Tutorial Lecture, ACT3/MNHTE2018 at NTU, 14:/30-15:30, 10/7/2018

Phonon Transports in Thermoelectric Materials

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1. Brief History of Thermoelectricity(TE)

A.F. Ioffe (1880-1960): A key person of modern TE

- ✓ He proposed to use doped n- and p-type semiconductors (1930s).
- ✓ These thermo-couples can be wired in series and thermally parallel.
- ✓ This generates **a large thermoelectric power, Bi-Te, Pb-Te,** (1950s).

See, for example, *Semiconductor Thermoelements(1956)*, by A. F. Ioffe, Infor. Ltd., London

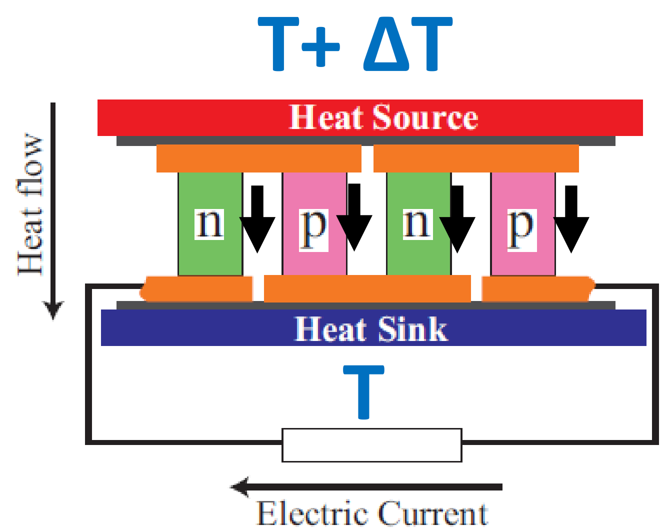


FIG. 1 (Color online) Thermoelectric devices contain many thermoelectric couples consisting of n-type and p-type thermoelectric elements wired electrically in series and thermally in parallel.

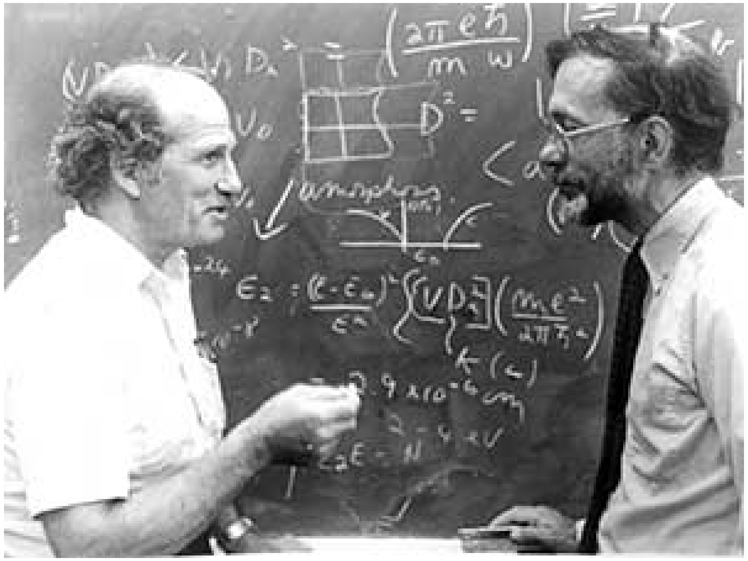
RMP, vol.86, (2014)669.

A F Ioffe (1880-1960)

Ukrainian Physicist, learned in Munich,
And worked with Roentgen as assistant.

Adoption of Si-Ge TE generator in spacecraft in 1960s For the supply of electric power

- ✓ **"Cody/Abeles"** employed **Si-Ge alloys** for Radio-isotope(Pu^{239}) TE generator in NASA's deep space probes (1960s).
  Apollo/Pioneer/Viking/Voyager/Galileo...
  Pu^{239}(→alpha) has a half-life time of 24×10^3 years.
- ✓ Their Si-Ge alloy system is **still working over 50years at 1000K** after the launch of space crafts in 1960s.



B. Abeles(left) and GC. Cody(right) in 1972

Cody/Abeles started to carefully measure **κ_L** of **Ge-Si alloys at 1,000 K** by eliminating the effects of thermal radiation and other sources of errors.

PHYSICAL REVIEW VOLUME 125, NUMBER 1 JANUARY 1, 1962

Thermal Conductivity of Ge-Si Alloys at High Temperatures*

B. ABELES, D. S. BEERS, G. D. CODY AND J. P. DISMUKES
RCA Laboratories, Princeton, New Jersey
(Received August 16, 1961)

The thermal conductivity of several Ge-Si alloys was determined in the temperature range 300° to 1200° K. A strikingly large decrease in the lattice thermal conductivity in the entire temperature range was found upon alloying. The temperature dependence and magnitude of the thermal conductivity can be obtained from current theory if it is modified to permit the dependence of anharmonic scattering on alloy composition. Justification for this dependence is given in terms of second order processes involving simultaneous two-phonon point defect scattering and three-phonon anharmonic scattering. The low-thermal conductivity, the high-thermal stability, and the low mass of the Ge-Si alloys makes these materials very useful for high-temperature thermoelectric power generation. A couple made up of heavily doped *n*- and *p*-type Ge-Si alloys, operated over a temperature range 300°–1140°K, had an energy conversion efficiency of 10%.

2. K_L involves rich information on dynamic properties of materials

Kinematic formula for κ_L under relaxation time approx.

$$\kappa_{\rm ph}(T) = \frac{1}{3}\sum_{\mu}\int_0^{\omega_{c\mu}} \hbar\omega_\mu \frac{\partial n_{\rm B}}{\partial T} v_\mu^2 \tau_\mu(T,\omega) D(\omega_\mu) d\omega_\mu,$$

Basic assumptions:

- ✓ This formula is valid under $\omega_{ph}\tau_{ph} > 1$ since the view of phonon modes are lost at $\omega_{ph}\tau_{ph} < 1$, where we can't identify heat-carrying phonons as vibrational states.
- ✓ It needs to propagate more than its wavelength λ, where the perturbation theory is applicable;

$$\ell_{ph} > \lambda$$

Another important remarks

- ✓ $1/\tau_{ph}(q)$ is additive from "Mathienssen rule":

  $$1/\tau_{ph}(q) = 1/\tau_R(q) + 1/\tau_{An}(q) + 1/\tau_{e\text{-}p}(q) + \ldots\ldots$$

- ✓ v_g is the group velocity of heat-carrying acoustic phonons. The phase velocity $v=\omega/k$ does not correspond to any physical observable.
- ✓ Only the group velocity $v_g=d\omega/dk$ is meaningful. So, the zone boundary acoustic phonons don't carry heat.

See, e.g.,
P Carruthers :Theory of thermal conductivities of solids at low temperatures, *Rev. Mod. Phys.(1961).*
RJ Hardy, : Energy flux operators for a lattice Phys. Rev. (1963)

Ordinary disordered systems

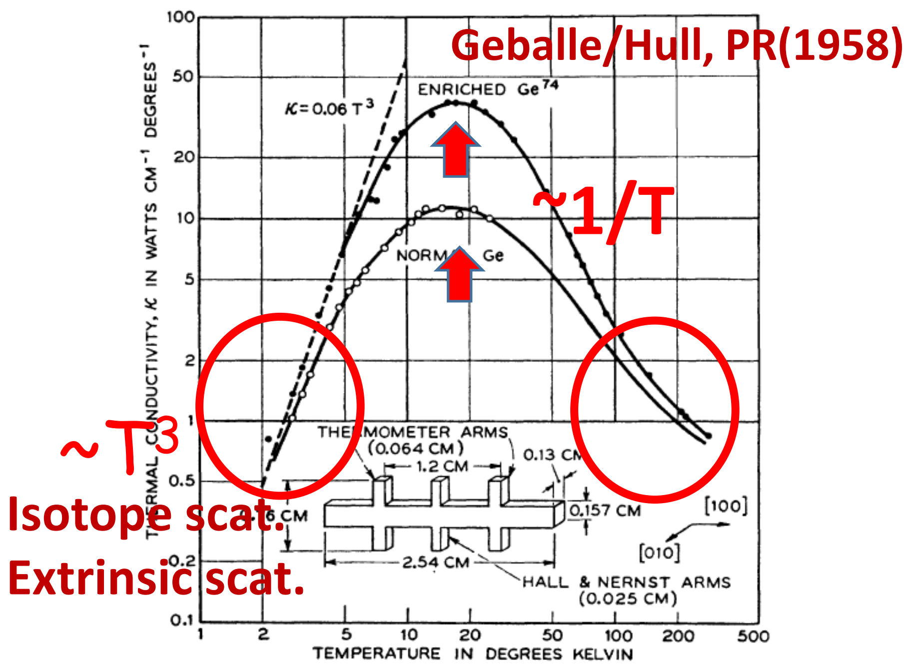


FIG. 2. Isotope effect on thermal conduction in germanium ... e how much higher the peak conductivity ... ure (96% Ge^{73}) sample. The boundary ... good agreement with the Casimir theory (Sec. VII) for the pure sample, but does not approach T^3 variation in the normal sample even at the lowest temperatures attained.

Ge with Isotope

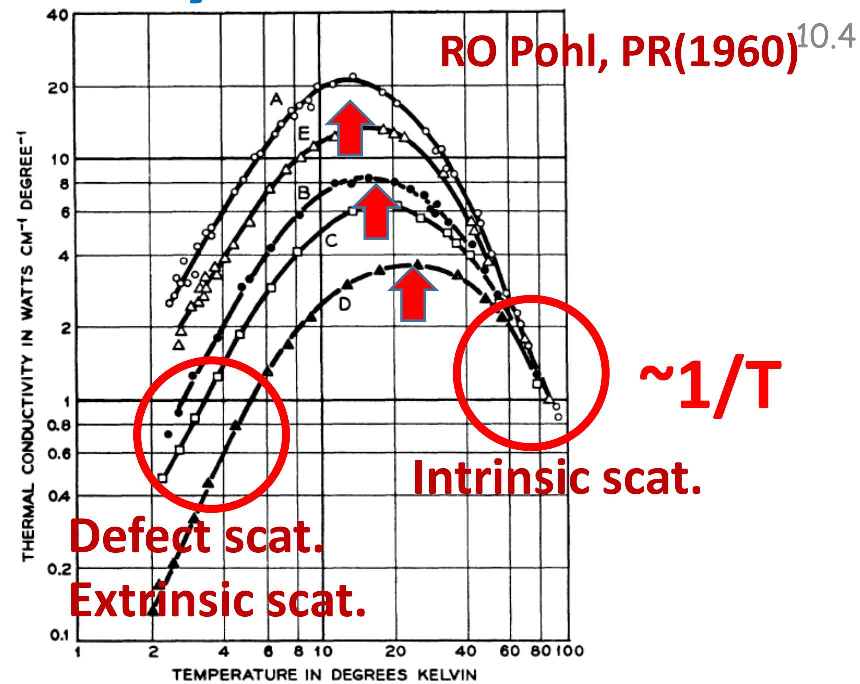


FIG. 4. ... by success... ment for e... are 6.7×7... n_F=7.1×... cm^{-3}; E, p...

Irradiation damaged LiF:
Li-ion are missing, percolated.

- ✓ What do peaks mean? **Periodic system has no localized states (Bloch theorem)**
- ✓ Heat-carrying phonons are mostly at 20Kx3.84(Wien's law)=2THz, λ=25A **in the middle of Brillouin zone, not at** the zone boundary phonons.
- ✓ v_g are not much changed in isotope systems, while irradiated ones change **DOS/v_g.**
- ✓ Why do κ_{ph} *decrease with increasing T as 1/T?* **3 phonon process. The deviation from 1/T is due to 4 phonon process.**

3. The phonon-glass electron-crystal concept

Contradicted concept “矛盾”

“κ_L of efficient TE materials should be very low”

The phonon-glass electron-crystal concept (G. A. Slack, 1995)

- ✓ It needs caution to use the term “glass-like”.
- ✓ Don’t mix glasses up with ordinary disorder materials such as Si-Ge mixed crystal.

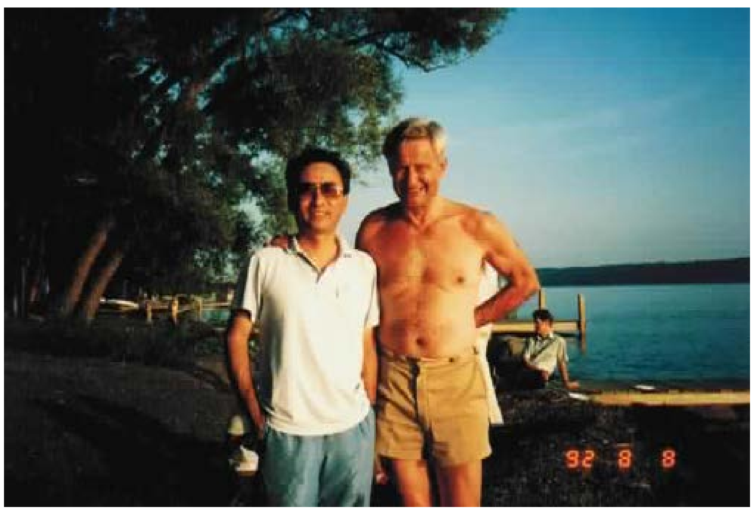
K_L of silica glass/α-quartz

●: Eucken,1911*

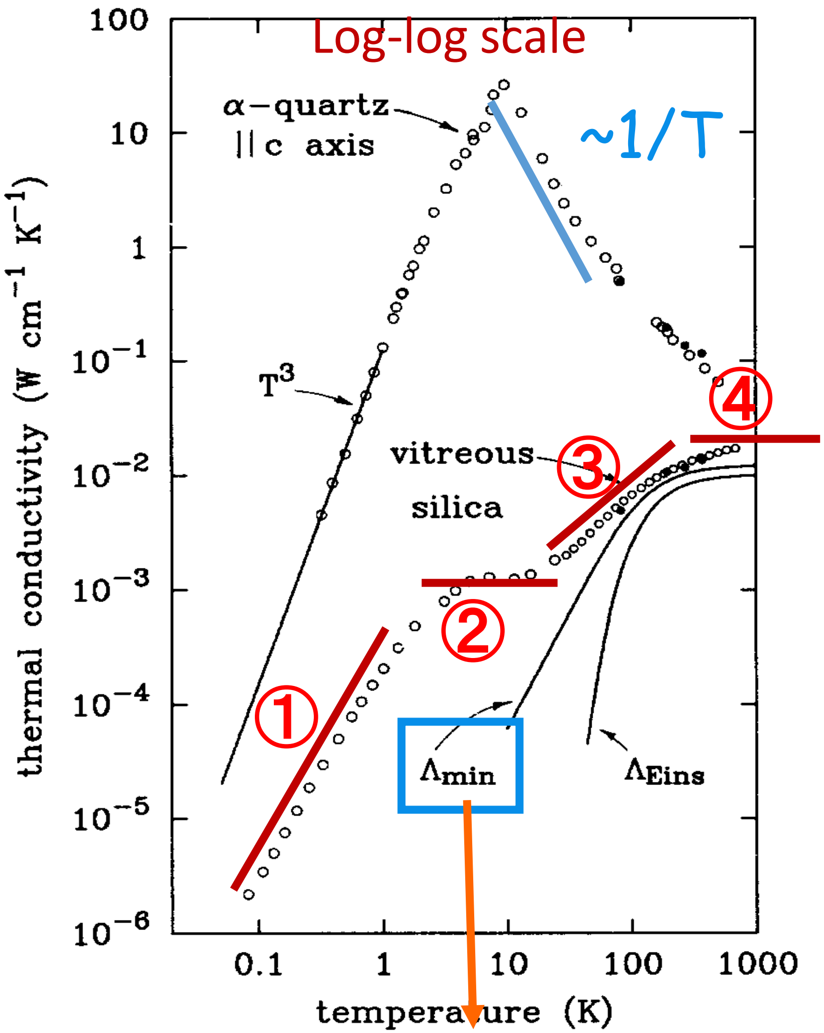
Nernst's coworker

○: Zeller/Pohl, 1971

*A. Einstein propose a model to explain these data.
Ann. Phys. Vol.35, 679(1911).



With R. O. Pohl
at Ithaca, 1992



The minimum K_{min} by Cahill/Pohl (1987)

“4 characteristic regions in κ_L of glasses”

① T < 2K, $\kappa_L \propto T^2$
② T～10K, Plateau region, $\kappa_L \propto T^0$
③ T=10 K～100 K, T-linear rise, $\kappa_L \propto T^1$
④ *T* >100 K, **Saturated** regime, $\kappa_L \propto T^0$

①-④ regions are independent of kinds of glasses, **“universal”**

- ✓ One of unsolved problems **remained** in condensed matter physics over 50 years.
- ✓ Difficulty is due to their complicated atomic-structure depending on kinds of glasses !!
- ✓ This has lead for a long time hand-waiving arguments on underlying mechanism, except ①.

4. What is the minimum K_{min}?

Slack(1979) & Cahill/Pohl(1989)

In glasses, κ_L "monotonically" increases with T, indicating the existence of the upper minimum of κ_L independent of T.

✓ The minimum K_{min} (Cahill/Pohl) has been cited in many literatures. The citation # is over 1,200 times , mostly without understanding its physical implications.

The Integral form of K_L from the kinetic equation:

$$\kappa_{\text{ph}}(T) = \frac{1}{3}\sum_{\mu}\int_0^{\omega_{c\mu}} \hbar\omega_\mu \frac{\partial n_{\text{B}}}{\partial T} v_\mu^2 \tau_\mu(T,\omega) D(\omega_\mu) d\omega_\mu,$$

V_μ : group velocity

Here, they put as $\omega_{ph}\tau_i = \pi$, the same as the Ioffe-Regel criterion.

Then, the formula for κ_{min} becomes

The number density of atoms

$$\kappa_{min}^{CP} = \frac{k_B v_s (6\pi^2 n)^{2/3}}{4\pi} I(x_D) \Rightarrow I(x_D) = \frac{2}{x_D^2}\int_0^{x_D} \frac{x^3 e^x dx}{(e^x - 1)^2}.$$

Here $x = \hbar\omega/k_B T$ and $x_D = \hbar\omega_D/k_B T$

The transport integral becomes $I(x_D)=1$ at high temperatures ($x_D<<1$).
Thus, the high temperature κ_{min} yields the simple formula

$$\kappa_{min} = \frac{k_B v_s (6\pi^2 n)2/3}{4\pi} \sim 0.36 \frac{k_B v_s}{a^2}$$

*G.A. Slack(1979) is the 1st to derive this formula κ_{min}.
The difference with Cahill/Pohl's (1989) is only factor 2.
This is due to the Ioffe-Regel condition employed:

$$\omega_{ph}\tau_i = \pi \text{ or } 2\pi.$$

The minimum K_{min} is based on the unreliable postulate:

"Debye" phonons are strongly localized (SL) with the localization length ℓ of the order of wavelength λ under Ioffe-Regel criterion.

"$\omega_{ph}\tau_i = \pi$" or "$q\ell = \pi$"

Is this postulate acceptable??

No, I will explain it in the next slides!

Some problems in the minimum κ_{min}

1. $\omega_{ph}\tau_i = \pi$ holds for all of acoustic modes in glasses. Single mechanism for whole temperature.
2. **This only asserts:** the minimum mean free-path **ℓ at high-T limit** becomes of the order of the inter-atomic spacing a_0.**
3. These SL modes **don't contribute to heat transfer** without being assisted by delocalized **(extended)** acoustic phonons.
4. This is because localized modes don't belong to the same eigenfrequency ω_1. : **Level repulsion from random matrix theory!!**
5. Furthermore, κ_{min} don't recover the data for **high density** systems.

**Ioffe and Regel (1960) argued that ℓ of electrons can never become shorter than the interatomic spacing a_0, since the concept of carrier velocity is lost at that point. Similar arguments were later expressed by Mott (1972) for electrical conductivity σ_{min} . This notion of a minimum metallic conductivity σ_{min} compatible with a minimum mean free path $\ell_{min} = a_0$ became known as the Ioffe-Regel-Mott (IRM) limit.

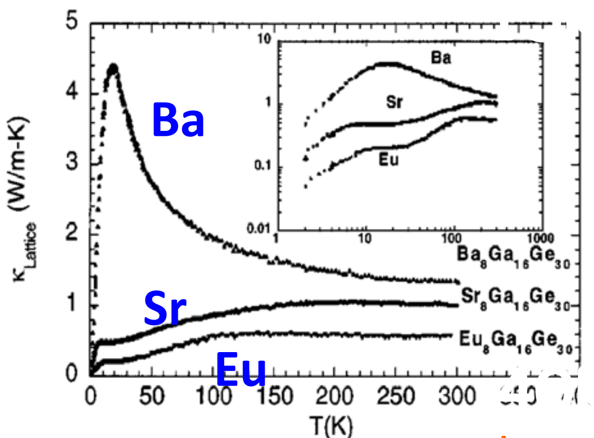
***See, Off-center rattling triggers high temperature κ_L in thermoelectric clathrates: Non-perturbative approach*, Q. Xi, et al., *Physical Review* B 97, 224308 (2018).**

5. Clathrates emerge glass-like K_L though crystalline

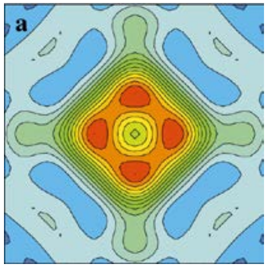
Glasses/Amorphous materials exhibit <u>very low</u> κ_L owing to the lack of lattice periodicity, but these also give <u>low σ_e</u>. However, clathrates are crystalline with lattice periodcity with high <u>σ_e</u>.

ZT: SGG=0.3~0.6, BGS=0.6, n-BGG= 0.8~1.35

Linear scale



Log-log



$\Delta r \sim 0.4 Å$

Sales et al. 2001, PRB (Type-I $\underline{R}_8Ga_{16}Ge_{30}$: Guest atoms: <u>R</u>=Ba, Sr, Eu)

Clathrates are composed of cages and guest ions

$Ba_8Ge_{16}Sn_{30}$

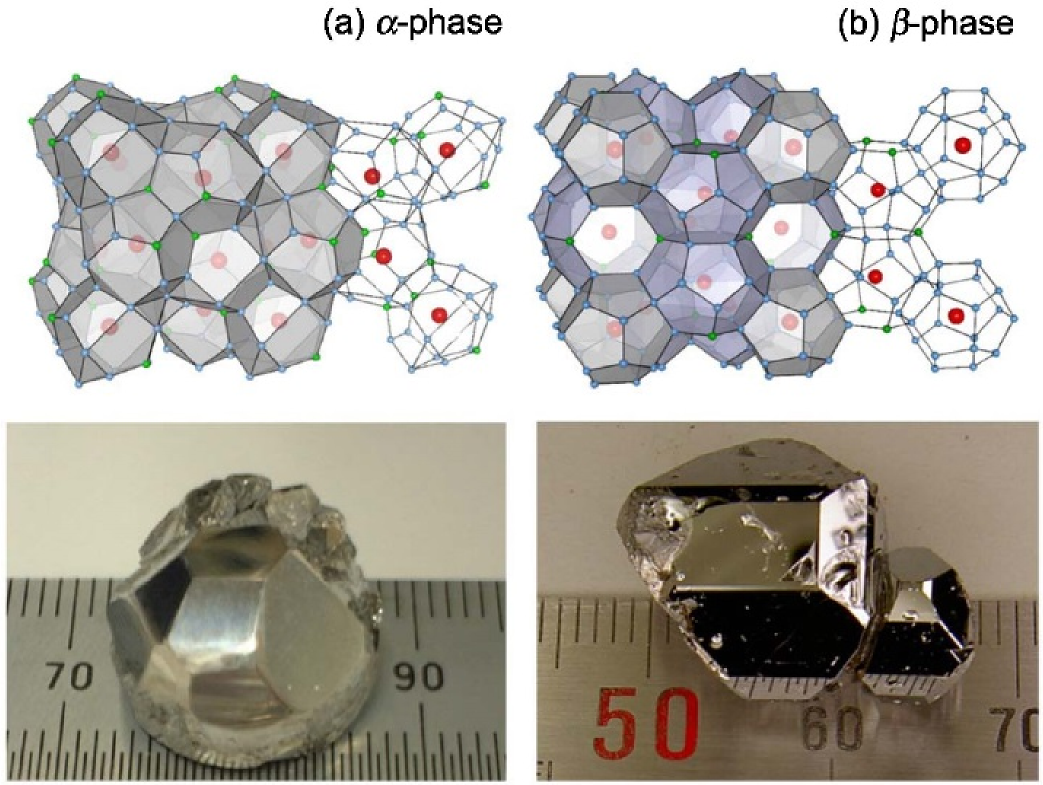


FIG. 1. (Color online) Crystal structures and corresponding as-grown single crystals of (a) α-$Ba_8Ga_{16}Sn_{30}$ and (b) β-$Ba_8Ga_{16}Sn_{30}$.

Phonon-glass electron-crystal thermoelectric clathrates: Experiments and Theory,
T. Takabatake, K. Suekuni, T. Nakayama, and K. Kaneshita,
Reviews of Modern Physics, vol. 86, 669-716 (2014)

The point for clathrates showing glass-like K_L:

Guests take "off-center" positions with random orientations.
While, cage-network keeps lattice periodicity!!

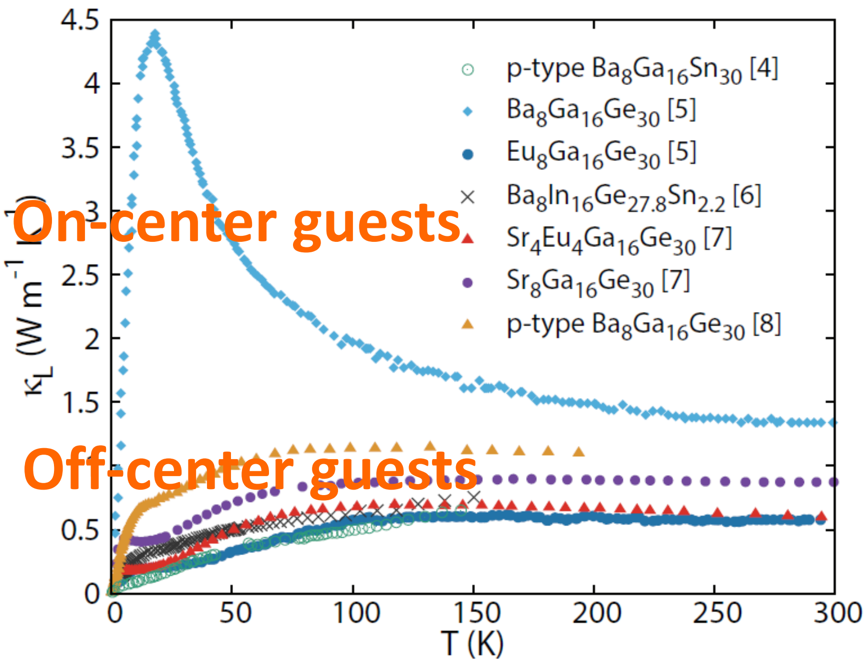


FIG. 1. (Color online) Temperature dependence of κ_L plotted in linear scale for various off-center type-I clathrates[4–8] and "on-center" type-I $Ba_8Ga_{16}Ge_{30}$[5]. The parentheses [...] in inset give reference numbers.

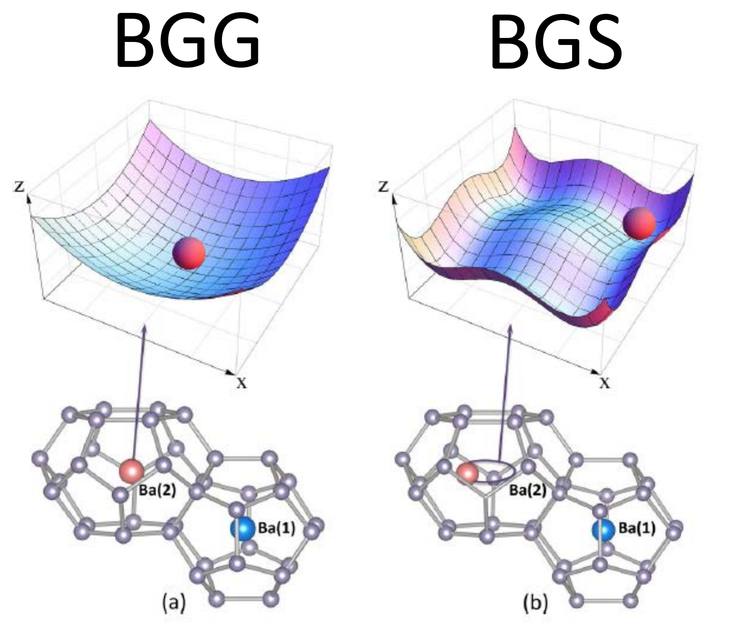


Figure taken from Q. Xi et al., PRB, vol. 97, 224308 (2018)

Characteristics of κ_L of off-center clathrates

- ✓ κ_L are the same as those of glasses, in magnitude and T-dependence!!

- ✓ The underlying mechanism should be the same as that of glasses, since both possess nanoscale open-spaces (voids$\approx a$).

- ✓ Clathrates have clear-cut atomic structures. Thus, those are tractable compared with glasses, which enables us elucidate theoretically the underlying mechanism of glass-like K_L.

6. Theory of glass-like κ_L in clathrates

The Mathiessen rule

$$1/\tau = 1/\tau_1 + 1/\tau_2 + 1/\tau_3 + 1/\tau_4 + \ldots$$

- ✓ ① *Tunneling States,* $\tau_3 \propto \coth(\omega/T)/\omega^2$: $\kappa_L \propto T^2$
  Kaneshita&TN, EPL 86, 56004(2009)
- ✓ ② *Anderson weak Localization: Onset of the plateau:* $\kappa_L \propto T^0$
  Y. Liu et al., PRB 93, 214305(2016)
- ✓ ③ *Hopping of Strongly Localized modes,* $\tau_4 \propto \omega^2/T$: $\kappa_L \propto T$
  Q. Xi et al., PRB 96, 064306(2017)
- ✓ ④ *Rattling regime: Breakdown of Perturb. Theory:* $\kappa_L \propto T^0$
  Q. Xi et al., PRB 97, 4308(2018)

τ_n can be obtained by the perturbation theory **at T < 100K** ①②③. This is because we can identify **excited modes as vibrational states.** While, **in the saturated-regime ④ at T>100K**, guest atoms execute **true rattling motion,** which we can't identify as vibrational modes.

Let's explain the theory on ③ and ④ in the next.

③ $K_L \propto T$ at 10~100 K: Hopping region of SL modes

Hopping processes explain linear rise in temperature of thermal conductivity in TE clathrates with off-center guest atoms, Q. Xi, et. al. , PRB **96**, 064306 (2017)

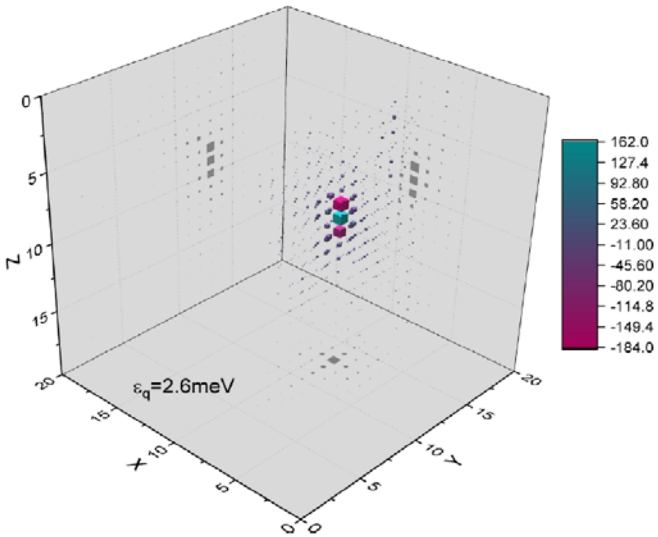


FIG. 3. The mode pattern of SL modes belonging to the eigenenergy $\varepsilon_q = 2.6$ meV. Both the color scale and the cubic size indicate the strength of amplitudes at each site. The mode pattern is obtained from the system size $20 \times 20 \times 20$ under a fixed boundary condition.

$$P(\varepsilon_q) = \frac{\left(\sum_{\ell=1}^{N} |\varphi_\ell(\varepsilon_q)|^2\right)^2}{N \sum_{\ell=1}^{N} |\varphi_\ell(\varepsilon_q)|^4},$$

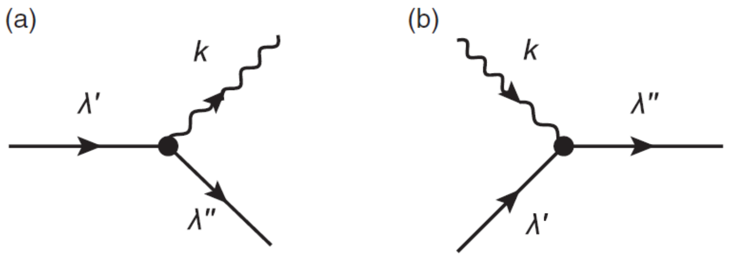
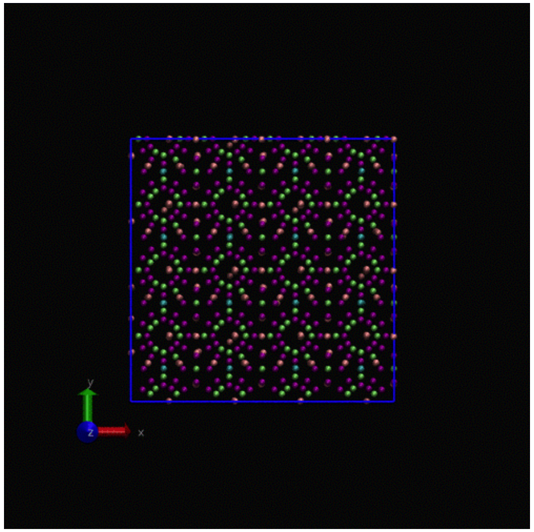


FIG. 5. The diagrams showing the hopping process for SL modes arising from anharmonic interaction between SL modes and extended modes: (a) SL → extended + SL and (b) extended + SL → SL. The solid lines denote the SL mode and the wavy lines the extended mode.

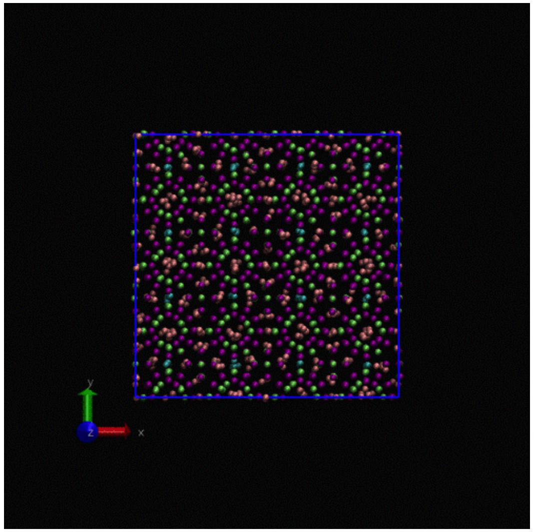
If all modes are localized, there is no heat transport. It needs to be assisted by extended acoustic modes via anharmonic interaction between these. Note that localized modes never take the same eigen-frequency.

④ Saturated-regime at T>100K

MD movie of rattling motion of guests at high temperature by Z. Zhang (Q. Xi et al., PRB 97, 224308, 2018)



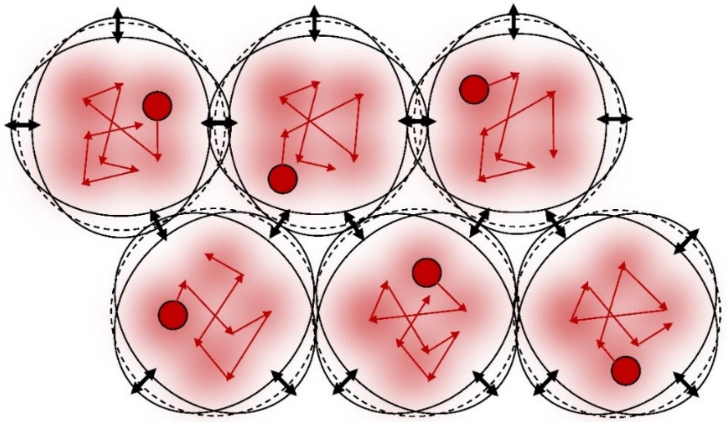
10K



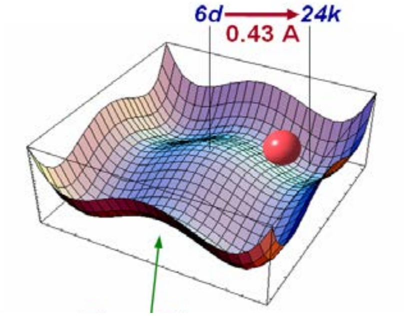
400K

- ✓ The perturbation theory is **<u>inapplicable</u>** for ④ since $\omega_{ph}\tau_i < 1$ or $\Delta u \approx a$, indicating **<u>non-vibrational</u>** states of rattlers, i.e., we can't describe those as vibrational states.
  This means that Mathienssen rule breaks down at T>100K!!
- ✓ Off-center rattling triggers heat transfer via deformation of cage-shell of the volume Ω.
- ✓ **The need of <u>non-perturbative</u> treatment.**

T+ΔT



T



Purely theoretical approach is possible for T>100K by taking into account the situation: Heat is carried via the cascade transfer of cage vibrations created by true rattling motion of guest atoms.

***Off-center rattling triggers high temperature κ_L in thermoelectric clathrates: Non-perturbative approach*, Q. Xi, et al., *Physical Review* B 97, 224308 (2018).**

Expression of heat current *J*(t)

$$J(t) = \frac{1}{V}\frac{d}{dt}\left[\sum_{\ell} r_{\ell}(t)\epsilon_{\ell}(t)\right] = \frac{1}{V}\sum_{i,j\in i}^{N}[x_i(t) - X_j(t)]F_{ij}\cdot\dot{x}_i(t).$$

By defining as

$$\sum_{j\in i} F_{ij}\cdot\dot{x}_i(t) = \dot{\varepsilon}_i.$$

The averaged heat current from a cage yields

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

Cage-shell emits energy into network cages via its surface vibration

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

Connection of velocity fields at r=R:

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

Then, we have

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

The definition of heat conductance $h_K(T)$

$$J(T+\Delta T) - J(T) = h(T)\Delta T \qquad h(T) = \partial_T J(T)$$

The result becomes

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

The form of κ_L in the rattling regime

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

Ω is the volume of cages, and the numerical factor γ takes a value of γ=4.2.

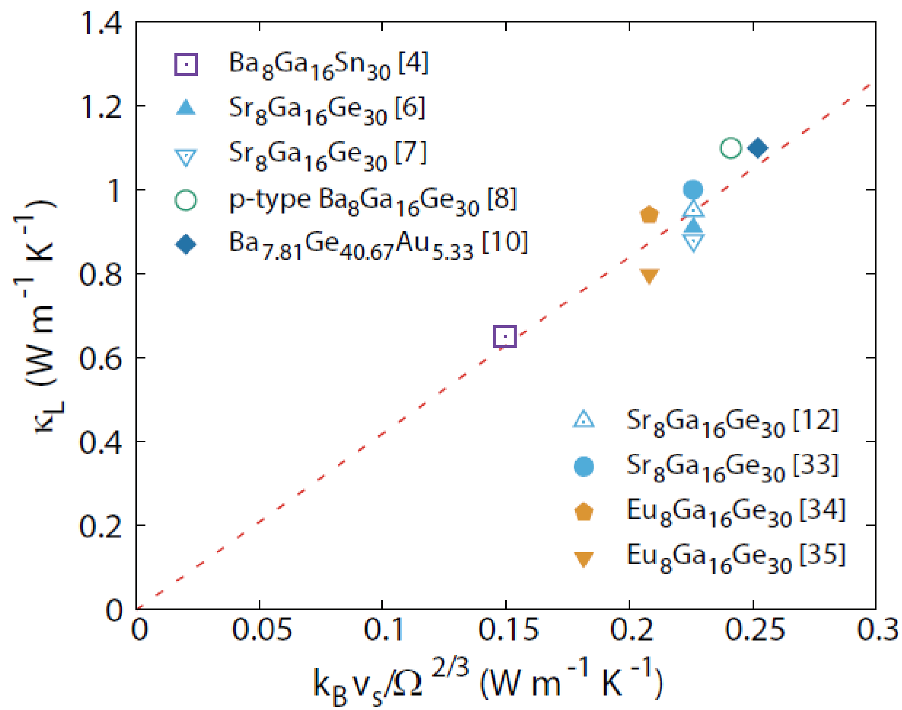


FIG. 2. (Color online) Observed κ_L for various off-center type-I clathrates as a function of $k_B v_s/\Omega^{2/3}$ [4,6–8,10,12,33–35]. Solid inverted-triangle on off-center Eu_8Ga_{16} ... Sn_{30} ... de-

*Off-center rattling triggers high temperature **κ_L** in thermoelectric clathrates: Non-perturbative approach*, Q. Xi, et al., *Physical Review* B 97, 224308 (2018).

give reference numbers.

Summary

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2. K_L involves rich information on dynamic properties of materials
3. The phonon-glass electron-crystal concept
4. The minimum K_L
5. Clathrates emerge glass-like K_L though crystalline
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