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The 4th OpenMX developer's meeting
2023/11/9

Material Design of Thermoelectric Materials through Experiments and Phonon Transport Calculations

Masanobu Miyata

Japan Advanced Institute of Science and Technology

M. Miyata and M. Koyano, Materials Research Express **9**, 5, 055901 (2022).
Masanobu Miyata, Journal of Applied Physics 130, 035104 (2021).

Contents

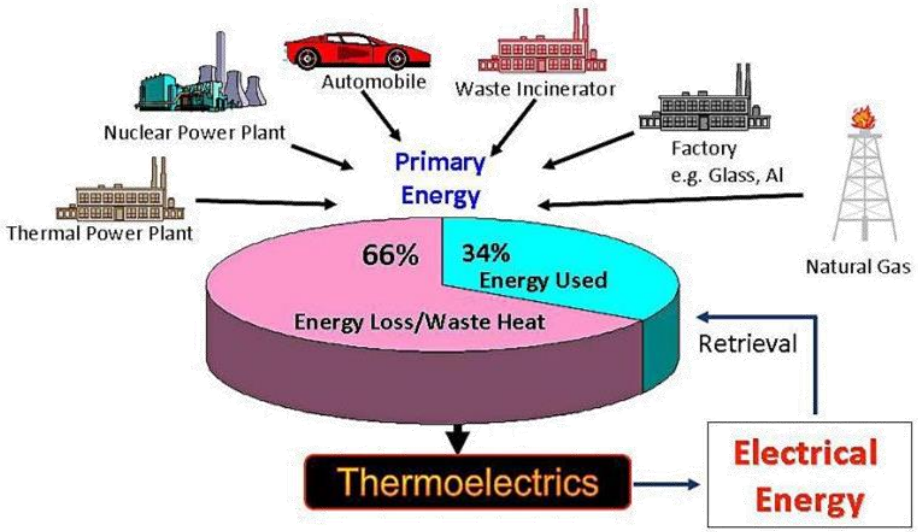
1. Introduction of thermoelectric conversion

2. Experimental and theoretical investigation of phonon transport properties for Ag-P compounds which shows low lattice thermal conductivity
   - Anisotropy bond of Ag-P cluster in AgP_2
   - 4^{th} order anharmonic phonons in Ag_3SnP_7

3. Summury

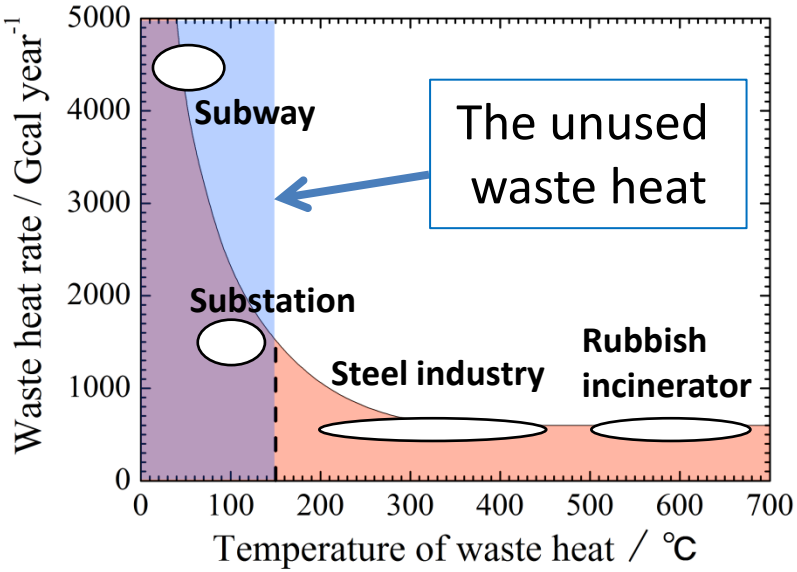
Energy problem

- The overview of industrial primary energy



Graphic: Oregon State University

The temperature profile of industrial waste heat

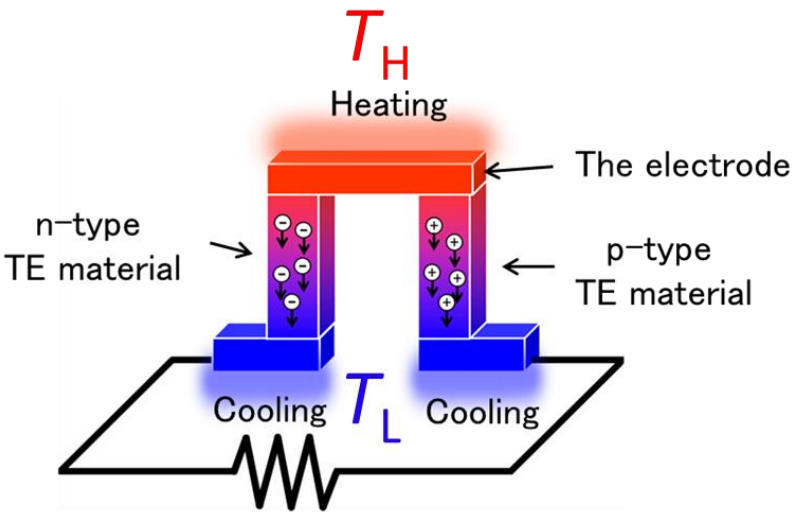


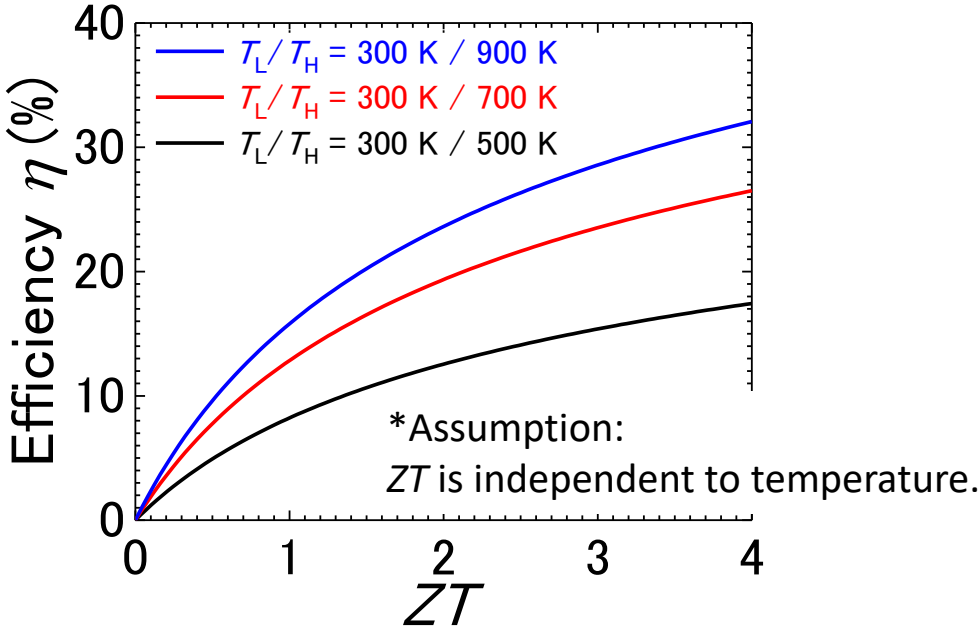
- The 1/3 of industrial primary energy is only used, meanwhile, that of **2/3** represents **a huge unused energy resource** available worldwide
- The waste heat below 150℃ accounts for a large percentage

Some technology that can regenerate that waste heat into available energy is necessary.

Thermoelectric conversion

- Thermoelectric (TE) effect enables a direct conversion from **thermal energy** into **electrical energy**





$$V = -S\Delta T$$

S : Seebeck coefficient
ΔT: Temperature difference
V : thermoelectromotive force

$$ZT = \frac{S^2\sigma}{\kappa_{el} + \kappa_{lat}} T$$

σ : Electrical conductivity
κ_{el} : Electron thermal conductivity
κ_{lat}: Lattice thermal conductivity
T : Absolute temperature

- The temperature deference of the module generates electromotive force by Seebeck effect
- We can evaluate the TE performance by using figure of merit *ZT*

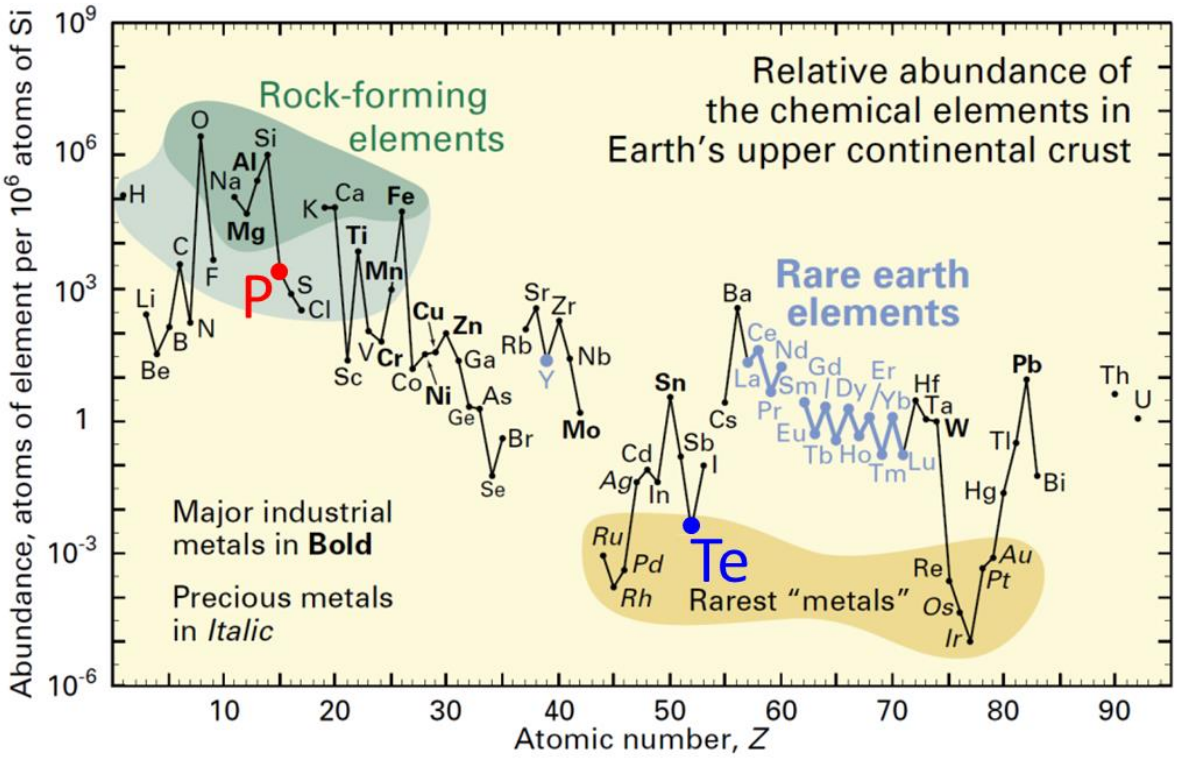
◆ **Conventional TE materials**

Bi_2Te_3, PbTe

☺ **High performance**

😢 **Te is rare**

Need to develop new thermoelectric materials to replace Te compounds



➢ Amount of Te: 38000 t ~ 8×10^9 modules: ~ 1 module / person

😢 **Too few amount of Tellurium**

Sulfide

Phosphide

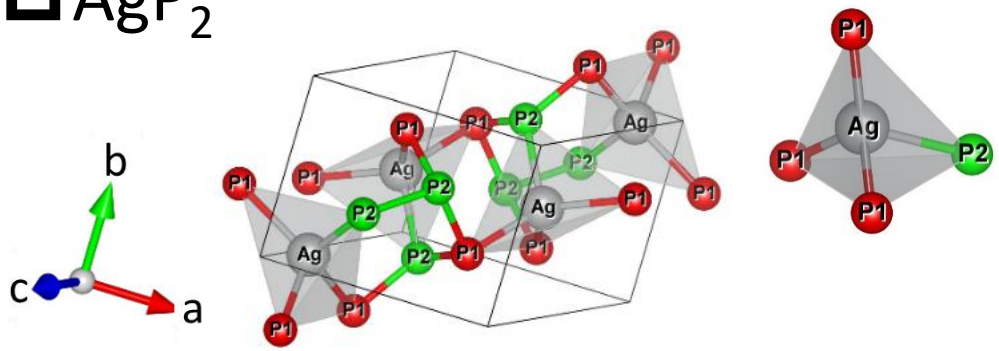
➢ Earth abundant elements in a crust.

➢ Lattice thermal conductivity tends to be comparative high due to including light mass element P phospher.

[1] G. B. Haxel *et al.*, *USGS Fact Sheet*, 087-02(2002).

Ag-P compounds which show low lattice thermal conductivity

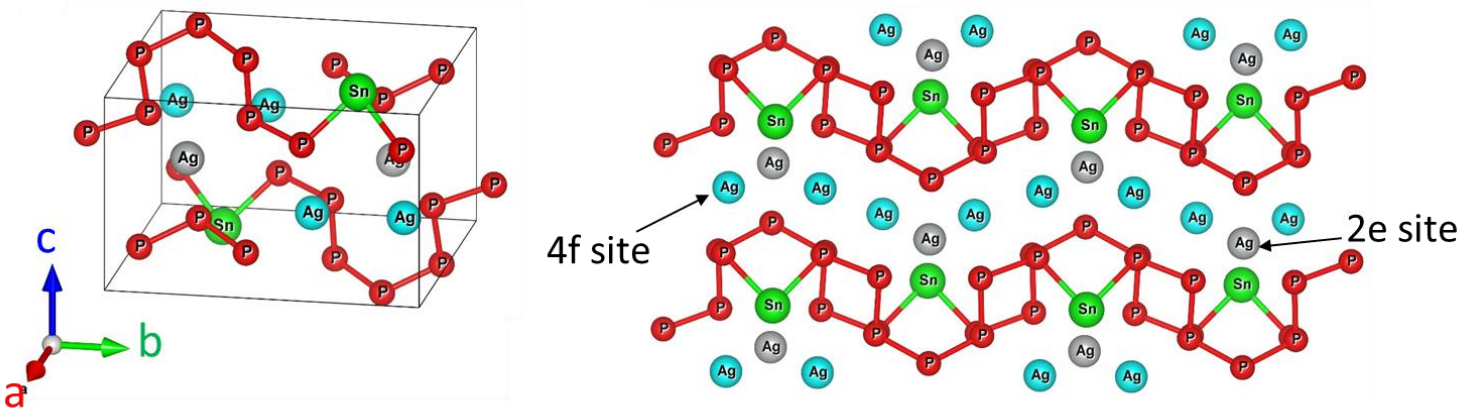
AgP_2



- Primitive cell of AgP_2 contains four Ag and eight P, and the Ag-P clusters whose P atoms locate around Ag, tetrahedrally.

*M. H. Moeller *et al.* Z. Anorg. Allg. Chem. **491**, 225 (1982).

Ag_3SnP_7



- The chain-structured phosphide Ag_3SnP_7 has P_7 chain structure extended to b-axis.

*M. M. Shatruk et al., Angew. Chem. Int. Ed. 39, 14, 2508(2000).

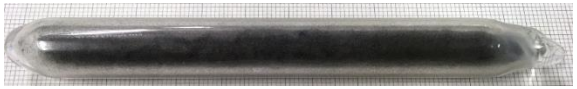
Electronic and phonon properties of the binary phosphide AgP_2

Experimental synthesis and transport properties of AgP_2

~~Melting method (600° C, 8h)~~

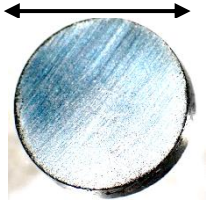
~~Unreacted P burns off and cannot be synthesized~~

Chemical vapor transport method
(600° C, 8hours, iodine added)
ΔT ~ 2 K (≈ temperature variation in furnace)

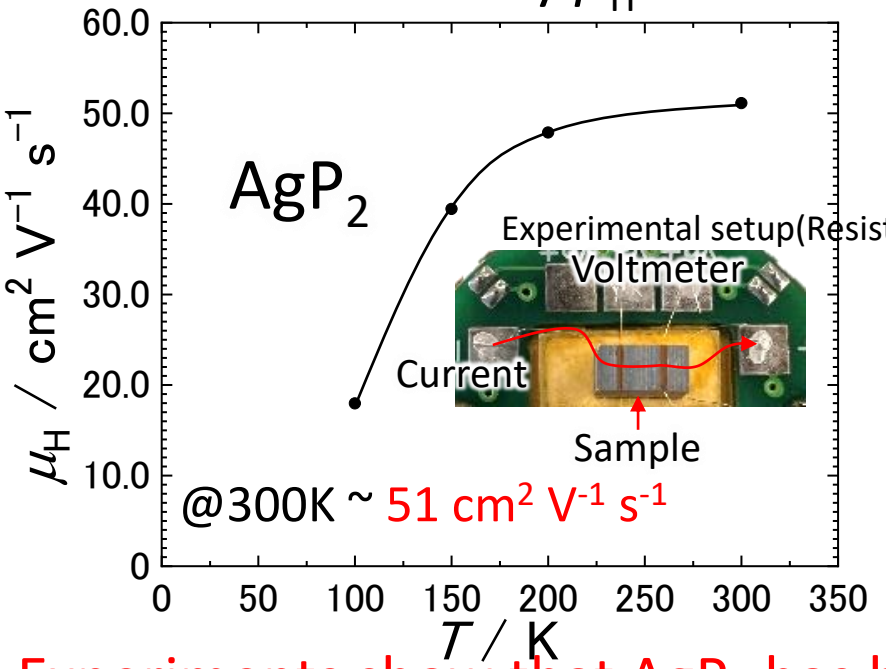


Hot press

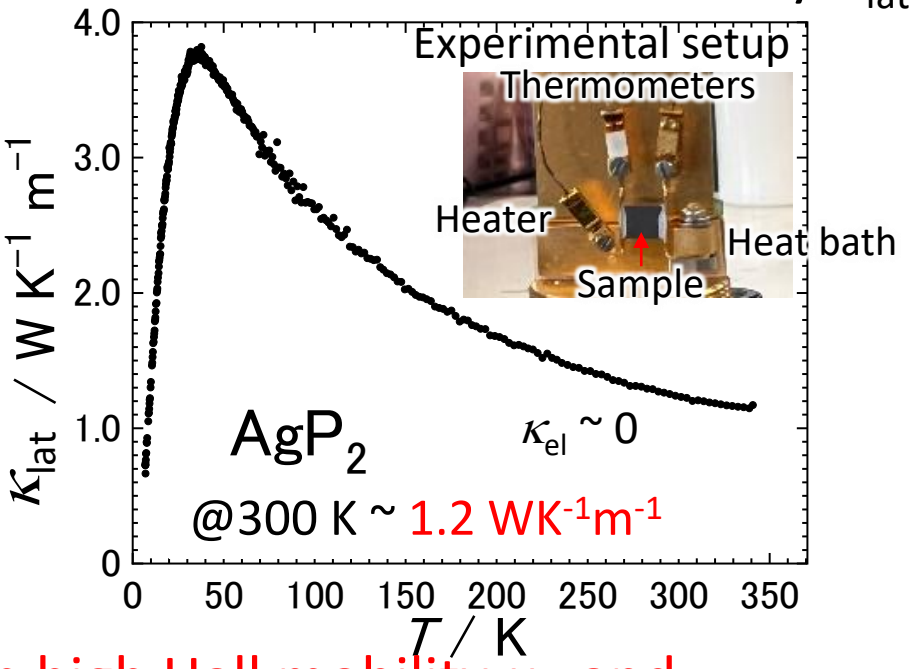
10 mm



Hall mobility μ_H



Lattice thermal conductivity κ_{lat}



Experiments show that AgP_2 has both high Hall mobility μ_H and low lattice thermal conductivity κ_{lat}

Condition of DFT calculation

Electronic structure and transport calculations

OpenMX

* T. Ozaki, Phys. Rev. **B 67**, 155108 (2003).
* M. Miyata, Taisuke Ozaki *et al.*, Journal of Electronic Materials, 47(6) 3254-3259 (2018)

- Variable cell relaxation
- *E-k* relation, density of states

- Exchange correlation potential: GGA-PBE
- Cutoff energy: 500 Ryd
- Max Force: 1.0×10^{-6} Hartree $Bohr^{-1}$

BoltzTraP

*G. K. H. Madsen and D. J. S. Singh, Comput. Phys. Commun. **175**, 67 (2006).

- Electron transport properties

- Number of k-points used for transport calculation: approx. 50000

Phonon Transport Calculations

ALAMODE

*T. Tadano *et al.* J. Phys.: Condens. Matter **26**, 225402 (2014).

- Phonon dispersion
- Density of states
- Lifetime of phonons
- Mean square displacement (MSD)
- Mode Grüneisen Parameters γ
- Lattice thermal conductivity

<Interatomic force constant>

- Harmonic term(2^{nd} order): Displacement = 0.04 Å
- Anharmonic term (3rd order): Displacement = 0.08 Å

- Supercell size
  $2 \times 2 \times 2$ primitive cell

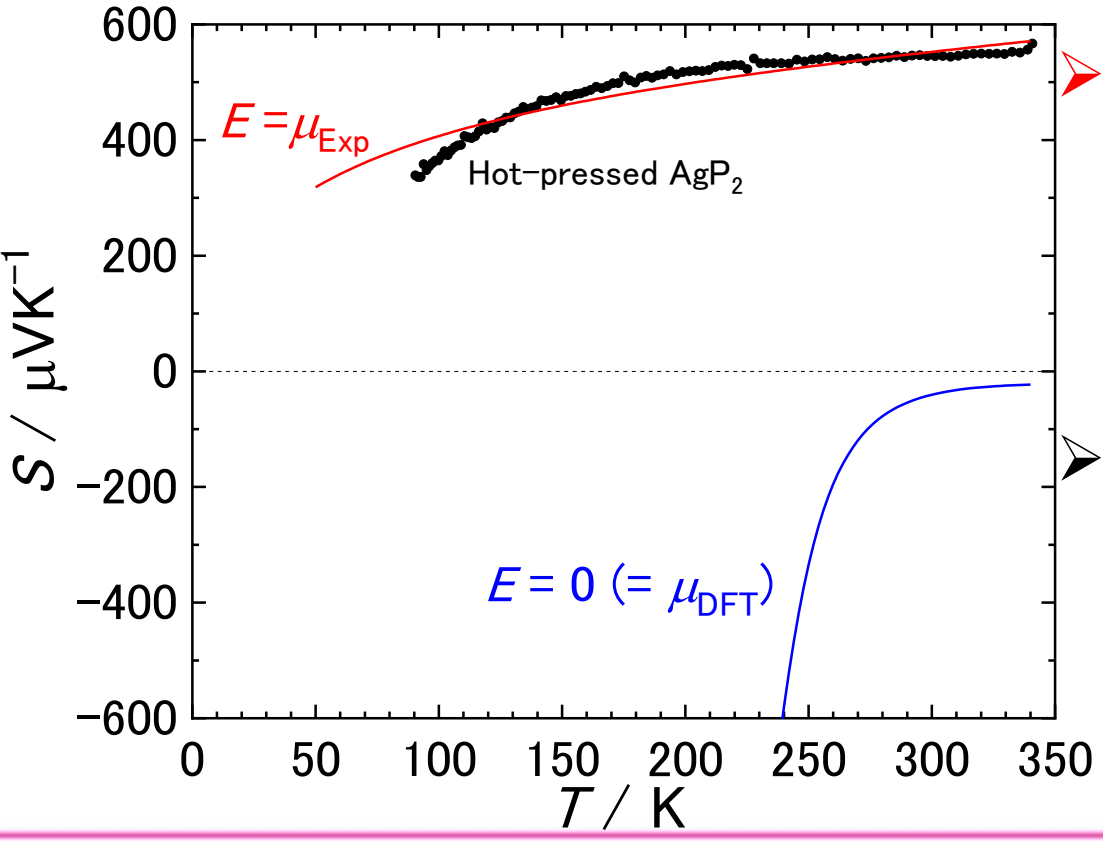
Determination of experimental chemical potential μ_{Exp}

＜Seebeck coeffieint＞

$$S = -\frac{1}{|e|T}\frac{K_1}{K_0} \qquad K_n = \int \zeta(\varepsilon,T)(\varepsilon-\mu)^n\left(-\frac{\mathrm{d}f(\varepsilon,T)}{\mathrm{d}\varepsilon}\right)\mathrm{d}\varepsilon,$$

$f(\varepsilon,T)$: Fermi-Dirac distribution function
μ : Chemical potential
$\zeta(\varepsilon,T)$: Spectrum conductivity

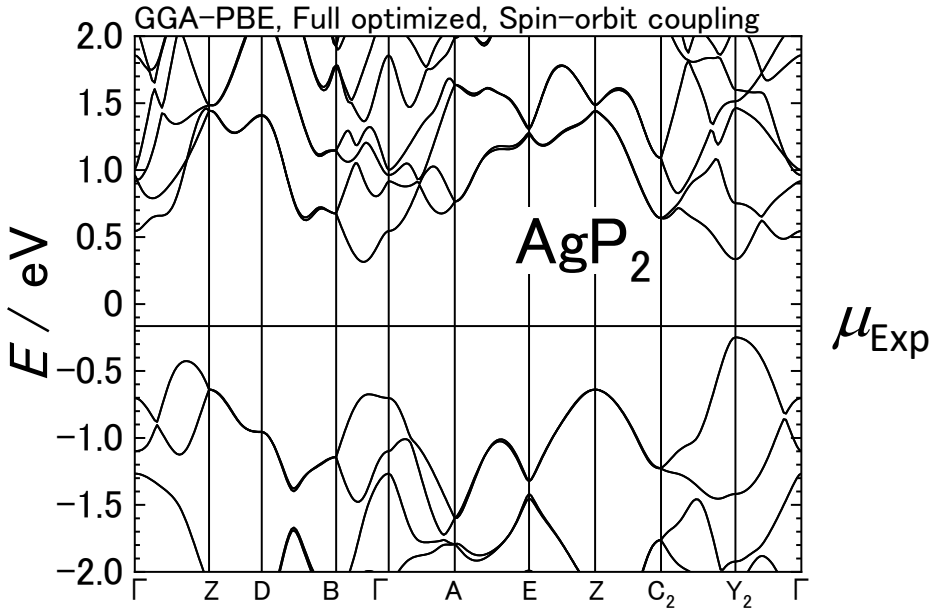
$\zeta(\varepsilon,T) \propto D(\varepsilon)\{v(\varepsilon)\}^2\tau(\varepsilon,T)$
$D(\varepsilon)$: Density of states
$v(\varepsilon)$: Group velocity of electrons



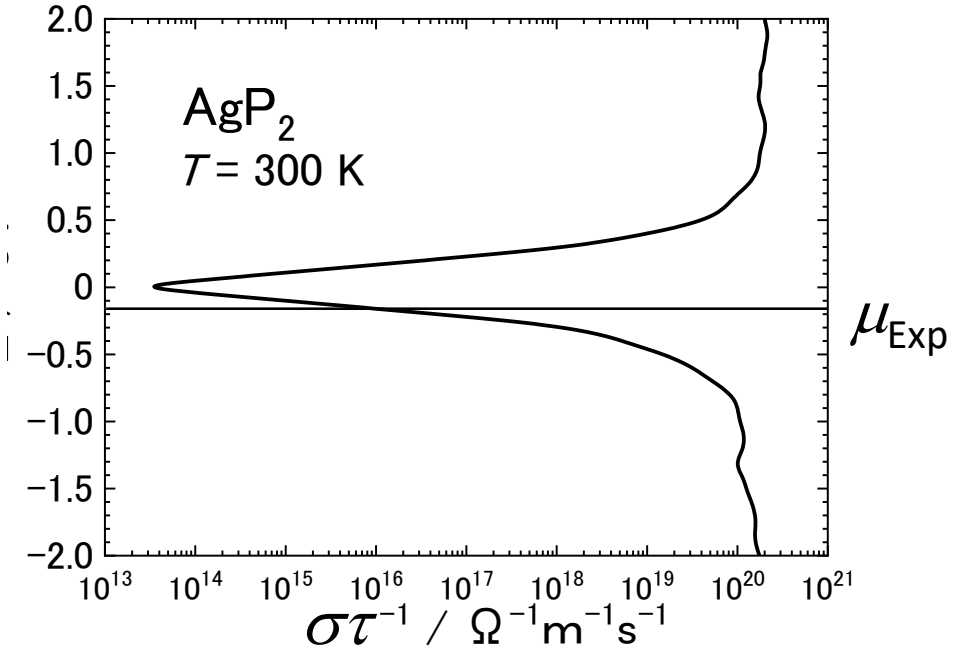
- We determined the chemical potential μ_{Exp} by comparison of experimental and theoretical *S*-*T* curves.
- The existence of excess holes in experimental sample of AgP_2 were clarified.

Electronic structure of AgP_2

E-k relation



Electrical conductivity $\sigma\tau^{-1}$



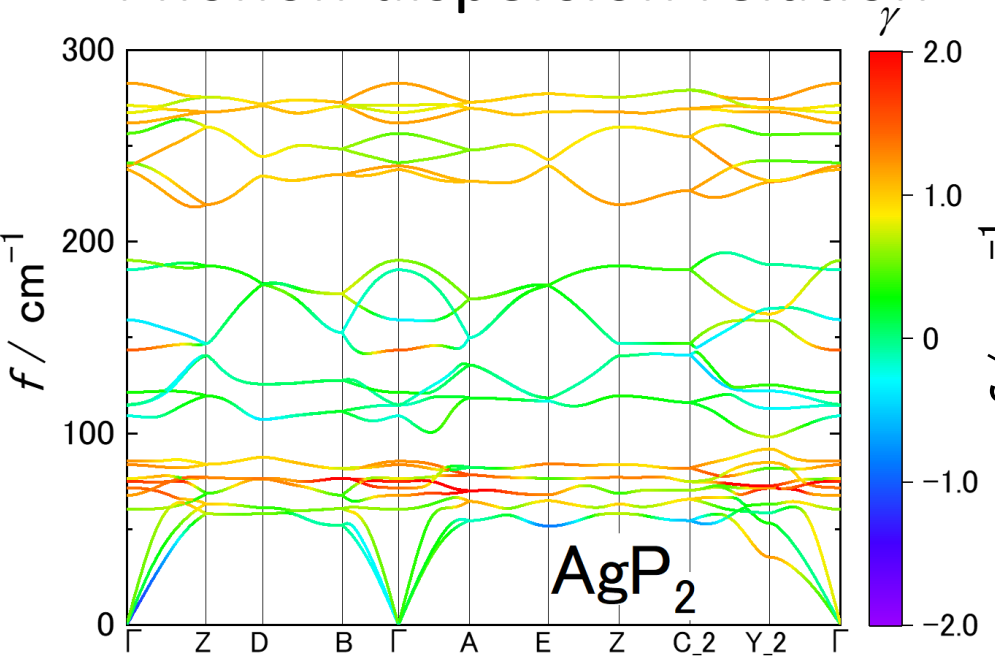
- The chemical potential μ_{Exp} is 300 K locates in the forbidden band.
  → Intrinsic semiconductor

- $\sigma\tau^{-1}$ at μ_{Exp} is 1.22×10^{16} Ω^{-1} m^{-1} s^{-1} .
  We estimated the relaxation time of electron for AgP_2.
  Relaxation time τ = 3.3 fs

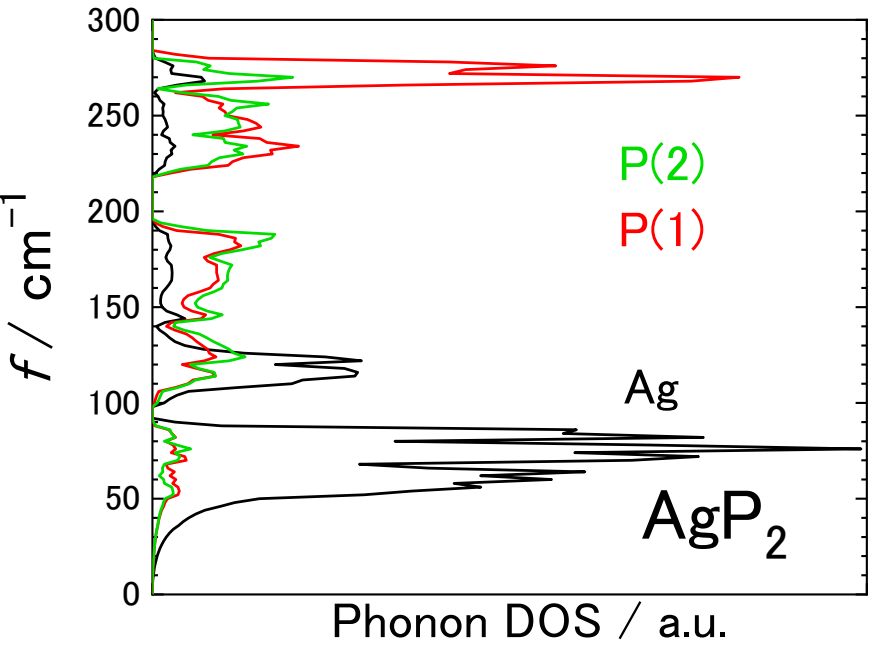
Relatively long carrier relaxation time τ are the origin of large μ_H

Phonon properties of AgP_2

Phonon dispersion relation



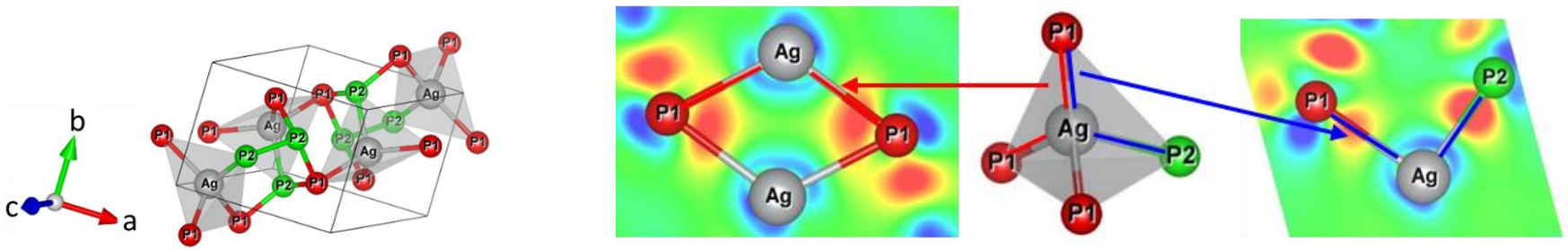
Phonon DOS



- The optical phonon modes which show large mode Grüneisen parameter γ are generated around 60 cm^{-1}.

- Ag phonon modes are dominant less than 100 cm^{-1}.
  → This result indicates that the large anharmonic phonons around 60 cm^{-1} are originated from Ag.

Analysis of bonding states using difference electron density

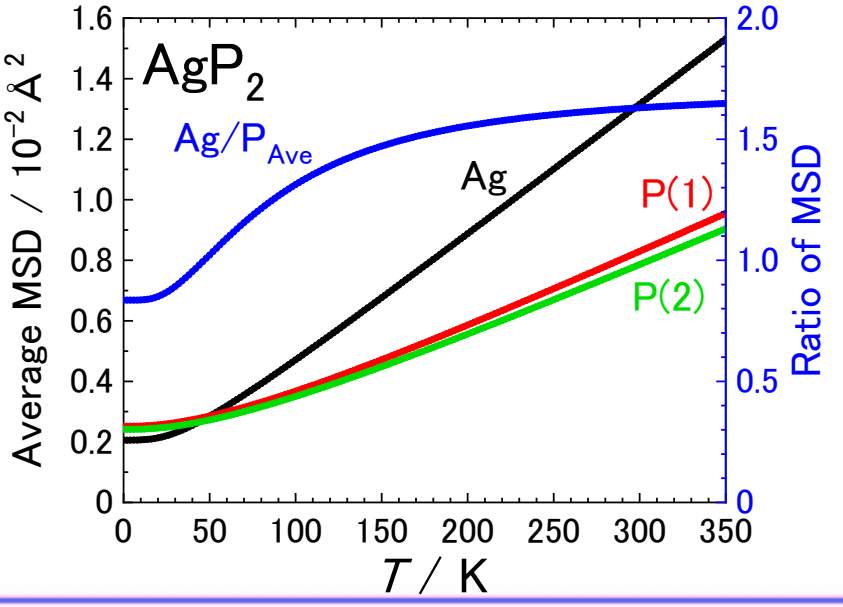


- From the point of view of the geometry and difference electron density, the anisotropy of Ag-P cluster in AgP_2 are large.

The mean square displacement (MSD) for each atom

- In AgP_2 , the MSD for Ag atoms is about 1.6-1.7 times larger than those of P atoms, indicating the scattering cross section for Ag with phonon-phonon process is large.

We compared AgP_2 and related materials that of phonon properties.

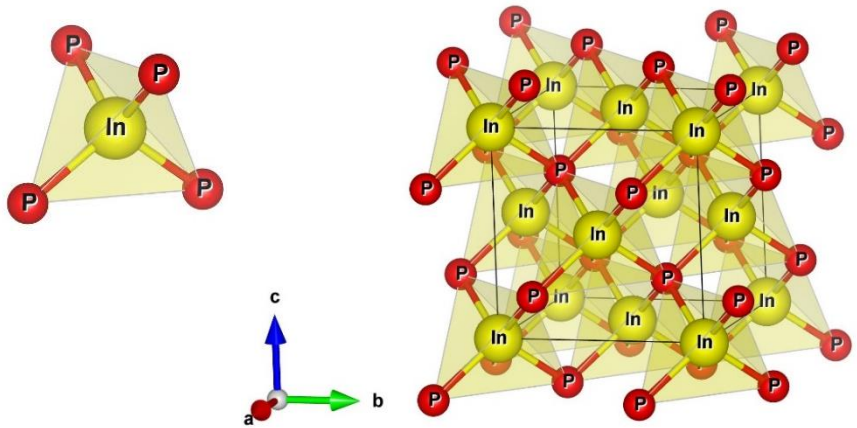


Comparison with phonon properties of other phosphides

☐ InP

Mass of ratio

P : In : Ag = 1 : 3.71 : 3.48



In-P Cluster

Bond distance (In-P): 2.541Å for all

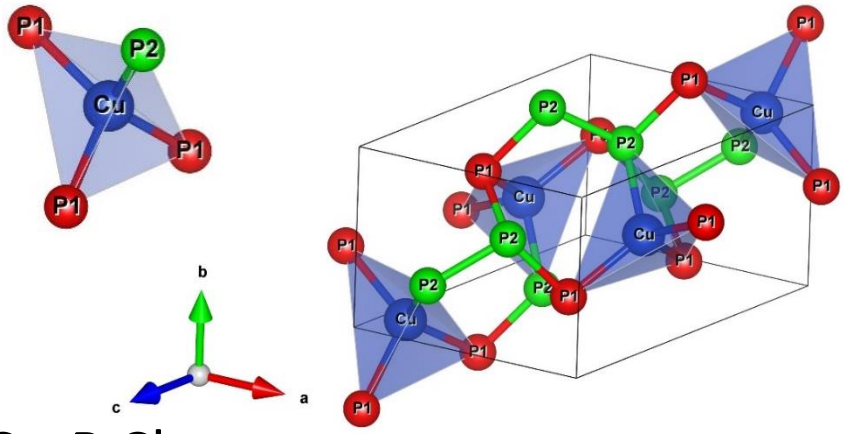
Bond angles (P-In-P): 109.47 deg.

✓ **Bonds and geometry: Isotropic**

☐ CuP_2

Mass of ratio

P : Cu : Ag = 1 : 2.05 : 3.48



Cu-P Cluster

Bond distance (Cu-P): 2.274- 2.500 Å

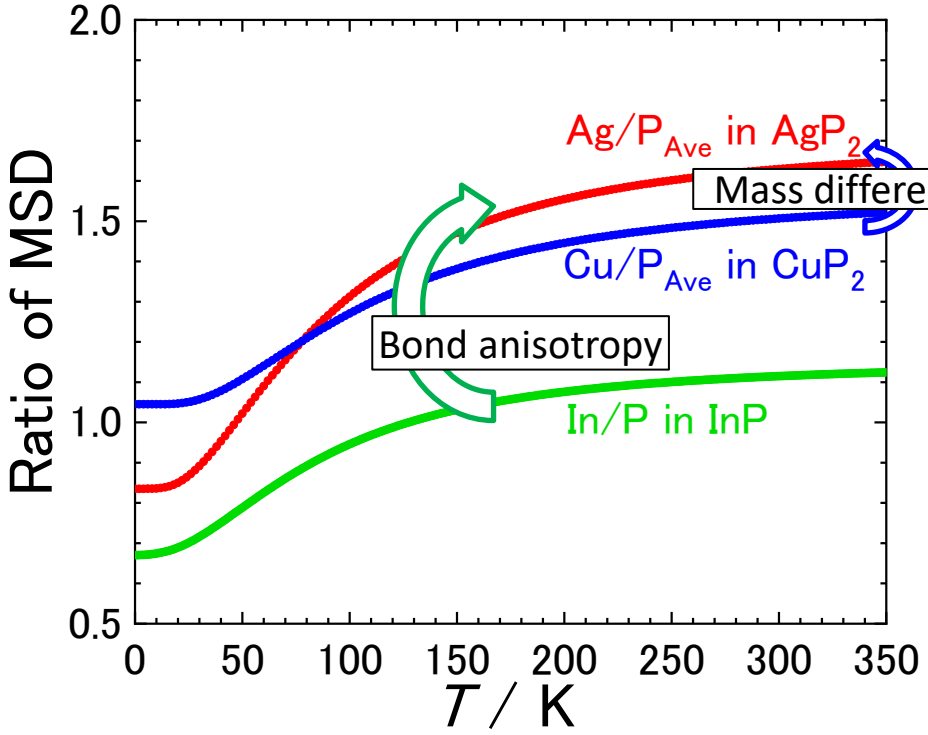
Bond angle (P-Cu-P): 95.18- 118.59 deg.

✓ **Bonds and geometry: Anisotropic**

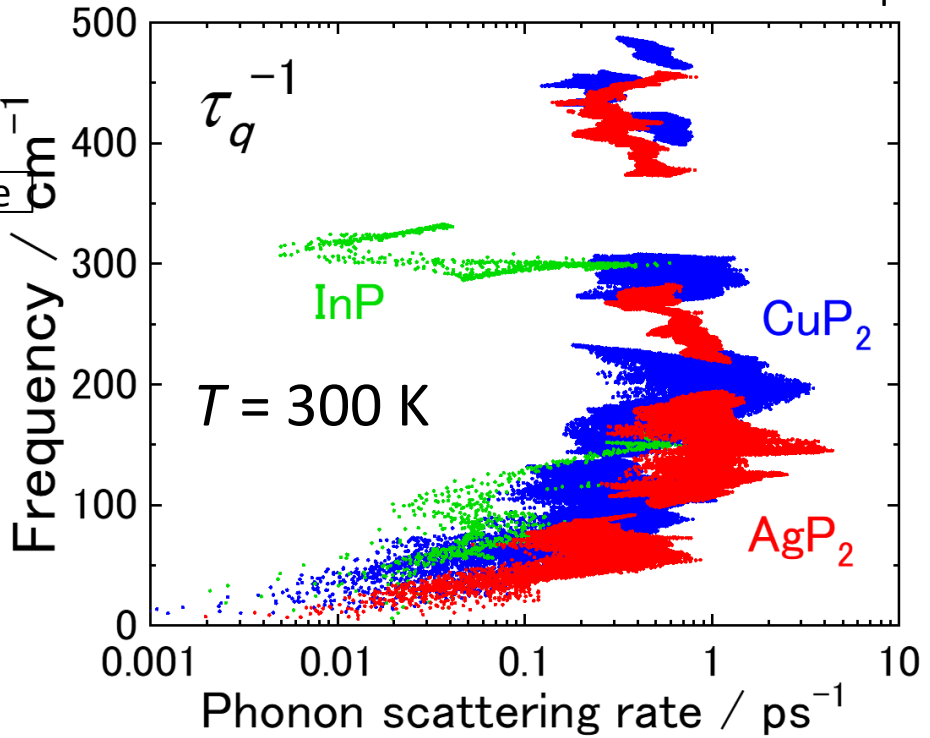
For clarifying the origin of large MSD, we investigated which is effective to MSD for mass of ratio or anisotropic bond.

The origin of large vibration of Ag atoms in AgP_2

Ratio of MSD



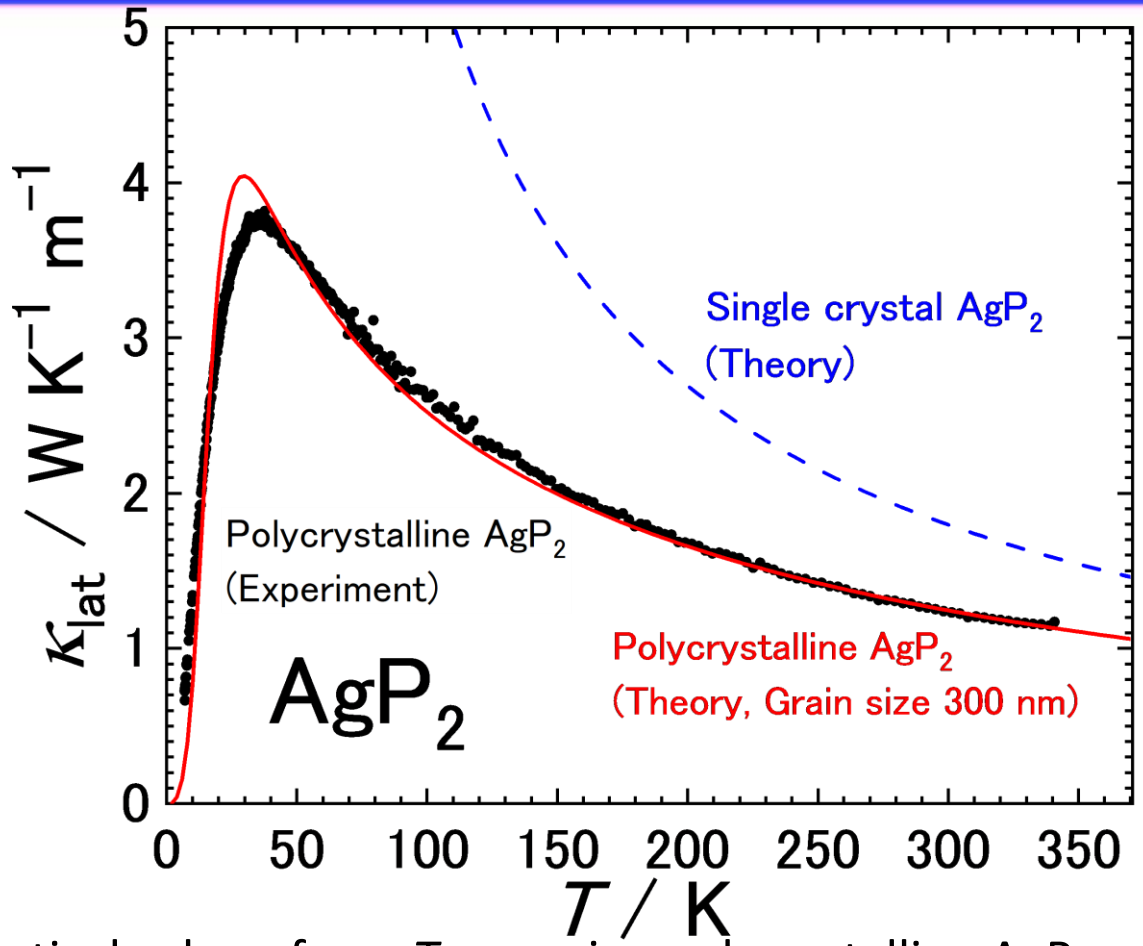
Phonon scattering probability τ_q^{-1}



- The ratio of MSD of Ag with P_{ave} is larger that of In in InP, denoting that the bond anisotropy is more effective to large MSD than that of mass difference.
- AgP_2 has a very high phonon scattering probability τ_q^{-1} in the low frequency region compared to that of CuP_2 and InP.

The anharmonic phonons of Ag is originated from the bond anisotropy of Ag-P cluster.

Comparison of lattice thermal conductivity for experiment and theory

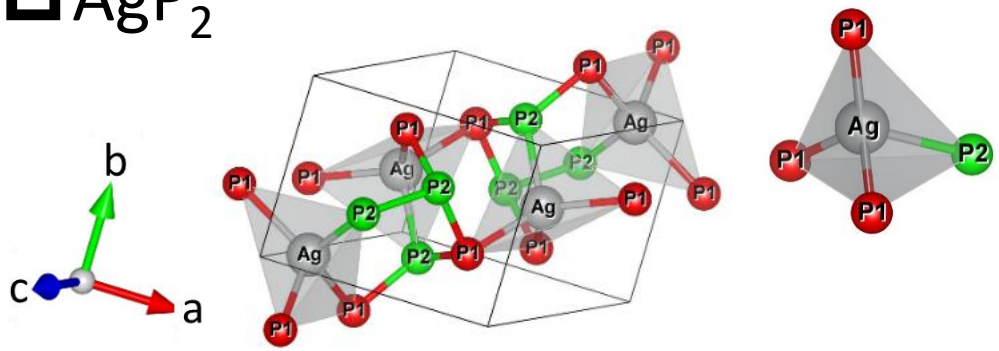


- The theoretical value of κ_{lat} -T assuming polycrystalline AgP_2 with a crystallite diameter of 300 nm is quantitatively reproduces the experimental value of κ_{lat} for the experimentally synthesized polycrystalline AgP_2

We clarified that AgP_2 exhibits low lattice thermal conductivity, experimentally and theoretically.

Ag-P compounds which show low lattice thermal conductivity

AgP_2

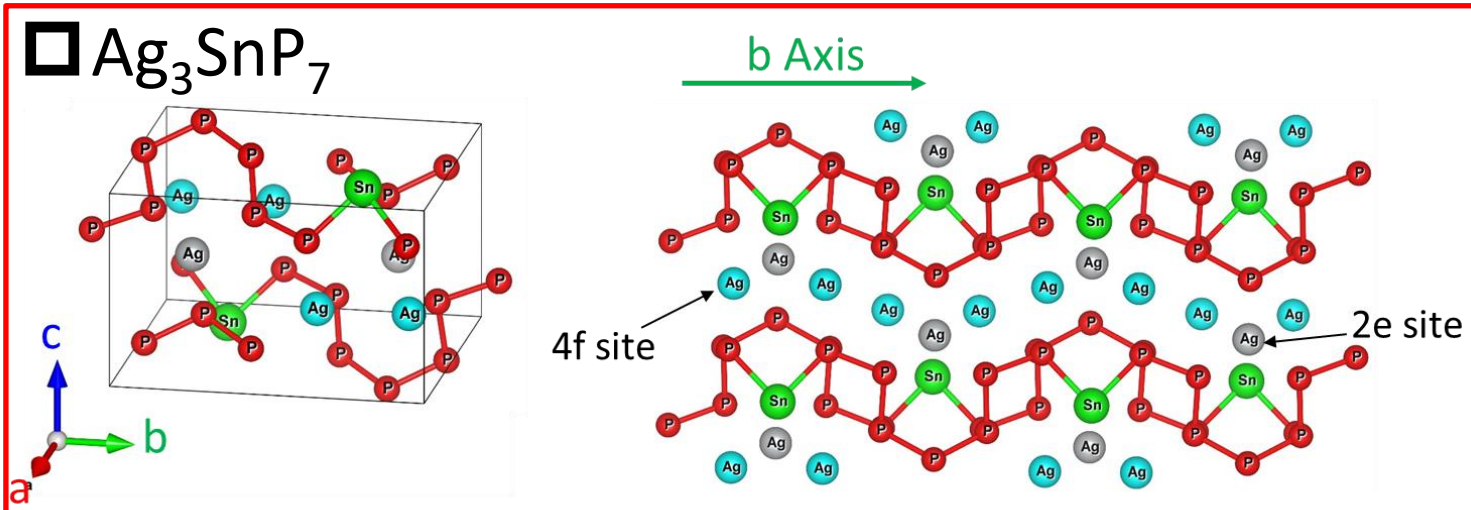


- Primitive cell of AgP_2 contains four Ag and eight P, and the Ag-P clusters whose P atoms locate around Ag, tetrahedrally.

Crystal system: Monoclinic $(P2/c)_1$

*M. H. Moeller *et al.* Z. Anorg. Allg. Chem. **491**, 225 (1982).

Ag_3SnP_7



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*M. M. Shatruk et al., Angew. Chem. Int. Ed. 39, 14, 2508(2000).

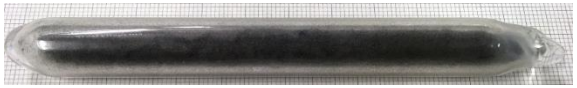
Sample Synthesis and Evaluation

Sample Synthesis

~~Melting method (550° C, 8h)~~

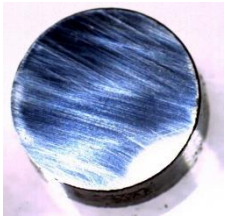
~~Unreacted P burns off and cannot be synthesized~~

Chemical vapor transport (CVT) method
(550℃, 1week, added iodine)
ΔT ~ 2 K (≈ temperature variation in furnace)

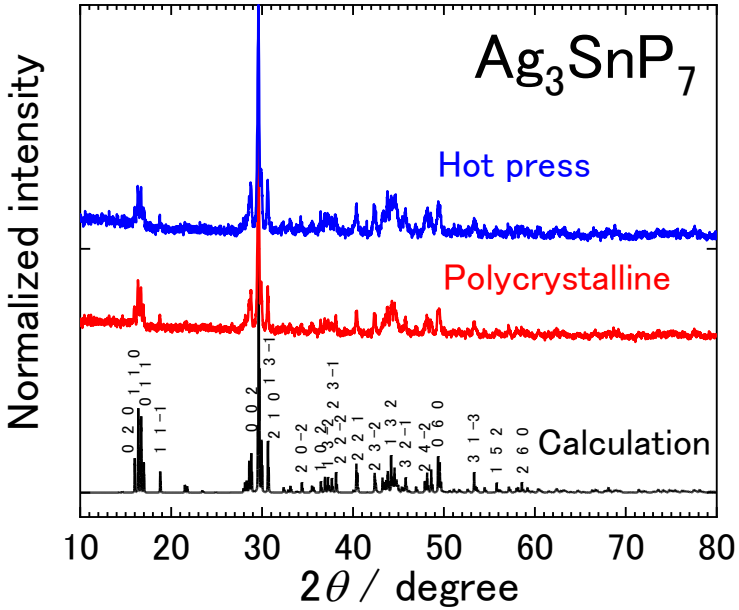


Hot press

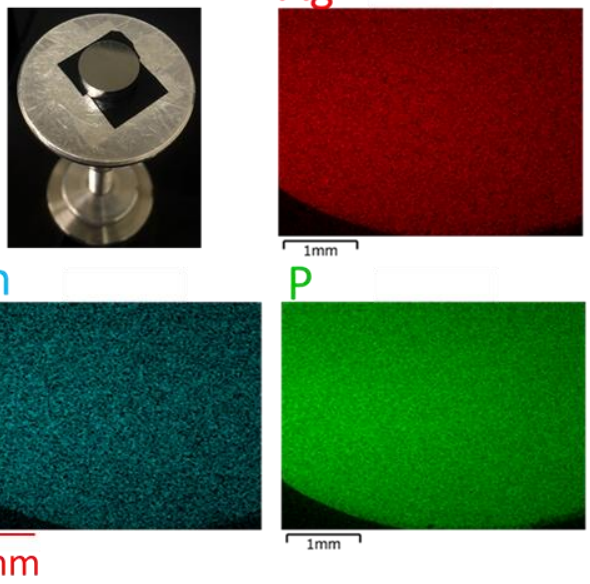
10 mm



XRD

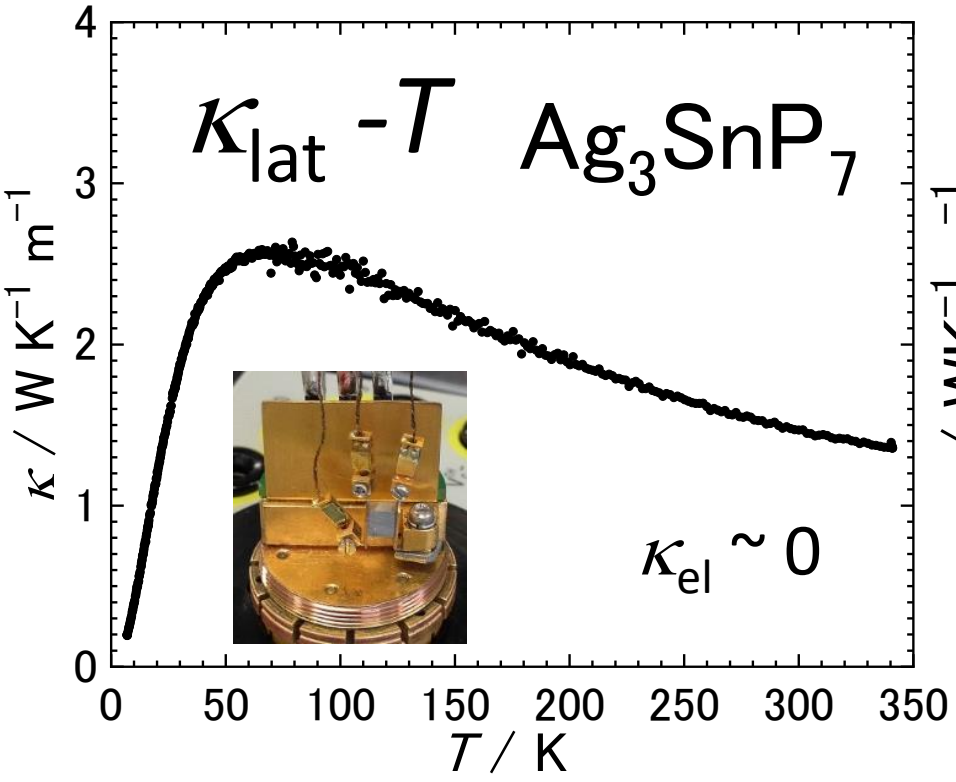


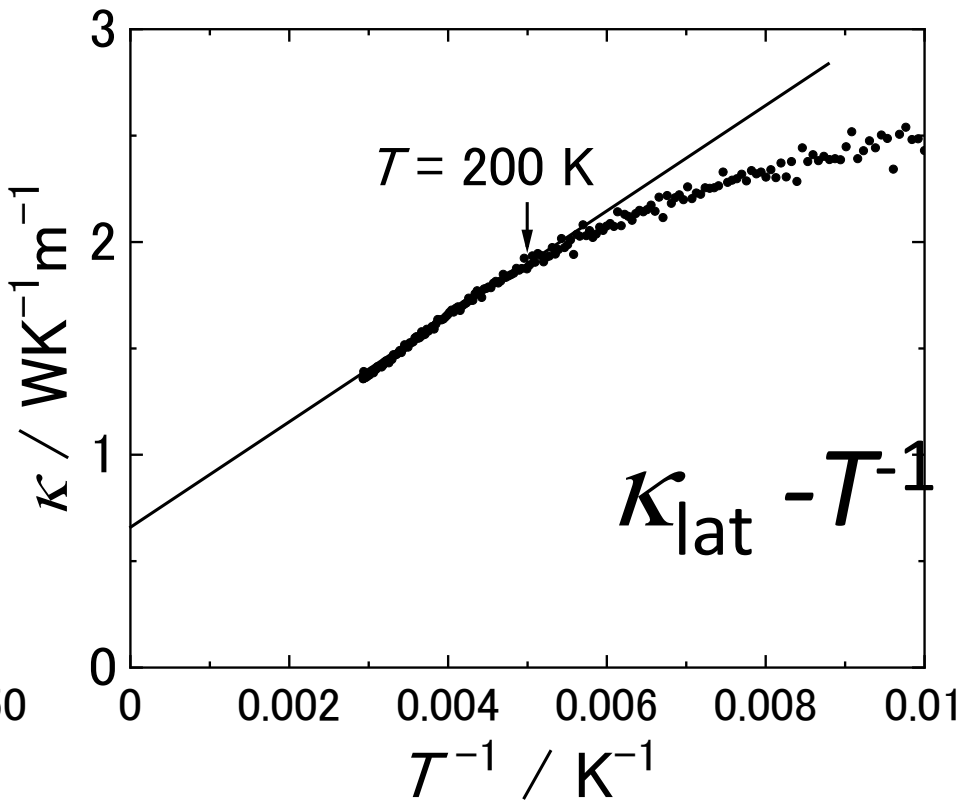
SEM-EDS



A homogeneous and single-phase Ag_3SnP_7 sample was successfully obtained using the CVT method.

Temperature dependence of thermal conductivity κ





- The lattice thermal conductivity κ_{lat} at room temperature is about 1.5 $WK^{-1}m^{-1}$.
- κ_{lat} - T^{-1} shows liner dependence more than 200 K, indicating phonon-phonon scattering is dominant more than 200 K.

Condition of DFT calculation

Electronic structure and transport calculations

OpenMX

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* M. Miyata, Taisuke Ozaki *et al.*, Journal of Electronic Materials, 47(6) 3254-3259 (2018)

- Variable cell relaxation
- *E-k* relation, density of states

- Exchange correlation potential: GGA-PBE
- Cutoff energy: 500 Ryd
- Max Force: 1.0×10^{-6} Hartree $Bohr^{-1}$

Phonon Transport Calculations

ALAMODE

*T. Tadano *et al.* J. Phys.: Condens. Matter **26**, 225402 (2014).

- Phonon dispersion
- Density of states
- Lifetime of phonons
- Mean square displacement (MSD)
- Mode Grüneisen Parameters γ
- Lattice thermal conductivity
- Self-consistent phonon calculation(SCPH)

<Interatomic force constant>

- Harmonic term(2^{nd} order): Displacement = 0.04 Å
- Anharmonic term (3^{rd} and 4th order): Displacement = 0.08 Å

- Supercell size
  $2 \times 2 \times 2$ primitive cell

Self-consistent phonon calculation

Solving the Dyson equation from the phonon Green's function finally yields the following equation

$$\Omega_q^2 = \omega_q^2 + \Omega_q I_q,$$

$$I_q = \sum_{q'} \frac{\hbar\Phi(q;-q;q';-q')}{4\Omega_q\Omega_{q'}}\left[1+2n(\Omega_{q'})\right]$$

ω_q: Harmonic phonon frequency at phonon $\boldsymbol{q}$

I_q : Self-energy of phonon at $\boldsymbol{q}$

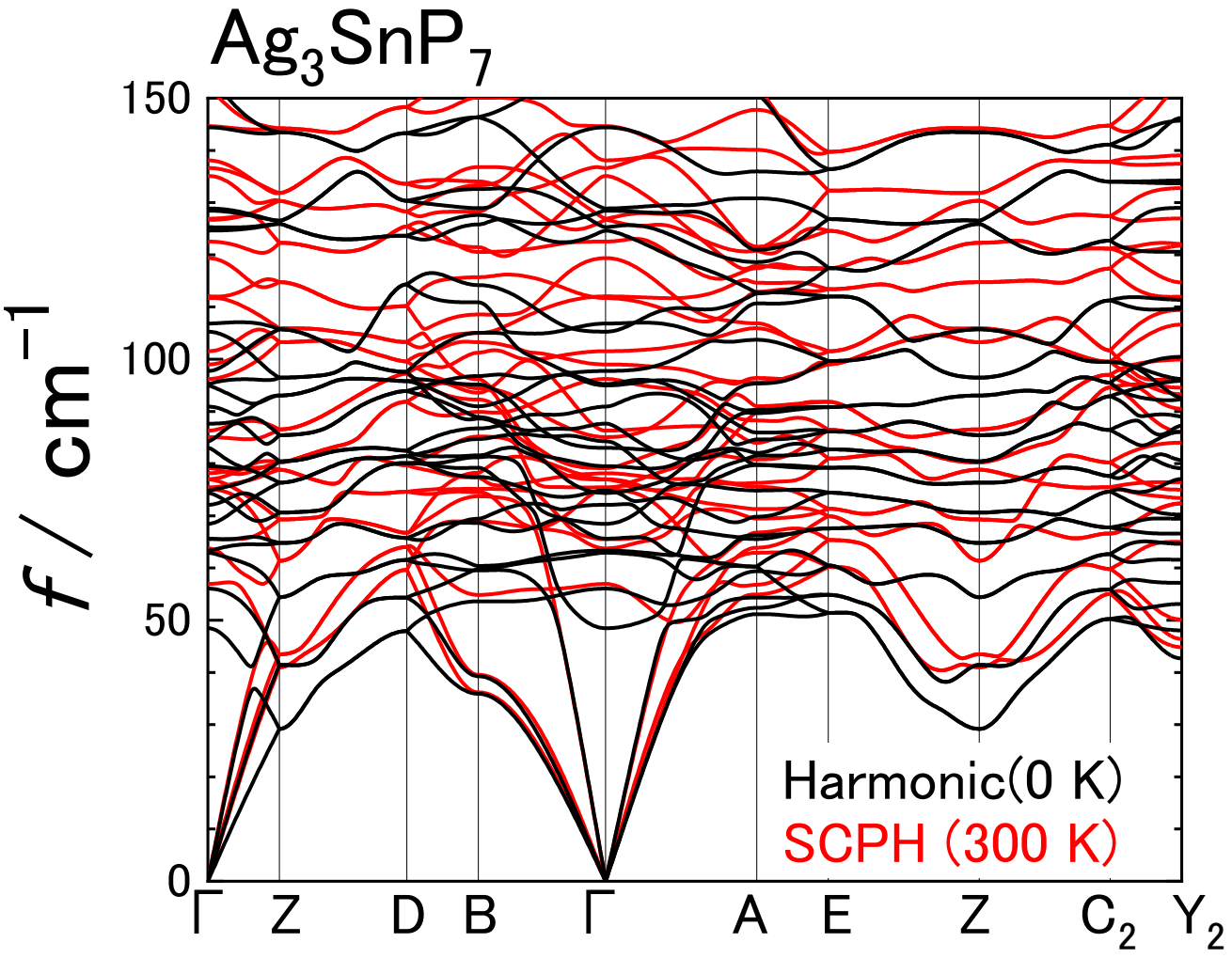
$\Phi(q;-q;q';-q')$: 4th order of anharmonic phonon term at $\boldsymbol{q}$, $-\boldsymbol{q}$, $\boldsymbol{q}'$ -$\boldsymbol{q}'$

n: Bose-Einstein distribution function

- Compute the two equations self-consistently until the renormalized frequency Ω_q convergence.

We finally obtain the Ω_q which include effective potential of 4th order anharmonic phonons.

Phonon dispersion

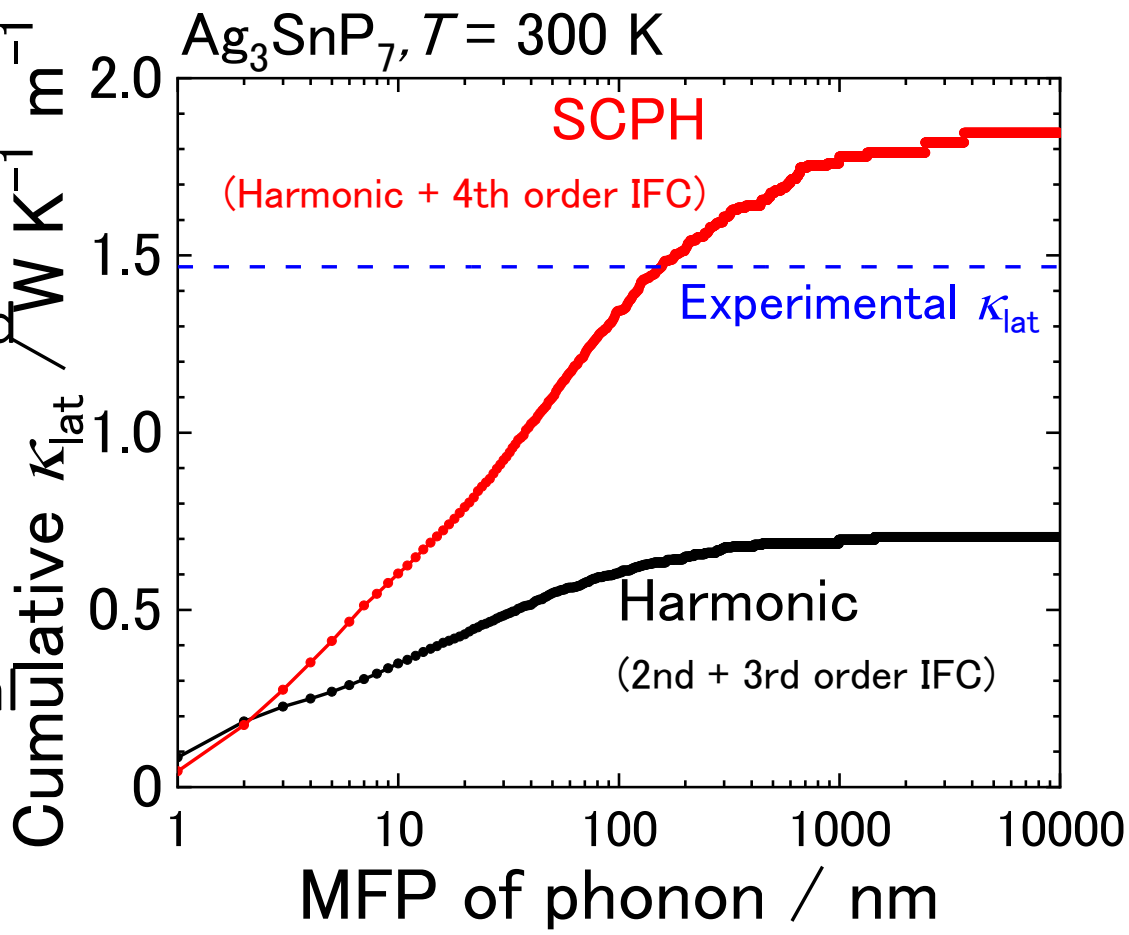


- In the SCPH calculation, in which the fourth-order anharmonic term is renormalized to the second-order harmonic term, the phonon dispersion relation shifts overall to the high-frequency side.

Comparison of lattice thermal conductivity κ_{lat}

Cumulative lattice thermal conductivity κ_{lat}

- Calculations using second-order IFC obtained from the harmonic approximation underestimate κ_{lat} compared to experimental values
- SCPH calculation with 4th order IFC renormalization reproduces the experimental value κ_{lat}

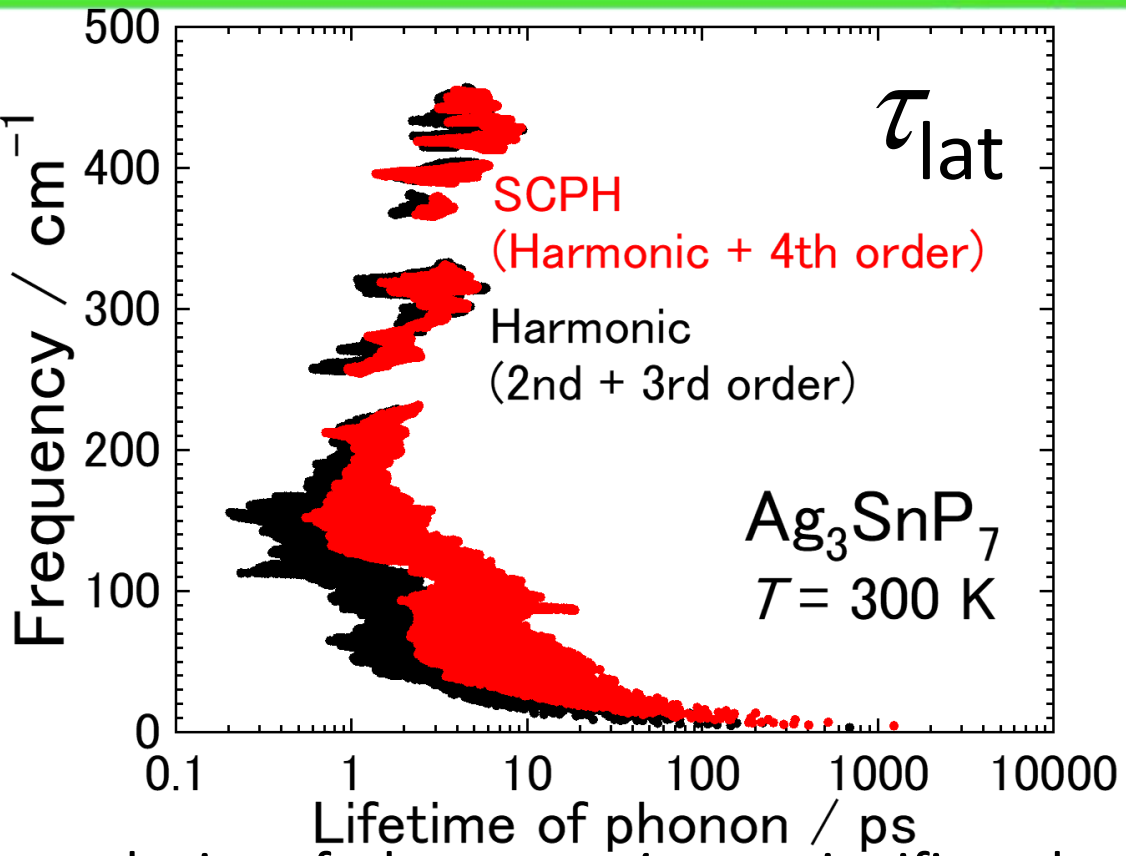


In the phonon transport of Ag_3SnP_7 , consideration of the 4th order anharmonic phonons are important.

Lattice specific heat C_v , Group velocity v, Lifetime of phonon τ_{lat}

$$\kappa_{lat} = \frac{1}{3} C_V v^2 \tau_{lat}$$

C_V	Harmonic ~ SCPH
v	Harmonic ≦ SCPH
τ	**Harmonic << SCPH**

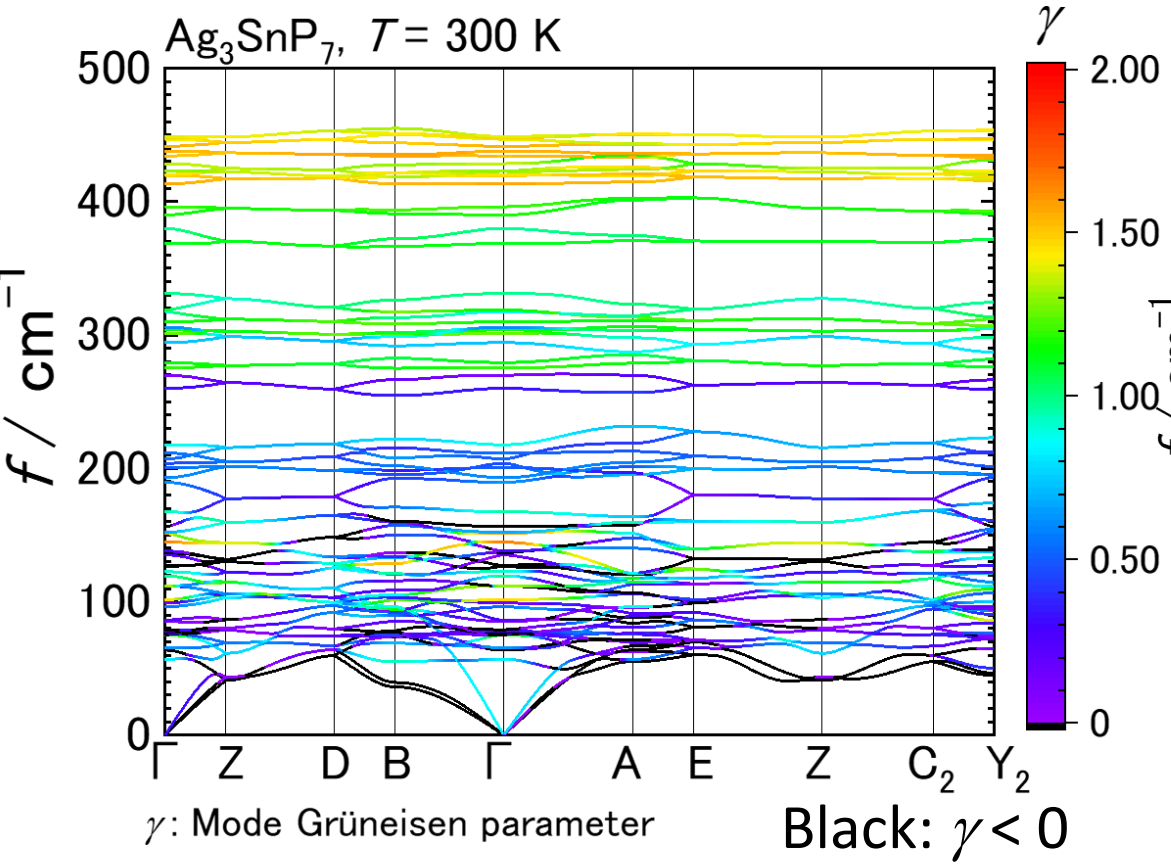


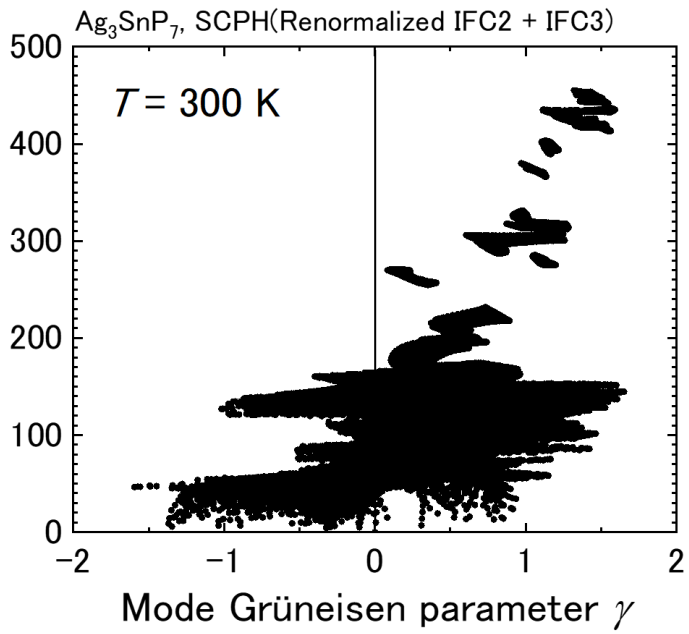
- Lattice specific heat C_v, group velocity of phonons v *is* not significantly different between harmonic calculation and SCPH.
- The underestimation of lifetime of phonon is occurred τ_{lat} caused by the lack of consideration of 4th order anharmonic phonon.

For Ag_3SnP_7 system, the consideration of 4th order anharmonic phonon is important!

Ag_3SnP_7 Anharmonic phonons in

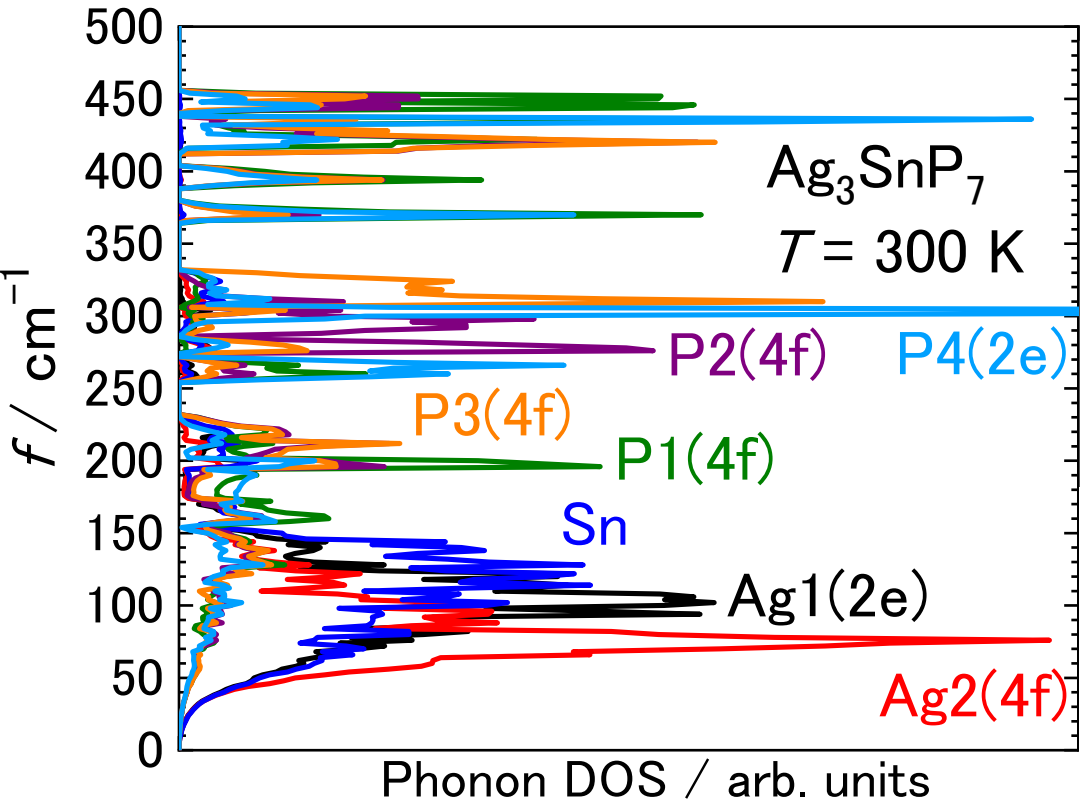
Phonon band , Mode-Grüneisen parameter γ

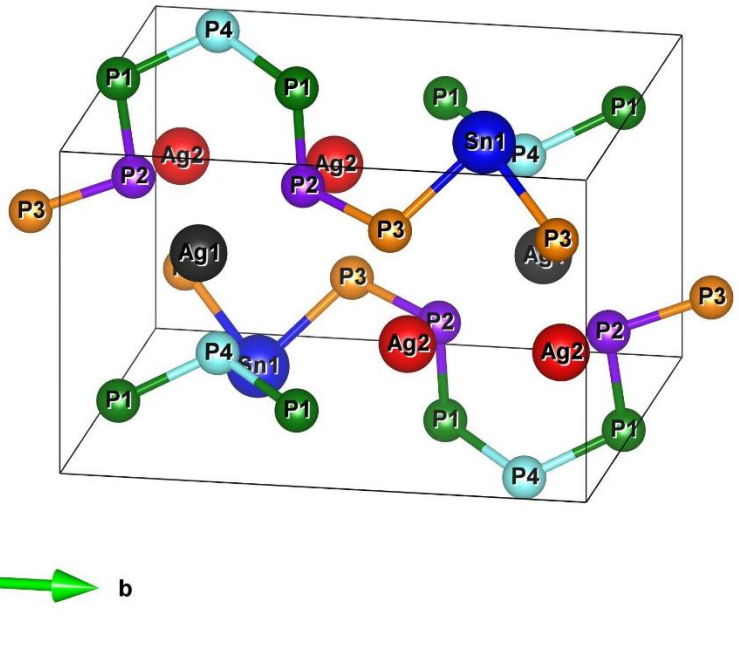




- In the frequency range below 160 cm^{-1}, γ is large negative value, indicating anharmonicity of phonon at low frequency region is large.

Phonon DOS with SCPH

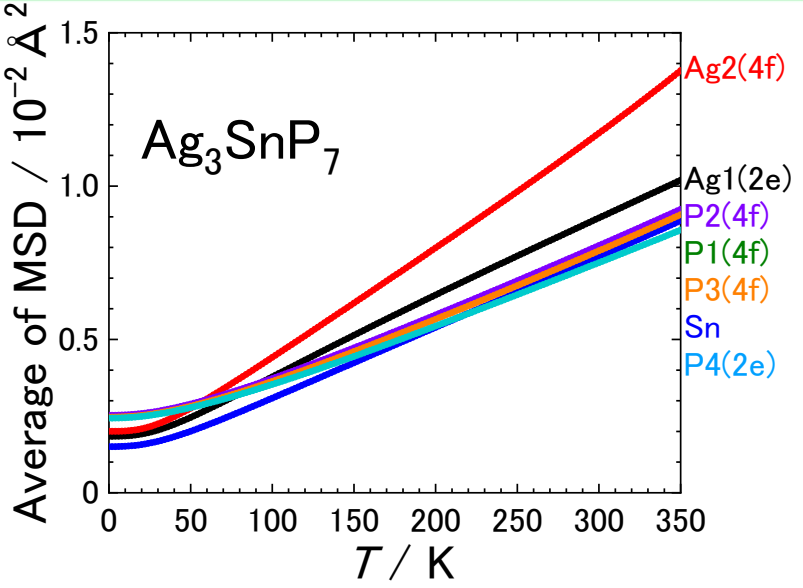


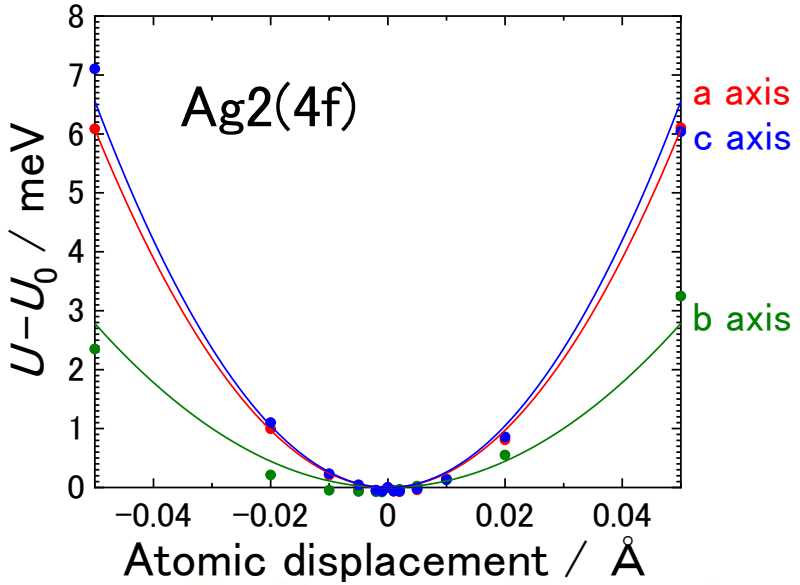


- In the frequency region below 160 cm^{-1} where γ shows large negative values, the PDOS of Ag atoms at the 4f site is the largest.

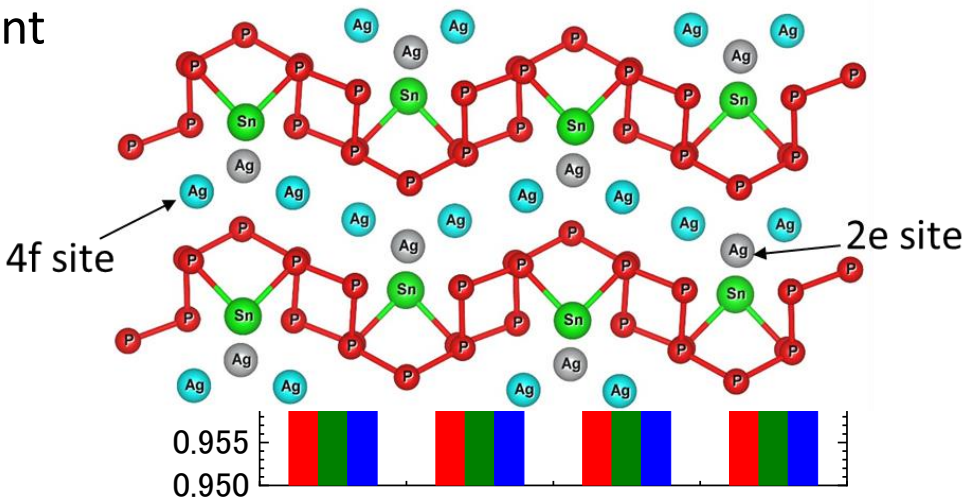
Phonon modes of Ag atoms at the 4f site contribute most to the anharmonicity of Ag_3SnP_7.

Large anharmonicity of Ag at 4f site



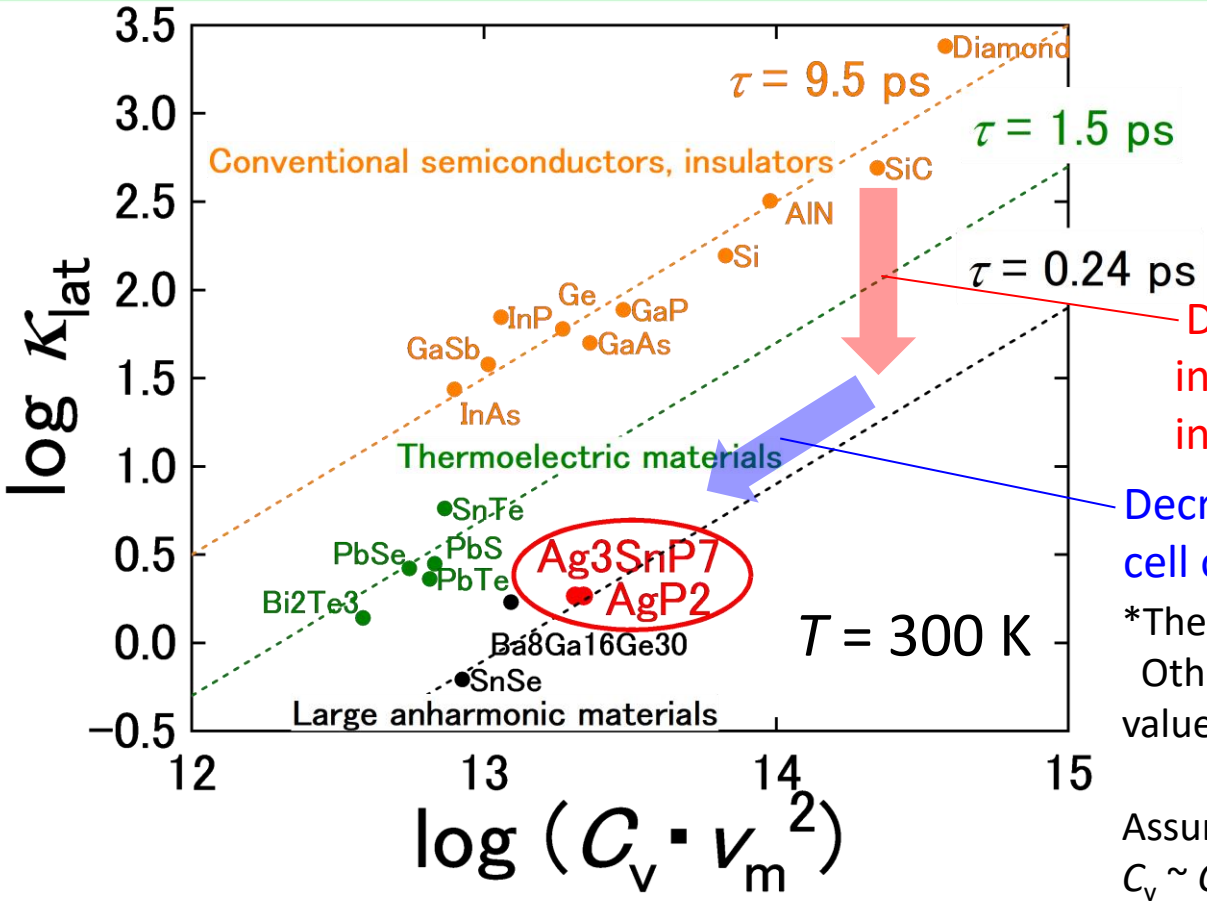


- At 300 K, the mean square displacement of the Ag atoms at the 4f site is large, signifying that the phonon scattering cross section of Ag at 4f site is the largest.
- For the Ag at 4f site, the atomic displacement dependence of total energy *U* is far from parabolic curve



The origin of the anharmonic phonon mode is the Ag atoms at the 4f site.

Comparison with experimental values for other inorganic materials



$$\kappa_{\mathrm{lat}} = \frac{1}{3} C_{\mathrm{V}} {v_m}^2 \tau$$

$$\log\kappa_{\mathrm{lat}} = \log C_{\mathrm{V}} {v_m}^2 + \log\frac{1}{3}\tau$$

Decrease τ due to the increase in phonon scattering intensity

Decrease C_v($\sim C_p$) , v_m due to large unit cell or heavy atoms

*Theoretical results: Ag_3SnP_7, AgP_2
Other materials were refered the reference value of experimental single crystal

Assumption:
$C_v \sim C_p$: Heat capacity at constant pressure

- Conventional semiconductors, insulators, and thermoelectric materials located in the dotted line at constant lifetime of phonons.
- The effective lifetime phonon τ of Ag_3SnP_7 is 0.24 ps and 1/40th of that of conventional semiconductors, and is comparable to SnSe and clathrate compounds which show large anharmonicity of phonons.

Summary

- We succeeded in creating Ag-P compounds with extremely low lattice thermal conductivity and elucidating the mechanism by making full use of experiments and first-principle calculations.
- The anharmonicity of the phonons in Ag-P compounds is due to the anharmonic phonons of the Ag atom, and the anisotropy of the bonds around the Ag atom is important.
- Using OpenMX and ALAMODE, we performed self-consistent phonon calculations considering fourth-order anharmonic phonons and found that fourth-order anharmonic phonons are important in the phonon transport of Ag_3SnP_7.

Acknowledgement

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科研費 KAKENHI