Off-center rattling triggers high-temperature thermal transport in thermoelectric clathrates: Nonperturbative approach

Qing Xi,[1,2,3] Zhongwei Zhang,[1,2,3] Tsuneyoshi Nakayama,[1,2,3,4,*] Jie Chen,[1,2,3] Jun Zhou,[1,2,3,†] and Baowen Li[5,‡]

[1]*Center for Phononics and Thermal Energy Science, School of Physics Science and Engineering, Tongji University, 200092 Shanghai, People's Republic of China*

[2]*China-EU Joint Lab for Nanophononics, Tongji University, 200092 Shanghai, People's Republic of China*

[3]*Shanghai Key Laboratory of Special Artificial Microstructure Materials and Technology, School of Physics Science and Engineering, Tongji University, 200092 Shanghai, People's Republic of China*

[4]*Hokkaido University, Sapporo 060-0826, Japan*

[5]*Department of Mechanical Engineering, University of Colorado, Boulder, Colorado 80309, USA*

(Received 24 May 2017; published 25 June 2018)

Lattice thermal conductivities κ_L of type-I clathrates encapsulating "off-center" guest atoms behave in a way that is sharply different from those of conventional crystals such as on-center type-I clathrates. The latter decreases with increasing temperature according to $1/T$ above a few tens K, while κ_L of off-center clathrates increase T linearly above a few tens of K. Further increasing temperature above $T \gtrsim 100$ K, κ_L saturates without exhibiting appreciable T dependence. In this temperature regime, the standard formulation of κ_L based on the perturbation theory is unfeasible. We herein present a theory of κ_L based on a "nonperturbative" approach by taking into account the interaction between nonvibrational off-center rattling states of guest atoms and cage shells. It is remarkable that our theory shows excellent agreement with observed $\kappa_L(T)$ for off-center clathrates in magnitudes, the cage volume Ω dependence, and T dependence.

DOI: 10.1103/PhysRevB.97.224308

I. INTRODUCTION

High-temperature thermal transport is a crucial issue in the search of efficient thermoelectric materials. This is because operating temperatures of thermopower devices are higher than room temperature. Efficient thermoelectric effects should be achieved by materials possessing both "glasslike" low lattice thermal conductivity and crystal-like high electrical conductivity [1–3]. Here, the glasslike thermal conductivity is characterized from low temperature regions as follows [2]. (i) κ_L is proportional to $T^{2+\delta}$ ($\delta \ll 1$) below a few K. (ii) The plateau region from a few K to a few tens of K. (iii) The T-linear rise above the plateau from ~10 K to 100 K. (iv) The saturated regime independent of T above $T \gtrsim 100$ K. These are the prominent hallmarks of glasslike thermal conductivities, almost identical to those of structural glasses.

Type-I clathrates are promising thermoelectric materials fulfilling the concept of the phonon-glass electron-crystal concept. In actuality, κ_L of type-I clathrates with off-center guest atoms behave like those of structural glasses [2,3]. See Fig. 1. Type-I clathrate $R_8M_{16}Z_{30}$ (R = Ba, Sr, Eu; M and Z = Al, Ga, In, Si, Ge, and Sn) has a $Pm\bar{3}n$ cubic structure, formed by the network cages consisting of face-sharing polyhedrons (dodecahedron and tetrakaidecahedron) and the encapsulated guest atoms [2]. Guest atoms in tetrakaidecahedral cages will take off-center positions when the ionic radius of guest atoms is relatively small compared with the cage radius [5], which has been observed in $Sr_8Ga_{16}Ge_{30}$ [5,9], $Eu_8Ga_{16}Ge_{30}$ [5], $Ba_8Ga_{16}Sn_{30}$ [4], and $Ba_{7.81}Ge_{40.67}Au_{5.33}$ [10] by means of x-ray and neutron diffraction methods. The off-center guest atoms break the translational invariance of the systems. More importantly, the weakly bounded guest atoms in cages with large open space execute nonvibrational motion above $T \gtrsim$ 100 K with large atomic displacement parameter [9,11–14]. In this context, we should mention the concept of part-crystalline part-liquid state which has been proposed for filled skutterudites [15,16], indicating that the nonvibrational state of rattling guest atoms is a general aspect at high temperature for host-guest systems.

Let us begin by giving a brief summary on previous theoretical results on $\kappa_L(T)$ of off-center type-I clathrates. The (i) described in the first paragraph in the Introduction has been successfully interpreted by the two-level tunneling states caused from frustrated electric-dipole configuration concerning off-center guest ions [17,18]. The relevance of the localization-delocalization (LD) transition on the onset of the plateau at a few K (ii) has been demonstrated for the first time by means of large-scale numerical simulations [19]. In addition, the T-linear rise above a few tens of K (iii) has been explained by the hopping of strongly localized modes assisted by acoustic phonons [20]. For these disordered systems, large-scale simulation based on *ab initio* calculation is difficult as seen from the discrepancy between simulation results and experimental measurements of room temperature lifetimes [10], while the coarse-grained Hamiltonian is quite effective since the wavelengths λ of acoustic phonons at THz frequency region are much larger than the size of unit cell $a_0 \simeq 1$ nm including eight guest atoms and 46 cage atoms bounded by strong covalent bonding. However, despite the importance of

*tnaka@eng.hokudai.ac.jp
†zhoujunzhou@tongji.edu.cn
‡Baowen.Li@colorado.edu

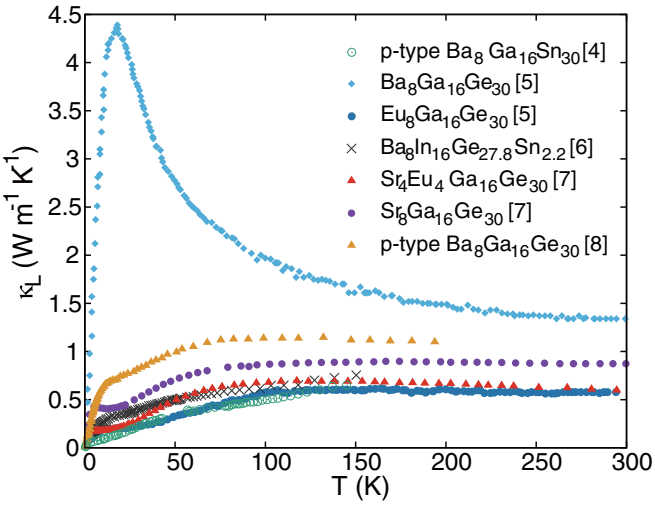

FIG. 1. Temperature dependence of κ_L plotted in linear scale for various off-center type-I clathrates [4–8] and "on-center" type-I $Ba_8Ga_{16}Ge_{30}$ [5]. The parentheses [...] in the inset give reference numbers.

the issue (iv) in the search of efficient thermoelectric materials, the underlying mechanism is yet to be explained. Here we aim at a theoretical elucidation of the underlying mechanism of heat transfer at $T \gtrsim 100$ K. For this purpose, we discuss the problem from a general point of view by proposing a theoretical model of heat transfer in host-cage systems with off-center rattling guest atoms. In this sense, the mechanism proposed here is applicable to a wide class of host-guest systems involving weakly bounded atoms in void/open structures.

II. ENERGY FLUX IN THE RATTLING REGIME $T \gtrsim T_R$

Type-I clathrates encapsulating off-center guest atoms in tetrakaidecahedron cages are composed of networked host cages of a simple cubic structure. We give a 3D video obtained from molecular dynamics (MD) simulations for type-I $Ba_8Ga_{16}Sn_{30}$ (BGS) involving off-center guest atoms in the Supplemental Material [21], which visualizes that guest atoms at 400 K perform off-center rattling motion, which are not assigned as vibrational states satisfying the condition $\omega\tau > 1$. Meanwhile, cage atoms vibrating with smaller amplitudes around their equilibrium positions can be described as vibrational states. At 10 K, however, guest atoms locate at off-center positions in cages, and vibrate there.

This aspect is consistent with THz-frequency spectroscopy data for off-center type-I BGS observed at various temperatures [22,23]. The data exhibit two peaks at 0.5 and 0.7 THz frequencies at $T_R \simeq 100$ K. Those are assigned as librational and stretching modes relevant to off-center guest atoms in type-I BGS [24]. Increasing temperature, these two peaks collapse into a single peak at 0.75 THz with comparable width. However, such a characteristic has not been observed for on-center type-I $Ba_8Ga_{16}Ge_{30}$ [22,23]. These spectroscopic data provide a strong evidence for off-center guest atoms to behave as off-center rattlers in cages at $T \gtrsim T_R$.

The rattling temperature T_R should play a crucial role for $\kappa_L(T)$ in type-I clathrates with off-center guest atoms. First, at $T \lesssim T_R$, the systems take a disordered configuration of guest atoms, and it converts into higher symmetry at $T \gtrsim T_R$ where guest atoms behave as rattlers in cages. Second, the strong covalent bonding between cage atoms ensures the existence of acoustic phonons in host cages even at $T \gtrsim T_R$ in contrast to rattling states of weakly bound guest atoms (see Supplemental Material [21]). At $T \lesssim T_R$, the standard kinetic formula $\kappa_L(T) = 1/(3V)\sum_{\mathbf{ks}} C_V(\omega_s)v_s^2\tau(\omega_s)$ is valid under the condition $\omega\tau > 1$ [25]. At $T \gtrsim T_R$, however, off-center guest atoms cannot be described as vibrational states and the perturbation treatment is unavailable in contrast to the case of on-center clathrates [26,27].

We employ the formulation of energy flux available for nonvibrational states of rattling atoms. Hardy [28] has presented the rigorous formulation on the heat transfer, from which it is straightforward to deduce the version of energy flux working at $T \gtrsim T_R$ by taking the limit $\hbar \to 0$. The local heat flux density $\boldsymbol{j}(\boldsymbol{x},t)$ is obtained from the continuity equation for the energy density $h(\boldsymbol{x},t) = \sum_\ell \epsilon_\ell(t)\delta(\boldsymbol{x} - \boldsymbol{r}_\ell)$ given by the time-dependent total energy $\epsilon_\ell(t)$ of ℓth atom at the position vector $\boldsymbol{r}_\ell$. The average energy flux is defined as $\boldsymbol{J} = (1/V)\int^V \boldsymbol{j}(\boldsymbol{x})dV$, which yields [29]

$$\boldsymbol{J}(t) = \frac{1}{V}\frac{d}{dt}\left[\sum_\ell \boldsymbol{r}_\ell(t)\epsilon_\ell(t)\right]. \tag{1}$$

By decomposing the contributions from guest atom i and cage atom j by taking $\ell = i$ or j, we have the following expression for the guest atom energy $\varepsilon_i(t)$ and the cage atom's $E_j(t)$, which are composed of the interaction potentials V_{ij}^{CG} between guest atoms (i) and cage atoms (j) and $V_{jj'}^{CC}$ between cage atoms (j, j'),

$$\begin{aligned}\varepsilon_i(t) &= \frac{1}{2}m\dot{\boldsymbol{x}}_i^2(t) + \frac{1}{2}\sum_j V_{ij}^{CG}(\boldsymbol{X}_j,\boldsymbol{x}_i),\\ E_j(t) &= \frac{1}{2}M_j\dot{\boldsymbol{X}}_j^2(t) + \frac{1}{2}\sum_{j'} V_{jj'}^{CC}(\boldsymbol{X}_j,\boldsymbol{X}_{j'})\\ &\quad + \frac{1}{2}\sum_i V_{ji}^{CG}(\boldsymbol{X}_j,\boldsymbol{x}_i),\end{aligned} \tag{2}$$

where m and M_j are masses of guest atoms and cage atoms, and the subscript j on cage atoms is combined with the subscript i of a guest atom since each cage involves only one guest atom, i.e., $j \in i$. The position vector $\boldsymbol{x}_i(t)$ of ith guest atom is expressed by the sum of the small displacement $\boldsymbol{q}_i(t)$ and the equilibrium position $\boldsymbol{R}_i$, $\boldsymbol{x}_i(t) = \boldsymbol{R}_i + \boldsymbol{q}_i(t)$, and the position vector of cage atom j is given by $\boldsymbol{X}_j(t) = \boldsymbol{R}_j + \boldsymbol{Q}_j(t)$ with $\boldsymbol{Q}_j(t)$ the small displacement of cage atom. $\dot{\boldsymbol{x}}_i(t)$ and $\dot{\boldsymbol{X}}_j(t)$ are time-dependent velocities of the ith guest atom and the jth cage atom, respectively.

The substitution of Eq. (2) into Eq. (1) leads to [28,29]

$$\begin{aligned}\boldsymbol{J}(t) = &\frac{1}{V}\sum_{i,j\in i}[\varepsilon_i(t)\dot{\boldsymbol{x}}_i(t) + E_j(t)\dot{\boldsymbol{X}}_j(t)]\\ &+ \frac{1}{V}\sum_{j,j'}\left[(\boldsymbol{X}_j(t) - \boldsymbol{X}_{j'}(t))\boldsymbol{F}_{jj'}^{CC}\cdot\dot{\boldsymbol{X}}_j(t)\right]\\ &+ \frac{1}{V}\sum_{i,j\in i}\left[(\boldsymbol{x}_i(t) - \boldsymbol{X}_j(t))\boldsymbol{F}_{ij}^{GC}\cdot(\dot{\boldsymbol{x}}_i(t) + \dot{\boldsymbol{X}}_j(t))\right],\end{aligned} \tag{3}$$

where the interatomic force $\boldsymbol{F}_{jj'}^{CC}$ between cage atoms j, j' and $\boldsymbol{F}_{ij}^{GC}$ between guest atom i and cage atom j are defined by

$$\boldsymbol{F}_{jj'}^{CC} = -\frac{\partial U_{j'}^{CC}}{\partial \boldsymbol{X}_j}, \quad \boldsymbol{F}_{ij}^{GC} = -\frac{\partial U_j^{GC}}{\partial \boldsymbol{x}_i}, \tag{4}$$

with

$$U_j^{CC} = \frac{1}{2}\sum_{j'} V_{jj'}^{CC}(\boldsymbol{X}_j, \boldsymbol{X}_{j'})$$

and

$$U_j^{GC} = \frac{1}{2}\sum_{i} V_{ji}^{GC}(\boldsymbol{X}_j, \boldsymbol{x}_i), \tag{5}$$

where U_j^{CC} is the cage atom–cage atom interaction potential for the cage atom j, and U_j^{GC} is the guest-cage potential for the cage atom j. Equation (3) is applicable for nonvibrational states in gases and liquids. The first parenthesis in the right in Eq. (3) describes the convective contribution to heat transfer, and the second and the third in the right are the conductive part. In off-center type-I clathrates, the location of guest atoms deviates significantly from the off-center equilibrium position at $T \gtrsim T_{\mathrm{R}}$. It is apparent, however, that guest atoms cannot diffuse to nearest-neighbor cages. Consequently, we do not take into account the convectional terms in Eq. (3).

The second parenthesis in the right in Eq. (3) expresses the energy transfer in host cage, whose constituent atoms are bound by short-range covalent bonding. Type-I clathrates consist of eight guest atoms and 46 cage atoms in unit cell, where optical modes attributing to these atoms are irrelevant to heat transfer. In addition, the time average of the relative distance between cage atoms in the same cage becomes $\overline{\boldsymbol{X}_j(t) - \boldsymbol{X}_{j'}(t)} = d_{jj'}$ for the dominant nearest-neighbor coupling, where $d_{jj'}$ is the nearest-neighbor distance due to short-range covalent bonding, which is much smaller than the size of cage $2R$, while, at $T \gtrsim T_{\mathrm{R}}$, the relations $\overline{\boldsymbol{x}_i - \boldsymbol{X}_j} \cong R$ and $\dot{\boldsymbol{x}}_i(t) \gg \dot{\boldsymbol{X}}_{j\in i}$ hold in the third parentheses (see Supplemental Material [21]). As a result, the third term stemming from rattling guest atoms should play a key role for the heat transfer at $T \gtrsim T_{\mathrm{R}}$. Thus the dominant term for energy flux at $T \gtrsim T_{\mathrm{R}}$ in Eq. (3) is given by

$$\boldsymbol{J}(t) = \frac{1}{V}\sum_{i,j\in i}^{N} [\boldsymbol{x}_i(t) - \boldsymbol{X}_j(t)]\boldsymbol{F}_{ij}\cdot\dot{\boldsymbol{x}}_i(t). \tag{6}$$

To assess more definitely the impact of guest atoms on energy flux, we consider another aspect of the part of $\boldsymbol{F}_{ij}\cdot\dot{\boldsymbol{x}}_i$ in Eq. (6) using the relation

$$\sum_{j\in i} \boldsymbol{F}_{ij}\cdot\dot{\boldsymbol{x}}_i(t) = \dot{\varepsilon}_i. \tag{7}$$

This relation yields the thermal/time-averaged energy flux (heat flux) at T given by

$$\langle\overline{\boldsymbol{J}(t)}\rangle = \frac{N}{V} R\dot{\varepsilon}_c(T), \tag{8}$$

where $\langle\cdots\rangle$ denotes the thermal average at a temperature T. The energy fluxes from individual cages are identical at each site because of the translational invariance of the system at the rattling regime $T \gtrsim T_{\mathrm{R}}$. So, we have employed the notation ε_c for ε_i.

Let us give a qualitative interpretation on the above formula. The kinetic energy ε_c can be related with the local pressure p_c in a cage and the cage volume v_c by the relation $\varepsilon_c = p_c v_c$. The volume change $v_c + \delta v_c$ caused by the interaction between guest atom and cage atoms yields the energy change $\delta\varepsilon_c(t) = \varepsilon_c\Delta_c(t)$, where the dilation is given by $\Delta_c(t) = \delta v_c/v_c$. Consequently, the off-center rattling motion of guest atom triggers the energy transfer to host cage via deformation of cage shells. In thermal equilibrium, guest atoms convert their energies into cage-shell modes, and those are recovered by the reverse process.

III. ENERGY FLUX FROM RATTLING GUEST ATOMS TO HOST CAGE AT $T \gtrsim T_{\mathrm{R}}$

Off-center rattling motion of guest atoms at $T \gtrsim T_{\mathrm{R}}$ triggers the energy exchange with host cages via the deformation of cages. This mechanism is identical to the emission of phonons from a small particle immersed in an elastic medium. We utilize the treatment on heat transfer from fine particles immersed in liquid He II [30] and liquid ^{3}He [31] by modifying those to be applicable at high temperatures $T \gtrsim T_{\mathrm{R}}$. The mean rate of energy emitted from dilation modes of a cage is given by the square of the velocity field $\boldsymbol{v}(\boldsymbol{r},t)$ [32],

$$\dot{\varepsilon}_{\mathrm{c}} = \rho_{\mathrm{s}} v_{\parallel} \oint_S |\boldsymbol{v}(\boldsymbol{r})|^2 dS, \tag{9}$$

where ρ_{s} and $v_{\parallel}$ are the mass density and the velocity of longitudinal phonons in the host cage. dS is the surface element surrounding a cage. Since the emitted energy is carried away by vibrations of a cage shell, it needs to relate the velocity field $\boldsymbol{v}(\boldsymbol{r})$ at $\boldsymbol{r}$ to $\boldsymbol{v}(\boldsymbol{R})$ at the surface $\boldsymbol{R}$ under the situation $|\boldsymbol{r}| \geqslant |\boldsymbol{R}|$.

The velocity fields at $\boldsymbol{r}$ and $\boldsymbol{R}$ can be related by introducing the scalar potential $\phi_q(\boldsymbol{r},t)$ defined by $\boldsymbol{v}(\boldsymbol{r},t) = \mathrm{grad}\,\phi(\boldsymbol{r},t)$ [30]. The radial component of the velocity field becomes

$$|\boldsymbol{v}^q(\boldsymbol{r})|^2 = \frac{R^4}{r^4}\frac{1+(qr)^2}{1+(qR)^2}\left|v_r^q(\boldsymbol{R})\right|^2, \tag{10}$$

where q represents the wave number of emitted phonon. This provides the emission of spherical pressure (longitudinal) waves [30]. The effect of shear (transverse) waves stemmed from the angular components $v_\theta^q(R)$ and $v_\phi^q(R)$ will be discussed later.

Substituting this relation into Eq. (9) and taking the closed surface of the integration to be a sphere of radius $r > R$, the mean energy emitted from a cage becomes

$$\dot{\varepsilon}_c^q = \rho_{\mathrm{s}} v_{\parallel}\frac{q^2R^4}{1+q^2R^2}\int_0^{2\pi}\int_0^{\pi}\left|v_r^q(\boldsymbol{R})\right|^2 d\Omega, \tag{11}$$

where $d\Omega = \sin\theta\, d\theta\, d\phi$. The velocity field $v_r(\boldsymbol{R})$ at the surface of a cage must be equal to the time derivative of the surface displacement of the cage, i.e., $\boldsymbol{v}(\boldsymbol{R},t) = \dot{\boldsymbol{u}}(\boldsymbol{R},t)$. The $\boldsymbol{u}(\boldsymbol{R},t)$ is expressed by the sum of the eigenmode J for shell vibrations of a cage, where J stands for a set of quantum numbers $(\ell,m,\omega_q^{\ell,m})$ specifying the eigenmodes. By defining the eigenmode belonging to the eigenfrequency ω_J as $\vec{\psi}_J(\boldsymbol{R})$,

the displacement operator is expressed by

$$\boldsymbol{u}(\boldsymbol{R},t) = \sum_J \sqrt{\frac{\hbar}{2\rho_s \omega_J \Omega}} (a_J \vec{\psi}_J(\boldsymbol{R}) e^{-i\omega_J t} + \text{H.c.}), \quad (12)$$

where Ω and ρ_s are the volume and the mass density of cage, respectively, and a_J and $a_J^\dagger$ are the boson operators of the mode J. The eigenfunction $\vec{\psi}_J(r)$ represents the spherical wave emitted from a cage.

The thermal-averaged total energy emitted from a cage via longitudinal phonons is obtained by summing up J for Eq. (11), which yields

$$\dot{\varepsilon}_c(T) = \rho_s v_\parallel \sum_J \frac{q^2 R^4}{1+q^2R^2} \int_0^{2\pi} \int_0^{\pi} d\Omega \times \langle \dot{u}_r^J(\boldsymbol{R},t)^\dagger \dot{u}_r^J(\boldsymbol{R},t) \rangle, \quad (13)$$

where $\dot{u}_r(\boldsymbol{R})$ represents the normal component of the velocity field at the surface of a cage. The thermal average is defined by

$$\langle \dot{u}_r^J(R)^\dagger \dot{u}_r^J(R) \rangle = \text{Tr}\left[e^{-\beta H} \dot{u}_r^J(R)^\dagger \dot{u}_r^J(R) \right], \quad (14)$$

where $H = \sum_J \hbar\omega_J a_J^\dagger a_J$ and $\beta = 1/k_B T$. Noting $\langle a_J^\dagger a_J \rangle = n(\omega_J, T)$ given by the Bose-Einstein distribution function, the integral in Eq. (13) yields [30]

$$\int_0^{2\pi} \int_0^{\pi} \langle \dot{u}_r^J(\boldsymbol{R})^\dagger \dot{u}_r^J(\boldsymbol{R}) \rangle d\Omega = \frac{\hbar\omega_J}{\rho_s \Omega} n(\omega_J, T) \times \int_0^{2\pi} \int_0^{\pi} d\Omega \left(\left. \frac{\partial j^\ell}{\partial x} \right|_{r=R}^2 + [\text{higher order terms}] \right), \quad (15)$$

where $j^\ell(x)$ with $x = qr$ is the ℓth order spherical Bessel function of the first kind. It should be emphasized that, since the size of the cage is small enough $2R \approx 5$ Å, the lowest symmetric mode of cavity cage dominantly contributes to the energy transfer. Higher order terms in the parenthesis in Eq. (15) provide small contribution. Thus the most effective process occurs in the fundamental mode ($\ell = 0$) with the eigenfrequency $\omega^0 = 2\pi v_s/\lambda_0$ attributing to the lowest spherical Bessel function $\ell = 0$ of the form $j^0(x) = \sin x/x$ in Eq. (15). The wavelength λ_0 should be $\lambda_0 = 4R$ for the cage with the radius R.

The heat conductance is defined by $h(T) = \partial_T J(T)$ from the relation $J(T+\Delta T) - J(T) = h(T)\Delta T$. By taking the high temperature relation $n(\omega_J, T) = k_B T/\hbar\omega_J$ in Eq. (15) and substituting the results of Eq. (13) into Eq. (8), we have the heat conductance due to the emission of longitudinal acoustic phonons from a cage as

$$h_\parallel(T) = \frac{4\pi k_B v_\parallel q_o^2 R^5}{(1+q_0^2R^2)\Omega^2} \left. \frac{\partial j^0(q_0 r)}{\partial x} \right|_{r=R}^2, \quad (16)$$

where we have used the relation $N/V = 1/\Omega$ for the number density of off-center guest atoms, not the number density of all atoms in the systems. It should be noted that $\hbar$ is canceled out in Eq. (16). This is consistent with the fact that the classical dynamics works in the rattling regime $T \gtrsim T_R$. The $\partial j^0(x)/\partial x\,|_{r=R}$ in Eq. (16) equals the first-order spherical Bessel function

$$j^1(x) = \sin x/x^2 - \cos x/x, \quad (17)$$

with $x = q_0 R = \pi/2$ from $4R = \lambda_0$. This gives rise to the heat conductance

$$h_\parallel(T) = \alpha_\parallel k_B v_\parallel/\Omega, \quad (18)$$

where the prefactor is given by

$$\alpha_\parallel = 3(q_0R)^2 j^1(q_0R)^2/\left(1+q_0^2R^2\right), \quad (19)$$

using the relation $\Omega = 4\pi R^3/3$. It is straightforward to incorporate the effect of shear (transverse $\perp$) waves stemming from the angular components of the velocities $v_\theta^q(\boldsymbol{R})$ and $v_\phi^q(\boldsymbol{R})$ according to the treatment of the heat transfer from small particles to liquid ^{3}He [31]. Note that transverse modes propagate in liquid ^{3}He, but not in liquid ^{4}He. The prefactor $\alpha_\perp$ is obtained by taking into account the dominant contribution from the lowest order of modes, i.e., by replacing $\partial j^0(x)/\partial x\,|_{r=R}^2$ and $v_\parallel$ in Eq. (16) with the eigenfunctions of shear modes and $v_\perp$ [31].

The thermal conductivity κ_L is obtained from the total conductance $h(T) = h_\parallel(T) + h_\perp(T)$ by multiplying the lattice constant a_0 of type-I clathrates with off-center guest atoms using the relation $a_0/2 = 2R$. This is expressed in terms of the cage volume Ω as

$$\kappa_L(T) = \gamma \frac{k_B v_s}{\Omega^{2/3}}, \quad (20)$$

where v_s is the average velocity of acoustic phonons defined by $v_s = (v_\parallel + 2v_\perp)/3$. This expression directly provides the relevance of guest atoms to high-temperature $\kappa_L(T)$ via the cage volume Ω. We can evaluate the prefactor as $\gamma = 2.61$ from the expressions of $\alpha_\parallel$ and $\alpha_\perp$. This γ value attributes to the contribution from fundamental modes of a cage, so it should be considered as the lower limit of $\kappa_L^{\min}$ at $T \gtrsim T_R$. The proper value of γ can be obtained by incorporating higher-order terms of modes. Thus the prefactor $\gamma = 4.2$ estimated in Fig. 2 can be recovered. Equation (20) shows T-independent saturated κ_L in accord with the observations shown in Fig. 1. The Ω dependence in Eq. (20) is consistent with the experimental data for off-center clathrates showing glasslike thermal conductivity as seen from Fig. 2, in addition to the agreement with observed magnitudes of $\kappa_L(T)$.

IV. RELEVANCE TO THE CONCEPT OF THE MINIMUM THERMAL CONDUCTIVITY

The concept of the minimum thermal conductivity (MTC) was first proposed by Slack [36] by employing the standard formula of thermal conductivity $\kappa(T) = (1/3V)\sum_k C_V v_s \ell$. This formula yields

$$\kappa_{min}^{SK}(T) = \frac{k_B v_s (6\pi^2 n)^{2/3}}{2\pi} I(x_D), \quad (21)$$

where the transport integral is given by

$$I(x_D) = \frac{2}{x_D^2} \int_0^{x_D} \frac{x^3 e^x dx}{(e^x-1)^2}. \quad (22)$$

Here, $x = \hbar\omega/k_B T$ and $x_D = \hbar\omega_D/k_B T$ with the Debye cutoff frequency ω_D. The number density of atoms n is

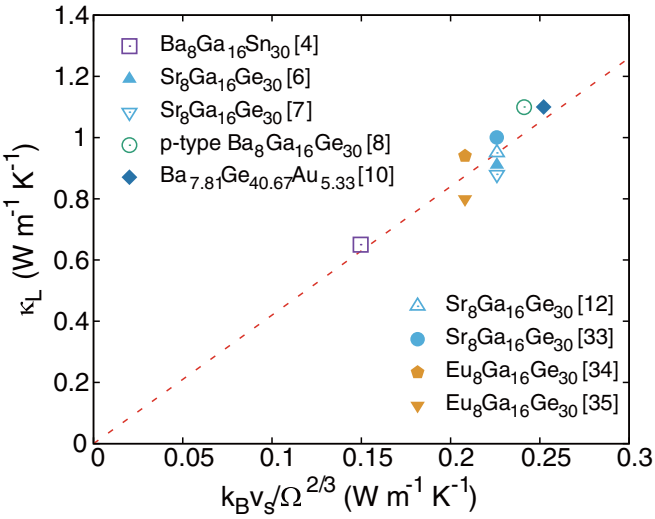

FIG. 2. Observed $\kappa_{\rm L}$ for various off-center type-I clathrates as a function of $k_{\rm B}v_s/\Omega^{2/3}$ [4,6–8,10,12,33–35]. Solid inverted triangle on off-center $Eu_8Ga_{16-x}Sn_{30+x}$ denotes the thermal conductivity averaged for $x = 0.47$–0.76 [35]. The dashed line is a guide for the eyes showing good agreement with Eq. (20) for $\gamma = 4.2$. The parentheses [...] in the inset give reference numbers.

related to the Debye temperature by $\theta_D = \hbar v_s(6\pi^2 n)^{1/3}/k_{\rm B}$ of "monoatomic" systems. The term x^3 in the transport integral comes from the combination of the Debye density of states and the postulated mean-free path of acoustic phonons of the form $\ell(\omega) = 2\pi v_s/\omega$ or equivalently $q\ell(\omega) = 2\pi$, which is identical to the Ioffe-Regel (IR) criterion for strongly localized (SL) modes except for the factor 2. In the SL regime, the mean-free path ℓ and the localization length collapse into a single length scale, i.e., those have the same meaning. The prefactor $k_{\rm B}v_s(6\pi^2 n)^{2/3}/2\pi$ in $\kappa_{min}^{SK}(T)$ provides the MTC at high temperatures.

Cahill and Pohl [37] have explicitly postulated that "all" acoustic phonons are strongly localized with the localization length $\ell \simeq \lambda/2$ according to the Ioffe-Regel (IR) criterion of $q\ell(\omega) = \pi$ [38]. The formula [37] is given by

$$\kappa_{min}^{CP} = \frac{k_{\rm B}v_s(6\pi^2 n)^{2/3}}{4\pi} I(x_D). \tag{23}$$

This is the same as κ_{min}^{SK} in Eq. (21) except the factor 2 in the denominator stemmed from the IR criterion employed. These $\kappa_{min}^{SK/CP}$ are proportional to the number density of atoms according to $n^{2/3}$. In applying the formula for actual systems with many atoms in unit cell such as the case of type-I clathrates with 54 atoms in unit cell or fullerene derivatives [39,40], it is crucial that the Debye model [36,37] not allowing modes $\omega \geqslant \omega_D$ exhausts the number of degrees of freedom. Thus the MTC formula gives rise to the overestimation of κ_{min} for these systems [39,40]. In addition, the formulas [36,37] give the temperature dependence proportional to T^2 at $T \lesssim \theta_D$. This prediction is in conflict with the experimental data $\kappa_L(T) \propto T$ above the plateau temperature region from a few tens of K to ∼100 K of off-center clathrates and structural glasses (iii) [2]. The discrepancy arises from their postulate that all excited phonons are strongly localized. This postulate is only valid for fracton excitations in fractal structures [41], in which heat transfer does not occur in the absence of anharmonic interaction [42]. Thus the physical basis of our theory based on a nonperturbative approach is distinct from these MTC.

V. SUMMARY

We have given a theory on the underlying mechanism governing high-temperature $\kappa_{\rm L}(T)$ of type-I clathrates with off-center guest atoms, focusing on the regime at $T \gtrsim T_R$. Our approach is based on nonperturbative treatment, different from the standard one according to the perturbation theory. As seen from the 3D video of MD simulations in the Supplemental Material [21], off-center rattling motion of guest atoms performs spontaneous displacement with large amplitude in cages, which induces the deformation of surrounding cages, and the energy exchange between cage and guest atom occurs via phonon emission/absorption. We point out that the theory proposed here is applicable for host-guest systems involving weakly bound atoms in void/open structures, although we have exemplified the systems of off-center clathrates. It is remarkable that the prediction of the formula Eq. (20) shows excellent agreement with observed $\kappa_{\rm L}(T)$ for off-center clathrates in magnitude, temperature dependence, and the cage-volume Ω dependence.

To conclude, our theoretical investigation based on a nonperturbative approach provides one of guiding principles for searching and designing efficient thermoelectric materials operating at high temperatures with very low lattice thermal conductivities. In addition, the principal mechanism described here works for a wide class of complex disordered systems such as structural glasses involving weakly bound atoms in void structures [43]. These are in some respects similar to those of clathrates with rattling guest atom.

ACKNOWLEDGMENTS

This work is supported by the National Natural Science Foundation of China Grant No. 11334007. T.N. acknowledges the support from Grand-in-Aid for Scientific Research from the MEXT in Japan, Grant No. 26400381. J.Z. is supported by the program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning No. TP2014012. J.C. acknowledges the support from the National Natural Science Foundation of China (Grant No. 51506153).

[1] G. A. Slack, in *CRC Handbook of Thermoelectrics*, edited by D. M. Rowe (CRC Press, Boca Raton, FL, 1995), pp. 407–440.
[2] T. Takabatake, K. Suekuni, T. Nakayama, and E. Kaneshita, Rev. Mod. Phys. **86**, 669 (2014).
[3] M. Beekman, D. T. Morelli, and G. S. Nolas, Nat. Mater. **14**, 1182 (2015).
[4] K. Suekuni, M. A. Avila, K. Umeo, H. Fukuoka, S. Yamanaka, T. Nakagawa, and T. Takabatake, Phys. Rev. B **77**, 235119 (2008).

[5] B. C. Sales, B. C. Chakoumakos, R. Jin, J. R. Thompson, and D. Mandrus, Phys. Rev. B **63**, 245113 (2001).
[6] K. Suekuni, S. Yamamoto, M. A. Avila, and T. Takabatake, J. Phys. Soc. Jpn. **77**, 61 (2008).
[7] J. L. Cohn, G. S. Nolas, V. Fessatidis, T. H. Metcalf, and G. A. Slack, Phys. Rev. Lett. **82**, 779 (1999).
[8] A. Bentien, M. Christensen, J. D. Bryan, A. Sanchez, S. Paschen, F. Steglich, G. D. Stucky, and B. B. Iversen, Phys. Rev. B **69**, 045107 (2004).
[9] B. C. Chakoumakos, B. C. Sales, D. G. Mandrus, and G. S. Nolas, J. Alloys Compd. **296**, 80 (2000).
[10] P.-F. Lory, S. Pailhès, V. M. Giordano, H. Euchner, H. D. Nguyen, R. Ramlau, H. Borrmann, M. Schmidt, M. Baitinger, M. Ikeda, P. Tomeš, M. Mihalkovič, C. Allio, M. R. Johnson, H. Schober, Y. Sidis, F. Bourdarot, L. P. Regnault, J. Ollivier, S. Paschen, Y. Grin, and M. de Boissieu, Nat. Commun. **8**, 491 (2017).
[11] B. C. Chakoumakos, B. C. Sales, and D. G. Mandrus, J. Alloys Compd. **322**, 127 (2001).
[12] L. Qiu, I. P. Swainson, G. S. Nolas, and M. A. White, Phys. Rev. B **70**, 035208 (2004).
[13] N. L. Okamoto, K. Kishida, K. Tanaka, and H. Inui, J. Appl. Phys. **100**, 073504 (2006).
[14] S. Christensen, M. A. Avila, K. Suekuni, R. Piltz, T. Takabatake, and M. Christensen, Dalton Trans. **42**, 14766 (2013).
[15] W. Qiu, L. Xi, P. Wei, X. Ke, J. Yang, and W. Zhang, Proc. Natl. Acad. Sci. U.S.A. **111**, 15031 (2014).
[16] W. Qiu, X. Ke, L. Xi, L. Wu, J. Yang, and W. Zhang, Sci. China-Phys. Mech. Astron. **59**, 627001 (2016).
[17] T. Nakayama and E. Kaneshita, Europhys. Lett. **84**, 66001 (2008).
[18] E. Kaneshita and T. Nakayama, Europhys. Lett. **86**, 56004 (2009).
[19] Y. Liu, Q. Xi, J. Zhou, T. Nakayama, and B. Li, Phys. Rev. B **93**, 214305 (2016).
[20] Q. Xi, Z. Zhang, J. Chen, J. Zhou, T. Nakayama, and B. Li, Phys. Rev. B **96**, 064306 (2017).
[21] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.97.224308. for the 3D video obtained from MD calculations. The Supplemental Video for the atomic dynamics in type-I BGS visualizes that off-center guest atoms at 400 K perform "off-center" rattling motion in cages by frequently changing their positions in cages, which cannot be assigned as vibrational states. Meanwhile, "cage atoms" vibrate with smaller amplitudes around their equilibrium positions at 400 K. These vibrations are described as vibrational states. At lower temperature 10 K, both cage atoms and guest atoms at off-center positions in cages manifest vibrational states satisfying $\omega\tau > 1$.
[22] T. Mori, K. Iwamoto, S. Kushibiki, H. Honda, H. Matsumoto, N. Toyota, M. A. Avila, K. Suekuni, and T. Takabatake, Phys. Rev. Lett. **106**, 015501 (2011).
[23] T. Kume, T. Sukemura, S. Nakano, S. Sasaki. K. Suekuni, and T. Takabatake, Photon Factory Activity Report No. 32B, 2015 (unpublished); T. Sukemura, T. Kume, T. Matsuoka, S. Sasaki, T. Onimaru, and T. Takabatake, J. Phys.: Conf. Ser. **500**, 182022 (2014).
[24] T. Nakayama and E. Kaneshita, J. Phys. Soc. Jpn. **80**, 104604 (2011).
[25] See, for example, E. M. Lifshitz and L. P. Pitaevskii, *Physical Kintetics*, Course of Theoretical Physics (Elsevier Ltd., Amsterdam, 1981), Vol. 10.
[26] T. Tadano, Y. Gohda, and S. Tsuneyuki, Phys. Rev. Lett. **114**, 095501 (2015).
[27] T. Tadano and S. Tsuneyuki, Phys. Rev. Lett. **120**, 105901 (2018).
[28] R. J. Hardy, Phys. Rev. **132**, 168 (1963).
[29] S. G. Volz and G. Chen, Phys. Rev. B **61**, 2651 (2000).
[30] T. Nakayama and N. Nishiguchi, Phys. Rev. B **24**, 6421 (1981).
[31] N. Nishiguchi and T. Nakayama, Phys. Rev. B **25**, 5720 (1982).
[32] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics*, 2nd ed. (Elsevier Ltd., Singapore, 2004), Chap. 74.
[33] S. Christensen, M. S. Schmokel, K. A. Borup, G. K. H. Madsen, G. J. Mclntyre, S. C. Capelli, M. Christensen, and B. B. Iversen, J. Appl. Phys. **119**, 185102 (2016).
[34] S. Paschen, W. Carrillo-Cabrera, A. Bentien, V. H. Tran, M. Baenitz, Yu. Grin, and F. Steglich, Phys. Rev. B **64**, 214404 (2001).
[35] A. Bentien, V. Pacheco, S. Paschen, Yu. Grin, and F. Steglich, Phys. Rev. B **71**, 165206 (2005).
[36] G. A. Slack, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1979), Vol. 14, pp. 1–71.
[37] D. G. Cahill and R. O. Pohl, Solid State Commun. **70**, 927 (1989); D. G. Cahill, S. K. Watson, and R. O. Pohl, Phys. Rev. B **46**, 6131 (1992).
[38] A. F. Ioffe and A. R. Regel, Prog. Semicond. **4**, 237 (1960).
[39] J. C. Duda, P. E. Hopkins, Y. Shen, and M. C. Gupta, Phys. Rev. Lett. **110**, 015902 (2013).
[40] X. Wang, C. D. Liman, N. D. Treat, M. L. Chabinyc, and D. G. Cahill, Phys. Rev. B **88**, 075310 (2013).
[41] T. Nakayama, K. Yakubo, and R. L. Orbach, Rev. Mod. Phys. **66**, 381 (1994).
[42] S. Alexander, O. Entin-Wohlman, and R. Orbach, Phys. Rev. B **34**, 2726 (1986).
[43] G. D'Angelo, C. Crupi, G. Carini, and C. Vasi, Phys. Rev. B **84**, 172201 (2011).