute the following heating profile into Eq. (5) and take the inverse Fourier transform:

$$\tilde{Q}(\Omega, \mathbf{k}) = \delta\left(\frac{2\pi}{l}\right) + \delta\left(-\frac{2\pi}{l}\right) \quad (6)$$

Second sound as damped temperature-wave equation

As discussed earlier⁴⁷, using the energy and momentum conservation equations derived from the PBTE with the Callaway model, a damped temperature-wave equation can be derived:

$$\frac{\partial^2 T}{\partial t^2} + \frac{1}{\tau_{ss}} \frac{\partial T}{\partial t} - v_{ss}^2 \frac{\partial^2 T}{\partial x^2} = 0 \quad (7)$$

with the second sound velocity v_{ss} and relaxation time τ_{ss} given by Eq. (8).

$$v_{ss}^2 = \frac{\langle \frac{c_q q_x v_x}{\omega_q} \rangle^2}{\langle \frac{c_q q_x^2}{\omega_q^2} \rangle \langle C_q \rangle} \quad (8a)$$

$$\tau_{ss} = \frac{\langle \frac{c_q q_x^2}{\omega_q^2} \rangle}{\langle \frac{c_q q_x^2}{\omega_q^2} \tau_{qR} \rangle} \quad (8b)$$

However, Eq. (8) does not capture the wavevector dependence of the decay length and or the second sound speed. Thus, we refer to the second sound velocity obtained from Eq. (8) as the intrinsic limit.

Ballistic limit

In the ballistic regime, phonons move without interactions. Each phonon at a given wavevector \mathbf{q} will simply move along the x -axis with a velocity equal to the x -component of the group velocity v_x . If we assume the initial heating is thermally distributed, i.e. each mode is excited proportional to its contribution to heat capacity, then the temperature response of the TTG can be expressed as:

$$\Delta T = 2Q \frac{\langle C_q \cos(qv_x t) \rangle}{C^2} \quad (9)$$

where Q is the total heating and C is total heat capacity. The TTG temperature response function at the ballistic limit at different temperatures obtained with Eq. (9) is shown in Fig. 2c. The time of the first dip t_d can be obtained the setting the derivative of ΔT to zero:

$$\left. \frac{d\Delta T}{dt} \right|_{t=t_d} = -2Q \frac{\langle C_q q v_x \sin(qv_x t_d) \rangle}{C^2} = 0 \quad (10)$$

Then thermal zero sound velocity can be obtained as:

$$v_{tzs} = \frac{l}{2t_d} \quad (11)$$

The detailed derivation of Eq. (9) is provided in SM3.

Dispersion of measured thermal wave

If the second sound wave is approximated as a damped wave, then the TTG signal can be written as:

$$\Delta T(t) = \exp(-\Omega_i t) \cos(\Omega_r t) \quad (12)$$

The Fourier transform is:

$$\widetilde{\Delta T}(\omega) = \frac{1}{\Omega_i + i(\omega - \Omega_r)} + \frac{1}{\Omega_i + i(\omega + \Omega_r)} \quad (13)$$

This is sharply peaked near Ω_r ; near this frequency, the frequency spectrum can be approximated as:

$$|\widetilde{\Delta T}(\omega)|^2 \approx \frac{1}{\Omega_i^2 + (\omega - \Omega_r)^2} \quad (14)$$

Therefore, the frequency of the temperature wave could be obtained by Lorentzian fitting of the temperature response function at a specified wavevector given by Eq. (5). The detailed derivation is provided in SM4.

Data availability

The data that support the findings of this study are available from the corresponding author on reasonable request.

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Authors Contributions Statement

Z.D. and K.C. contributed equally to this work. K.C. and Z.D. carried out the experiment. Z.D. performed the first principles calculations. Z.D. and G.C. analyzed the data and wrote the manuscript, with contribution from K.C., B.S., J.S., A.A.M. and K.A.N.. G.C. and K.A.N. supervised the research. All authors comment on, discussed and edited the manuscript.

Competing interests Statement

The authors declare no competing interests.

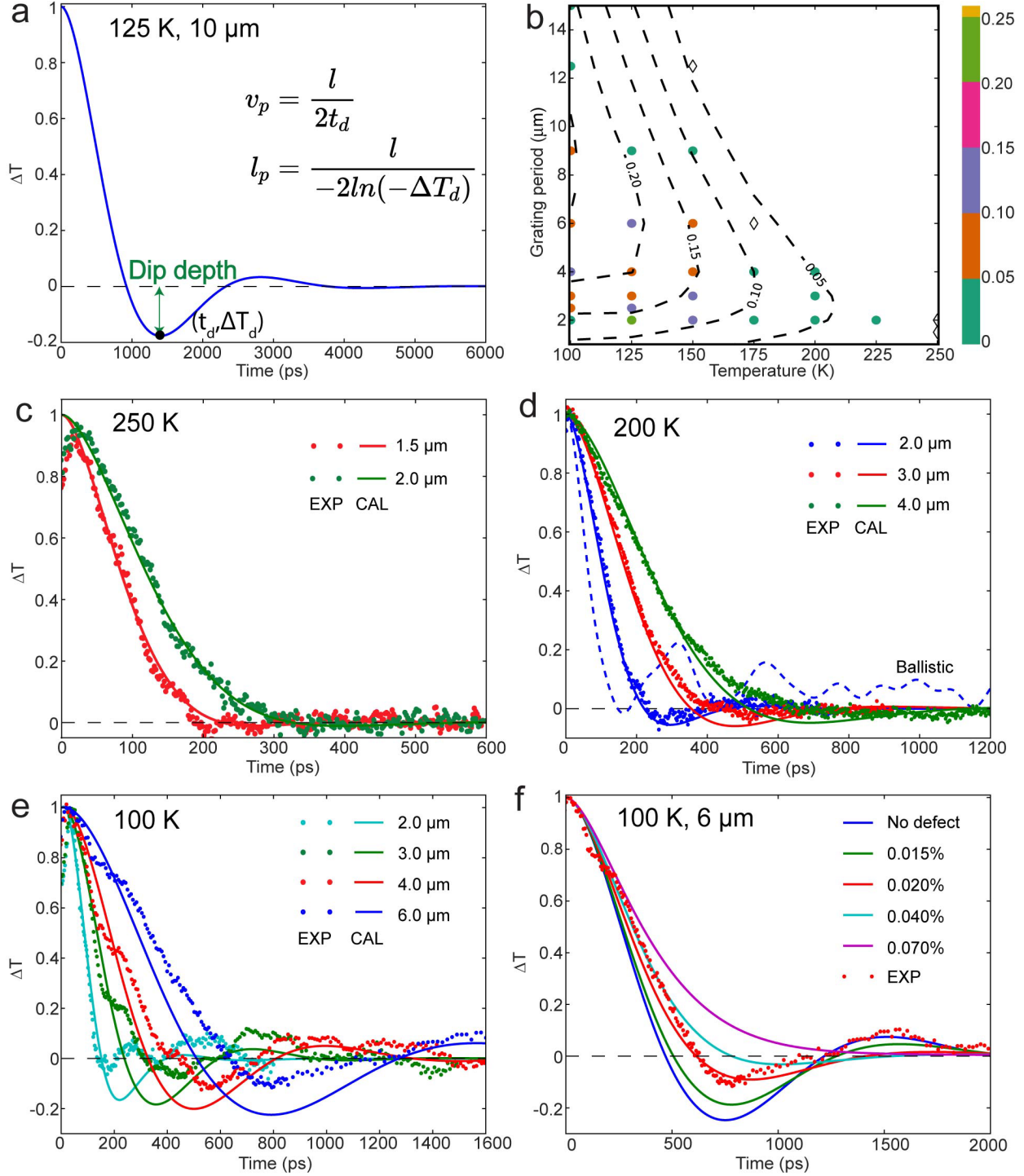


Figure 1. Measured (points) and simulated (curves) heterodyned TTG signals for graphite after normalization with respect to the peak height at early times. (a) The simulated temperature response at 125 K with a 10 μm grating period. The negative dip is the hallmark of wavelike thermal transport and its depth represents the second-sound strength. (b) TTG second-sound temperature window at different grating periods. The color bar shows the normalized dip depth. The circles (diamonds) indicate observation (no observation) of wavelike transport. TTG signals at (c) 250 K, (d) 200 K, and (e) 100 K for various grating periods. (f) The calculated effect of vacancies on TTG signal at 100 K for a 6 μm period.

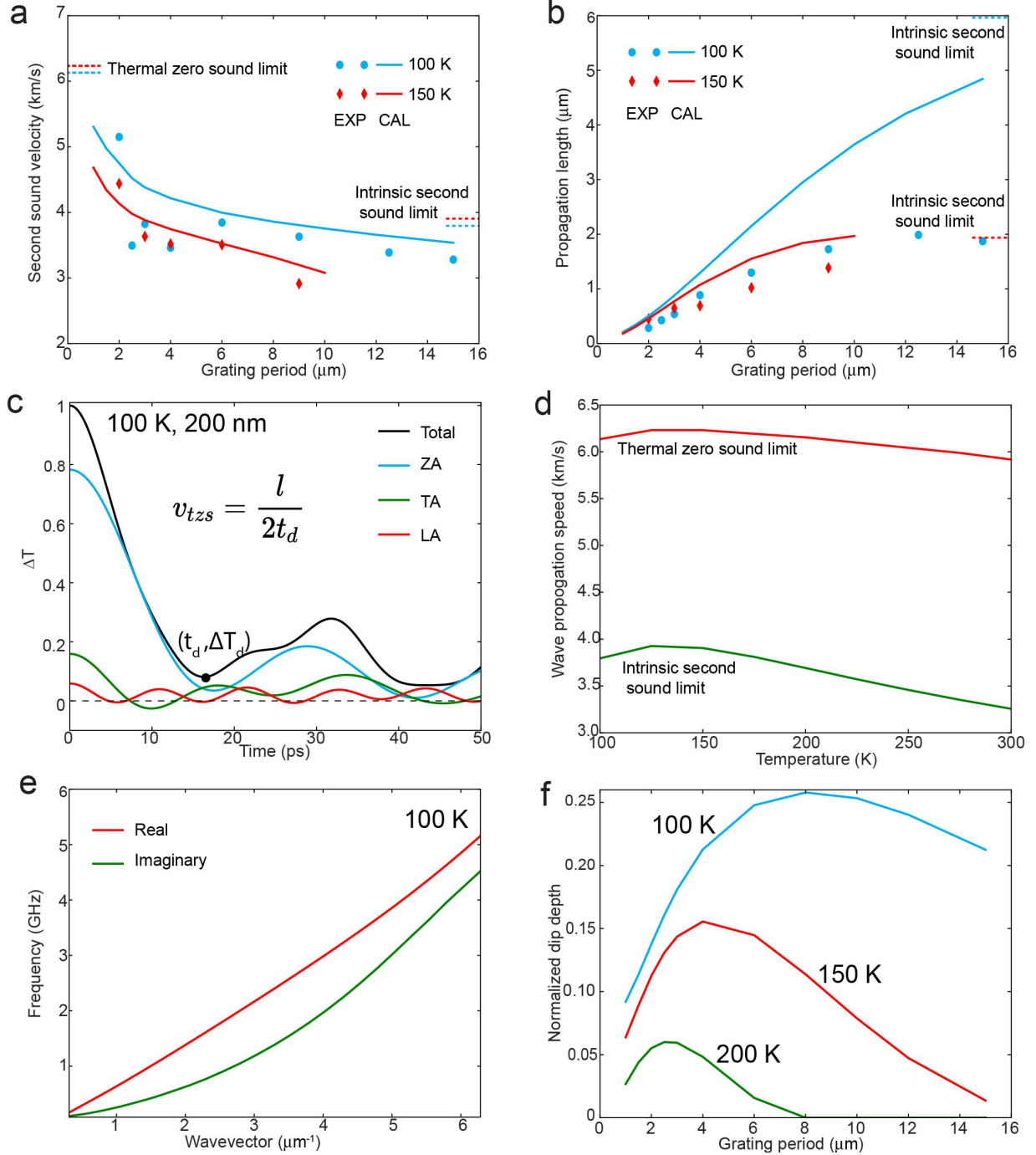


Figure 2. Dispersion of thermal waves. The measured and calculated data are represented by points and curves, respectively. (a) Dependence of wave velocity on grating period. Also shown are the intrinsic second sound limit from Eq. (2) and the thermal zero sound limit discussed in Methods. Damping reduces the second sound velocity below the intrinsic limit at large grating periods, while zero sound increases the measured wave velocity at small grating periods. (b) Propagation length variation with grating period at different temperatures. (c) Calculated ballistic limit of the TTG signal at 100 K and its contributions from flexural, longitudinal, and transverse acoustic modes (ZA, LA, and TA respectively). (d) Variation of the calculated ballistic and intrinsic second sound limits with temperature. (e) Dispersion of second sound at 100 K. (f) Variation of the calculated normalized dip depth with grating period at 100 K, 150 K and 200 K.

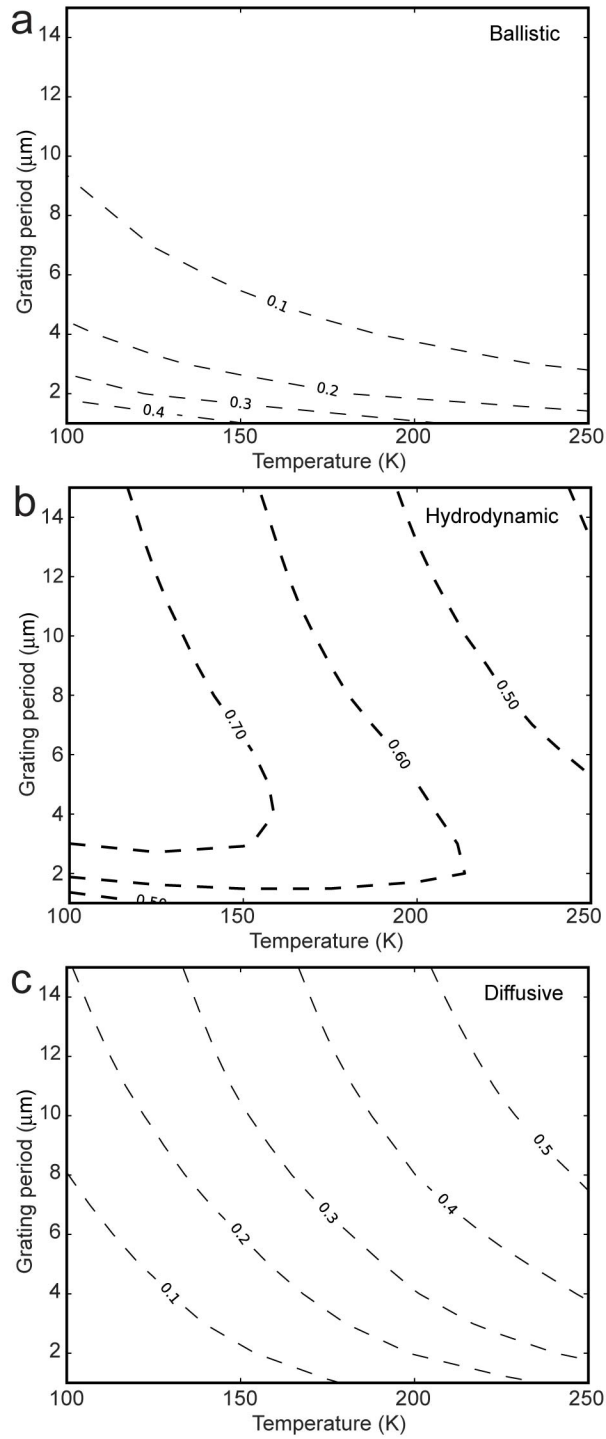


Figure 3. The three groups of phonons. Approximated fraction of excited phonons in the (a) Ballistic, (b) Hydrodynamic and (c) Diffusive regime based on Eq. (4).

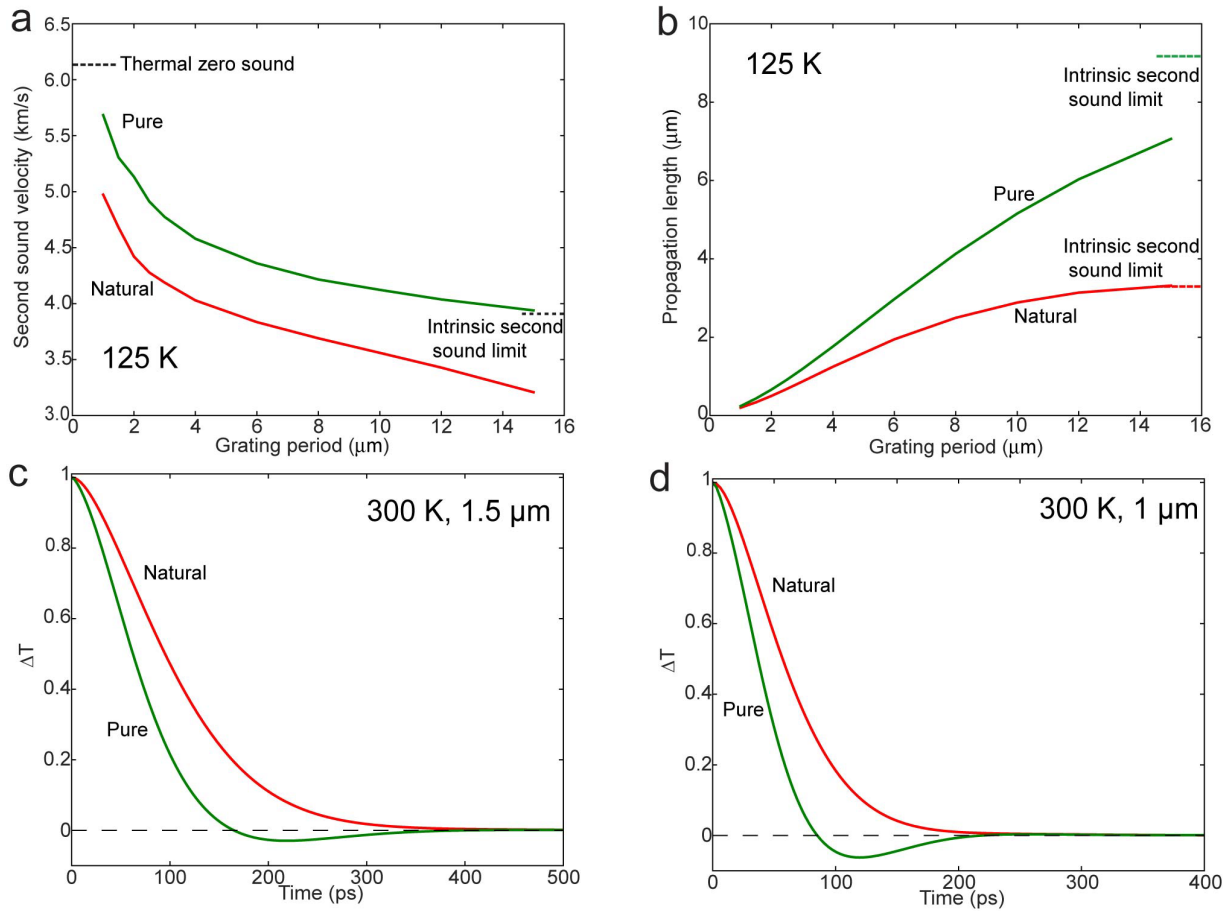


Figure 4. Isotope effect on second sound. Variation of (a) second sound velocity and (b) propagation length with grating period at 125 K in natural and isotopically pure graphite. (c) Calculated TTG signals at 300 K with a grating period of 1.5 μm and (d) 1 μm .

Supplementary Materials

Observation of Second Sound in Graphite over 200 K

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1. Thermal transient grating measurements and analysis

The measured second sound signals using the upgraded TTG system are shown in Fig. S2a. By changing the heterodyne phase difference between the reference beam and the probe light, one could identify and separate the amplitude grating and phase grating signals in the TTG measurement, representing the change of the real and the imaginary part of the complex reflection coefficient, respectively¹. As discussed in Ref. 2, because the thermorefectance coefficient of graphite is quite small, the red curve in Fig. S2a, which shows only spikes at zero time delay and oscillations around 0 after that, should be the “amplitude grating” signal, and the black curve, which is taken at maximized second peak, should be the “phase grating” signal. The first peak of the black curve can be attributed to the excitation of electron-hole pairs, while the second peak of the black curve indicates the build-up of the temperature grating profile through electron-phonon and phonon-phonon scattering. The red curve shows obvious oscillations, corresponding to a speed of ~ 20600 m/s, very close to sound speed of the LA mode in graphite (~ 21000 m/s). One possible interpretation of this oscillation is that the in-plane standing wave modulates the density and thus the refractive index, and such modulation is sensed by the real part of the reflectance and contributes to the amplitude signal. Fast Fourier transformation analysis shows that the black curve also has the oscillation at this frequency but with a weaker magnitude, which may arise from a slight mixing of amplitude grating as the heterodyne phase might not be perfectly set at the pure phase grating point. In order to filter out this unwanted oscillation, we adopt the Savitzky-Golay method³ to smooth our phase grating signal, as shown in Fig. S2b. It can be seen that the smoothed curve captures the profile of our raw data but filters out the high frequency acoustic oscillations. With the smoothed curve, we can clearly identify the position and the magnitude of the second sound “dip”. All our measurements and data processing were performed as described in this section.

The statistical error of the data points in the signal waveforms can be estimated by the standard deviation of the negative-time-delay signals, as shown in Fig. S2b. In our pump-probe experiments, the negative-time-delay signals should be 0 in the ideal case. While in the real case, the randomness of the measurement system cause fluctuation around the 0 baseline (Fig. S2b). The magnitude of the fluctuation could be used to estimate the measurement errors. Most of our measurement errors are around 0.01, while the “dip” amplitude of those signals which we claimed to be second sound observations are much larger than their errors, indicating the “dips” are intrinsic and reliable.

2. Temperature response calculation

All the calculation are based on the temperature response with an arbitrary heating profile derived in Ref.4. Here we briefly recap its derivation.

We start with the PBTE,

$$\frac{\partial f_\mu}{\partial t} + \vec{v}_\mu \cdot \nabla f_\mu = Q_\mu \frac{Nv}{\hbar\omega_\mu} + \sum_\nu W_{\mu\nu} (f_\nu^0 - f_\nu) \quad (\text{S1})$$

where μ is a short-hand index for a given phonon mode (branch and wavevector in the Brillouin zone), ω_μ is the frequency of the given phonon mode, f_μ is the non-equilibrium distribution function, N is the number of discretized points in the Brillouin zone, v is the unit cell volume and f_μ^0 is the equilibrium (Bose-Einstein) distribution function. \mathbf{W} is the phonon scattering matrix.

We write Eq. (S1) in terms of deviational phonon energy density:

$$\frac{\partial g_\mu}{\partial t} + \vec{v}_\mu \cdot \nabla g_\mu = Qp_\mu + \sum_\nu \frac{\omega_\mu}{\omega_\nu} W_{\mu\nu} (c_\nu \Delta T - g_\nu) \quad (\text{S2})$$

where $g_\mu = \frac{\hbar\omega_\mu}{Nv} [f_\mu - f_\mu^0(T_0)]$ and the volumetric heat generation rate Q_μ is replaced by Qp_μ , where Q is the macroscopic volumetric heat generation rate, and p_μ corresponds to how much a given mode is excited by the heating. We assume initial heating is thermally distributed, i.e. $p_\mu = c_\mu/C$, where $C = \sum_\mu c_\mu$ is the heat capacity.

We take the spatial and temporal Fourier transform of Eq. (S2):

$$\tilde{g}_\mu = \tilde{Q} A_{\mu\nu}^{-1} p_\nu + \Delta\tilde{T} (\delta_{\mu\nu} - iA_{\mu\gamma}^{-1} D_{\gamma\nu}) c_\nu \quad (\text{S3})$$

Where the dummy index indicates summation as in Einstein notation, i.e. $a_\mu b_\mu = \sum_\mu a_\mu b_\mu$, with $D_{\mu\nu} = \delta_{\mu\nu} (\Omega + \vec{k} \cdot \vec{v}_\mu)$ and $A_{\mu\nu} = \frac{\omega_\mu}{\omega_\nu} W_{\mu\nu} + iD_{\mu\nu}$. Ω and \vec{k} represent the frequency and wavevector from the Fourier transform.

We sum the Eq. (S3) over all the phonon modes and express the temperature deviation as:

$$\Delta\tilde{T} = \sum_\mu \frac{\tilde{g}_\mu}{c} \quad (\text{S4})$$

We obtain a general expression for temperature response for heating with frequency Ω and wavevector \vec{k} as:

$$\Delta\tilde{T}(\Omega, \vec{k}) = \tilde{Q}(\Omega, \vec{k}) \frac{\text{sum}[\mathbf{A}^{-1}\vec{p}]}{\text{sum}[i\mathbf{A}^{-1}D\vec{c}]} \quad (\text{S5})$$

where we define the sum operation of a vector to add up the values of its elements, i.e. $\text{sum}[\mathbf{a}] = \sum_{\mu} a_{\mu}$.

To obtain the time-dependent response of the TTG measurement with a grating period l , we need to substitute the following heating profile:

$$\tilde{Q}(\Omega, \vec{k}) = \delta\left(\frac{2\pi}{l}\right) + \delta\left(-\frac{2\pi}{l}\right) \quad (\text{S6})$$

and take the inverse Fourier transform.

3. Ballistic limit

In the ballistic limit, the 1D-PBTE for the TTG takes the form

$$\frac{\partial f}{\partial t} + v_x \frac{\partial f}{\partial x} = 0 \quad (\text{S7})$$

where v_x is the group velocity along the TTG grating period direction, with the initial condition

$$f_o(x) = f_A \cos(qx) \quad (\text{S8})$$

where $q = \frac{2\pi}{l}$, and f_A is the amplitude of the initial distribution due to the laser heating. If the initially excited phonon population is thermally distributed, then $f_A = \frac{c_q Q}{\hbar\omega C}$, where Q is the total heating and C is total heat capacity.

Then the distribution at $t \geq 0$ is:

$$f(x, t) = f_o(x - v_x t) = f_A \cos[q(x - v_x t)] \quad (\text{S9})$$

The measured TTG signal is proportional to the temperature difference between $T(x = 0)$ (the peak) and $T(x = l/2)$ (the null) and can be written as:

$$\begin{aligned} \Delta T &= \frac{\langle f(0, t) \hbar\omega \rangle}{C} - \frac{\langle f\left(\frac{l}{2}, t\right) \hbar\omega \rangle}{C} \\ &= 2 \frac{\langle f(0, t) \hbar\omega \rangle}{C} \\ &= 2Q \frac{\langle c_q \cos(qv_x t) \rangle}{c^2} \end{aligned} \quad (\text{S10})$$

As in the main context, $\langle \rangle$ means summation over all the phonon modes.

4. Dispersion of the measured temperature waves and second sound

For a damped temperature wave with wavevector $k = \frac{2\pi}{l}$ and frequency Ω_r and decay rate Ω_i , the temperature excursion can be written as:

$$\Delta T(x, t) = \exp(-\Omega_i t) \cos(\Omega_r t - kx) \quad (\text{S11})$$

The TTG measured signal ΔT is proportional to the temperature difference between $T(0, t)$ and $T(l/2, t)$:

$$\Delta T(t) = \exp(-\Omega_i t) \cos(\Omega_r t) \quad (\text{S12})$$

The comparison of Eq. (S12) with the TTG signal is shown in Fig. S7. The Fourier transform of $\Delta T(t)$ is:

$$\Delta T(\omega) = \frac{1}{\Omega_i + i(\omega - \Omega_r)} + \frac{1}{\Omega_i + i(\omega + \Omega_r)} \quad (\text{S13})$$

This is sharply peaked near Ω_r ; near this frequency, we could ignore the second term in Eq. (S13) as its magnitude is much smaller than the first term, and the frequency spectrum can be approximated as:

$$|\widetilde{\Delta T}(\omega)|^2 \approx \frac{1}{\Omega_i^2 + (\omega - \Omega_r)^2} \quad (\text{S14})$$

Therefore, the frequency of the temperature wave could be obtained by Lorentzian fitting with the temperature response function at a specified wavevector given by Eq. (5) of the main text as shown in Fig. S7.

5. Heat-pulse experiment and three groups of phonons

In the heat-pulse experiment^{5,6}, two opposite surfaces of the crystal are covered with metal films are deposited onto opposite surfaces of a crystal to serve as the heater and the detector, as shown in Fig.S8a. An electrical pulse is applied to the heater on one side of the crystal. The detector on the right side measures the arrival of the heat pulse via resistance change (Fig. S8a). The propagation speed of the ballistic pulse is close to the sound velocity^{5,6}. However, it has been shown theoretically that thermal excitation as conducted in these experiments cannot excite a mechanical wave of significant amplitude⁷. Therefore, the ballistic heat pulses observed in the heat-pulse experiments^{5,6} are actually thermally excited ballistic phonons as in three groups of phonons picture. A similar three groups of phonons picture was used to explain the heat-pulse experiments as detailed in Ref. 8. The heat pulses arrived with speeds close to the longitudinal and transverse phonon speeds. The finite sizes of the heater and detector result in a range of propagation directions for phonons that reach the detector, as shown in Fig. S8a, and therefore a range of arrival times is measured yielding an average velocity that is determined from the measurement. For a Debye material of sound velocity v , the average speed of ballistic phonons over the solid angle θ that the detector sustained can be estimated as:

$$v_{ave} = \frac{v \sin^2(\theta)}{2[1-\cos(\theta)]} \quad (\text{S15})$$

This average speed is shown in Fig. S8b. For example, as reported in Ref. 9, the detector size was 6 mm, while the sample length was 7.8 mm. Therefore, the maximum solid angle for phonons recorded by the detector could be estimated to be 21° , which yields to a propagation velocity greater than 95% of the sound velocity (Fig. S8b).

6. Contribution from ballistic/diffusive phonons to the TTG signals

The signal in the TTG experiment is proportional to the temperature difference $\Delta T = T(0) - T(l/2)$. The initially excited phonons follow a cosinusoidal spatial distribution and their subsequent transport determines this temperature difference. For a phonon traveling in the positive x -direction, the distance d it travels to reach $\frac{l}{2}$ is $\frac{l}{2} - x$. Whether this phonon's contribution is ballistic or diffusive is determined by the relationship between d and the total MFP Λ_o and R-scattering length Λ_R . If $\Lambda_R < d$, it is diffusive transport. If $\Lambda_o > d$, it is ballistic. Phonons satisfying $\Lambda_o < d < \Lambda_R$ experience hydrodynamic transport. Figure S9a shows in pink and green the ballistic/diffusive components contributions to the measured signal.

The variations of the ballistic and diffusive phonon contributions to the TTG signal with respect to MFP are shown in Figs. S9b and S9c. Summing over all the phonon modes with weights $c_q v_x^2$ as the approximated mode contribution to heat conduction, we obtain Fig. 3a and 3b in the main text. It should be noticed that this is not a rigorous estimation of the ballistic/diffusive contribution, but it should be qualitatively reliable.

7. Mean free path analysis at 200 K

A detailed mean free path analysis is performed to further confirm the observation at 200 K is indeed second sound instead of ballistic signals. Since the ZA phonon dominates the contribution to second sound, we provide a comparison of the grating period and ZA phonon MFP of different scatterings at 200 K (Fig. S10). A characteristic frequency, $k_B T / 2\pi\hbar$, is also marked, below which phonons can be readily activated at a given temperature. The average phonon MFP is computed as: $\Lambda_l = \langle C_q v \tau_l \rangle / \langle C_q \rangle$. At 200 K, the Average N-scattering and R-scattering MFP are around 0.2 μm and 5.6 μm respectively. Therefore, our investigated grating periods i.e. 2~3 μm are indeed larger than the MFP of normal scattering and smaller than the MFP of resistive scattering (including Umklapp scattering and isotopic scattering).

8. Thermal zero sound and intrinsic second sound velocity in a Debye material

In this section, we compare the thermal zero sound and intrinsic second sound velocities using the Debye model for phonon dispersion. The TTG signal in the ballistic transport regime is given by Eq. (9) of the main text. For a Debye material with sound velocity v , we can replace the summation over phonon modes in Eq. (9) by integration, and the TTG signal can be written as:

$$\Delta T = \text{sinc}(qvt) \quad (\text{S16})$$

The time of the first dip t_d can be obtained the setting the derivative of the ΔT to zero, which gives:

$$qvt_d \approx 4.4934 \quad (\text{S17})$$

Substitute $q = \frac{2\pi}{l}$ into the above equation, we obtain what we define as the thermal zero sound velocity:

$$v_{tzs} \approx 0.7 v \quad (\text{S18})$$

Eq. (2a) for a Debye material gives the intrinsic second sound velocity:

$$v_{ss} = \frac{v}{\sqrt{3}}$$

Therefore $v_{tzs} > v_{ss}$ for a Debye material.

9. Characterization of the sample

We observe several graphite crystallites larger than 1 mm in length, which are highlighted in different colors in Fig. S11(a). We performed atomic force microscopy (AFM) to further analyze the surface defects, step edges and grain boundaries. Fig. S11(b) shows AFM height image of the natural graphite crystal. The dashed arrows show step edges where the height changes across the lines. The solid arrows indicate grain boundaries where height does not vary across the line. ImageJ was used to estimate the average area of grains that are surrounded by the step edge or grain boundaries in the AFM image. The average grain area is estimated as $382 \pm 270 \mu\text{m}^2$ where the largest longer axis could be larger than $100 \mu\text{m}$ and the typical grain size is larger than $20 \mu\text{m}$.

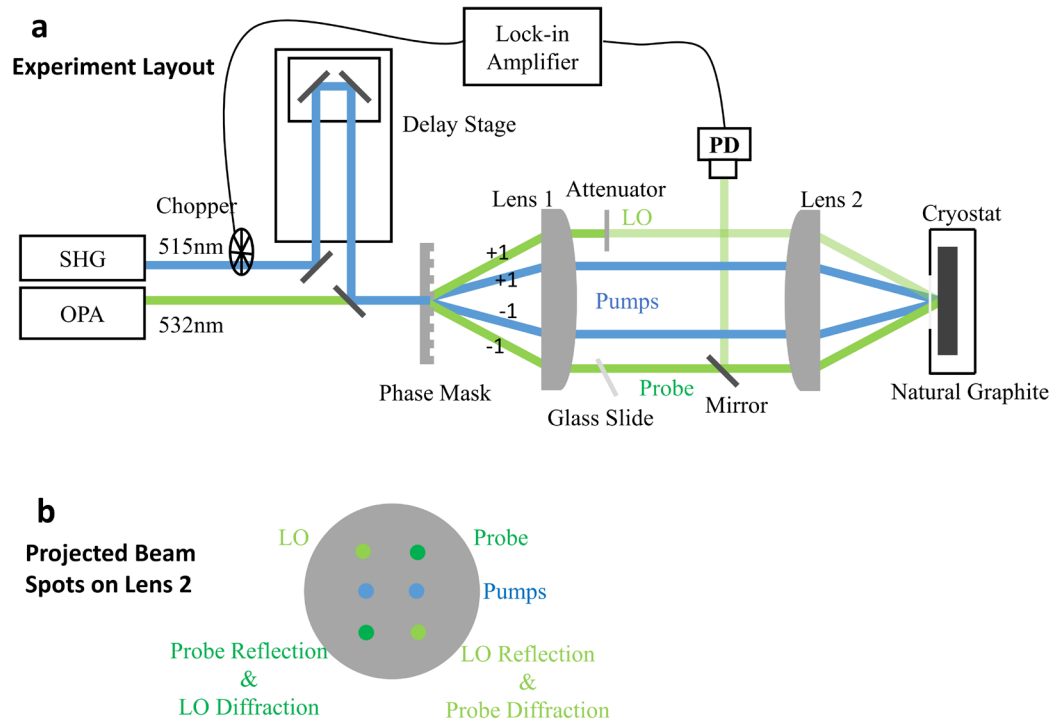


Figure S1. Schematic illustration of the femtosecond laser TTG setup. (a) Top view. The difference in the diffracted angle after the phase mask between the 515 nm and the 532 nm laser beams is exaggerated for better drawing. (b) Side view [from left to right in Fig. S1(a)] of various laser spots at Lens 2.

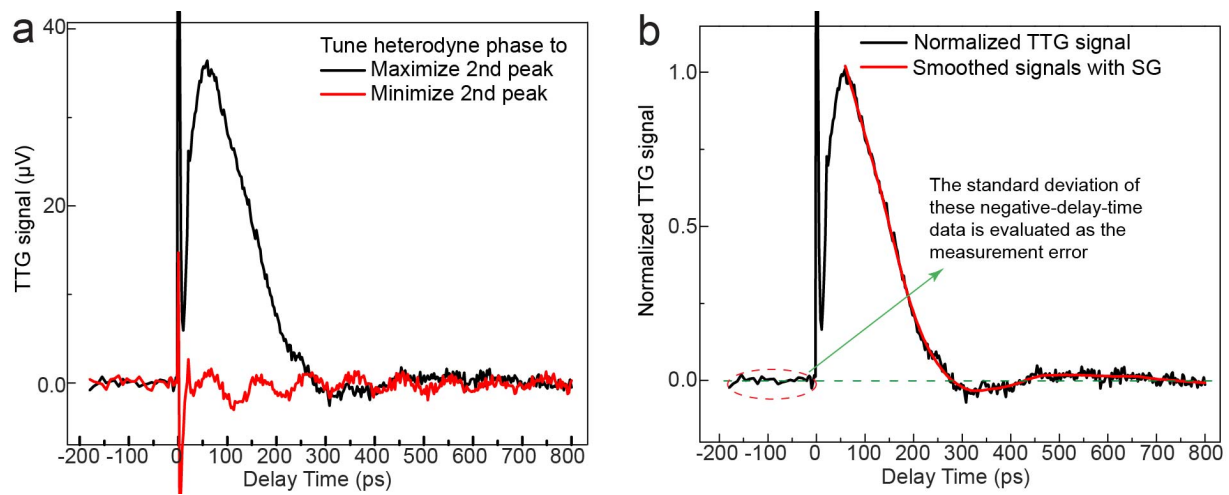


Figure S2. (a) Measured TTG signals at 200 K and 2 μm grating period at two heterodyne phases. One phase is set to maximize the second peak, corresponding to the phase grating signal, while the other phase is set to minimize the second peak, corresponding to the amplitude grating signal. (b) Normalized phase grating signal and the smoothed response obtained using the Savitzky-Golay method. The negative-time-delay signals are used to estimate the measurement error.

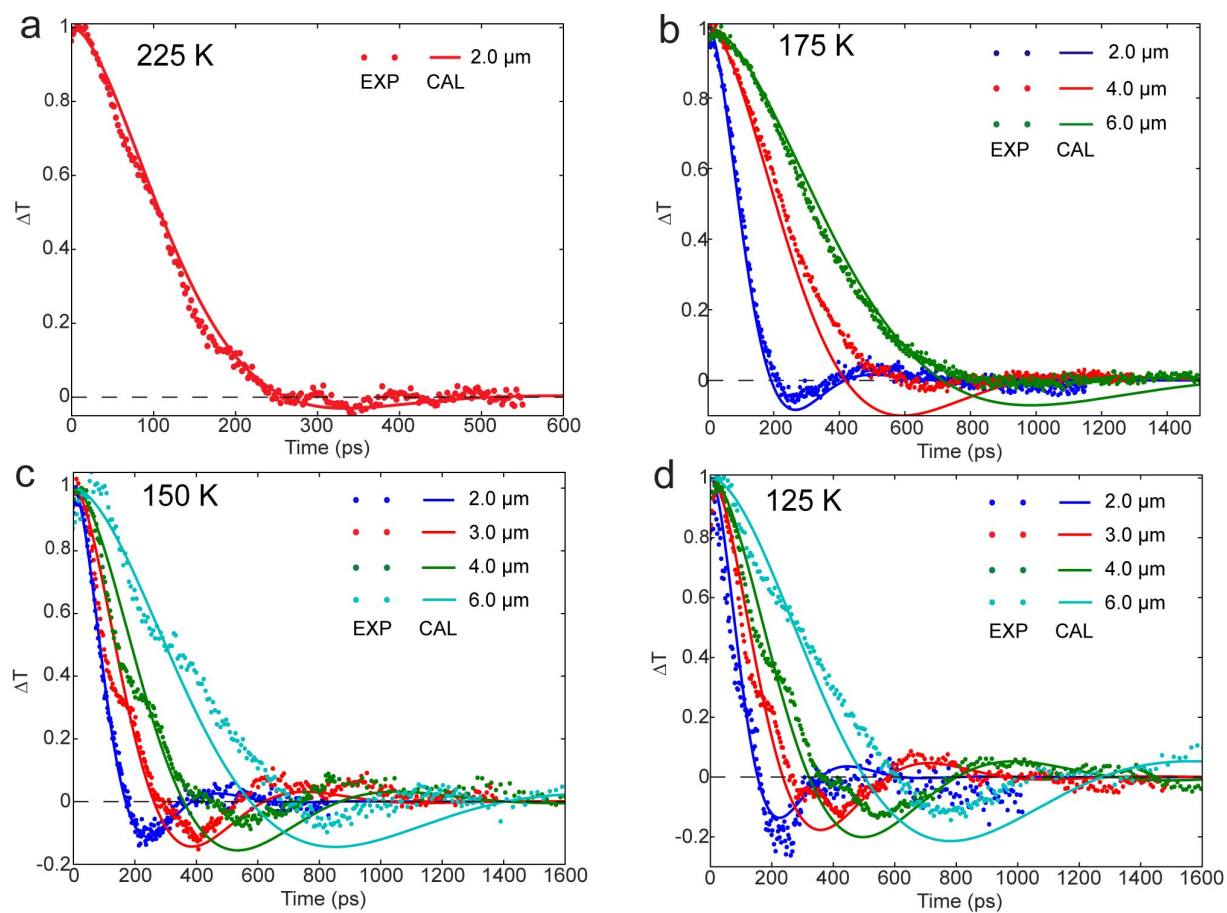


Figure S3. Temperature response of TTG at (a) 225 K, (b) 175 K, (c) 150 K, and (d) 125 K.

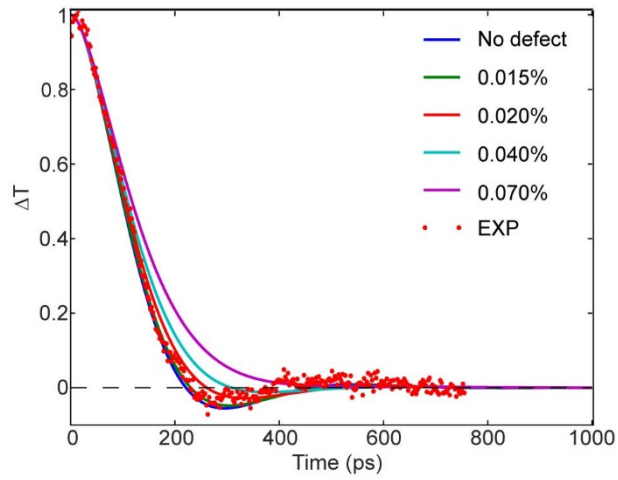


Figure S4. Dependence of the TTG temperature response on vacancy defects at 200 K for a grating period of 2 μm . Dots are the experimental data and curves are the calculations.

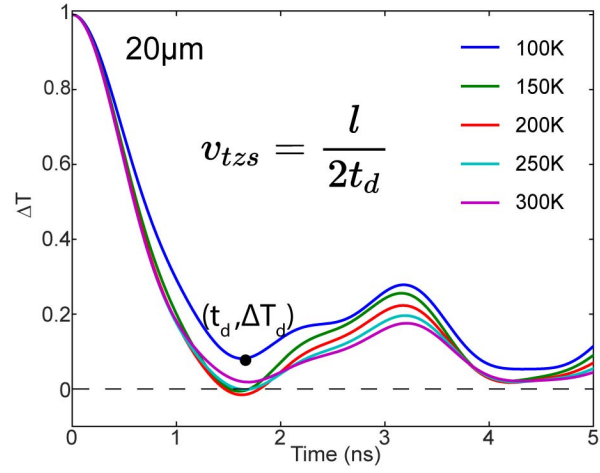


Figure S5. Simulated TTG signal in the ballistic limit at different temperatures.

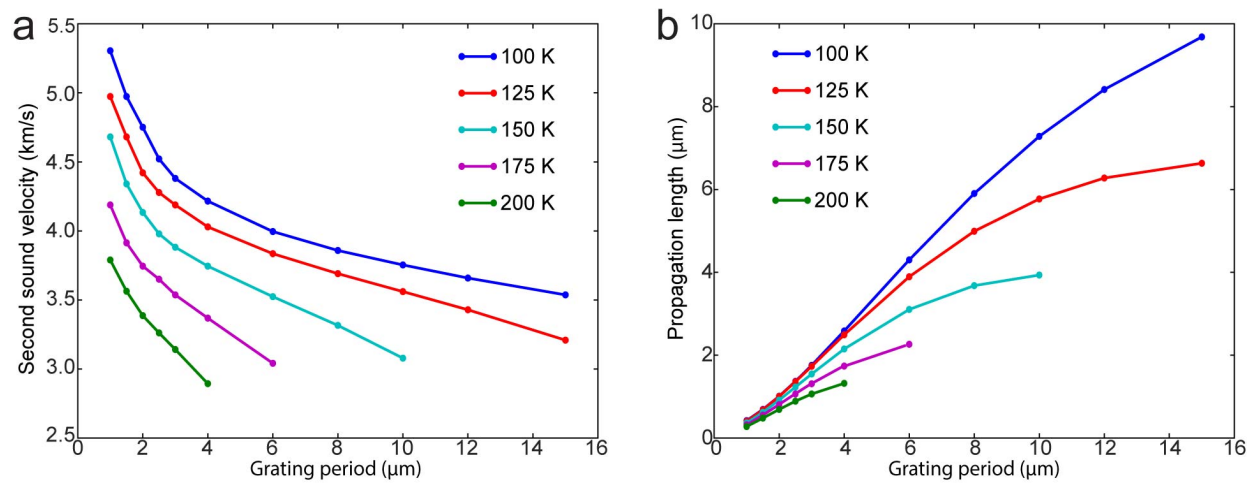


Figure S6 Calculated dependence of (a) second sound speed and (b) propagation length on the grating period at different temperatures.

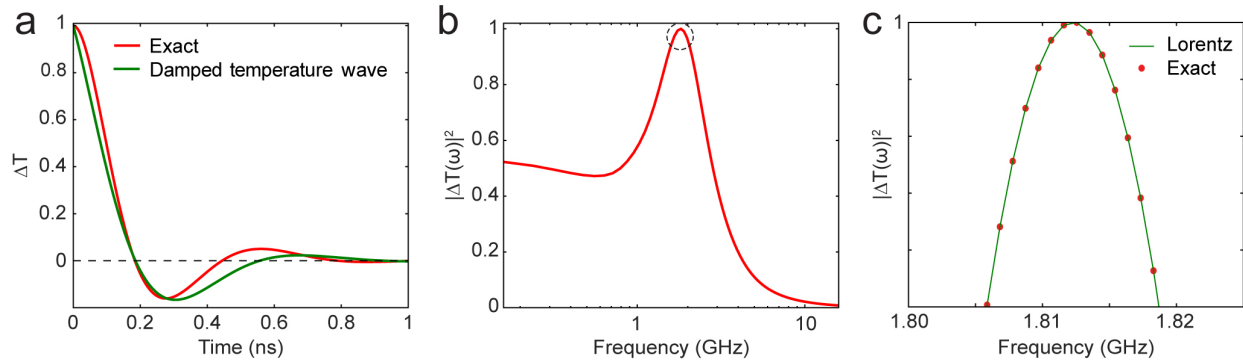
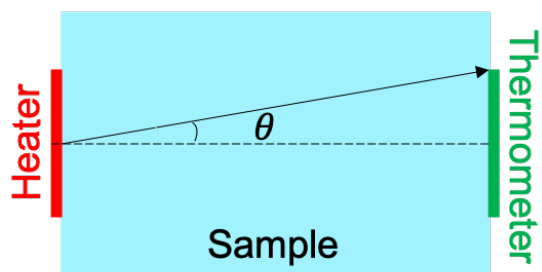


Fig S7 (a) Comparison of a damped temperature wave according to Eq.(S12) with an exact solution of the PBTE (b) The frequency spectrum of temperature response obtained from the Fourier transform of the exact solution, (C) The Lorentz fitting to obtain the real part and imaginary part of the temperature wave.

a



b

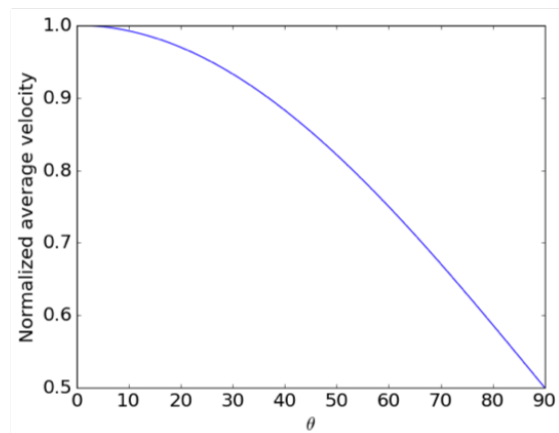


Fig S8 (a) Schematic illustration of the heat-pulse experiment set up, and (b) variation of the average velocity of ballistic phonons with solid angle.

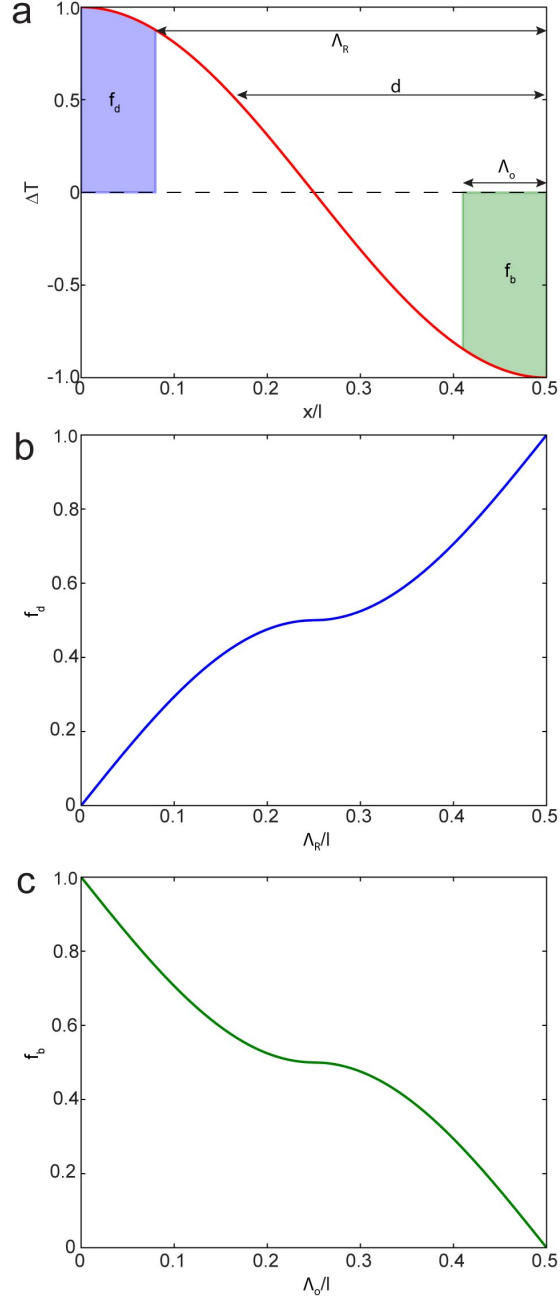


Figure S9. Illustration of diffusive, ballistic, and hydrodynamic phonon contributions to the TTG signal. Λ_o is the total mean free path and Λ_R the resistive mean free path. Phonons are excited between the peak ($x/l=0$) and the null ($x/l=0.5$), and their subsequent transport dictates the measured signal. (a) For phonons traveling in the positive x -direction (in reality, excited phonons travel to both positive and negative directions), phonons in the purple region (marked “ f_d ”) reach the temperature valley at $x/l=0.5$ via diffusive transport, while phonons in the green region (marked “ f_b ”) reach the same location ballistically. Phonons in between the two regions are hydrodynamic contributions. (b) Variation of the diffusive phonon contribution to the TTG signal with respect to R-scattering MFP to grating period l ratio, Λ_R/l , (c) Variation of the ballistic phonon contribution to the TTG signal with respect to total MFP to grating period ratio, Λ_o/l .

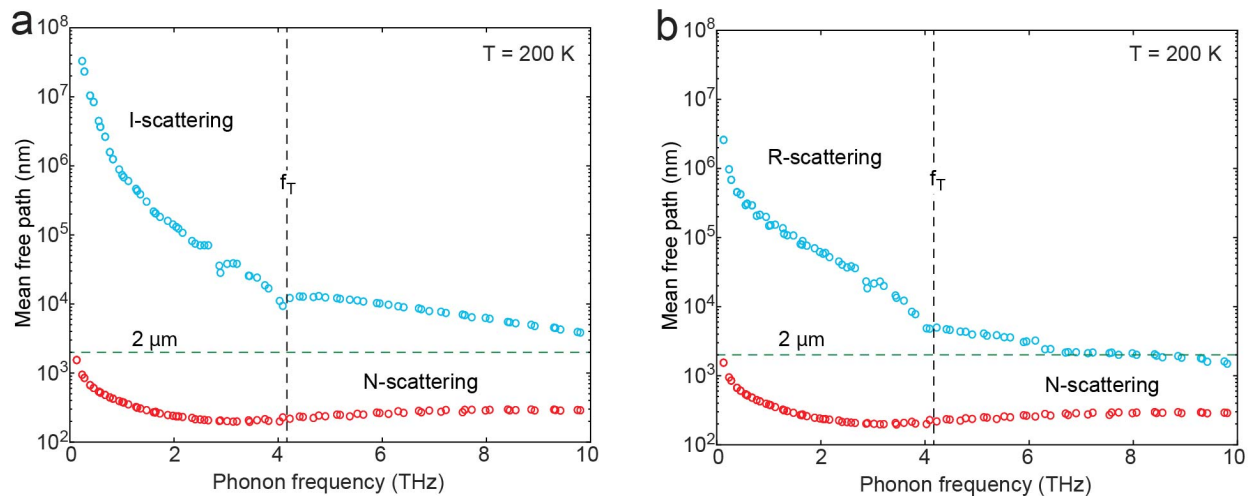


Figure S10. Comparison of mean free path at 200 K (a) N-scattering and I-scattering (b) N-scattering and R-scattering, where the characteristic frequency $f_T = kT/2\pi\hbar$ is marked

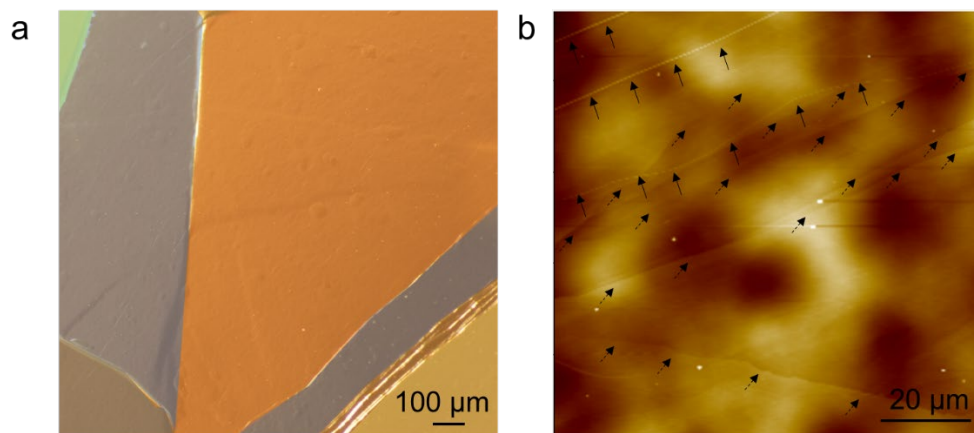


Figure S11 (a) Optical image of the natural graphite crystal. Individual graphite flakes are highlighted in different colors. (b) AFM z -height image of the natural graphite crystal. The dashed arrows show step edges where the height changes across the lines. The solid arrows indicate grain boundaries where height does not vary across the line.

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