Impact of Rattlers on Thermal Conductivity of a Thermoelectric Clathrate: A First-Principles Study

Terumasa Tadano,[1,*] Yoshihiro Gohda,[2] and Shinji Tsuneyuki[1,3]
[1]Department of Physics, The University of Tokyo, Tokyo 113-0033, Japan
[2]Department of Materials Science and Engineering, Tokyo Institute of Technology, Yokohama 226-8502, Japan
[3]Institute for Solid State Physics, The University of Tokyo, Kashiwa 277-8581, Japan
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We investigate the role of rattling guest atoms on the lattice thermal conductivity of a type-I clathrate $Ba_8Ga_{16}Ge_{30}$ by first-principles lattice dynamics. Comparing phonon properties of filled and empty clathrates, we show that rattlers cause tenfold reductions in the relaxation time of phonons by increasing the phonon-phonon scattering probability. Contrary to the resonant scattering scenario, the reduction in the relaxation time occurs in a wide frequency range, which is crucial for explaining the unusually low thermal conductivities of clathrates. We also find that the impact of rattlers on the group velocity of phonons is secondary because the flattening of phonon dispersion occurs only in a limited phase space in the Brillouin zone.

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An intermetallic clathrate is an inclusion complex where guest atoms are enclosed in cavities formed by the host crystal lattice [1]. One of the most characteristic features of clathrates is an unusually low lattice thermal conductivity κ_L ($\sim$1 W/mK) [2], which makes clathrates promising for thermoelectric applications with high figure of merit $ZT = \sigma S^2 T/(\kappa_c + \kappa_L)$. Here, T is the absolute temperature, σ is the electrical conductivity, S is the Seebeck coefficient, and $\kappa_{c(L)}$ is the thermal conductivity by electrons (phonons), respectively. Since the κ_L value of a clathrate is intrinsically low without introducing micro- or nanostructures such as grain boundaries or nanoscale precipitates, semiconductor clathrates are one of the prototype materials that follow the phonon-glass electron-crystal concept proposed by Slack [3].

The origin of low κ_L of host-guest structures such as clathrates and skutterudites has commonly been attributed to the "rattlers," i.e., guest atoms loosely bound inside oversized cages [4–7]. However, its actual role is not fully understood. In the simple kinetic theory, the lattice thermal conductivity is given by

$$\kappa_L = \frac{1}{3} C v^2 \tau, \tag{1}$$

where C is the lattice specific heat, v is the average group velocity, and τ is the average relaxation time of phonons, respectively. Historically, the reduction in κ_L has been attributed to resonant scatterings by localized rattling modes [4], which reduce the τ value of heat-carrying acoustic modes in a limited energy region near avoided-crossing points. This mechanism was originally introduced to explain the κ_L observed in a solid solution of KCl and KNO_2 [8], and it was also applied to a clathrate hydrate assuming the guest as an isolated point defect [5]. However, although the resonant phonon scattering has repeatedly been employed to explain the low κ_L values of host-guest structures [4–6], little attention has been paid to the validity of that mechanism itself. Recently, the validity of resonant scattering was questioned by experimental and theoretical studies in skutterudites [9,10].

Another important role of rattlers that has recently been recognized is their impact on the group velocity [11,12]. On the basis of inelastic neutron scattering (INS) of a type-I clathrate $Ba_8Ga_{16}Ge_{30}$ (BGG), Christensen *et al.* [11] claimed that a major effect of rattlers is to reduce the v value of acoustic phonons at the avoided-crossing points rather than to reduce τ. This mechanism clearly conflicts with the resonant scattering scenario, where τ is the main source of low κ_L. It is still an open question as to whether the group velocity v or the relaxation time τ is mainly affected by rattlers, which should be understood precisely for further reducing κ_L and thereby enhancing ZT.

In this Letter, we analyze the effect of rattlers on κ_L in a type-I clathrate BGG from first principles to answer the questions raised above. In particular, we extract harmonic and anharmonic interatomic force constants from *ab initio* calculations based on density-functional theory, and then we calculate the phonon frequency and phonon lifetime of filled and empty clathrates. As will be shown in the following, we observe a tenfold reduction in τ and thereby in κ_L due to rattlers, whereas the change in the group velocity is less significant. We also show that the reduction in τ occurs in a wide frequency range, thus indicating that the phonon scatterings in BGG is nonresonant.

For a reliable estimation of phonon relaxation times, one needs to consider dominant phonon scattering processes. Generally, phonons can be scattered by other phonons,

charged carriers, disorders, isotopes, and grain boundaries [13]. In clathrates with off-center rattlers, phonon scatterings due to tunneling between the two-level system should also be considered to explain glasslike κ_L at low temperature [2]. In this study, we only consider the three-phonon interactions that are dominant in a relatively high-temperature range for the on-center systems which we are interested in. Then, by considering the lowest-order perturbation of cubic anharmonicities, which has successfully been applied for many solids [14,15], the linewidth of phonon mode q is given as [16]

$$\Gamma_q(\omega) = \frac{\pi}{2N}\sum_{q',q''}|V_3(-q,q',q'')|^2 \times [(n_{q'}+n_{q''}+1)\delta(\omega-\omega_{q'}-\omega_{q''}) - 2(n_{q'}-n_{q''})\delta(\omega-\omega_{q'}+\omega_{q''})]. \quad (2)$$

Here, ω_q is the phonon frequency, N is the number of $\boldsymbol{q}$ points, $n_q = 1/(e^{\beta\hbar\omega_q}-1)$ is the Bose-Einstein distribution function, $\beta = 1/kT$ with the Boltzmann constant k, and $\hbar$ is the reduced Planck constant, respectively. In Eq. (2) and in the following, we use the variable q defined by $q = (\boldsymbol{q}, j)$ and $-q = (-\boldsymbol{q}, j)$ where $\boldsymbol{q}$ is the crystal momentum and j is the branch index of phonons. The matrix element for three phonon interaction V_3 is given as

$$V_3(q,q',q'') = \frac{1}{N}\sqrt{\frac{\hbar^3}{8\omega_q\omega_{q'}\omega_{q''}}} \times \sum_{\{\ell,\alpha,\mu\}}\Phi_{\mu_1\mu_2\mu_3}(\ell_1\alpha_1;\ell_2\alpha_2;\ell_3\alpha_3) \times \frac{e^{\mu_1}_{\alpha_1}(q)e^{\mu_2}_{\alpha_2}(q')e^{\mu_3}_{\alpha_3}(q'')}{\sqrt{M_{\alpha_1}M_{\alpha_2}M_{\alpha_3}}} \times e^{i(\boldsymbol{q}\cdot\boldsymbol{r}(\ell_1)+\boldsymbol{q}'\cdot\boldsymbol{r}(\ell_2)+\boldsymbol{q}''\cdot\boldsymbol{r}(\ell_3))}, \quad (3)$$

where $e^{\mu}_{\alpha}(q)$ is the polarization vector of atom α along the μ direction that corresponds to phonon mode q, M_α is the atomic mass of atom α, and $\boldsymbol{r}(\ell)$ is the coordinate of the ℓth cell. The phonon frequency ω_q and the polarization vector $\boldsymbol{e}(q)$ can be obtained straightforwardly by diagonalizing the dynamical matrix. Once the phonon linewidths are obtained, the lattice thermal conductivity is estimated by the Boltzmann transport equation (BTE) within the relaxation time approximation (RTA)

$$\kappa_L^{\mu\nu} = \frac{1}{N\Omega}\sum_q C_q v_q^\mu v_q^\nu \tau_q, \quad (4)$$

where Ω is the unit-cell volume and $\tau_q = [2\Gamma_q(\omega_q)]^{-1}$ is the phonon lifetime. Although RTA can underestimate the thermal conductivity of high-κ_L materials because it incorrectly considers normal phonon-phonon processes as resistive [17], it has been reported that, in most of the materials, the RTA gives κ_L values that do not differ much from the full solution to the BTE, especially for low-κ_L systems [15,18].

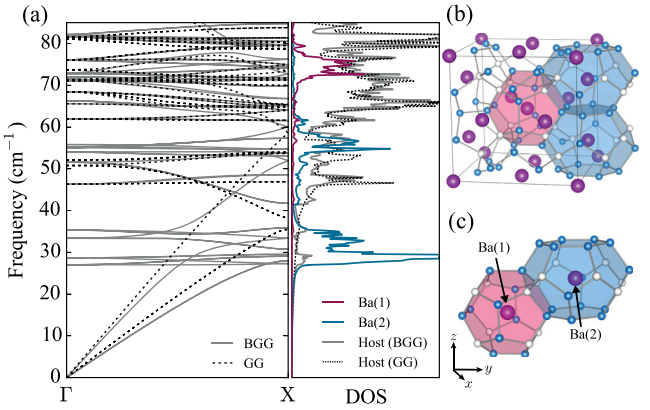

FIG. 1 (color online). (a) Calculated phonon dispersion and projected phonon DOS of BGG (solid lines) and GG (dotted lines). (b) Crystal structure of BGG. Ba, Ga, and Ge atoms are represented by magenta, white, and blue spheres, respectively. (c) Representation of two inequivalent Ba rattlers in dodecahedral (red) and tetrakaidecahedral (blue) polyhedra.

The calculation of the phonon linewidth requires $\Phi_{\mu_1\mu_2}(\ell_1\alpha_1;\ell_2\alpha_2)$ and $\Phi_{\mu_1\mu_2\mu_3}(\ell_1\alpha_1;\ell_2\alpha_2;\ell_3\alpha_3)$, which are harmonic and cubic force constants in real space. We computed these by the finite-displacement approach [19,20] where atomic forces for displaced configurations were calculated with the VASP code [21], with the Perdew-Burke-Ernzerhof functional [22] and the PAW method [23,24] (see the Supplemental Material [25]). Calculations were performed for a unit cell containing 54 atoms with the crystal symmetry of $Pm\bar{3}n$ [see Figs. 1(b) and 1(c)]. The optimized lattice constant was 10.95 Å, which slightly overestimates the experimental value, 10.76 Å [26].

The calculated phonon dispersion and the phonon DOS of BGG are shown in Fig. 1(a) with solid lines. The avoided crossing of the longitudinal acoustic (LA) mode and the rattling modes of Ba(2) atoms inside tetrakaidecahedral cages is clearly observed in the band structure around $\omega_q = 28$–34 cm^{-1}. The rattling modes in this energy range correspond to the vibration in the xy plane, whereas those observed in ~55 cm^{-1} are the vibration of Ba(2) atoms along the z direction. Experimentally measured Raman shifts of these rattling modes are 31–33 cm^{-1} and 64 cm^{-1}, respectively [27], in good agreement with the computational results. We found that the small underestimation of the vibration energy along direction z can be cured by employing a smaller lattice constant comparable with the experimental value. In this study, we neglect the temperature dependence of the Raman spectra reported by Takasu *et al.* [27] due to computational limitations. We consider that such an effect is not essential to understand the low κ_L

of BGG, but could be important to explain the temperature dependence of κ_L, especially for off-center systems. To better understand the localization of the Ba motions and their hybridization with Ga/Ge atoms, we estimated the participation ratio $P_q = [\sum_\alpha |\boldsymbol{u}_\alpha(q)|^2]^2 / N_\alpha \sum_\alpha |\boldsymbol{u}_\alpha(q)|^4$ where $\boldsymbol{u}_\alpha(q) = M_\alpha^{-1/2} \boldsymbol{e}_\alpha(q)$ as in Ref. [28]. We then obtained small P_q (~0.1) for all the rattling modes including the vibrations of Ba(1) atoms inside dodecahedral cages observed in 70–80 cm^{-1}, thus indicating the localized nature of the vibrations of Ba guests (see the Supplemental Material [25]). Localization of guest atoms is significant in the rattling modes around $\omega_q = 28$–34 cm^{-1}, whereas a little hybridization with cage atoms is observed in the higher energy rattling modes, in accordance with previous computational results [28,29].

To investigate the effect of Ba rattlers directly, we also calculated phonon properties of an empty clathrate $Ga_{16}Ge_{30}$(GG). Since Ba atoms are necessary as electron donors to complete the sp^3 framework of host cages, one cannot perform first-principles calculations directly on the fictitious material GG. Therefore, we estimated harmonic and cubic force constants of GG from the displacement-force data set obtained for the original system BGG by neglecting force constants related to Ba guests. We found that this procedure can extract force constants of the hypothetical system GG without degrading the numerical accuracy of host-host force constants (see the Supplemental Material [25]). By using the extracted force constants of GG, we can turn off host-guest interactions, and the crossing behavior is recovered as shown in Fig. 1(a) (dotted lines).

Figure 2 shows the temperature dependence of κ_L calculated by the BTE-RTA [Eq. (4)]. The lattice thermal conductivity of BGG calculated with $6 \times 6 \times 6\,\boldsymbol{q}$ points was 0.78 W/mK at 100 K [30]. The value may be slightly increased by using denser $\boldsymbol{q}$ grids, although such calculations were not performed due to computational limitations. In addition, we observed that the κ_L value of BGG is sensitive to the lattice constant, and a smaller lattice constant corresponding to the experimental value yielded $\kappa_L = 1.35$ W/mK. This value agrees well with experimental values of 1.5 W/mK (p type) and 1.9 W/mK (n type) [31], thus indicating the validity of the BTE-RTA with considering dominant three-phonon scattering processes even for the complex system BGG. The thermal conductivity of a empty system GG calculated with $8 \times 8 \times 8\,\boldsymbol{q}$ points was 18.94 W/mK at 100 K (16.74 W/mK with $6 \times 6 \times 6\,\boldsymbol{q}$ points), which is more than 20 times greater than that of BGG. We also estimated κ_L of another empty clathrate Ge_{46} and obtained a higher value of 57.59 W/mK ($8 \times 8 \times 8\,\boldsymbol{q}$ points), which can be attributed to the smaller anharmonicity of the Ge framework. These results clearly show the impact of rattlers on κ_L of type-I clathrates, which was also demonstrated by previous classical molecular dynamics studies on a hypothetical material Sr_6Ge_{46} [32]. In Fig. 2, we also show a theoretical result of BGG with the effect of phonon-boundary scattering considered by using Matthiessen's rule, for which the phonon lifetime in Eq. (4) is substituted by $\tau_{q,\mathrm{eff}}^{-1} = \tau_q^{-1} + 2v_q/L$ with the grain size of $L = 2$ μm. The result agrees well with the experimental values of the n-type sample [31] in a wide temperature range. The lower thermal conductivity of the p-type sample can be attributed to the off-center rattling motion as suggested by Fujiwara and co-authors [33].

To understand the microscopic origin of the 20-fold reduction in κ_L, we analyzed the role of rattlers on the phonon lifetime τ. In Fig. 3, we compare the phonon

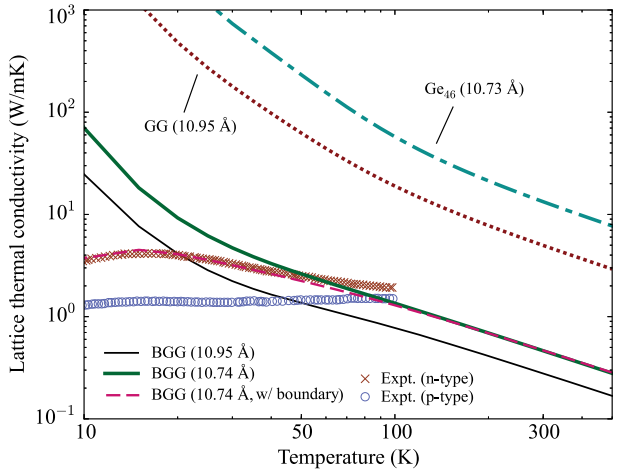

FIG. 2 (color online). Temperature dependence of the lattice thermal conductivity calculated for filled (BGG) and empty (GG, Ge_{46}) clathrates. For BGG, we also show the result with the boundary effect considered by Matthiessen's rule with the grain size of $L = 2$ μm, which is comparable with experimental results (symbols) [31].

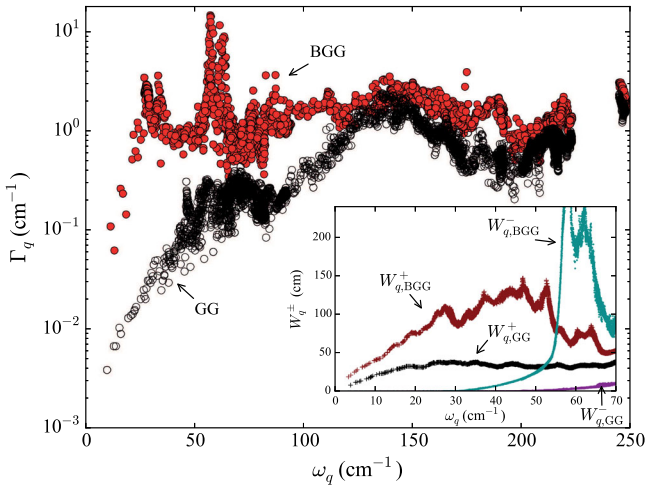

FIG. 3 (color online). Calculated phonon linewidth of BGG (filled circles) and GG (open circles) at 300 K. Inset: Energy- and momentum-conserving phase space $W_q^\pm$ in the low-energy region at 300 K.

linewidth Γ_q of BGG and GG at room temperature calculated by Eq. (2), which is inversely proportional to the phonon lifetime $\tau_q = (2\Gamma_q)^{-1}$. Contrary to the resonant scattering picture where one expects $\Gamma_q(\omega) \propto [\omega^2/(\omega^2-\omega_0^2)^2]$ with a localized rattling frequency ω_0 [8], the phonon linewidth of BGG is increased from that of GG in the entire frequency range. Therefore, phonon scattering by rattlers is *not* resonant. The difference is significant in the low-frequency region (< 120 cm^{-1}), and the tenfold increase in Γ_q is observed even for low-frequency acoustic phonons. To elucidate the reason for this considerable increase in Γ_q due to rattlers, we also estimated the energy- and momentum-conserving phase space for three-phonon scattering processes

$$W_q^{\pm} = \frac{1}{N}\sum_{q',q''}{}' \begin{Bmatrix} n_{q''} - n_{q'} \\ n_{q'} + n_{q''} + 1 \end{Bmatrix} \delta(\omega_q - \omega_{q'} \pm \omega_{q''}). \quad (5)$$

Here, W_q^+ and W_q^- are the phase spaces corresponding to absorption and emission of phonon q, respectively, and the summation is restricted to the pairs (q', q'') satisfying $\boldsymbol{q} + \boldsymbol{q}' + \boldsymbol{q}'' = n\boldsymbol{G}$. At room temperature, the phase space of absorption W_q^+ is significantly greater than that of emission W_q^- for low-energy modes as shown in the Fig. 3 inset. Moreover, additional phonon modes induced by rattlers increase the phase space W_q^+ for low-energy acoustic phonons; $W_{q,\text{BGG}}^+$ is greater than $W_{q,\text{GG}}^+$ by more than a factor of 2. However, this increase in $W_q^{\pm}$ is not sufficient to explain the tenfold increase in Γ_q. Actually, the increase in the matrix element $|V_3(-q, q', q'')|^2$ appearing in Eq. (2) is also significant in BGG. In Fig. 4(a), we show the difference in the matrix element $|V_3(-q, q', q'')|^2$ of heat-carrying transverse acoustic (TA) and LA modes at $\boldsymbol{q} = (0.1, 0, 0)$ whose frequencies are 8.0 and 11.4 cm^{-1}, respectively. As clearly seen in the figure, the matrix elements of BGG are increased at the frequencies $\omega_{q'}$ corresponding to the vibrational energies of localized rattling modes (see Fig. 1). This indicates the significant role of rattlers for enhancing $|V_3(-q, q', q'')|^2$, a measure of anharmonicity of the system. Not only the LA mode but also the TA mode at small $\boldsymbol{q}$ is strongly affected by the localized Ba motions, which is made possible by the anharmonic effects. In the frequency above 100 cm^{-1}, we observed no significant difference in $|V_3(-q, q', q'')|^2$ between BGG and GG. Therefore, the difference of the matrix elements in the low-frequency region should be essential for understanding the tenfold change in τ and very low κ_L value of BGG. It should be noted that our results shown in Figs. 3 and 4 clearly support the increased umklapp scattering scenario proposed by Lee *et al.* [34] and therefore question the validity of the phononic filter mechanism recently proposed by Euchner and Pailhès [28,29].

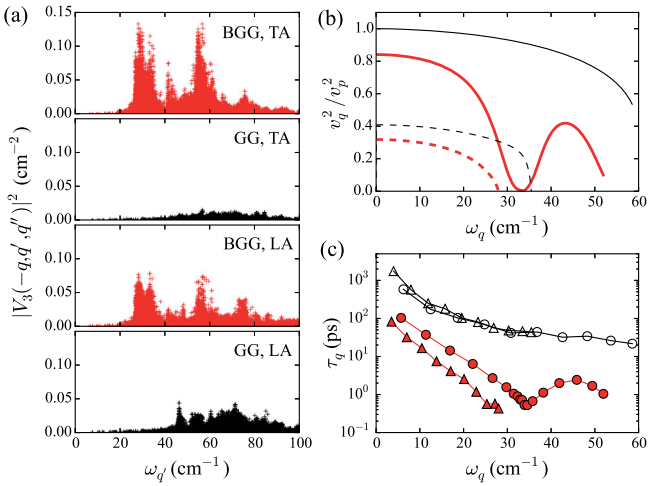

FIG. 4 (color online). Calculated phonon properties of the acoustic and the anticrossing rattling modes along the [100] direction. (a) Magnitude of anharmonic interactions of the TA and LA modes at $\boldsymbol{q} = (0.1, 0, 0)$. (b) Square group velocity of transverse (dashed line) and longitudinal (solid line) modes of BGG (thick line) and GG (thin line) normalized by the square sound velocity v_p^2. (c) Phonon lifetime of transverse (triangles) and longitudinal (circles) modes of BGG (filled symbols) and GG (empty symbols) at 300 K.

Next, we discuss the effect of rattlers on the group velocity v of heat-carrying acoustic modes. To this end, we calculated group velocities and phonon lifetimes of the TA and LA modes (and the anticrossing rattling mode for BGG) along the [100] direction. In Fig. 4(b), we compare the square group velocities of the transverse and longitudinal modes of BGG and GG. The values are normalized by the group velocity of the LA mode of GG, $v_p = 4100$ m/s. It can be seen that the group velocity of the LA mode is significantly reduced around $\omega_q = 33$ cm^{-1} due to the flattening of the band dispersion, whereas the TA mode is less affected. The reduction in v seems great, but is too local in energy to explain the 20-fold reduction of the integrated quantity $\kappa_L \propto \int d\omega D(\omega) C(\omega) v^2(\omega) \tau(\omega)$, where $D(\omega)$ is the phonon DOS. From the ω integral of $v_{\text{LA}}^2(\omega)$, we can roughly estimate that the reduction in v due to rattlers results in a reduction in κ_L by no more than a factor of 2. Moreover, if the frequency dependence of $\tau(\omega)$ is considered, the significance of the group velocity reduction becomes much less. In Fig. 4(c), we also compare the phonon lifetimes of the acoustic modes at room temperature. As already noted in Fig. 3, the rattler-induced reduction in $\tau(\omega)$ occurs in the wide frequency range rather than in a limited range around 33 cm^{-1}. This is because the phonon-rattler scattering is described by precise three-phonon processes rather than the phenomenological resonant scattering. The calculated phonon lifetimes of the TA and LA modes at room temperature are $\tau \sim 1$ ps near the avoided-crossing point and increase rapidly as decreasing $\boldsymbol{q}$, in good agreements with previous

INS studies [28,29]. We also estimated the mean-free-path $\ell_q = |v_q|\tau_q$ of acoustic phonons and found that the ℓ_q value of low-energy modes can be as long as 100 nm even at room temperature. In the previous INS study [11], phonon mean-free paths in BGG were assumed to be restricted by the separation of rattlers ($\ell_q \sim 5.5$ Å). Such an assumption, however, is artificial because we observed $\ell_q > 1$ nm in a wide range of frequency.

To summarize, we performed anharmonic lattice dynamics calculations of a type-I clathrate BGG from first principles and analyzed the effect of on-center rattlers on the relaxation time τ and the group velocity v of acoustic phonons. Then, we observed massive reduction of τ in a wide frequency range, thus indicating that the resonant scattering scenario is not appropriate to describe phonon scatterings in BGG. This tenfold reduction in τ was achieved due to the enhancement of the anharmonicity and the energy- and momentum-conserving phase space induced by rattlers. The nonresonant and significant reduction of τ is crucial to understand unusually low lattice thermal conductivities ($\kappa_L \sim 1$ W/ mK) of clathrates, whereas the effect of the group velocity is secondary because its reduction occurs only in a limited frequency range.

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*tadano@cms.phys.s.u-tokyo.ac.jp

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