

Evidence of fifth- and higher-order phonon scattering entropy of zone-center optical phonons

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Authors of recent studies have established the significance of fourth-order anharmonicity in the linewidth of zone-center optical phonons, while it is unknown whether the fifth- and even higher-order phonon scattering is important. In this paper, we estimate the convergence of phonon scattering entropy with respect to perturbation orders. Using density functional perturbation theory, we calculate the three- and four-phonon linewidths for zone-center optical phonons in a series of zinc-blende III–V compounds including InP, c-GaN, BN, AlSb, GaP, InSb, AlAs, InAs, GaSb, and AlP. Our results show that, although the agreement between theory and experiment is greatly improved by incorporating four-phonon scattering, considerable discrepancies still exist, especially at high temperatures. We reveal that, on average, the phonon scattering entropy converges well at the eighth order, and the fifth- and higher-order phonon scattering entropy is about 37% of that of four-phonon scattering at Debye temperature and increases with temperature. With four-, five-, and higher-order phonon scattering included, the linewidth deviates largely from the linear scaling with temperature. In this paper, we provide evidence of the higher-than-fourth-order lattice anharmonicity in zone-center optical phonon linewidths as well as Raman and infrared spectra.

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I. INTRODUCTION

Zone-center optical phonon linewidth is a basic quantity in condensed matter, essential for a wide range of applications including material characterizations, infrared (IR) spectra, Raman spectra, and radiative heat transfer [1,2]. While three-phonon scattering had been considered the dominating mechanism for phonon linewidth [3–8], recently, fourth-order phonon anharmonicity has been predicted to have a significant or sometimes leading role [9–11]. First-principles predictions with four-phonon scattering have explained well the measured Raman or IR linewidths for a wide range of materials [11], and the method has been further extended to strongly anharmonic materials by including phonon frequency shift [12]. Although these works have facilitated increasing acceptance of the four-phonon scattering theory in spectroscopy techniques and radiative transport, a natural question is: What is the impact of the fifth- and even higher-order phonon scattering?

In this paper, we define and calculate the phonon *scattering entropy* of different orders of scattering for the zone-center optical phonons, using rigorous density functional theory (DFT) calculations for 10 zinc-blende III–V semiconductors including InP, c-GaN, BN, AlSb, GaP, InSb, AlAs, InAs, GaSb, and AlP. We find that, although four-phonon scattering can largely remedy the discrepancies between previous theory based on

three-phonon scattering and experiment, the fifth- and even higher-order phonon scattering can still be nonnegligible or even significant, especially above Debye temperature T_D .

II. METHODOLOGY

Phonon linewidth 2Γ is a Matthiessen sum of contributions from isotope (τ_{iso}^{-1}) [13,14], three-phonon ($\tau_{3,\lambda}^{-1}$) [15–17], four-phonon ($\tau_{4,\lambda}^{-1}$) [9,10,18], and higher-order phonon scattering rates [3,19]:

$$2\Gamma = \tau_{\text{iso}}^{-1} + \tau_{3,\lambda}^{-1} + \tau_{4,\lambda}^{-1} + \tau_{5,\lambda}^{-1} + \dots \quad (1)$$

The formalisms and calculations of τ_{iso}^{-1} , $\tau_{3,\lambda}^{-1}$, and $\tau_{4,\lambda}^{-1}$ are well established on the first-principles perturbation theory, and here, we follow the method as detailed in Ref. [11]. The second-, third-, and fourth-order interatomic force constants for calculating phonon frequencies and scattering rates were calculated from DFT within the local density approximation, as implemented in the Vienna *Ab initio* Simulation Package (VASP) [20,21]. The computational details as well as phonon dispersions of all materials studied are given in the Supplemental Material [22], including Refs. [23–37] therein. Direct evaluation of the five-phonon ($\tau_{5,\lambda}^{-1}$) and higher-order phonon scattering rates is currently not available. To estimate their significance, we define the scattering entropy of a phonon mode as

$$\begin{aligned} S &\equiv \frac{\hbar 2\Gamma}{T} = \frac{\hbar \tau_{\text{iso}}^{-1}}{T} + \frac{\hbar \tau_{3,\lambda}^{-1}}{T} + \frac{\hbar \tau_{4,\lambda}^{-1}}{T} + \frac{\hbar \tau_{5,\lambda}^{-1}}{T} + \dots \\ &\equiv S_2 + S_3 + S_4 + S_5 + \dots, \end{aligned} \quad (2)$$

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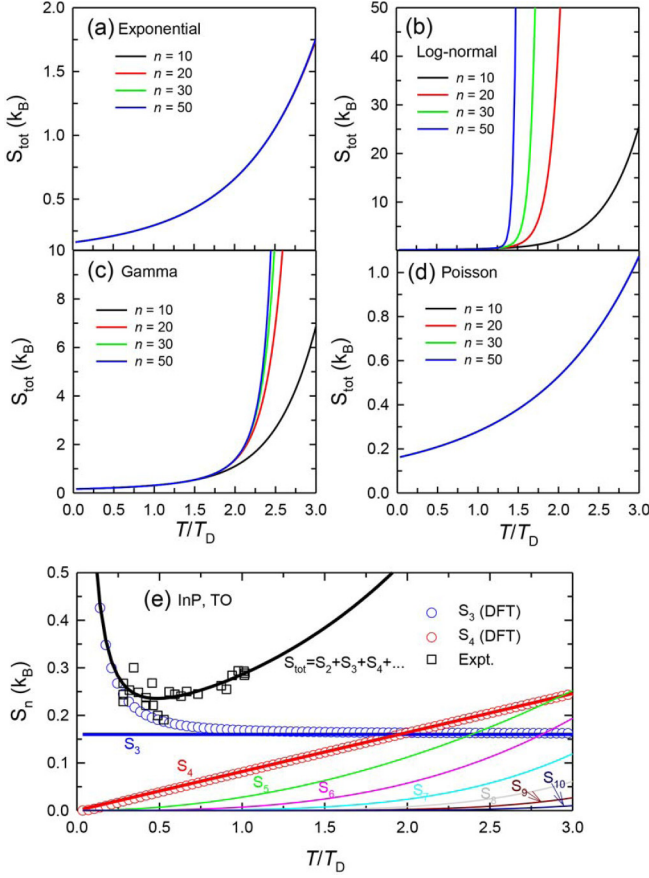


FIG. 1. (a) T -dependent entropy series summation of the transverse optical (TO) mode of InP with respect to n based on the exponential form, (b) log-normal function, (c) Gamma function, and (d) Poisson function. (e) Phonon scattering entropies of different order as a function of T for the TO mode of InP. The blue (red) circles represent the calculated S_3 (S_4), the black squares denote the experimental data from Ref. [38], and the solid curves represent the fitted results through Eq. (5). The total scattering entropy [$S_{\text{tot}} = (S_2 + S_3 + S_4)_{\text{DFT}} + S_5 + S_6 + \dots + S_{10}$] is provided for comparison with experiment.

considering that the quantity $\hbar 2\Gamma$ has a unit of energy and its temperature sensitivity has a unit of entropy. With this definition, S_2, S_3, S_4 , and S_5 are the phonon scattering entropies due to two- (isotope scattering), three-, four-, and five-phonon scattering, respectively. They count the multiplicities of phonon scattering reactions allowed by energy and momentum conservations. They should all have units of k_B , the Boltzmann constant, allowing easy numerical comparison of contributions at a particular temperature. They may themselves be T dependent: S_4, S_5 , and above grows strongly with increasing T .

Since $\tau_{3,\lambda}^{-1}$ increases approximately linearly and $\tau_{4,\lambda}^{-1}$ quadratically with T as shown before [9–11], and by analogy, $\tau_{5,\lambda}^{-1}$ increases cubically with T , $\hbar 2\Gamma$ can be asymptotically expanded as

$$\begin{aligned} \hbar 2\Gamma &= A + BT + CT^2 + DT^3 \dots \\ &= T(S_2 + S_3 + S_4 + S_5 + \dots), \end{aligned} \quad (3)$$

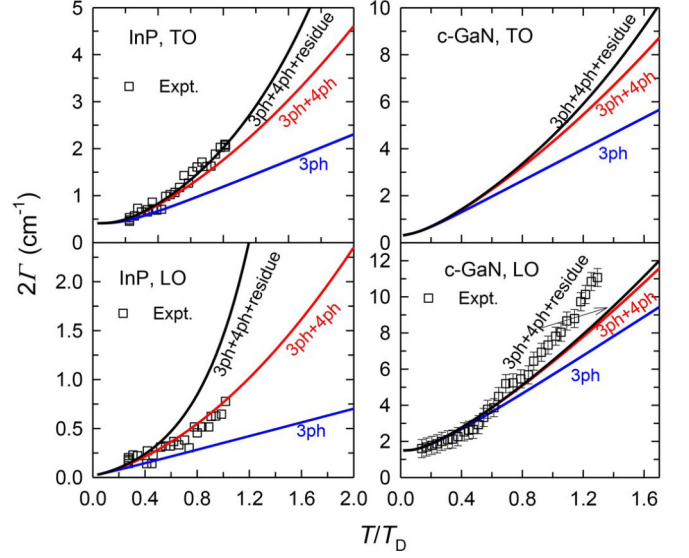


FIG. 2. T -dependent phonon linewidths 2Γ of the zone-center transverse optical (TO) and longitudinal optical (LO) phonons in InP and c-GaN. The solid red and blue curves represent our calculations with and without $\tau_{4,\lambda}^{-1}$; the solid black curves are the fitting results considering the higher-than-fourth-order phonon scattering terms; the squares denote experimental data for InP [38] and c-GaN [50]. Note that, for c-GaN, the T -independent background contribution arising from scattering by lattice defects is excluded from the original experimental data.

where the constant A accounts for the T -independent contribution from scattering with isotopes, impurities, and defects, BT for $\hbar\tau_{3,\lambda}^{-1}$, CT^2 for $\hbar\tau_{4,\lambda}^{-1}$, and DT^3 for $\hbar\tau_{5,\lambda}^{-1}$. Since different materials have different Debye temperatures, for cross-comparing between different materials, we introduce the dimensionless temperature scale $\tilde{T} \equiv T/T_D$ for normalization, and Eq. (3) can thus be rewritten as

$$\frac{\hbar 2\Gamma}{T} \equiv S = CT_D \left(\frac{\tilde{A}}{\tilde{T}} + \tilde{B} + \tilde{T} + \tilde{D}\tilde{T}^2 + \dots \right), \quad (4)$$

where CT_D is the four-phonon scattering entropy at $T = T_D$ ($\tilde{T} = 1$), which is used to normalize all the other scattering entropies, the dimensionless coefficients $\tilde{A} \equiv (A/T_D)/CT_D$, $\tilde{B} \equiv B/CT_D$, and $\tilde{D} \equiv DT_D/C$. If $\tilde{B} < 1$, then the three-phonon scattering is less important than the four-phonon scattering at $T = T_D$, and vice versa. If $\tilde{D} > 1$, the five-phonon scattering is more important than the four-phonon scattering at $T = T_D$, and vice versa.

Note that the higher the T , the more orders of scattering terms need to be included, and the absolute convergence of the linewidth will always be achieved. However, the higher-than-fourth orders are impractical to calculate directly at present. In this context, we attempt to establish an asymptotic form for estimating the higher-order phonon scattering entropy and for illustrating the convergence rate of the linewidth. In view of the variation law of phonon scattering of different order with T , we can easily deduce that the scattering entropy of different orders of phonon anharmonicity should have the form $k_B(T/T_D)^{n-3}f(n)$, with $f(n)$ representing the coefficient function associated with the scattering order n ($n \geq 3$). In

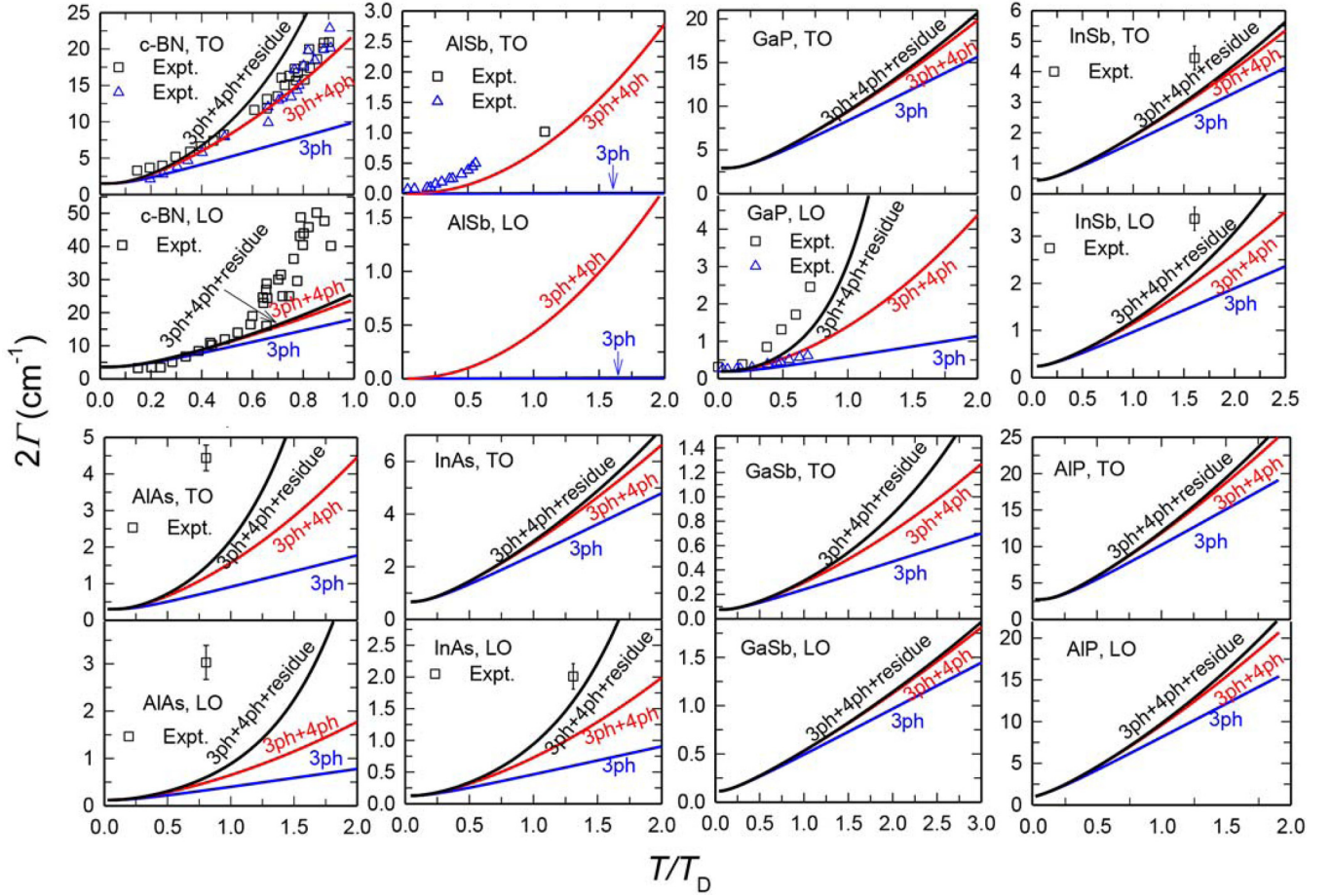


FIG. 3. Zone-center optical phonon linewidths 2Γ of the transverse optical (TO) and longitudinal optical (LO) phonons for group III-V zinc-blende compounds. The solid red and blue curves represent our calculated results with and without $\tau_{4,\lambda}^{-1}$, and the solid black curves are the fitting results considering the higher-than-fourth-order phonon scattering terms. Experimental data are taken from the following references: c-BN [39,40], AlSb [41,42], GaP [43,44], InSb [45], AlAs [45], and InAs [46,47].

principle, the scattering entropy must be absolutely convergent with n for any temperatures, thus $f(n)$ should be in the form of attenuation. By Occam's razor, the simplest analytical form is almost always the best. Here, we try to describe $f(n)$ with several different typical attenuation functions including the exponential form, log-normal function, Gamma function, and Poisson distribution. Once these functions allow the scattering entropy series summation to converge to a reasonable value for $T < T_{\text{melt}}$, where T_{melt} is the melting point, it makes sense for us to choose them as the coefficient function $f(n)$.

Taking the transverse optical (TO) mode of InP as an example, we apply these four functions to test the convergence rate of phonon scattering with increasing T . For the exponential form, $f(n) = \exp[-\alpha(T)n^2 + \beta(T)]$, and hence, the asymptotic form can be expressed as $S_n = k_B(T/T_D)^{n-3} \exp[-\alpha(T)n^2 + \beta(T)]$. By determining the parameters α and β from S_3 and S_4 at a given T , one can extrapolate the magnitude of higher-order phonon scattering and illustrate the convergence rate at different temperatures, especially above T_D . Figure 1(a) shows the entropy series summation with respect to n based on this fitting. It can be seen that, for $T/T_D < 3$, the convergence is achieved well at $n = 10$. For the log-normal function, $f(n) =$

$\frac{1}{(n-2)\alpha\sqrt{2\pi}} \exp\left\{-\frac{[\ln(n-2)-\beta]^2}{2\alpha^2}\right\}$. In Fig. 1(b), it appears that the entropy series summation obtained by log-normal function cannot give a convergent trend. For the Gamma function, $f(n) = \frac{(n-2)^{\alpha-1} \exp[-(n-2)/\beta]}{\Gamma(\alpha)\beta^\alpha}$, where α is a shape parameter, β is a scale parameter, and Γ is the usual generalized factorial $\Gamma(\alpha) = \int_0^\infty t^{\alpha-1} e^{-t} dt$. Note that n is set to 2 as the origin of the Gamma distribution since two-phonon scattering gives no contribution to the phonon anharmonicity. The entropy series summation obtained by the Gamma function is shown in Fig. 1(c). We can see that the convergence rate of scattering entropy is rather slow, and the convergence is not achieved even at $n = 50$. For the Poisson distribution, $f(n) = \frac{\alpha^{n-2} e^{-\alpha}}{(n-2)!}$, with the single parameter α being the expected rate of occurrences. Since the Poisson function has only one adjustable parameter, it cannot describe the scattering entropy of different order. To increase flexibility of the function, we introduce an additional parameter β to the original Poisson function to scale the amplitude of $f(n)$. Hence, the eventual form should be written as $f(n) = \beta \frac{\alpha^{n-2} e^{-\alpha}}{(n-2)!}$. Similarly, n is set to 2 as the origin of the Poisson distribution. It is observed in Fig. 1(d) that, at $T/T_D < 3$, the convergence of phonon scattering by fitting the Poisson distribution is well achieved at $n = 10$.

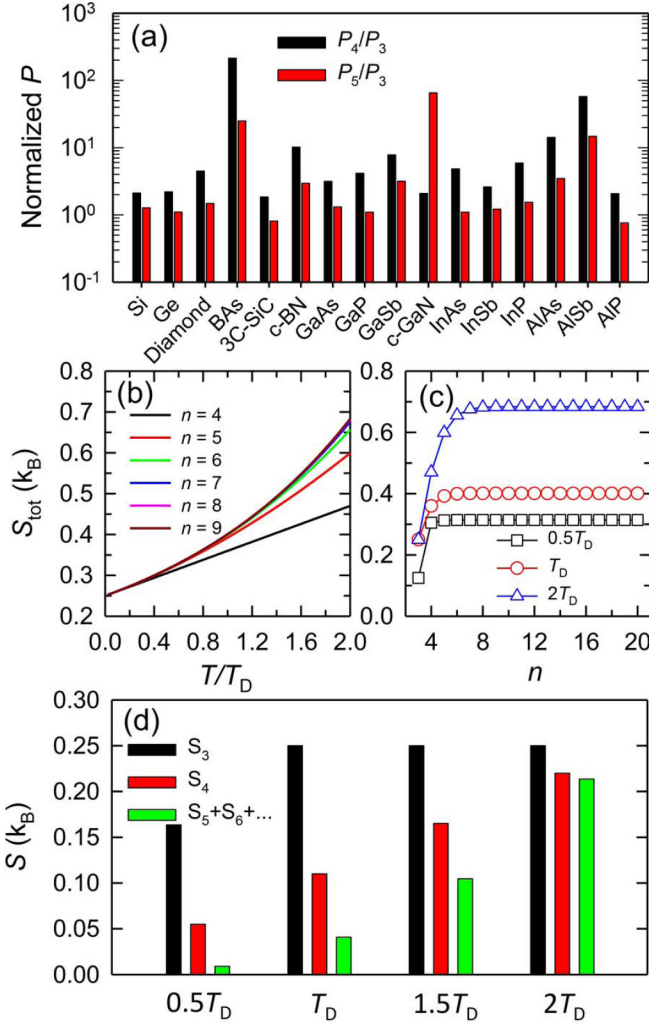


FIG. 4. (a) The normalized four- and five-phonon phase spaces of the zone-center transverse optical (TO) mode for materials studied. (b) The overall convergence speed of phonon scattering entropy with respect to the reduced temperature (T/T_D) when truncated to the different orders, and (c) with respect to the scattering order n at different temperatures. (d) The average scattering entropies S_3 , S_4 , and $S_5 + S_6 + \dots$ for materials studied at different temperatures.

From the above results, we conclude that, among these four functions, the exponential form and Poisson function are optimal for the convergence of phonon scattering. The exponential form, however, only works for the case where the scattering entropy decays monotonically with increasing n , whereas the Poisson function has the asymmetric shape and can thus reasonably reflect the nonmonotonic variation of scattering entropy, e.g., $S_3 < S_4 > S_5$. Given the realistic trend of scattering entropy with n , the Poisson distribution is preferred for describing $f(n)$. For further verifying the reliability of the Poisson function in terms of the convergence rate, we also show different orders of scattering entropy up to the tenth order in Fig. 1(e). It can be seen that the calculated S_4 (red circles) from the DFT is fitted well over the entire T range, whereas the calculated S_3 (blue circles) deviates from the fitted value below the T_D , due to the fact that $\tau_{3,\lambda}^{-1} \sim T$ is strictly satisfied only above T_D . Given that the higher-order

contributions are negligible below T_D , our proposed asymptotic form is valid in estimating higher-order entropy at high temperatures. It is clear from Fig. 1(e) that, in combination with the DFT calculations for S_2 , S_3 , and S_4 and the analytical fit for higher-order contributions, our estimated total scattering entropy [$S_{\text{tot}} = (S_2 + S_3 + S_4)_{\text{DFT}} + S_5 + S_6 + \dots + S_{10}$] (solid black line) can reasonably explain the experimental results (black squares), implying the validity of the Poisson function in estimating the convergence rate of phonon scattering.

Hence, in this paper, we propose the asymptotic form as

$$S_n = k_B \left(\frac{T}{T_D} \right)^{n-3} \beta \frac{\alpha^{n-2} e^{-\alpha}}{(n-2)!}, \quad (5)$$

which is the simplest analytical form of estimating the phonon anharmonicity ($n \geq 3$) to achieve absolute convergence following Occam's razor. Here, α and β are the fitting parameters related to the truncation order of scattering entropy and scattering strength, respectively, which are different for different phonon modes in different materials.

III. RESULTS AND DISCUSSION

The calculated zone-center phonon linewidths that include τ_{iso}^{-1} , $\tau_{3,\lambda}^{-1}$, and $\tau_{4,\lambda}^{-1}$ for the TO and longitudinal optical (LO) phonons in InP, c-GaN, c-BN, AlSb, GaP, InSb, AlAs, InAs, GaSb, and AlP are shown in Figs. 2–3 in comparison with available experimental data. For InP, we find that, with $\tau_{4,\lambda}^{-1}$ included, our calculated results are in good agreement with available experimental data [38], indicating that four-phonon scattering does account for the discrepancies between previous theoretical and experimental works. Remarkably, for other materials including c-GaN, c-BN, AlSb, GaP, InSb, AlAs, and InAs, our predictions of 2Γ , even after including four-phonon scattering, still deviate considerably from the experimental data in Refs. [39–47]. This implies that the fifth- and even higher-order phonon scatterings may become significant. For AlSb, the three-phonon contribution is nearly zero due to the large acoustic-optical (a-o) bandgap, and the four-phonon and higher-order processes dominate the linewidths in the entire T range. A similar case was also reported in BAS [11,48]. The large a-o phonon bandgap prevents two acoustic phonons from combining as an optical phonon due to the restriction of energy and momentum conservation as illustrated in Ref. [49]. For AlP and GaSb, which have no experimental data reported yet, our predictions provide a theoretical basis for the Raman measurements.

To assess the importance of fifth- and higher-order phonon scattering terms, we apply Eq. (5) to fit to S_3 and S_4 of the zone-center phonon linewidths of all the materials except AlSb, and the phonon scattering entropy of different order along with the fitting parameters is given in the Supplemental Material [22]. Note that, for AlSb, where the three-phonon contribution is nearly zero, our asymptotic form is not applicable anymore. The convergent linewidths obtained from the analytical fit are compared with the available experimental results in Figs. 2–3. For a certain mode of some of the materials studied, such as the TO mode of InP, LO mode of GaP, TO and LO modes of InSb, TO and LO modes of AlAs, LO mode of InAs, including the higher-order

TABLE I. Calculated characteristic scattering entropies $S_2 = A/T_D$, $S_3 = B$, and $S_4 = CT_D$ in terms of k_B , and the dimensionless coefficients $\tilde{A}$ and $\tilde{B}$ for materials examined in this paper. The relative contribution of four- to three-phonon scattering entropy at RT, $S_4(300\text{K})/S_3(300\text{K})$, is also given.

Materials	T_D (K)	S_2 (k_B)	S_3 (k_B)	S_4 (k_B)	$\tilde{A}$	$\tilde{B}$	RT- S_4/S_3
Si	645	0.039	0.34	0.076	0.51	4.39	10.59%
Ge	360	0.025	0.28	0.043	0.58	6.60	12.62%
Diamond	2280	0.026	0.12	0.091	0.28	1.32	9.93%
BAs	651	0.34	0.00023	0.12	2.76	0	52 173.91%
3C-SiC	1106	0.013	0.16	0.36	0.037	0.45	35.68%
c-BN	2025	0.030	0.19	0.24	0.13	0.65	9.73%
GaAs	313	0.021	0.23	0.13	0.16	1.74	51.86%
GaP	412	0.0044	0.69	0.096	0.046	7.19	8.89%
GaSb	240	0.0036	0.037	0.011	0.34	3.41	30.55%
c-GaN	584	0.0019	0.23	0.072	0.011	3.17	12.08%
InAs	229	0.032	0.41	0.082	0.39	5.04	24.70%
InSb	187	0.022	0.35	0.042	0.51	8.29	18.75%
InP	286	0.021	0.16	0.082	0.25	1.90	49.89%
AlAs	373	0.012	0.086	0.073	0.17	1.18	59.07%
AlSb	276	0.00031	0.00093	0.10	0.003	0.009	12 132.14%
AlP	525	0.092	0.71	0.12	0.74	5.70	8.50%
Average $\bar{S}$	—	0.043	0.25	0.11	—	—	—

scattering terms can considerably improve the agreement between the four-phonon theory-based calculations and experiments, showing the importance of higher-order effects. For both the LO modes of c-GaN and c-BN, our estimations show that the contribution of higher-order scattering terms is negligible, so we speculate that the difference between experiments [40,50] and our calculations may be due to the background scattering in the experiment, which is generally inevitable especially at higher temperatures. It should be noted that, in general, four-phonon scattering has a larger impact for optical phonons than for the heat-carrying acoustic phonons. Our previous studies [11,49] have shown that, for zone-center optical phonons, the four-phonon scattering is dominated by the recombination process $\lambda_1 + \lambda_2 \rightarrow \lambda_3 + \lambda_4$. The optical branches bunch together and allow the four modes λ_1 , λ_2 , λ_3 , and λ_4 to have similar energies, so they can easily satisfy the energy conservation rule for the recombination process. In contrast, the low-frequency acoustic phonons which carry heat rarely participate in the recombination process of the four-phonon scattering of optical phonons due to large energy differences. Therefore, it is understandable in certain materials, four-phonon scattering can significantly affect the linewidth of zone-center optical phonons, while not affecting much the thermal conductivity, e.g., in c-BN [51]. For the LO mode of InP and the TO mode of c-BN, the analytical fit reveals the significant contribution from higher-order terms at higher temperatures and overestimates the linewidth in varying degrees as compared with the experimental results. In addition to the limitations of the accuracy of our general model, this overestimation, at least in part, should be attributed to the T -induced phonon renormalization, which was not considered in this paper but has been demonstrated to considerably weaken the phonon scattering rates especially above T_D [52–54]. We also note that, with higher-order phonon scattering included, the linewidth deviates largely from the linear scaling with T , which offers an important theoretical basis

for experimentalists to study the Raman spectra at different temperatures.

To explore the significance of fifth-order phonon scattering, we further calculate the phase space P , which describe the probabilities of all the possible scattering events, of the zone-center TO phonon for three- (P_3), four- (P_4), and five-phonon (P_5) scattering in these materials, as given in the Supplemental Material [22]. Generally, the larger the phase space, the stronger the phonon scattering. For ease of comparison between different orders of scattering terms, we normalize P_4 and P_5 against P_3 , and results are shown in Fig. 4(a). As is seen in Fig. 4(a), P_5 is generally comparable with P_4 , especially for certain materials, e.g., c-GaN, P_5 is even an order of magnitude larger than P_4 , providing the evidence that the five-phonon scattering is indeed nonnegligible.

Table I lists the calculated detailed characteristic scattering entropies $S_2 = A/T_D$, $S_3 = B$, and $S_4 = CT_D$ in terms of k_B , and $\tilde{A}$ and $\tilde{B}$ for aforementioned compounds as well as some important materials studied in our recent work [11], including Si, Ge, diamond, BAs, and 3C-SiC. Also, for ease of appreciating the practical significance of the calculated numbers, the relative contribution of four- to three-phonon scattering entropy at room temperature (RT) $S_4(300\text{K})/S_3(300\text{K})$ is shown. The salient smallness of $\tilde{T}_3$ in some materials (BAs, AlSb, 3C-SiC, AlAs, and to a degree, InP) has to do with the peculiar phonon dispersion relation in these crystals, where the large a-o gap and the flatness of the optical bands make the satisfaction of three-phonon selection rules very difficult if not impossible. From the data, we have compiled the average entropies at their respective Debye temperatures, as shown in Table I. As is made explicit by the dimensionless expression in Eq. (4), when $\tilde{T} \ll \tilde{A}$, the linewidth is dominated by isotope/defect scattering. When $\tilde{T} > \tilde{B}$, four-phonon scattering is more important than three-phonon scattering. We also notice that the absolute magnitude of $S_4(T_D) = CT_D$ varies

TABLE II. Calculated phonon linewidth (in units of cm^{-1}) of the zone-center TO mode for materials studied in this paper as compared with the experimental values at around $T = T_D$.

Materials	T (K)	2Γ (exp) (cm^{-1})	2Γ ($\tau_{3,\lambda}^{-1}$) (cm^{-1})	2Γ ($\tau_{3,\lambda}^{-1} + \tau_{4,\lambda}^{-1}$) (cm^{-1})	2Γ [$\tau_{3,\lambda}^{-1} + \tau_{4,\lambda}^{-1} + (0.4\tau_{4,\lambda}^{-1})$] (cm^{-1})
Si	686	7.50 [55]	5.13	7.47	8.34
Ge	337	2.93 [56]	2.50	2.84	2.97
Diamond	1037	4.97 [57]	3.48	4.51	4.89
BAs	485	0.98 [11]	0.000017	0.97	1.33
InP	286	2.073 [38]	1.21	1.79	2.00
InSb	300	4.45 ± 0.39 [45]	2.66	3.16	3.35
c-BN	1826	20.96 [39]	8.98	18.79	22.42
AlAs	373	4.44 ± 0.35 [45]	0.91	1.56	1.80
AlSb	276	1.02 [42]	0.0021	0.80	1.10
GaAs	313	2.32 [38]	1.79	2.29	2.48
Average 2Γ	—	5.16	2.67	4.42	5.07

quite a lot, ranging from $0.011k_B$ in GaSb to $0.36k_B$ in 3C-SiC, implying that the four-phonon scattering strength is strongly correlated to the inherent phononic structure of the material such as the a-o gap, phonon bunching, and the flatness of the optical bands. On average, $\bar{S}_4$ ($0.11k_B$) is comparable with $\bar{S}_3$ ($0.25k_B$).

To provide insights on the overall convergence speed, we apply Eq. (5) to fit to $\bar{S}_3$ and $\bar{S}_4$ to extrapolate the total scattering entropy S_{tot} . Figure 4(b) shows the overall convergence speed of the total entropy below $T = 2T_D$ when truncated to the different orders. It is seen that the rate of convergence obviously depends on T : the higher the temperature, the slower the convergence rate. To look into the convergence rate more closely, Fig. 4(c) also shows the overall convergence speed with respect to the scattering order n for three certain temperatures. It is important to find that, within 0.01% error, the scattering entropy at $T = 0.5T_D$, T_D , and $2T_D$ converges well at the 6th, 8th, and 11th order, respectively. Physically significant is the fact that the Taylor expansion sum in Eq. (3) appears to have reasonable convergence rate on average but is not exceedingly rapid either, which one probably should have expected at the outset. More specifically, we find that the resulting higher-order scattering entropy $S_5 + S_6 + \dots$ is $0.041k_B$ at T_D , as much as $\sim 37\%$ of $\bar{S}_4$. By carefully examining the T -dependent residual entropy between the experimental and the calculated scattering entropies $\Delta S \equiv S_{\text{exp}} - S_2 - S_3 - S_4$ for these materials, it appears that, on average, scattering processes higher than four-phonon scattering could still contribute considerably to the linewidth, as shown in Table II. On average, at $T = T_D$, the three-phonon scattering contribution to the linewidth is 2.67 cm^{-1} , and after including four-phonon scattering, the linewidth is 4.42 cm^{-1} , still lower than the experimental value of 5.16 cm^{-1} . When an additional $\sim 0.37\tau_{4,\lambda}^{-1}$ is included at $T = T_D$, the sum will approximately converge to the experiment value, demonstrating the robustness of our proposed asymptotic form in evaluating the high-order scattering terms. Thus, the total scattering entropies from all-order phonon scattering at $T = T_D$ should be about $S_2 + S_3 + S_4 + (S_5 + S_6 + S_7 + S_8) = 0.043k_B + 0.25k_B + 0.11k_B + (0.041k_B) = 0.44k_B$. The fact

that the average total scattering entropy is of the order of k_B is physically significant since it indicates universally that the zone-center optical phonon has a linewidth comparable with the average phonon energy at T_D . As is seen in Fig. 4(d), the residual entropy from higher-order terms increases rapidly with T : from our *ab initio* calculated data, we see that, at $T = 0.5T_D$, the residual contribution from the fifth- and higher-order scatterings is $< 2.86\%$, but at $T = 2T_D$, that is almost the same as $\bar{S}_4$ ($0.22k_B$).

IV. CONCLUSIONS

In summary, we have calculated the zone-center optical phonon linewidths of a series of technologically important III-V compound semiconductors by first principles. Including four-phonon scattering brings the predictions much closer to experimental data than the three-phonon theory. However, for many materials including c-GaN, c-BN, AlSb, GaP, InSb, AlAs, and InAs, the predictions, even after including four-phonon scattering, still deviate considerably from the experimental data. To examine the convergence of the phonon linewidth, we use the phonon scattering entropy concept, and an error-scale estimate for the previously untreated fifth- and higher-order phonon scattering entropies is provided for these materials on average. We find that, at T_D , on average, the convergence is well achieved at the eighth order, and the average entropy of fifth- and higher-order scattering is $\sim 37\%$ of that of four-phonon scattering. The total scattering entropy is of the order of k_B , which is physically significant since it indicates universally that the zone-center optical phonon has a linewidth comparable with the average phonon energy at T_D .

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Supplemental Material for “Evidence of fifth- and higher-order phonon scattering entropy of zone-center optical phonons”

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Sec.1. METHODS

A. Phonon Linewidth

The vibrational properties of crystals are described by the vibrational Hamiltonian, which can be Taylor expanded as $\hat{H} = \hat{H}_0 + \hat{H}_3 + \hat{H}_4 + \dots$, where $\hat{H}_0$, $\hat{H}_3$ and $\hat{H}_4$ are the harmonic, cubic, and quartic terms, respectively. Within anharmonic perturbation theory, $\hat{H}_3 + \hat{H}_4$ contributes a T -dependent linewidth 2Γ to the second order self-energy [1]. The contribution from $\hat{H}_3$ is the well-known three-phonon scattering rate $\tau_{3,\lambda}^{-1}$ [2–5], which is computed by the summations of the probabilities of all the possible scattering events calculated by Fermi's golden rule (FGR) from density functional theory (DFT) :

$$\tau_{3,\lambda}^{-1} = \sum_{\lambda_1 \lambda_2} \left[\frac{1}{2} (1 + n_{\lambda_1}^0 + n_{\lambda_2}^0) \mathcal{L}_- + (n_{\lambda_1}^0 - n_{\lambda_2}^0) \mathcal{L}_+ \right]. \quad (\text{S.1})$$

here λ stands for $(\mathbf{q}, j)$ with $\mathbf{q}$ and j labeling the phonon wave vector and dispersion branch, respectively. $n^0 = (e^{\hbar\omega/k_B T} - 1)^{-1}$ is the phonon occupation number, and ω is the phonon angular frequency. $\mathcal{L}$ is the transition probability matrix, and the $+$ and $-$ superscripts denote sums over allowed absorption and emission processes, respectively, under the constraints of conservation of momentum and energy. Full expressions for all terms are not included here for brevity; readers are referred to Ref. [6] for details.

Similar to the derivation of the three-phonon scattering rate, the four-phonon scattering rate $\tau_{4,\lambda}^{-1}$ [6–8] including all possible four-phonon interaction events can be written by

$$\begin{aligned} \tau_{4,\lambda}^{-1} = \sum_{\lambda_1 \lambda_2 \lambda_3} & \left(\frac{1}{6} \frac{n_{\lambda_1}^0 n_{\lambda_2}^0 n_{\lambda_3}^0}{n_{\lambda}^0} \mathcal{L}_{--} + \frac{1}{2} \frac{(1 + n_{\lambda_1}^0) n_{\lambda_2}^0 n_{\lambda_3}^0}{n_{\lambda}^0} \mathcal{L}_{+-} \right. \\ & \left. + \frac{1}{2} \frac{(1 + n_{\lambda_1}^0)(1 + n_{\lambda_2}^0) n_{\lambda_3}^0}{n_{\lambda}^0} \mathcal{L}_{++} \right). \end{aligned} \quad (\text{S.2})$$

Apart from the phonon-phonon scattering, isotopic disorder also has an effect on the phonon linewidth, with rates given by [9, 10]

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$$\tau_{\text{iso}}^{-1} = \frac{\pi\omega^2}{2} \sum_{i \in u.c} g(i) |\mathbf{e}_\lambda^* \mathbf{e}_{\lambda'}(i)|^2 \delta(\omega_\lambda - \omega_{\lambda'}), \quad (\text{S.3})$$

where $g(i) = \sum_s f_s(i) [1 - M_s(i)/\bar{M}(i)]^2$ is the Pearson deviation coefficient of the isotope masses $\{M_s(i)\}$ of element i with isotopic abundance $f_s(i)$ and $\bar{M}(i) = \sum_s f_s(i) M_s(i)$.

The full width at half maximum (FWHM) of phonons 2Γ thus can be calculated as a Matthiessen sum of contributions from isotope scattering, three-phonon scattering, and four-phonon scattering rates

$$2\Gamma = \tau_{\text{iso}}^{-1} + \tau_{3,\lambda}^{-1} + \tau_{4,\lambda}^{-1} + \dots \quad (\text{S.4})$$

B. Three-phonon, four-phonon, and five-phonon phase spaces

The contribution to the phonon linewidth from three-phonon, four-phonon, and five-phonon scatterings depends on the phase space and the scattering matrix. The former is directly determined by the phonon dispersion, while the latter is determined by the third-order, fourth-order, and fifth-order IFCs, which are very difficult if not impossible to calculate due to the extremely expensive computational cost. The strength of phonon scattering of different orders can somehow be measured by their phase spaces, which describe the probabilities of all the possible scattering events. Generally, the larger the phase space, the stronger the phonon scattering. All phonon-phonon scattering processes including three-phonon, four-phonon, and five-phonon scattering processes are constrained to satisfy energy and momentum conservation:

$$\omega_\lambda \pm \omega_{\lambda_1} = \omega_{\lambda_2}, \quad \mathbf{q}_\lambda \pm \mathbf{q}_{\lambda_1} = \mathbf{q}_{\lambda_2} + \mathbf{G}, \quad (\text{S.5})$$

$$\omega_\lambda \pm \omega_{\lambda_1} \pm \omega_{\lambda_2} = \omega_{\lambda_3}, \quad \mathbf{q}_\lambda \pm \mathbf{q}_{\lambda_1} \pm \mathbf{q}_{\lambda_2} = \mathbf{q}_{\lambda_3} + \mathbf{G}, \quad (\text{S.6})$$

$$\omega_\lambda \pm \omega_{\lambda_1} \pm \omega_{\lambda_2} \pm \omega_{\lambda_3} = \omega_{\lambda_4}, \quad \mathbf{q}_\lambda \pm \mathbf{q}_{\lambda_1} \pm \mathbf{q}_{\lambda_2} \pm \mathbf{q}_{\lambda_3} = \mathbf{q}_{\lambda_4} + \mathbf{G}. \quad (\text{S.7})$$

Here ω_λ is the phonon frequency of mode λ , $\mathbf{G}$ is a reciprocal lattice vector that is zero for normal processes and non-zero for Umklapp processes, and the $\pm$ signs correspond to the two types of possible phonon-phonon processes. We define the phase space of each mode at each $\mathbf{q}$ point available for three-phonon, four-phonon, and five-phonon processes, as the sum over all possible modes subject to the constraints of Eqs. S.5-S.7:

$$P_3 = \frac{2}{3\Omega} \left(P_3^{(+)} + \frac{1}{2} P_3^{(-)} \right), \quad (\text{S.8})$$

$$P_4 = \frac{6}{7\Omega} \left(\frac{1}{2}P_4^{(++)} + \frac{1}{2}P_4^{(+-)} + \frac{1}{6}P_4^{(--)}\right), \quad (\text{S.9})$$

$$P_5 = \frac{24}{15\Omega} \left(\frac{1}{6}P_5^{(++++)} + \frac{1}{4}P_5^{(+++-)} + \frac{1}{6}P_5^{(+-+-)} + \frac{1}{24}P_5^{(----)}\right), \quad (\text{S.10})$$

where

$$P_3^{(\pm)}(\mathbf{q}) = \sum_{\lambda_1\lambda_2} \int_{BZ} d\mathbf{q} \delta(\omega_\lambda \pm \omega_{\lambda_1} - \omega_{\lambda_2}), \quad (\text{S.11})$$

$$P_4^{(\pm\pm)}(\mathbf{q}) = \sum_{\lambda_1\lambda_2\lambda_3} \int_{BZ} d\mathbf{q} \delta(\omega_\lambda \pm \omega_{\lambda_1} \pm \omega_{\lambda_2} - \omega_{\lambda_3}), \quad (\text{S.12})$$

$$P_5^{(\pm\pm\pm)}(\mathbf{q}) = \sum_{\lambda_1\lambda_2\lambda_3\lambda_4} \int_{BZ} d\mathbf{q} \delta(\omega_\lambda \pm \omega_{\lambda_1} \pm \omega_{\lambda_2} \pm \omega_{\lambda_3} - \omega_{\lambda_4}), \quad (\text{S.13})$$

where the integration in Eqs. S.11-S.13 is taken over the first Brillouin zone (BZ). The quantity, $\Omega = n^j V_{BZ}^2$ ($j=3, 4, 5$ for three-phonon, four-phonon, and five-phonon processes, respectively) with n phonon branches whose BZ has volume, V_{BZ} , is a normalization factor equal to the unrestricted phase space for each type of process. Herein the conservation of energy in all processes is enforced by the Dirac delta distributions, which is further approximated by Gaussian functions in our calculation. The factors on the right side of the Eqs. S.8-S.10 arise to prevent multi-counting of scattering events. Additional factors (2/3, 6/7, 24/15) in Eqs. S.8-S.10 give $P_3, P_4, P_5 = 1$ when the energy-conserving delta functions in Eqs. S.11-S.13(4) are removed.

Table S1 lists three-phonon, four-phonon, and five-phonon phase spaces of the zone-center TO phonon for sixteen materials.

C. Computational details

To obtain phonon scattering rates described above, the second, third- and fourth-order interatomic force constants (IFCs) are needed. All force constants are calculated via real-space finite displacement difference method, with 0.01Å of the magnitude of displacements. The second-order force constant and phonon frequencies are calculated within the DFT based on VASP [11, 12] as implemented in the open-source software packages Phonopy [13], and the supercell is $5 \times 5 \times 5$ primitive cells. To capture LO/TO splitting the non-analytical interaction is determined by the Born effective charges. The third-order force constants are calculated through Thirdorder [14], a package of ShengBTE, considering up

TABLE S1: The phase spaces of the zone-center TO mode for materials studied for three-phonon (P_3), four-phonon (P_4), and five-phonon (P_5) scatterings.

Materials	$P_3(10^{-6})$	$P_4(10^{-6})$	$P_5(10^{-6})$
Si	0.2357	0.4983	0.3002
Ge	0.4997	1.1036	0.5501
Diamond	0.05536	0.2475	0.08199
BAs	0.002628	0.5625	0.06547
3C-SiC	0.2211	0.4094	0.1789
c-BN	0.02848	0.2899	0.08383
GaAs	0.3891	1.2250	0.5102
GaP	0.2625	1.0917	0.2881
GaSb	0.1739	1.3574	0.5513
c-GaN	0.1947	0.4053	12.7081
InAs	0.4350	2.1005	0.4782
InSb	0.6113	1.5936	0.7444
InP	0.2169	1.2808	0.3345
AlAs	0.07516	1.0686	0.2607
AlSb	0.01642	0.9460	0.2414
AlP	0.3978	0.8231	0.3029

to the fifth nearest neighbor. The fourth-order force constant are calculated via the in-house code by considering up to the second nearest neighbors. The third- and fourth-order IFCs for all of materials examined in this work are performed with VASP using $4 \times 4 \times 4$ primitive cells and $4 \times 4 \times 4$ Monkhorst-Pack grid. The LDA is used for the exchange-correlation functional with projector-augmented-wave method [15]. The plane-wave energy cutoff of all the materials studied is set by adding 30% to the highest energy cutoff for the pseudopotentials. Cell parameters and internal atomic positions are fully relaxed until the

total energy and maximum ionic Hellmann-Feynman force converge to 10^{-10} eV and 10^{-6} eV/Å, respectively. The phonons are taken with a $16 \times 16 \times 16$ $\mathbf{q}$ -mesh in the Brillouin zone (BZ), which has been proven to afford good convergence of phonon scattering rates [7].

Considering that the large computational cost and the high memory requirement are needed for third- and fourth-order IFCs calculations, herein we harness the space-group symmetries of all crystals by calling the Atsushi Togo's spglib which can greatly reduce the required number of DFT calculations. In addition, it is noted that numerical uncertainties will cause small violations in crystal translational and rotational invariance constraints that has a large influence on phonon scattering calculation. Here a Lagrange-multiplier symmetrization technique is employed to overcome this issue.

Sec.2. PHONON DISPERSIONS FOR ALL OF MATERIALS

To perform the phonon linewidth calculations, the accurate phonon frequencies and corresponding eigenvectors are required, which can be extracted from the diagonalization of the dynamical matrix. Here we present the calculated phonon dispersions in the high-symmetry directions for all of the materials considered in this work, along with available experimental data for comparison(see Figs. S1–S10).

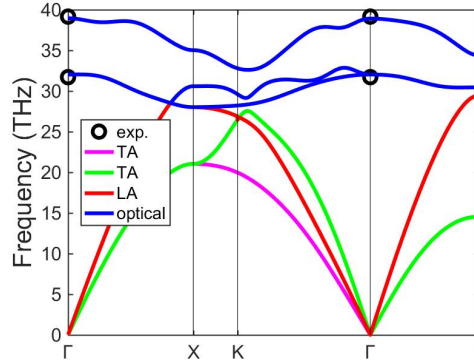


FIG. S1: Calculated phonon dispersion for c-BN in the high symmetry directions (solid curves). Experimental data from Ref. [16] are given by black circles.

In the Table S2, we also list our calculated frequencies of TO and LO mode at Γ point along with the values of ϵ_∞ for each material considered in this work, comparing with the existing experimental data.

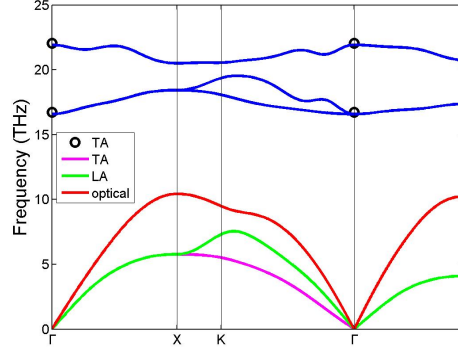


FIG. S2: Calculated phonon dispersion for GaN in the high symmetry directions (solid curves). Experimental data from Ref. [17] are given by black circles.

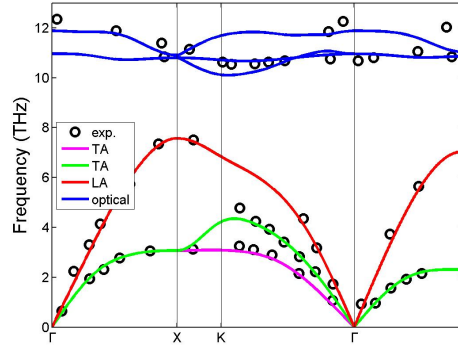


FIG. S3: Calculated phonon dispersion for GaP in the high symmetry directions (solid curves). Experimental data from Ref. [18] are given by black circles.

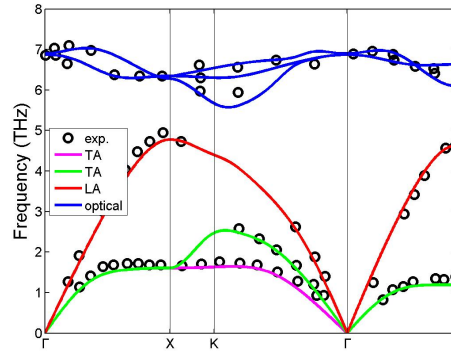


FIG. S4: Calculated phonon dispersion for GaSb in the high symmetry directions (solid curves). Experimental data from Ref. [19] are given by black circles.

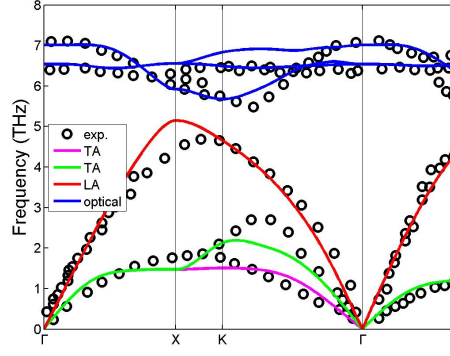


FIG. S5: Calculated phonon dispersion for InAs in the high symmetry directions (solid curves). Experimental data from Ref. [20] are given by black circles.

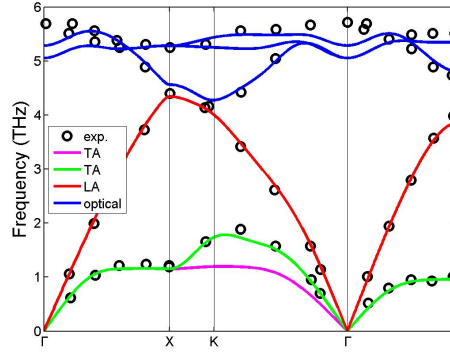


FIG. S6: Calculated phonon dispersion for InSb in the high symmetry directions (solid curves). Experimental data from Ref. [21] are given by black circles.

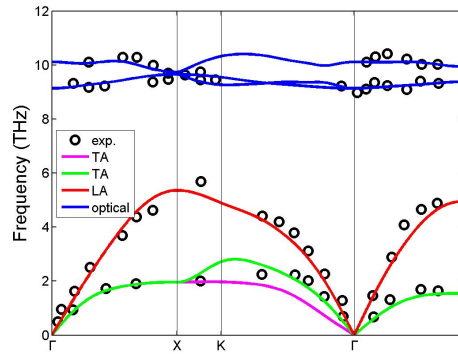


FIG. S7: Calculated phonon dispersion for InP in the high symmetry directions (solid curves). Experimental data from Ref. [22] are given by black circles.

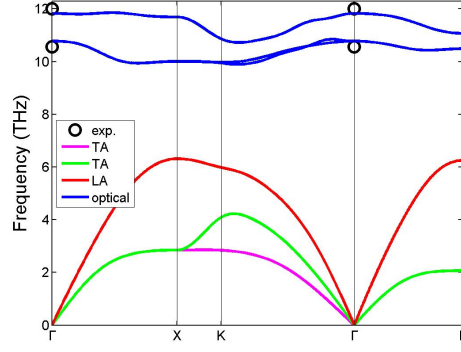


FIG. S8: Calculated phonon dispersion for AlAs in the high symmetry directions (solid curves). Experimental data from Ref. [23] are given by black circles.

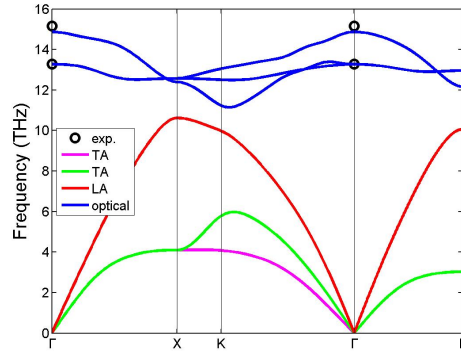


FIG. S9: Calculated phonon dispersion for AlP in the high symmetry directions (solid curves). Experimental data from Ref. [24] are given by black circles.

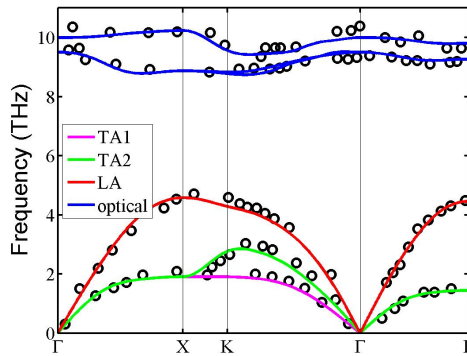


FIG. S10: Calculated phonon dispersion for AlSb in the high symmetry directions (solid curves). Experimental data from Ref. [25] are given by black circles.

TABLE S2: The optical phonon frequencies (in the units of cm^{-1}) at the Γ point, along with static dielectric constant ϵ_∞ for all of the materials listed in this work.

Materials	TO mode		LO mode		ϵ_∞	
	Present	Exp.	Present	Exp.	Present	Exp.
c-BN	1068	1056 [26]	1298	1304 [26]	4.561	4.46 [27]
GaAs	270.8	267.5	287.89	285.2	13.7426	12.85 [28]
GaP	365.3	365 [29]	396.1	403 [29]	10.60	-
GaSb	228.98	228.2 [19]	230.3	229.3 [19]	169.50	-
GaN	565.9	552 [30]	730.7	740 [30]	5.72	-
InAs	218	221 [31]	233.8	246 [31]	19.643	-
InSb	169	181.5 [21]	183.5 [21]	194.7	20.94	-
InP	304.6	320.3 [31]	337.1	341 [31]	11.98	-
AlAs	359	352 [20]	394.2	400 [20]	9.48	-
AlSb	316.8	318.8 [25]	333.4	350 [25]	11.74	-
AlP	442.2	442.5 [24]	495	504.5 [24]	8.312	-

Sec.3. CONVERGENCE TEST FOR PHONON SCATTERING

If the coefficient function $f(n)$ has physical meaning, the scattering entropy series summation must converge to a reasonable value for $T < T_{\text{melt}}$, where T_{melt} is the melting point. Table S3 lists the Debye temperature T_D , melting temperature T_{melt} , and T_{melt}/T_D for all the materials studied for reference.

We use Formula (5) in the main text to fit to S_3 and S_4 of all the materials except BAs and AlSb, and the fitting parameters are summarized in Table S4. To assess the reliability of the fit, we also show different orders of scattering entropy for the TO and LO modes of materials we are studying in Figs. S11-S19. It is clear that our proposed Eq.(5) in the main text is able to fit well the calculated S_3 and S_4 for all materials near the Debye temperature and above. Also, we display our defined Poisson distributions for different α at a fixed value of $\beta = 1$ in Fig. S20. It can be seen that the fitting parameter α is closely associated with the peak position (corresponding to the maximum of scattering entropy at $T = T_D$) and the truncation order n . On this basis, we evaluate the order of maximum scattering entropy and

TABLE S3: The Debye temperature, melting temperature, as well as $T_{\text{melt}}/T_{\text{D}}$ for all the materials.

Materials	T_{D} (K)	T_{melt} (K)	$T_{\text{melt}}/T_{\text{D}}$
Si	645	1687	2.62
Ge	360	1211	3.36
Diamond	2280	4300	1.89
BAs	651	2349	3.61
3C-SiC	1106	3003	2.72
c-BN	2025	3246	1.60
GaAs	313	1511	4.83
GaP	412	1750	4.25
GaSb	240	985	4.10
c-GaN	584	2773	4.75
InAs	229	1215	5.31
InSb	187	800	4.28
InP	286	1335	4.67
AlAs	373	2013	5.40
AlSb	276	1333	4.83
AlP	525	2803	5.34

truncation order for different materials at $T = T_{\text{D}}$, as listed in Table S4. Note that for all the materials the truncation order is obtained within an error of less than 0.01%. It can be seen that at $T = T_{\text{D}}$, the scattering entropy is dominated by three-phonon scattering in most materials, while four-phonon scattering is dominant in c-BN, and six-phonon scattering is dominant in 3C-SiC.

TABLE S4: The fitting parameters α and β , and the order of maximum scattering entropy as well as the truncation order at $T = T_D$ for the TO mode of different materials.

Materials	α	β	Order of maximum entropy (n)	Truncation order (n)
Si	0.4471	1.1892	3	6
Ge	0.3071	1.2394	3	6
Diamond	1.5167	0.3606	3	9
3C-SiC	4.5000	3.2006	6	15
c-BN	2.5263	0.9406	4	12
GaAs	1.1304	0.6301	3	8
GaP	0.2783	3.2752	3	6
GaSb	0.5946	0.1128	3	7
c-GaN	0.6261	0.6871	3	7
InAs	0.4000	1.5291	3	6
InSb	0.2400	1.8539	3	5
InP	1.0250	0.4351	3	8
AlAs	1.6977	0.2767	3	10
AlP	0.3380	2.9452	3	6
Average	0.8800	0.6849	3	8

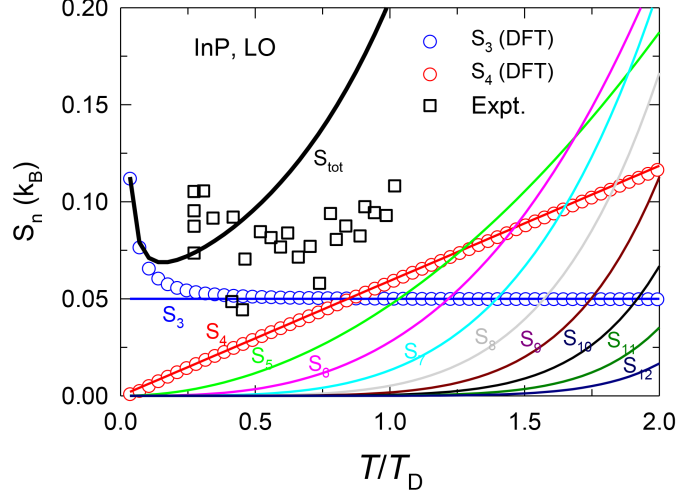


FIG. S11: Phonon scattering entropies of different order as a function of T for the LO mode of InP. The blue (red) circles represent the calculated S_3 (S_4), and the solid curves represent the fitted results through Eq.(5) in the main text.

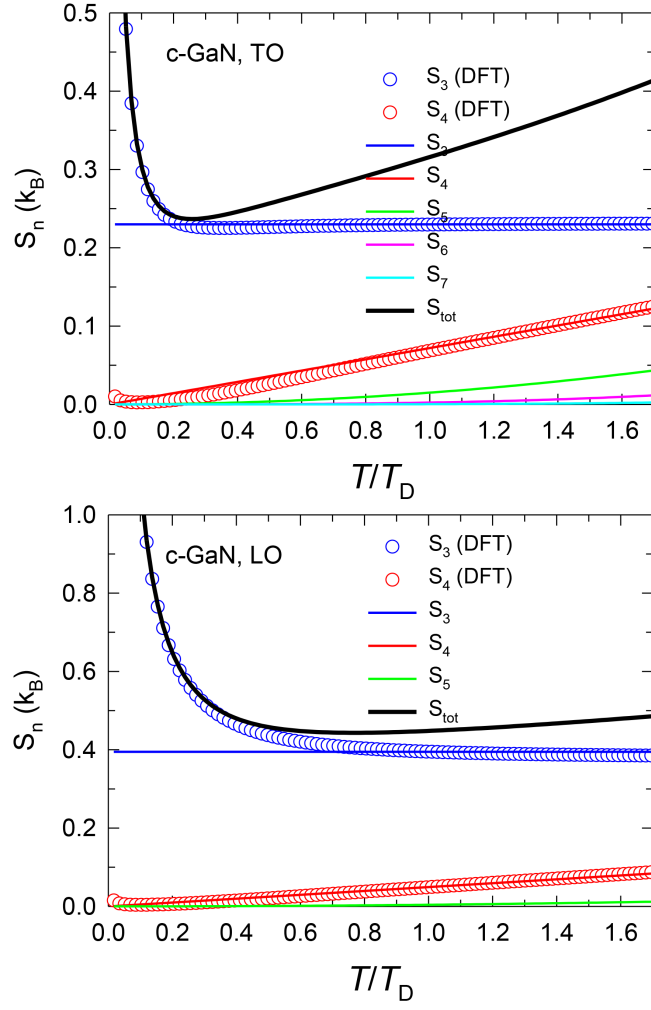


FIG. S12: Phonon scattering entropies of different order as a function of T for the TO and LO modes of GaN. The blue (red) circles represent the calculated S_3 (S_4), and the solid curves represent the fitted results through Eq.(5) in the main text.

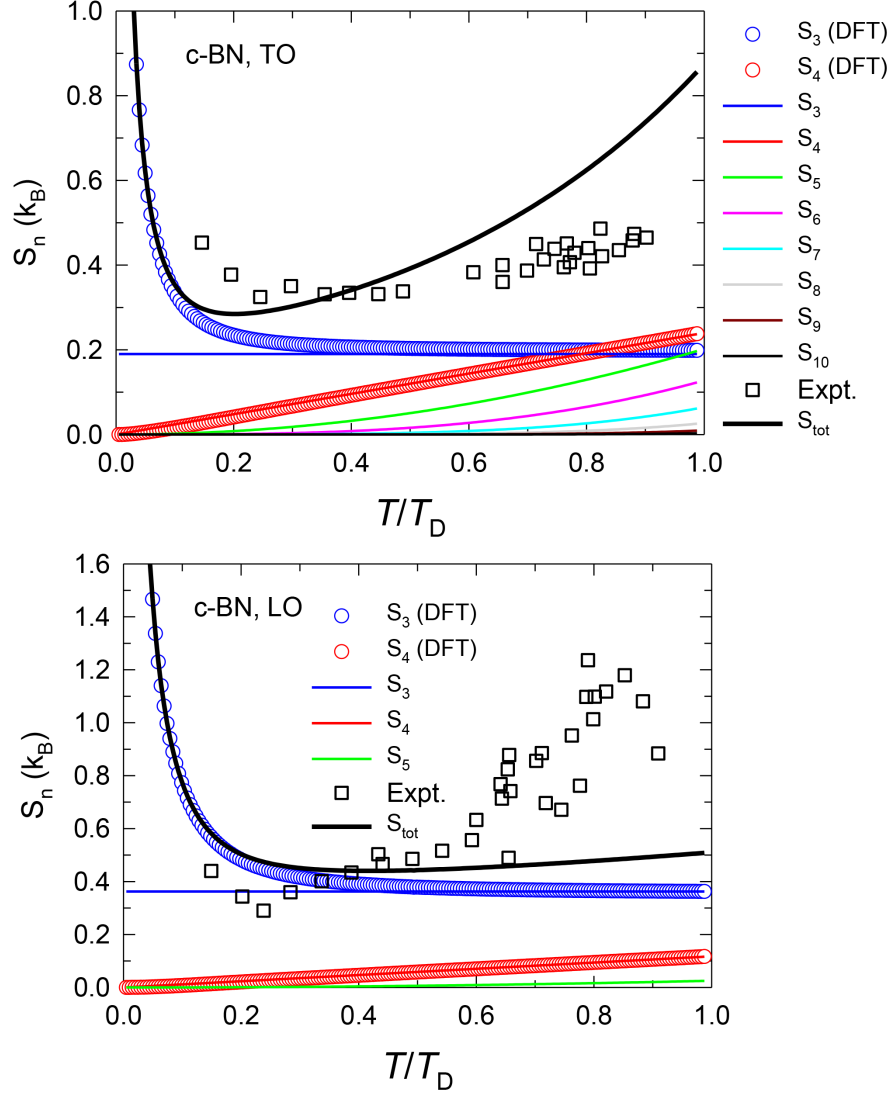


FIG. S13: Phonon scattering entropies of different order as a function of T for the TO and LO modes of c-BN. The blue (red) circles represent the calculated S_3 (S_4), and the solid curves represent the fitted results through Eq.(5) in the main text.

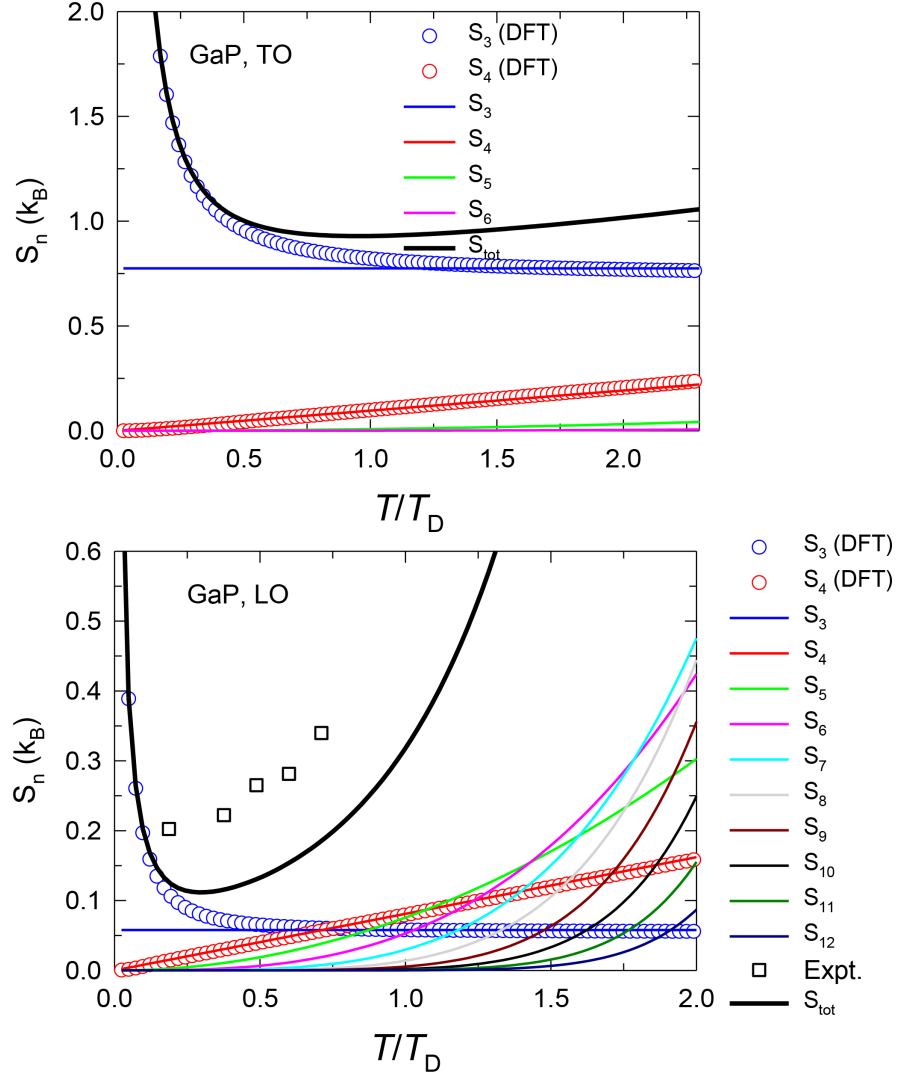


FIG. S14: Phonon scattering entropies of different order as a function of T for the TO and LO modes of GaP. The blue (red) circles represent the calculated S_3 (S_4), and the solid curves represent the fitted results through Eq.(5) in the main text.

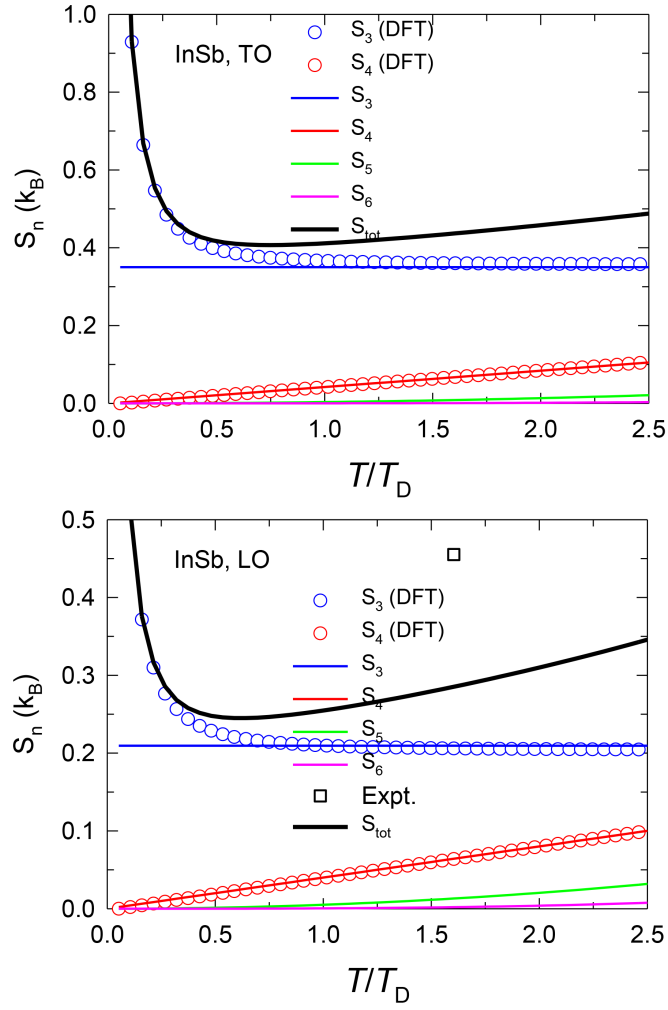


FIG. S15: Phonon scattering entropies of different order as a function of T for the TO and LO modes of InSb. The blue (red) circles represent the calculated S_3 (S_4), and the solid curves represent the fitted results through Eq.(5) in the main text.

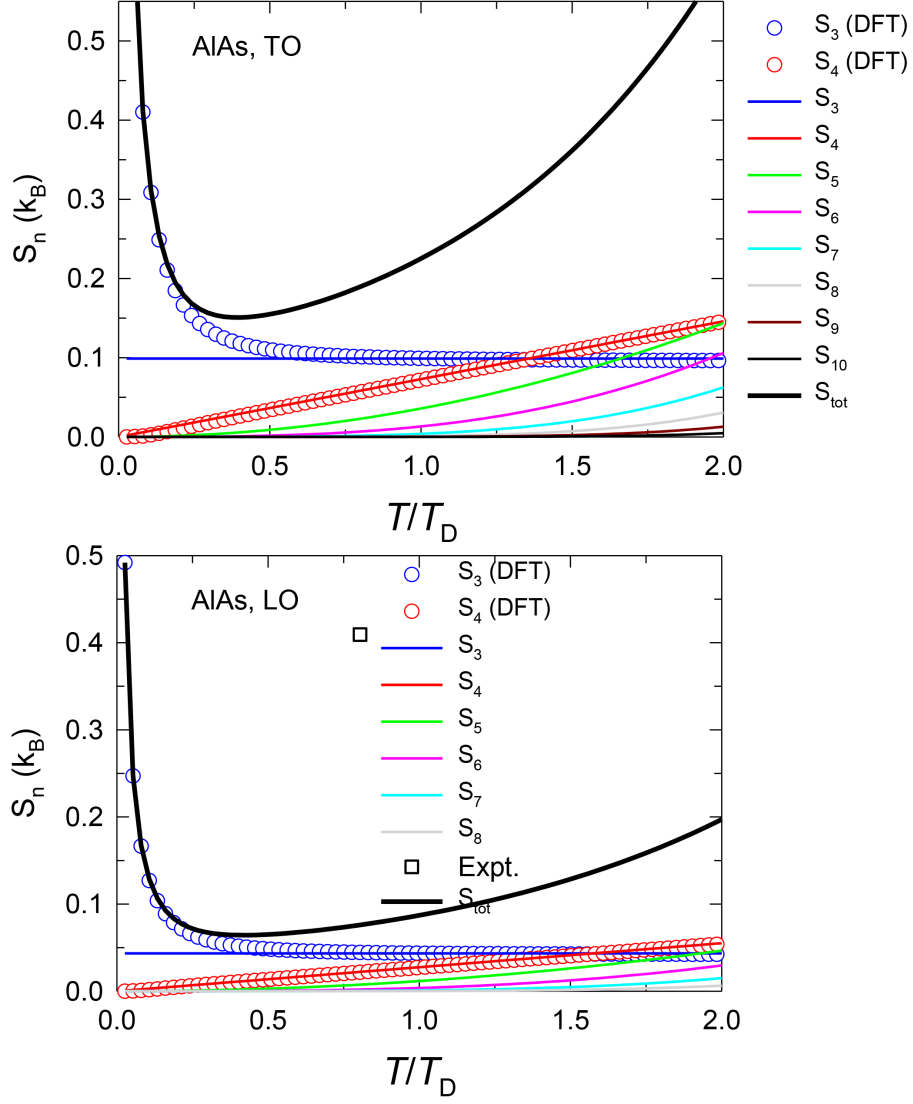


FIG. S16: Phonon scattering entropies of different order as a function of T for the TO and LO modes of AlAs. The blue (red) circles represent the calculated S_3 (S_4), and the solid curves represent the fitted results through Eq.(5) in the main text.

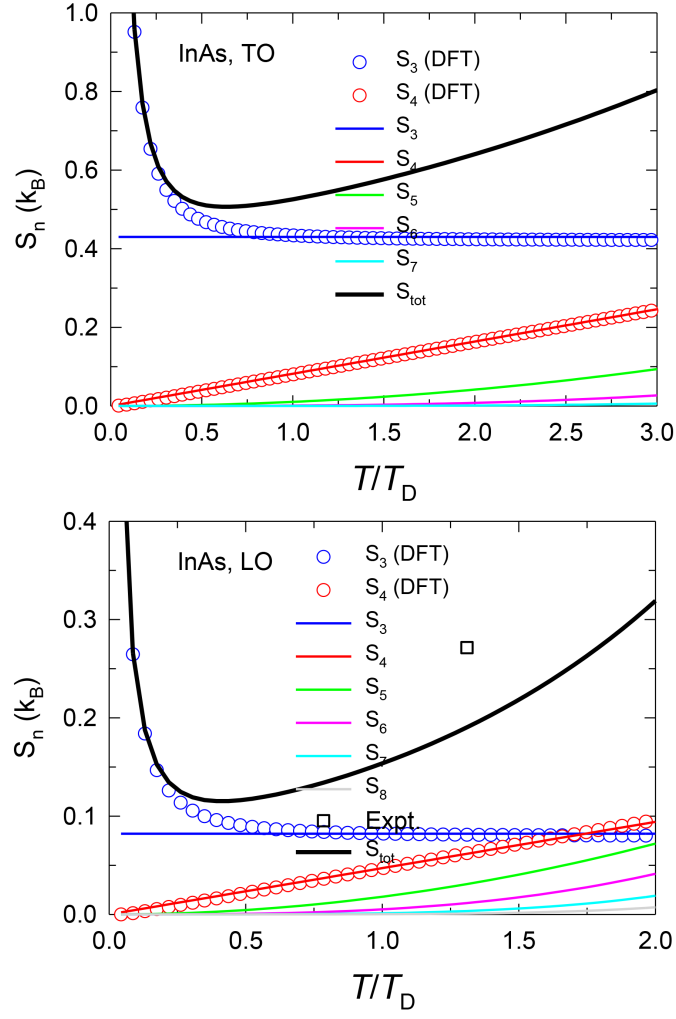


FIG. S17: Phonon scattering entropies of different order as a function of T for the TO and LO modes of InAs. The blue (red) circles represent the calculated S_3 (S_4), and the solid curves represent the fitted results through Eq.(5) in the main text.

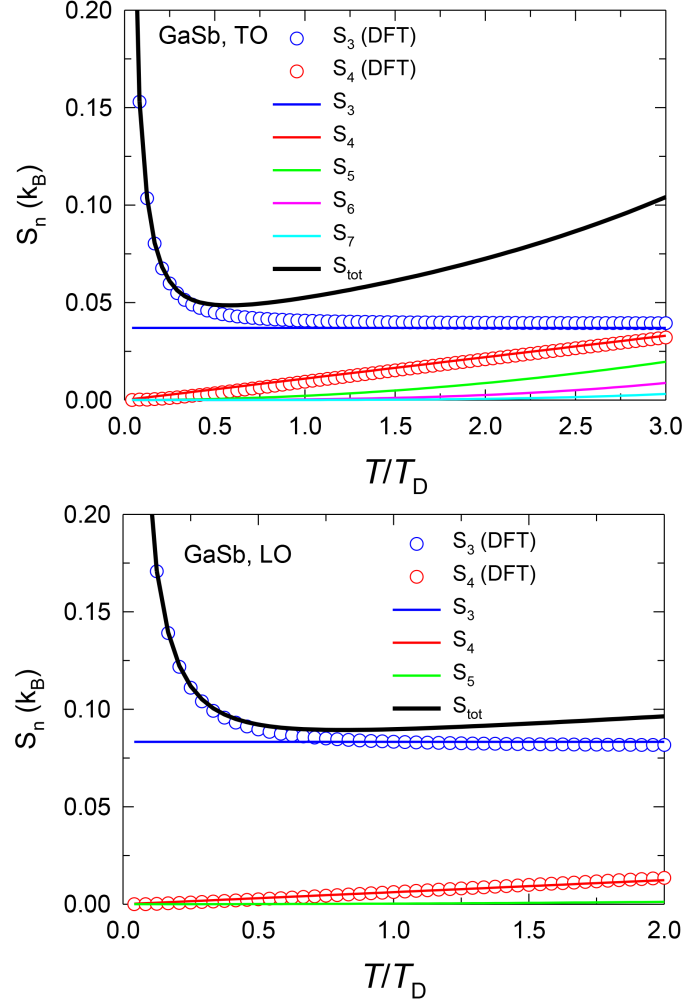


FIG. S18: Phonon scattering entropies of different order as a function of T for the TO and LO modes of GaSb. The blue (red) circles represent the calculated S_3 (S_4), and the solid curves represent the fitted results through Eq.(5) in the main text.

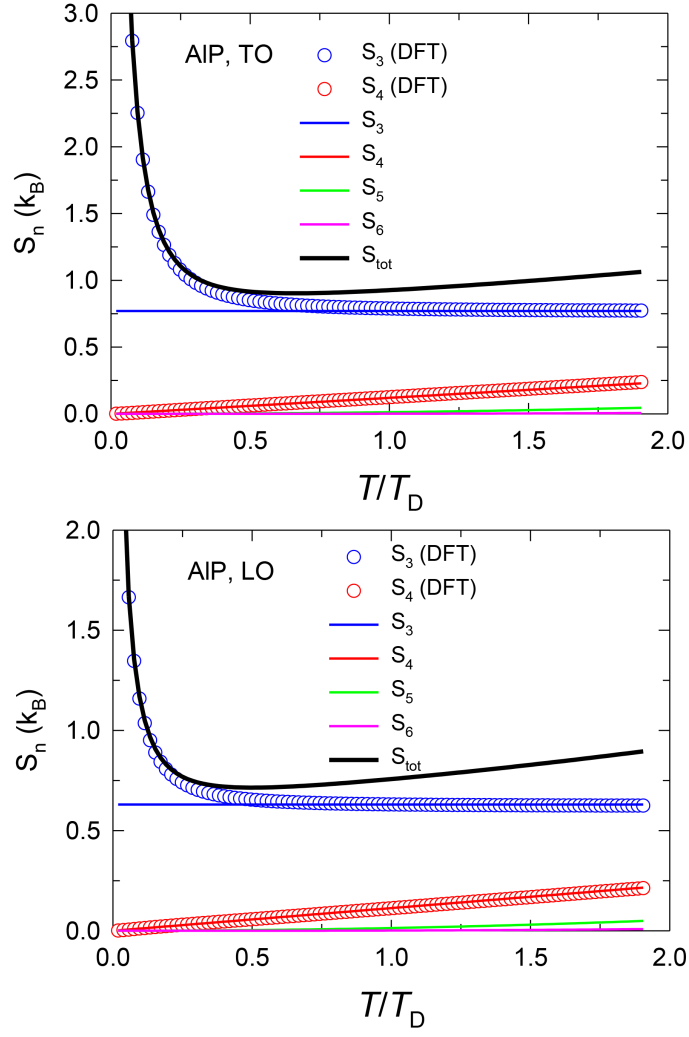


FIG. S19: Phonon scattering entropies of different order as a function of T for the TO and LO modes of AIP. The blue (red) circles represent the calculated S_3 (S_4), and the solid curves represent the fitted results through Eq. (5) in the main text.

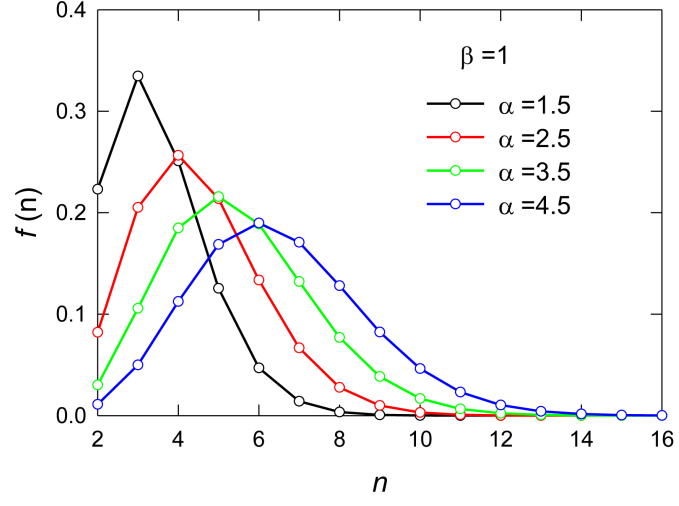


FIG. S20: Our defined Poisson distributions for different α at a fixed value of $\beta = 1$.

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