
Report of Referee A -- LB17640/Tadano

General comment: In this work the authors propose a method for calculating phonon quasiparticle energies of strongly anharmonic systems. Central to the method is the treatment of the frequency dependent 'bubble' diagram in the anharmonic self-energy. A new GW-like approximation scheme is proposed and analyzed on the cubic-to-tetragonal phase transition of CsPbBr3.

The results are interesting and of broad interest. In addition, the paper is clear and well-written.

Reply: We sincerely appreciate the referee's supportive and insightful comments on our manuscript. We believe the paper can attract researchers in the field of thermoelectrics, thermal transport, electron-phonon physics and beyond. Following the suggestions of the referee, we have amended the manuscript appropriately. The point-by-point responses to the referee's comments/questions are provided below:

コメントの追加 [SWA1]: Can we respond to all reviewers in the same way.

Question #1: How sensitive are the results to the DFT functional? The PBEsol is chosen, but without motivation. Fig. 1 b suggests that the lattice constant at zero temperature is incorrect with this functional. SC1 would then probably perform better if a better functional was used, at least for this property.

Reply: We chose PBEsol because it is known to give better prediction accuracy of cell parameters than LDA or other conventional GGA functionals such as PBE and PW91. LDA tends to underestimate the lattice parameters, PBE/PW91 shows an opposite tendency, and PBEsol results are often located between them **[1]**. In the case of $CsPbBr_3$, the PBEsol-predicted lattice constant was 5.868 Å. The experimental value is 5.873 Å at 473 K and increases gradually with heating (ref. [35] of the manuscript). If we fit the experimental temperature dependence of lattice constant with a linear function and extrapolate to 0 K, we obtain ~5.787 Å. Compared to this value, the PBEsol lattice constant is larger by ~1.4%.

We agree with the referee that a better functional would improve the accuracy of lattice constants. As a quick demonstration, we have tested with PBEsol + D3 method and obtained the value of 5.821 Å, which agrees better with ~5.787 Å. However, we did not use PBEsol+D3 in the present manuscript because the D3 approach is empirical and not justified theoretically in CsPbBr3.

Although an independent and more systematic investigation for $CsPbBr_3$ would be more informative, we have already performed a benchmarking calculation of $BaTiO_3$ using the same approach with different functionals, including LDA, PBE, PBEsol, AM05, and SCAN. There, we observed that the predicted phase transition temperature is sensitive to the exchange-correlation functional and shows a similar tendency with the lattice constants. Thus, we think that the accurate description of lattice constants (at finite temperature) is crucial for achieving a reliable prediction of soft-mode frequencies and phase transition temperatures. The paper on $BaTiO_3$ is under preparation and will be submitted as a separate topic.

To address the important role of the exchange-correlation functional more clearly, we have added the following sentence in the revised manuscript:

Main text (page 3): "Since a DFT lattice constant depends on the choice of the exchange-correlation functional and pseudopotential, the present result indicates the importance of carefully choosing them in quantitative predictions of T_c for $CsPbBr_3$."

Please also read our response to **Question #2 below** for more details about the lattice constant dependence of anharmonic properties.

コメントの追加 [SWA2]: It would be better if we can add a sentence to main manuscript or something to SI to make the reviewer happier?

[1] Zhang, G.-X., Reilly, A. M., Tkatchenko, A. & Scheffler, M. Performance of various density-functional approximations for cohesive properties of 64 bulk solids. *New J Phys* **20**, 063020 (2018).

Question #2: According to the results in Table 1, SC1 is far less sensitive to the volume than the QP approximations. For this reason it is not clear whether the observed sensitivity is specific to the QP approximation or inherent to the bubble diagram. The sentence "This result clearly highlights the important role of the lattice constants in accurate predictions of Tc." makes it sound as a very general conclusion. Furthermore, the QP[0] and QP-NL results are more sensitive to the volume than QP[S]. Is there a reason for this?

Reply: We appreciate the referee's insightful comments. We agree that the soft-mode frequencies obtained by the QP approximations are more sensitive to the SC1 frequencies. This can be attributed to the rather strong sensitivity of the bubble self-energy with respect to the lattice constant, as shown in the following figure (**Fig. 1a**).

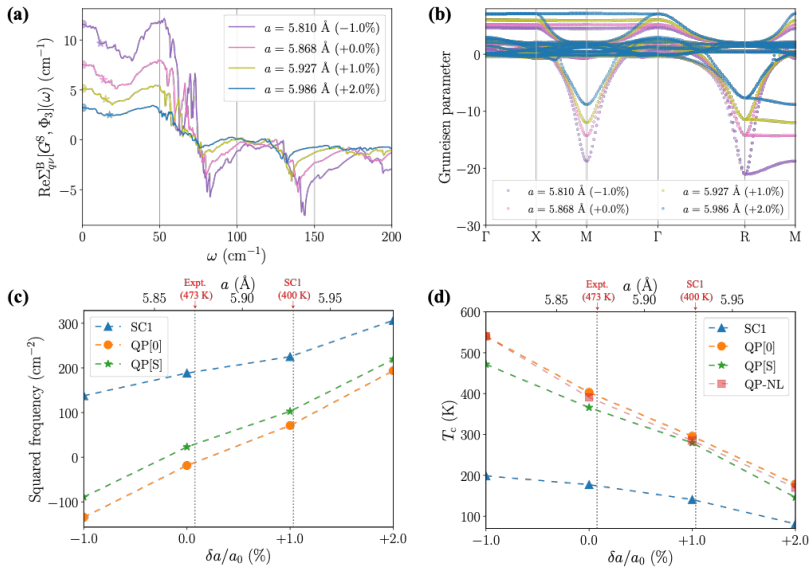

Figure 1. Lattice constant dependence of various anharmonic properties of cubic CsPbBr3. **(a)** Real part of the bubble self-energy of the soft mode at the R point as a function of frequency computed with various lattice constants. The circle symbols indicate the values used in the QP[0] approximation ($\boldsymbol{\omega = 0}$), and the star symbols indicate those used in the QP[S] method. The temperature is set to 400 K. **(b)** Grüneisen parameters along the high-symmetry lines of the Brillouin zone **(c)** Squared frequencies of the R-point soft mode computed with SC1, QP[0], and QP[S]. The temperature is set to 400 K. (d) Estimated T_c obtained from the temperature-dependence of the soft mode frequency at the R point.

The larger the lattice constant is, the greater the bubble self-energy becomes for the soft mode at the R point.

The same behavior was also observed for the soft mode at the M point. These soft modes are well characterized as tilting of $PbBr_6$ octahedra, which is often termed "rigid unit motion (RUM)". The RUM tends to become more anharmonic with decreasing the lattice constant, or equivalently nearest Pb-Pb distance. Therefore, the larger bubble self-energy in the smaller lattice constant can be explained mostly by the enhancement of the third-order force constants. We have also confirmed that the Grüneisen parameters of the soft modes, which were computed from third-order force constants, are negative and their magnitude increases with decreasing the lattice parameter, as shown in **Fig.1b**.

The rather strong dependence of *T*c on the lattice parameters is also related to the large Grüneisen parameters of the soft modes. We believe that this sensitivity is common to non-metal perovskite materials where the phonon frequency, or the curvature of the potential energy surface, is determined by the subtle competition between the long-range dipole-dipole interaction and the short-range interaction. We have confirmed the sensitivity of *T*c in $CsPbBr_3$. Similar results for $BaTiO_3$ were also reported in a very recent study by another group **[2]**.

Since we are not sure if the observed sensitivity of T_c to lattice constant is general, we have revised the sentence as follows:

Original: "Consequently, the estimated T_c value decreases by ∼20% even though the difference in the lattice constant is only ∼1%. This result clearly highlights the important role of the lattice constants in accurate predictions of T_c."

Revised: "Consequently, the estimated T_c value decreases by ∼20% even though the difference in the lattice constant is only ∼1%, whose details are also shown in Sec. S3 of the SM [41]. Since a DFT lattice constant depends on the choice of the exchange-correlation functional and pseudopotential, the present result indicates the importance of carefully choosing them in quantitative predictions of T_c for $CsPbBr_3$. A similar sensitivity has also been reported for $BaTiO_3$ [44]."

In addition, we have added **Fig. 1 above** to the revised SM.

[2] S. Ehsan, M. Arrigoni, G. K. H. Madsen, P. Blaha, and A. Tröster, First-Principles Self-Consistent Phonon Approach to the Study of the Vibrational Properties and Structural Phase Transition of BaTiO3, *Phys Rev B* **103,** 094108 (2021).

Comments:
Typos:
1. IFC on page 2 is not defined.
2. In Table 1 SC1 is denoted SCP.
3. 'optical model' on page 3 probably refers to 'optical mode'

Reply: We thank the referee for pointing out the errors. We have fixed them.

Report of Referee B -- LB17640/Tadano

General comment: The authors present three approaches to estimate quasiparticle peaks, including bubble self-energy on top of the self-consistent phonons (SCP). They compare the phonon frequencies of quasiparticles estimated by their methods to those directly from SCP based on a case study of CsPbBr3, a strongly anharmonic compound that displays phonon instability. They find that their approach can improve the predicted structural phase transition temperature and lattice thermal conductivity.

Reply: We sincerely appreciate the referee's insightful comments on our manuscript. We believe the paper can attract researchers in the field of thermoelectrics, thermal transport, electron-phonon physics and beyond. Following the suggestions of the referee, we have amended the manuscript appropriately. The point-by-point responses to the referee's comments/questions are provided below:

コメントの追加 [SWA3]: Can we respond to all reviewers in the same way.

Comment #1: While the comparison of different approaches to estimate phonon quasiparticle peaks is of interest, one should bear in mind the limitations of such methods based on the quasiparticle picture, since strong anharmonicity can significantly alter such a picture. This is the situation with a-CsPbBr3. Recent experimental measurements using momentum-resolved neutron and X-ray scattering have reported overdamped phonon modes in a-CsPbBr3 (Nat Mater. 2021: Two-dimensional overdamped fluctuations of the soft perovskite lattice in CsPbBr3). Moreover, molecular dynamics simulations using a machine learning potential, capable of precisely predicting the phase transition temperature, have reported a clear breakdown of the phonon quasiparticle picture in a-CsPbBr3, wherein many phonon modes exhibit non-Lorentzian line-shapes and multi-peak spectra (arXiv:2101.06099).

This brings out my largest concern about the current approach to study a-CsPbBr3, i.e., the phonon quasiparticle picture is no longer proper in a-CsPbBr3. Therefore, I cannot recommend this manuscript for publication in PRL unless the authors convince me of the validity of phonon quasiparticle in a-CsPbBr3.

Reply: We thank the referee for raising these important points. Indeed the quasiparticle picture has limitations as we allude to on page 2 *"Although the QP approximation cannot describe satellite peaks, i.e., incoherent parts of spectra, …"*. However, we would like to emphasize that the QP approximation is still powerful and helpful in first-principles calculations, as we elaborate below:

First, the QP picture is often necessary for performing subsequent calculations. For example, in the calculation of electron-phonon related quantities, including the superconducting transition temperature, band-gap renormalization, and polaron self-energy, it is necessary to give *time-independent* second-order force constants as inputs. Also, a QP dynamical matrix allows us to generate a quantum mechanical distribution of atomic displacements at finite temperature, which can be used to calculate various physical quantities, such as magnetic moment renormalized by phonons at finite temperature. All of these calculations are difficult to achieve if the full time-dependent information, i.e., full information of spectral function, is retained. We would like to emphasize that the harmonic phonon dispersion, SC1 phonon dispersion, and any other effective harmonic model such as TDEP **[3]** are also based on a QP picture. Still, these methods, particularly SC1 and TDEP, have been successfully used to study lattice dynamics of strongly anharmonic materials. The purpose of the present work is to provide a better one-body description of lattice vibration under inelastic phonon-phonon scatterings. Similar theoretical approaches have been developed and successfully employed in the community of strongly correlated electron systems. For example, Taranto *et al.* have reported that quasiparticle G_0W_0+DMFT gives better results for electronic structures of $SrVO_3$ than LDA+DMFT **[4]**. Our present

manuscript aims to achieve similar improvements in lattice dynamics calculations.

Second, we are not claiming that the developed QP theory alone is adequate for describing lattice dynamics in $CsPbBr_3$. We also think lattice dynamics in $CsPbBr_3$ are strongly damped near the phase transition. Indeed, we observed that the phonon spectral function $A_q(\omega) = |\mathrm{Im}G_q(\omega)|/\pi$, which was computed from the Green's function obtained from Eq. (3) of the manuscript, represents a non-Lorentzian shape near the phase transition temperature, as shown in **Fig.2** below. For the TA1 mode at $\boldsymbol{q}$=(0,1/5,0), the spectral function shows a well-defined peak which can be well represented with a Lorentzian function. By contrast, for the soft modes at $\boldsymbol{q}$=(1/2,1/2,0) and $\boldsymbol{q}$=(1/2, 1/2, 1/2), the spectral function shows a clear peak when the temperature is far above the phase transition temperature (~400 K), which becomes less clear as the temperature decreases. At 420 K, the spectral function shows a clear non-Lorentzian shape, in agreement with the recent molecular dynamics result (arXiv:2101.06099. Now published as Phys. Rev. B 105, 024302 (2022)).

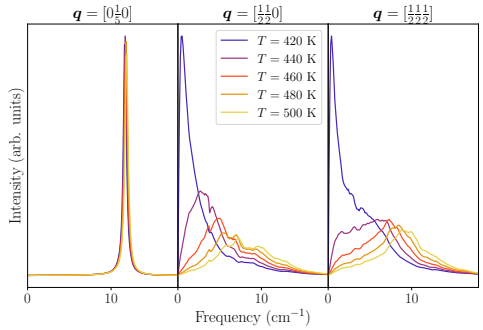

Figure 2 Spectral function of lowest-energy phonons at various $\boldsymbol{q}$ points. As the temperature decreases, the shape tends to display a non-Lorentzian character at $\boldsymbol{q}$=(1/2,1/2,0) and $\boldsymbol{q}$=(1/2, 1/2, 1/2).

Since the importance of the QP treatment was not addressed clearly in the original submitted version of the manuscript, we have modified the corresponding paragraph in the introduction in the revised version as follows:

Main text (page 1): "To mitigate these challenges, several quasiparticle (QP)-like approaches have been proposed in the last decade [11-15]. Although QP approximation cannot describe satellite peaks, i.e., incoherent parts of spectra, it has several advantages. Namely, it simplifies the evaluation of physical quantities that can be directly compared with experiments, such as group velocity and heat capacity. Besides, the QP treatment gives an *effective* one-body Hamiltonian of interacting phonons that is necessary as input for calculations of electron-phonon and phonon-phonon couplings in functional materials."

[3] O. Hellman, I. A. Abrikosov, and S. I. Simak, "Lattice Dynamics of Anharmonic Solids from First Principles", *Phys. Rev. B* **84**, 180301 (2011).

[4] C. Taranto et al., "Comparing quasiparticle GW+DMFT and LDA+DMFT for the test bed material $SrVO_3$", *Phys. Rev. B* **88**, 165119 (2013).

コメントの追加 [TT4]: (**removed paragraph**)

Even though the QP picture is incomplete, we found that the developed QP theory can give an improved estimate of phonon linewidth that agrees with the full spectral function better than the SC1 theory. The definition of the full spectral function is

$$A_q(\omega) = \frac{1}{\pi}|\mathrm{Im}G_q($$

where the frequency dependence of self-energy is retained. In a QP approximation, the frequency dependence of the self-energy is dropped, and the spectral function may be approximated as

$$A$$

Here, ω_q is the quasiparticle frequency, and Γ_q is the quasiparticle linewidth, which is inversely proportional to the phonon lifetime as $\tau_q = \hbar/2\Gamma_q$. The way to compute ω_q and Γ_q differs depending on the type of the QP approximation. By comparing the full (Eq. (1)) and QP spectral function (Eq.(2)), we have investigated which QP method gives the most reasonable value of Γ_q.

コメントの追加 [SWA5]: Terumasa: The first comment of the reviewer why the QP is important and relevant is not addressed. The questions deserves few new lines to be added to the main manuscript because this is why the reviewer does not think the paper deserves to be in PRL.

Comment #2: I suggest that the authors directly compare the phonon lifetime and spectra with the experiments to verify their phonon quasiparticle picture. Note that the agreement between experiments and theory in quantities such as transition temperature and lattice thermal conductivity, unfortunately, cannot be used as the ultimate evidence to support the validity of phonon quasiparticle picture due to potential cancellation of errors, as will be discussed below.

Reply: We thank the reviewer for bringing an excellent point. Following the referee's suggestion, we have compared the calculated phonon frequencies and linewidths along the G-X and G-M lines with the experimental data of Ref. **[5]**. As shown in the **top panels** of **Fig.3** below, the calculated frequencies of the acoustic modes agree well with the experimental data of Songvilay *et al.* **[5]**. Notably, for the G-M line, we have obtained better agreement by the QP[0] and QP-NL method than by the SC1 theory. As for the phonon linewidth (**bottom panels** of **Fig.3**), we have found that the linewidth associated with the three-phonon scattering process is significantly smaller than the experimental values. As pointed out by the referee, this may indicate the importance of the four-phonon scattering process. To confirm this point numerically, we have also

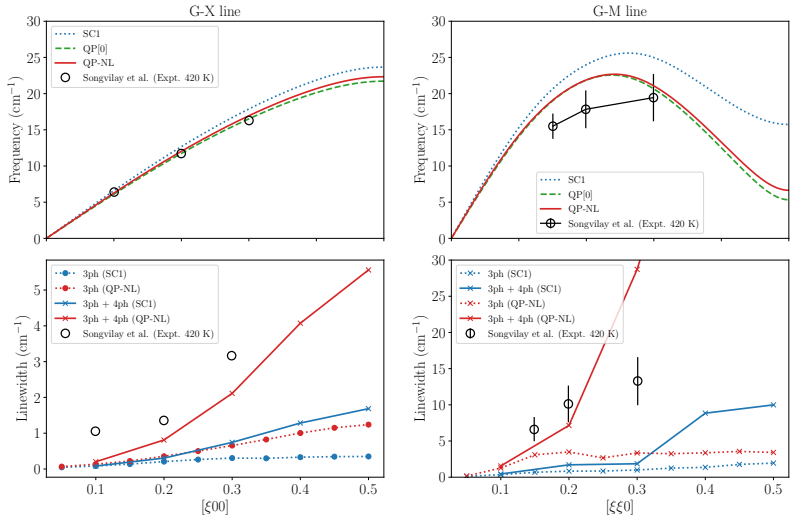

Figure 3 Phonon dispersion (top panels) and linewidth (bottom panels) of transverse acoustic modes of cubic $CsPbBr_3$ along the G-X and G-M lines. The calculations are performed at 440 K, which is slightly above the theoretical phase transition temperature.

computed the phonon linewidth associated with the most significant four-phonon scattering process, whose mathematical form is described in **Sec. S1 E** of the revised manuscript. As shown in **Fig.3** (solid lines), the calculated phonon linewidth is still smaller than the experimental one when the SC1 dynamical matrix is employed. We have found that this underestimation problem can be cured by employing the QP-NL dynamical matrix as input, as shown by red crosses in **Fig.3**, highlighting the importance of using the refined QP eigenenergy and eigenvector in the calculation of phonon linewidth.

In the revised manuscript, we have added the following discussion to address the agreement and disagreement between theoretical and experimental linewidth as follows:

Main text (page 4): "We compared the calculated phonon frequency and linewidth with the experimental values [46] for the transverse acoustic modes along the G-X and G-M lines. As shown in Fig. S5 of the SM

[41], the SC1 overestimates the TA phonon frequencies, while QP[0] and QP-NL agree better with the experimental data. As for the linewidth, the calculated $\Gamma_{q\nu}^{3\mathrm{ph}}$ was smaller than the experimental values even when the QP-NL dynamical matrix was used, which indicates the possible role of higher-order phonon scattering processes. To examine this, we also computed the four-phonon scattering rate $\Gamma_{q\nu}^{4\mathrm{ph}}$ following Refs. [47,48]. As shown in Fig. S5, the total linewidth $\Gamma_{q\nu} = \Gamma_{q\nu}^{3\mathrm{ph}} + \Gamma_{q\nu}^{4\mathrm{ph}}$ agrees reasonably well with the experimental values, but the agreement is observed only when the QP-NL dynamical matrix is used."

Also, we have added the above **Fig.3** in the revised supplementary material.

[5] M. Songvilay et al., "Common Acoustic Phonon Lifetimes in Inorganic and Hybrid Lead Halide Perovskites", *Phys Rev Mater* **3**, 093602 (2019).

Comment #3: As pointed out by the authors, the cubic-to-tetragonal phase transition is first order. This invites a question that whether it is proper to use the temperature-dependent phonon frequency to estimate the transition temperature. With this said, the seemingly underestimated transition temperature by SCP1 might indicate that the structural phase transition occurs before the frequency at R/M becomes zero. To verify their approach, I suggest that the authors estimate the transition temperature by calculating the free energies of both the cubic and the tetragonal phases and checking whether it is consistent with their estimation based on temperature-dependent phonon frequencies.

Reply: We thank the referee for the insightful suggestion. The experimental temperature hysteresis of the cubic-to-tetragonal phase transition of $CsPbBr_3$ is as small as 7 K **[6]**. Hence, while the phase transition is first-order in a rigorous sense, it is very close to the second-order, which validates the present approach based on the Curie–Weiss law. As suggested by the referee, it is also possible to estimate the phase transition temperature from the crossing point of the Helmholtz free energies of the cubic and tetragonal phases. Indeed, one of the present authors has demonstrated its potential capability in predicting T_c of $SrTiO_3$ [7]. However, the approach based on the free energy is trickier and computationally more demanding because it demands reaching convergence of the SC1 free energy not only for the cubic phase but also for the tetragonal phase. Moreover, to make the prediction more reliable, we have found that it is necessary to consider the anisotropic thermal expansion of the tetragonal phase, which makes the calculation even more expensive (this effect was not considered in the previous calculation on $SrTiO_3$ due to the computational limitation). Therefore, we do not employ the free-energy-based approach as it is computationally not well trackable using standard DFT calculations. We believe the proper approach for doing these investigations requires developing an SC1-based scheme for computing anisotropic thermal expansion in concert with a machine learning approach to accelerate the DFT calculations.

[6] Š. Svirskas *et al.*, "Phase transitions, screening and dielectric response of $CsPbBr_3$", *J. Mater. Chem. A* **8**, 14015-14022 (2020).

[7] T. Tadano and S. Tsuneyuki, "Ab initio prediction of structural phase-transition temperature of $SrTiO_3$ from finite-temperature phonon calculation", *J. Ceram. Soc. Jpn.* **127**, 404–408 (2019).

Comment #4: Another critical, yet missing, aspect is the effects of higher-order anharmonicity on phonon lifetimes. It has been reported in recent Letters [PRL 125, 245901 (2020) and PRL 125, 085901(2020)] that four-phonon resonance scattering is significant in systems containing rattling phonon modes. Therefore, in the present study, the reasonably good agreement between the experiment and the theory in the lattice thermal conductivity may be accidental due to the lack of higher-order phonon scattering. I suggest that the authors compare their calculated phonon lifetimes to the experimental ones to exclude or confirm this possibility.

Reply: We thank the reviewer for raising an important omission from our study. Following the referee's suggestion, we have additionally considered the four-phonon scattering rates and compared the total phonon linewidth with the experimental data. These calculations were not trivial and took considerable time and effort. As discussed in **our reply to Comment #1** above, we find that the four-phonon scattering rate was indeed significant and necessary for obtaining reasonable agreements with the experimental linewidth of the TA phonons of $CsPbBr_3$. Namely, the agreement was obtained only when the QP dynamical matrix was employed (please see **Fig.3** above). Moreover, we have calculated the thermal conductivity with the effect of four-phonon scattering and obtained the values of $\lesssim 0.2$ W/mK at 440 K, which are lower than the experimental value of $CsPbBr_3$ at 300 K (~0.4 W/mK) and that of $CsSnBr_3$ at 500 K (~0.46 W/mK). We attribute this underestimation to the anharmonic heat flux contribution **[8]**, which is not included in the present theory [Eq. (5) of the main text]. Therefore, following the previous successful study by Simoncelli *et al.* for the tetragonal $CsPbBr_3$ **[9]**, we only consider the three-phonon scattering when computing thermal conductivity.

Following the referee's comment, we have added **Sec. S1 E** and **Sec. S3** in the supplementary material and discussion about the potential contribution from the anharmonic heat flux in the main text as follows:

Main text (page 4): "Simoncelli *et al.* applied Eq. (5) to orthorhombic $CsPbBr_3$, combined with $\Gamma_{q\nu} \approx \Gamma_{q\nu}^{3\mathrm{ph}}$, and obtained excellent agreements with experimental LTC [29]. Hence, we employ the same approximation for $\Gamma_{q\nu}$ in this study. Note that the inclusion of the four-phonon scattering process in Eq. (5) is technically straightforward, but it can underestimate LTC of strongly anharmonic materials because of the missing contributions from anharmonic heat flux [50]."

[8] T. Sun and P. B. Allen, "Lattice thermal conductivity: Computations and theory of the high-temperature breakdown of the phonon-gas model", *Phys. Rev. B.* **82**, 224305 (2010).
[9] M. Simoncelli, N. Marzari, and F. Mauri, "Unified theory of thermal transport in crystals and glasses", *Nat. Phys.* **15**, 809 (2019).

Report of Referee C -- LB17640/Tadano

General comment: The present manuscript deals with the theory of strongly anharmonic phonons. The state-of-the art method to compute lattice vibrations in this case is based on the first-order self-consistent-phonon (SC1) scheme, in which nonperturbative quantum averages involving cubic and quartic interatomic force constants may be computed. In particular, the SC1 method yields renormalized real phonon frequencies. In order to take into account anharmonic phonon lifetimes, then, an additional self-energy term, the "bubble" diagram, is used, because it's the lowest-order contribution with a nonzero imaginary part. It was noticed in a couple of recent works (of which one of the authors of the present manuscript is co-author) that the real part of the "bubble" self-energy may also have a non-negligible effect on the renormalized phonon frequencies of strongly anharmonic crystals.

In this work, the authors propose an effective "one-shot" quasiparticle (QP) scheme to obtain such frequency corrections, to be used on top of the SC1 scheme.

They apply the present method to alfa-CsPbBr, a material which undergoes a phase transition above 400K and for which few theoretical studies are available, finding relevant changes to phonon frequencies, critical temperature and lattice thermal conductivity.

The work is well presented: it is clear in its premises and development as well as in the discussion of the results. It is detailed and thorough. The supplementary information are also very detailed and useful. In fact, I have very few comments (see below).

Reply: We sincerely appreciate the referee's supportive and insightful comments on our manuscript. We believe the paper can attract researchers in the field of thermoelectrics, thermal transport, electron-phonon physics and beyond. Following the suggestions of the referee, we have amended the manuscript appropriately. The point-by-point responses to the referee's comments/questions are provided below:

コメントの追加 [SWA6]: Can we respond to all reviewers in the same way.

Comment #1: Despite the solidity of the work, however, I believe that it lacks the novelty and "breakthrough" character that might be required for PRL, mainly because it consists of a refinement in the treatment of a problem already recognized and tackled – if only partially – in Refs. 17 and 30 of the main text of the manuscript. Therefore, I would recommend submitting this manuscript to Physical Review B.

Reply: We thank the referee for raising an important point about the impact of our study, and how it differs from previous studies. First, the importance of the bubble diagram has been noticed only recently (Refs. 17, 30, and 33 of the manuscript) and we believe its impact is still not well-recognized or well-understood by the community of condensed matter physics and computational material science due to requiring excessive computational demands. Recently, several studies calculated the phonon linewidth and thermal conductivity either using the SC1 or TDEP methods. However, the potential impact of the bubble frequency shift is greatly overlooked. Moreover, the theory for treating the bubble frequency shift is still immature compared with the well-established and diverse approximations in *GW* calculations employed in the electronic theory. Therefore, the impact of the present manuscript is in developing a rigorous foundation to study phonon bandstructure, particularly in anharmonic systems, which we are confident will prompt further theoretical development. Besides, the present work is novel and differs from previous studies (including Refs. 17 and 30) because (1) it formulates self-consistent phonon theory in the modern language employed in the *GW* community for the electronic degrees of freedom, (2) develops new QP approximations, (3) demonstrates their superiority over

SC1 for the first time, and (4) investigates a challenging new system $CsPbBr_3$ that is relevant for solar cell applications. Please note that the new developments in the current manuscript are general and apply to all materials, and we believe will present a new paradigm shift into developing phonon bandstructure theory akin to what is very established in the electronic structure community.

To address this point clearer, we have modified the main manuscript as follows:

Original: "The developed method incorporates the frequency shift by the bubble self-energy within the QP approximation and thereby solves the overestimation problem inherent to the SC1 theory."

Revised: "The developed method, which we formulate using the modern language employed in the GW approximation in electronic structure theory [28], incorporates the frequency shift by the bubble self-energy within the QP approximation and thereby solves the overestimation problem inherent to the SC1 theory."

Comment #2: Lack of experimental comparison beyond the critical temperature. While alfa-CsPbBr is certainly an interesting system to consider for the proposed QP approach, it is not possible to understand unambiguously if the resulting corrections in the phonon frequencies -and all the properties that depend on these corrections - are the relevant ones to essentially capture the behavior of the real material, as unforeseen effects more important than the present corrections are possible (e.g., related to the poorly described lattice constant). Maybe the authors can insert a small discussion about the expected generality of the proposed approach, which systems they believe will be strongly affected by this and which would still be well described by just the SC1 scheme, etc.

Reply: We thank the referee for pointing out this important omission in the manuscript. In addition to the T_c comparison, we have added a new comparison of theoretical and experimental phonon lifetimes in the revised manuscript. To that end, we have additionally computed the four-phonon scattering rates, which were not trivial and took considerable time and effort. As shown in **Fig.3** above, we obtained a reasonable agreement with the experimental linewidth only for the QP approach, while SC1 underestimated the linewidths. This also supports the advantage of the QP approach over SC1. Regarding the impact of the bubble correction, it is difficult to unambiguously determine which physical properties and materials are strongly affected by the correction and which are not. However, we know from our experience in $CsPbBr_3$, $BaTiO_3$, and $SrTiO_3$ that the correction is impactful to the soft mode frequencies in perovskite materials and thereby the predicted T_c as well as the dielectric permittivity. By contrast, we think that physical properties involving all phonon modes in the Brillouin zone, such as vibrational free energy and LTC, are less affected by the correction. However, as we show in the present manuscript, the correction noticeably changed the LTC of $CsPbBr_3$, which implies that the correction is also influential in the LTC of low-LTC materials.

To enrich the comparison between the present theory and experiment, we have added the **above Fig.3** to the revised SM (please see Sec. S4). In addition, the associated discussion has been added to the main text as follows:

Main text (page 4): "We compared the calculated phonon frequency and linewidth with the experimental values [46] for the transverse acoustic modes along the G-X and G-M lines. As shown in Fig. S5 of the SM [41], the SC1 overestimates the TA phonon frequencies, while QP[0] and QP-NL agree better with the experimental data. As for the linewidth, the calculated $\Gamma_{q\nu}^{3\mathrm{ph}}$ was smaller than the experimental values even when the QP-NL dynamical matrix was used, which indicates the possible role of higher-order phonon scattering processes. To examine this, we also computed the four-phonon scattering rate $\Gamma_{q\nu}^{4\mathrm{ph}}$ following Refs.

[47,48]. As shown in Fig. S5, the total linewidth $\Gamma_{q\nu} = \Gamma_{q\nu}^{3\mathrm{ph}} + \Gamma_{q\nu}^{4\mathrm{ph}}$ agrees reasonably well with the experimental values, but the agreement is observed only when the QP-NL dynamical matrix is used."

Besides, in relation to the expected generality of the proposed approach, we have added the following sentence in the revised manuscript:

Main text (page 3) "Although a more comprehensive study is needed, we expect the bubble frequency correction will affect the soft-mode frequencies and associated physical properties, such as T_c and dielectric permittivity, in a broad range of materials that exhibit structural phase transition."

コメントの追加 [SWA7]:
This sounds weak…. It does not say we have new results related to the four-phonon scattering rates, and new results related to linewidths.

You say above that "As shown in **Fig.3** above, we obtained reasonable agreement with the experimental linewidth only for the QP approach, while SC1 underestimated the linewidths. This also supports the advantage of the QP approach over SC1."
We should say this in the revised manuscript. This is a positive finding that address the reviewers comment.

Also, we should say that we have added Figure 3 in the SI in relation to this comment.

Comment #3: Consistency of the theory in describing lattice vibrations and unit cell volume. The agreement with the experimental critical temperature Tc is only reached when the phonon frequencies are corrected with the SC1+one-shot bubble approach, while at the same time the unit cell volume is kept at the DFT level. Otherwise, the values turn out to be very different because Tc is extremely dependent on the lattice parameter. This inconsistency introduces a degree of arbitrariness in the results which questions the general applicability of the method. In this system it is clear that the QP method gives a strong correction to Tc with respect to SC1, but what if I had another system where the difference is less clear? Does the SCP introduce a systematic error in the lattice constant for all systems? How can I be sure that the DFT volume, so dependent on pseudopotential choices, will be a good starting point? I think this point could be better addressed in the manuscript.

Reply: We thank the reviewer for the comment. Since SC1 is based on a variational principle, the SC1 free energy is always larger than the exact free energy of anharmonic systems. Hence, should an "exact" calculation of free energy be possible, it would give lattice constants that are different from the SC1 prediction. However, this is not the origin of the 1% difference between the SC1 and experimental lattice parameters. Instead, the difference should be attributed to the approximations in DFT itself (exchange-correlation functional, PAW, etc.). While PBEsol is known to give better lattice constants than PBE or LDA, the present calculation using PBEsol underestimates the lattice constants only slightly (please see Fig.1 (b) of the manuscript, where the PBEsol lattice constant at 0 K agrees accidentally with the experimental lattice constant at 473 K). Therefore, whether the DFT volume is a good starting point or not depends on the XC functional as well as studied materials.

To make these points clearer, the following modification has been made in the revised manuscript:

Original: "Consequently, the estimated T_c value decreases by ~20% even though the difference in the lattice constant is only ~1%. This result clearly highlights the important role of the lattice constants in accurate predictions of T_c."

Revised: "Consequently, the estimated T_c value decreases by ~20% even though the difference in the lattice constant is only ~1%, whose details are also shown in Sec. S3 of the SM [41]. Since a DFT lattice constant depends on the choice of the exchange-correlation functional and pseudopotential, the present result indicates the importance of carefully choosing them in quantitative predictions of T_c for $CsPbBr_3$. A similar sensitivity has also been reported for $BaTiO_3$ [44]."

In addition, we have added new data showing the lattice constant dependence of various anharmonic properties to the revised SM (please see **Sec. S3** of the SM).

Comment #4: Minor question about the possible QP schemes. Since QP[0] works better close to the phase transition, while QP[S] is supposed to become the better one away from Tc, what do the authors suggest as a possible efficient scheme for temperature-dependent phonon frequency calculations? Use QP[S] for a certain T<Tc, then switch to QP[0] close to Tc, then go back to QP[S]? Or is it just better to always use QP-NL? If the authors feel that this could be interesting, they may address it in the manuscript.

Reply: We believe the QP-NL is most accurate because it best represents the peak position of the spectral function. The calculation cost of QP-NL is not very different from QP[0] and QP[S], so using QP-NL for all temperature ranges is most straightforward. To make this point clearer, we have slightly changed the expression on page 5 as follows:

Original: "Furthermore, we expect that QP-NL is more reliable than QP[0],"

Revised: "We expect that calculations based on QP-NL are most reliable, "

Comment #5: [4] Minor comment about Figure 2. I would change the color scheme, as the white and yellow dashed lines – the latter called dotted in the caption – are barely distinguishable.

Reply: We thank the referee for pointing this out. We have changed line styles and linewidth to make the lines easier to distinguish.

List of changes made:
(These are highlighted by red in the attached highlighted manuscript and SM.)

- The description of the importance of the QP treatment has been enriched and moved to the introduction part (2nd paragraph on page 1).

- The novelty of this work compared to the previous studies has been addressed more clearly in the introduction part (3rd paragraph on page 1).

- The discussion about the sensitivity of the predicted T_c to the lattice constant has been enriched at the end of the 3rd paragraph on page 3. In addition, new supplementary data showing the lattice-constant dependence has been added to the SM.

- On page 4, a new sentence discussing the expected generality of the influence of the bubble self-energy correction has been added.

- The sentences discussing the influence of the input dynamical matrix on the resulting phonon lifetime have been moved to a more appropriate position. In the revised version, we first discuss the phonon linewidth, which is followed by the discussion about thermal transport.

- The phonon linewidths associated with the four-phonon scattering process have been calculated and an associated discussion has been added on page 4. In addition, new sections and figures related to the four-phonon scattering rate have been added to the revised SM. (Secs. S1E, S4 and Fig. S5)

- Figures 1c and 1d have been slightly improved. In the original version, the QP-NL data below T_c was not an actual QP-NL result; instead, we used the QP[0] result below T_c simply because the QP-NL equation does not have a solution below T_c. We have noticed that this point was not addressed clearly in the original version. To avoid any confusion, we have deleted the QP-NL data points below T_c and added the QP[0] data using translucent markers in the same figure. Note that this does not affect the predicted T_c because the Curie–Weiss fitting is performed using the data points *above* T_c. In addition, we have commented on the convergence of the QP-NL equation in Sec. S1C of the SM.

- The quality of Fig.2 has been improved.

- Some minor English corrections have been made to improve readability and clarity.

- Grant information has been slightly changed.