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CMD® Case Studies (2)

Theoretical Calculations by Computations to Go beyond Theories

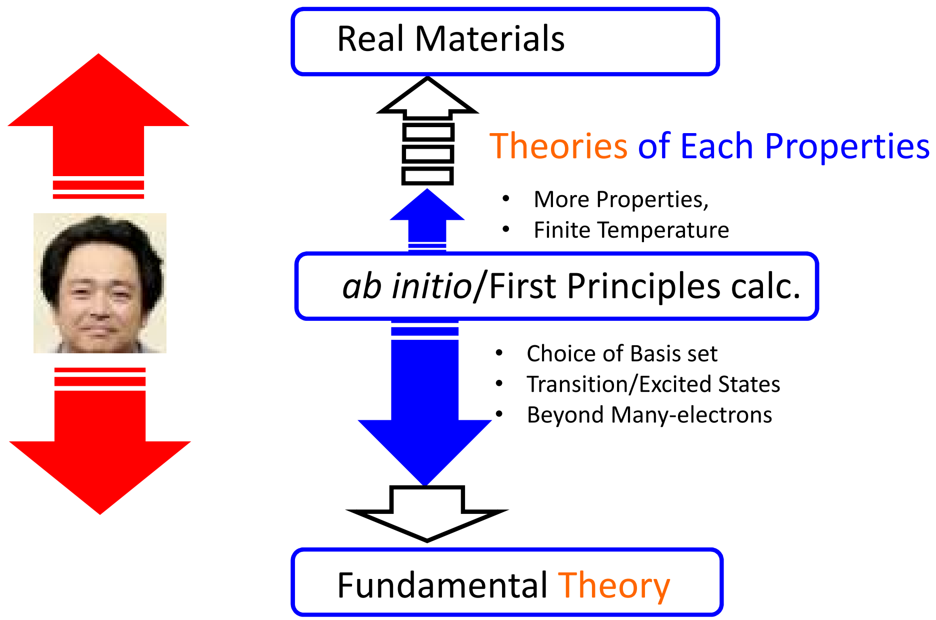
Masato YOSHIYA, Students and Collaborators

Graduate School of Engineering, Osaka University Japan
Nanostructure Lab., Japan Fine Ceramics Center, Japan

Contents

- ✓Introduction to Computation (ab initio and beyond)
- ✓Thermal Conductivity
- ✓Thermal Expansion
- ✓Conclusions

Theories & *ab initio* Calculations



Three Ways of Computations

✓Simulation

To reproduce something, and identify governing factors

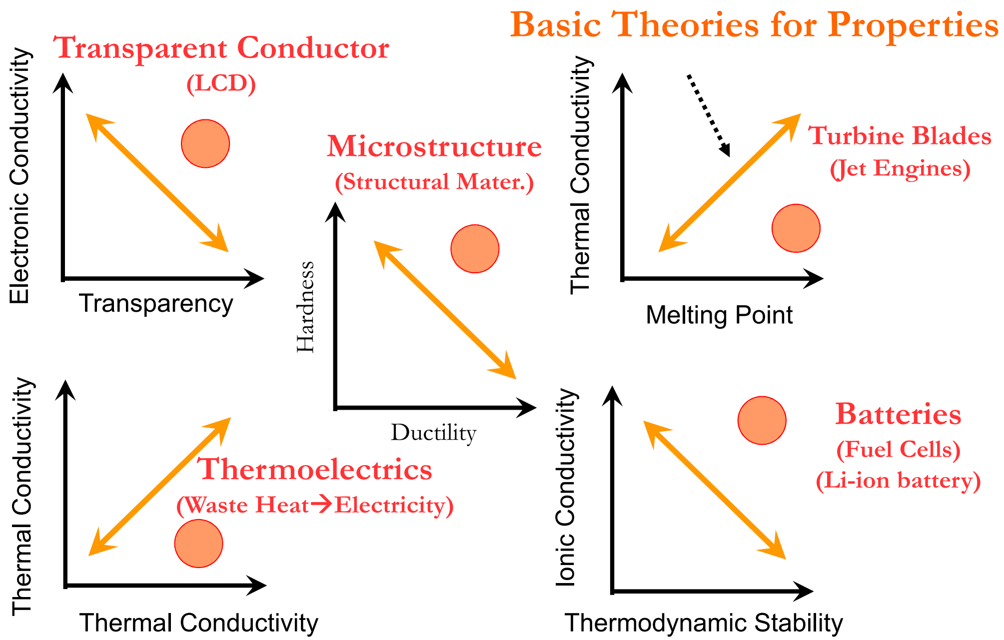
✓Theoretical Calculation

To use no theory for properties, but fundamental theory

✓Computational Experiment

To do experiments in computers

Conflicting Demands for Materials



吉矢真人 Masato Yoshiya : yoshiya@ams.eng.osaka-u.ac.jp, http://www.cmdc.ams.eng.osaka-u.ac.jp

Layered Thermoelectric Oxides

✓Introduction to Computation (ab initio and beyond)

✓Thermal Conductivity

✓Thermal Expansion

✓Conclusions

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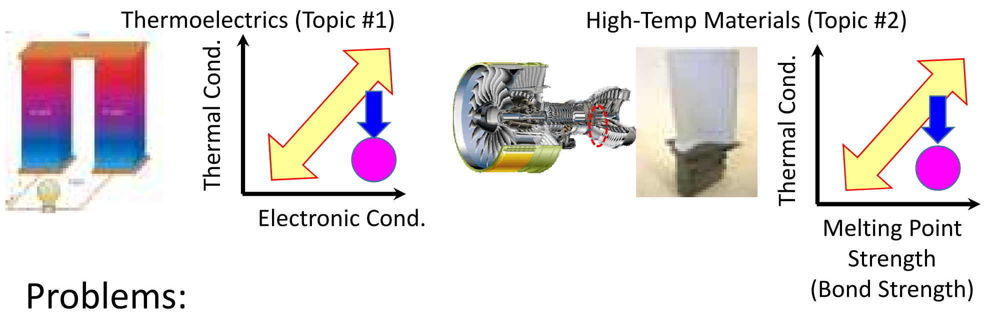
Selective Control of Thermal Conduction



Problems:

- Easy to decrease thermal conductivity ALONE
- Conventionally, discussing "Mean Free Path" ← Length of Defects
  → Remains qualitative → No quantitative guideline
- Unclear: Selective control of thermal conduction
  without deteriorating other properties needed

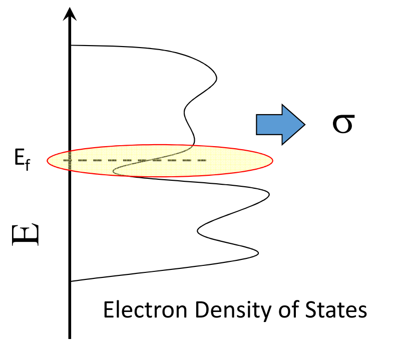
➡ Through computations,
Guidelines to control beyond correlation or trade-off

Masato Yoshiya : yoshiya@ams.eng.osaka-u.ac.jp, http://www.cmdc.ams.eng.osaka-u.ac.jp

Similarities and Differences: (Electrons and Phonons)

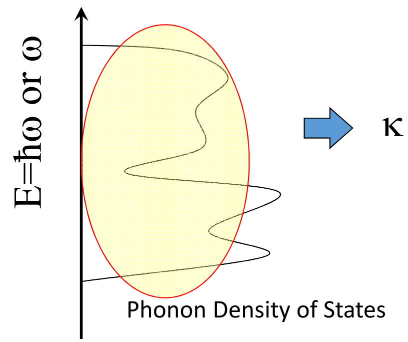
- ～1960: Equally discussed and theories developed
- After discovery of semiconductors: Phonons left behind electrons
- Reactivated in 21st century → Phonon conduction is complicated

Electrons
Fermi-Dirac statistics



Only Electrons near Fermi level contribute to σ

Phonons
Bose-Einstein statistics



All the phonons contribute to κ

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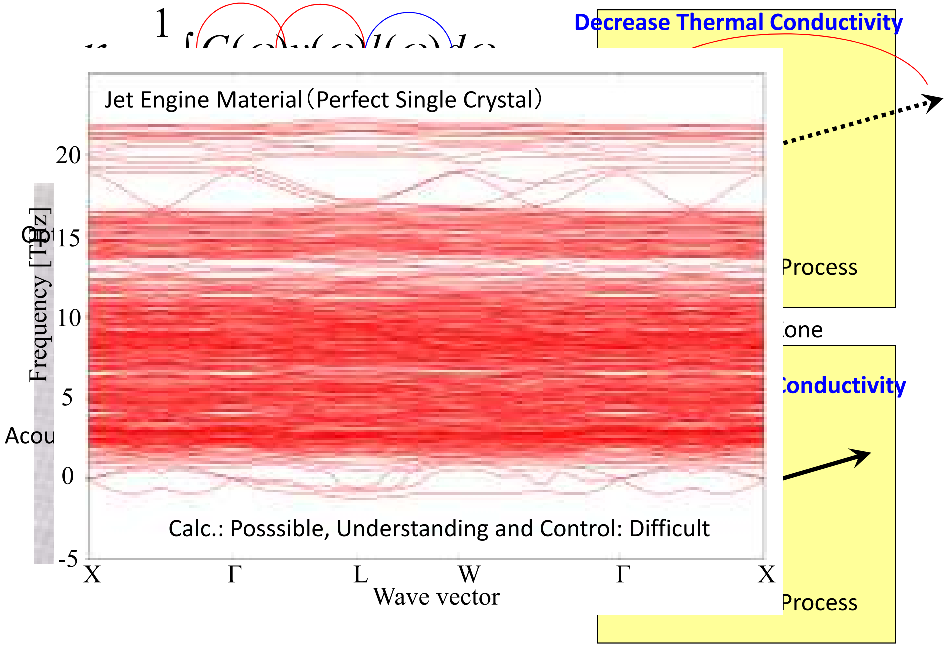
Theories and Reality



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Approaches to Thermal Conduction

1. Phonons：　Classical MD（Modeling）
2. Force-Field：　From *ab initio* calc.
3. Mechanism：　Original ways
3. Guideline for control　Computational Experiment

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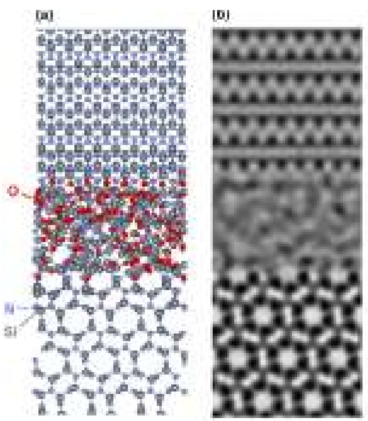
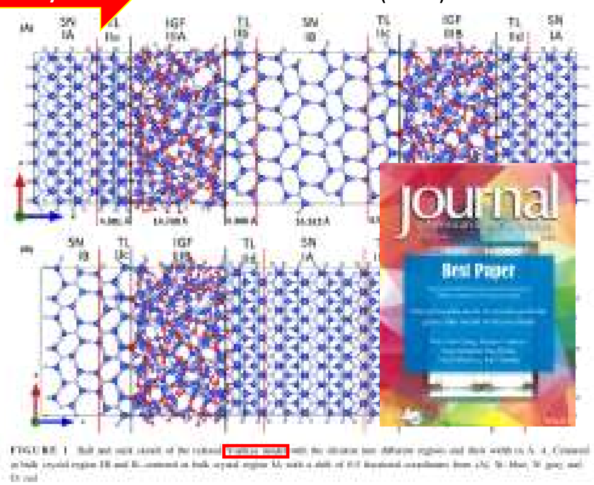
Intergranular Film (~ 1nm)

Classical FF Calc.(1998-2000)　20 yrs !　*ab initio* Calc. (2018)



M. Yoshiya, et al, (1999, 2000)



W-Y. Ching, M. Yoshiya, et al, J. Am. Ceram. Soc. (2018)

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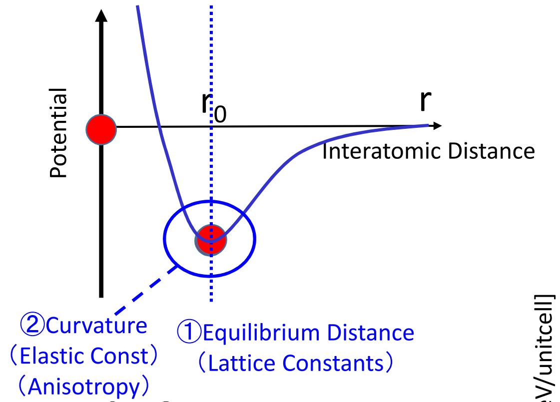
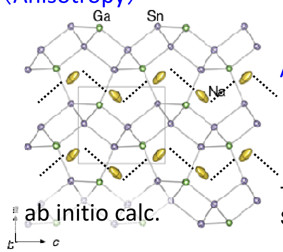
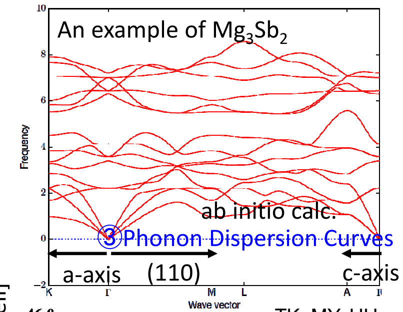
Example: ab initio calc.→Force Field

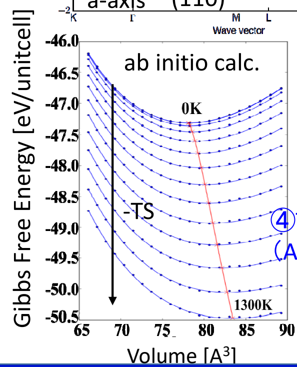




⑤Dynamics of Atomic Vibrations
$Na_2Ga_2Sn_4$

TY, MK, HT, MY, et al., Sci. Adv., submitted.





TK, MY, HU,, Nature Mater., in prep

EBC Material
$Gd_2Zr_2O_7$

④Thermal Expansion
（Anharmonicity）

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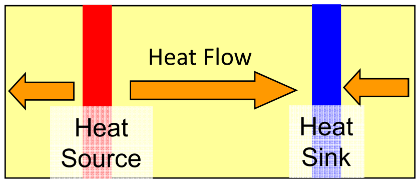
Thermal Conductivity: Existing Methods

Direct Method (1975)



Advantage: Path of Heat flow
Disadvantage: Artificial Scattering
Problem: Only κ

Equilibrium MD

Green-Kubo Equation (1957)

$$\kappa = \frac{V}{k_B T^2}\int_0^\infty \langle J_x(\tau) J_x(0)\rangle d\tau$$

Advantage: No artificial Scattering
Disadvantage: Slow convergence
Problem: Only κ

New Method (From Theory to Implementation)

- Not only greater/lower κ
- How κ is determined

→ Extension of existing theories

Original Method: Calc. & Analyses

- Perturbed MD — M. Yoshiya et al., (2004)

$$\dot{\mathbf{r}}_i = \mathbf{p}_i / m$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i + \overleftrightarrow{\mathbf{D}}_i \mathbf{F}_{ext}$$

R. Kubo (1957)

Linear Response Theory
Fluctuation Dissipation Theorem

D. J. Evans (1982), M. J. Gillan (1983)

$$\kappa = \frac{1}{T}\lim_{t\to\infty}\lim_{F_{ext}\to 0}\frac{\langle J_{Qx}(t)\rangle}{F_{ext}}$$

Sum over atoms → Further Analyses

$$J_{Qx}(t) = \left\{\sum_i \left\{ e_i \mathbf{v}_i + \mathbf{r}_{ij}(\mathbf{F}_{ij}\cdot\mathbf{r}_{ij})\right\}\right\} / V$$

- Advantage: Enables various analyses → Enable to identify mechanisms

Quantification of each elements' contribution to κ

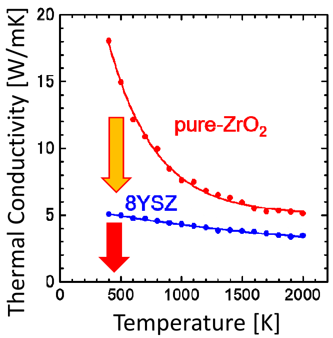
$$\kappa = \kappa_{Na} + \kappa_{Co} + \kappa_{O}$$

Idea from LCAO of ab initio calc.

Comparison #1: Jet Engine Material

~ RT

	Calc.	Exp.	Error
ZrO_2	18.5	8.1	228%
8YSZ	5.1	2.3	222%
Decrease	71.9%	71.6%	



Relative change: Okay
↓
Phonon Scattering: Okay
↓
Discussion on the safe side can be made (confined to Relative change)

Origins (through comparison with ab inito)

- Neglect of Quantum Effect ($T < \Theta_D$)
- Overestimation of group velocities

Comparison #2: Thermoelectrics

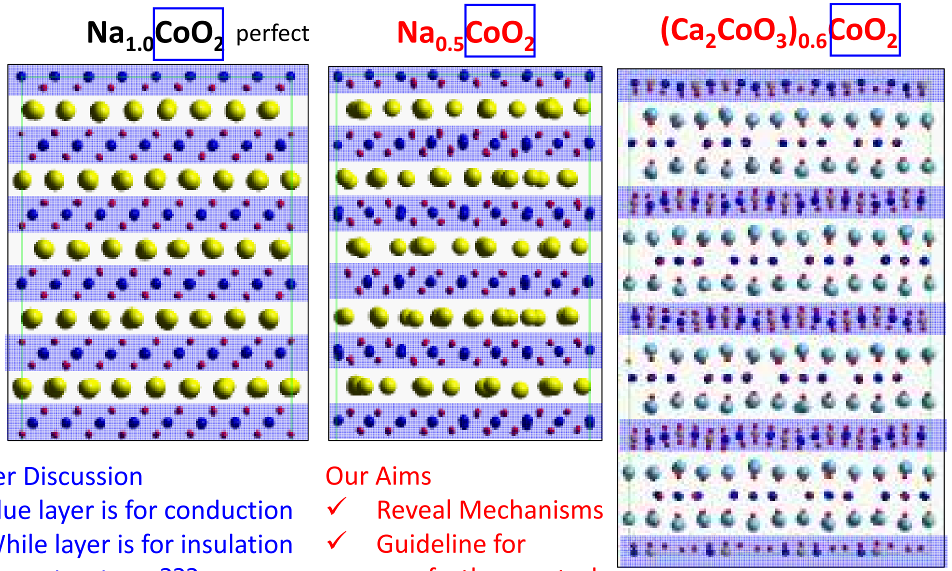
[W/mK]	300 K	800 K	
(a) $NaCoO_2$	41.6	14.9	
(b) $Na_{0.5}CoO_2$	20.7	10.9	Co^{3+}/Co^{4+} Ordered
(c) $Na_{0.5}CoO_2$	6.52	5.45	Co^{3+}/Co^{4+} Disordered
(d) $Na_{0.5}CoO_2$ †	19.0	5.1	Experiment (Single Xtal)

† K. Fujita et al., 2001

Fine to find agreement, but why?
→ Cancellation of two opposite errors
(Group Vel. & Formal Charges)

Layered Thermoelectric Oxides

Electronic properties: Understood Low Thermal Conductivity: ???



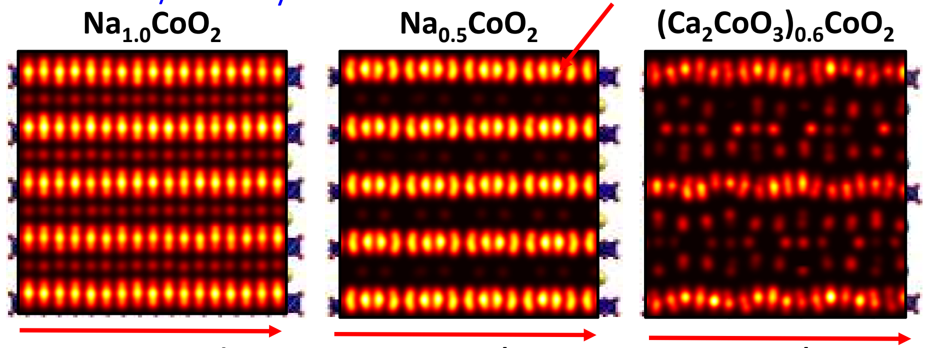
Earlier Discussion

- Blue layer is for conduction
- While layer is for insulation
- Nanostructures???

Our Aims

✓ Reveal Mechanisms
✓ Guideline for further control

Observations beyond Experiment



κ_{neigh} : 6.02 W/mK 0.37 W/mK 2.29 W/mK

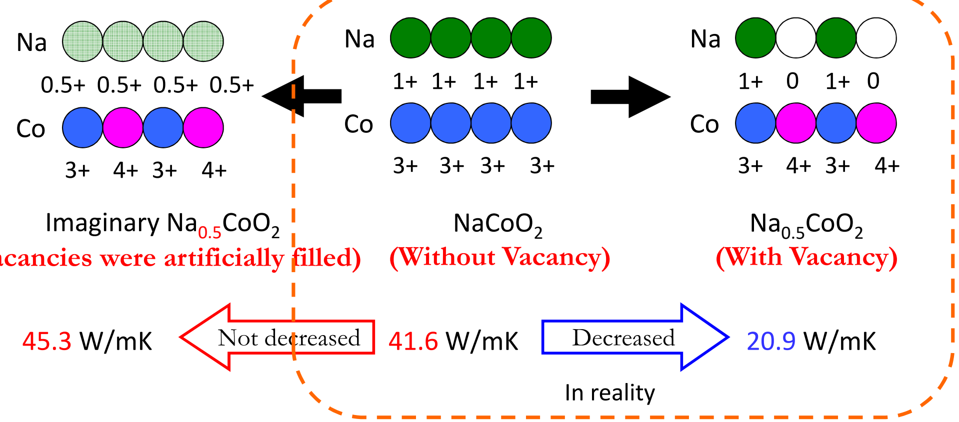
κ_{CoO2} : 37.40 W/mK 13.84 W/mK Drastic 4.91 W/mK

- Interlayer interaction suppress thermal conduction
- Without deteriorating electronic properties

SF, MY, CAJF, Sci. Rep. (2018)

Computational Experiment #1

Impact of Na Vacancies (with Co valence ordered)



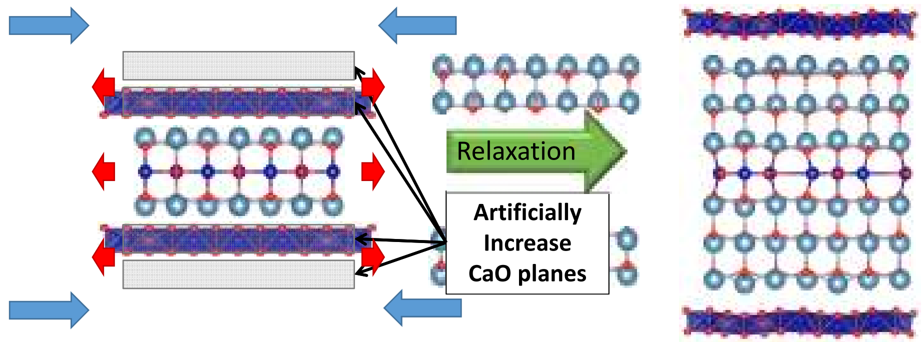
These results tell us that

- Presence of Na vacancies causes significant reduction of κ
- Mixture of Co^{3+}/Co^{4+} does not change κ very much when ordered

The story would not be changed even if Co charge conf. is disordered at high *T*.

Computational Experiment #2

$(Ca_2CoO_3)_{0.6}CoO_2$: Misfit-layered Structure

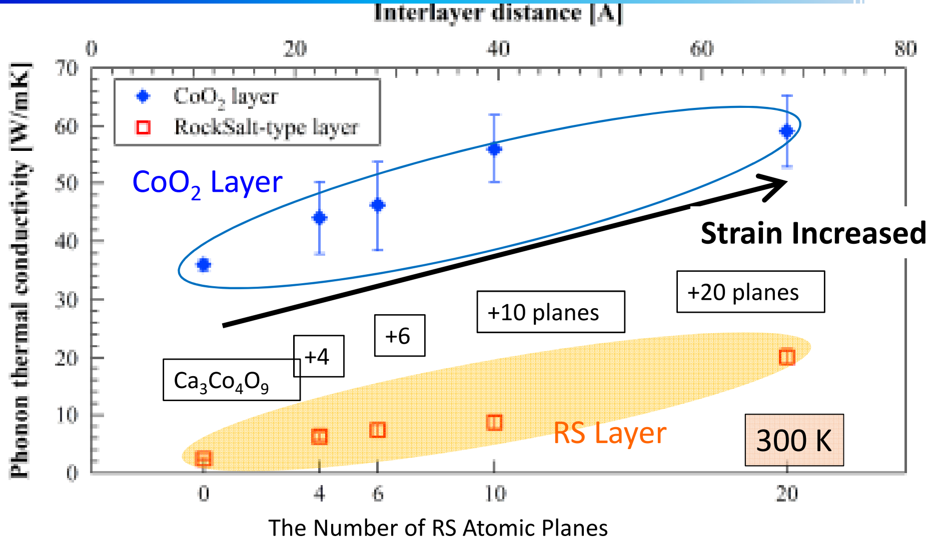


Artificially increase the number of atomic planes Misfit is rather increased

→Imposes more misfit and strain to CoO_2 layer

→Question: Whether thermal conductivity will increase or decrease?

Understanding through Comp. Exp.



With the increase of misfit, thermal conductivity is increased

➡ **Interlayer Dynamic Interaction determines κ**

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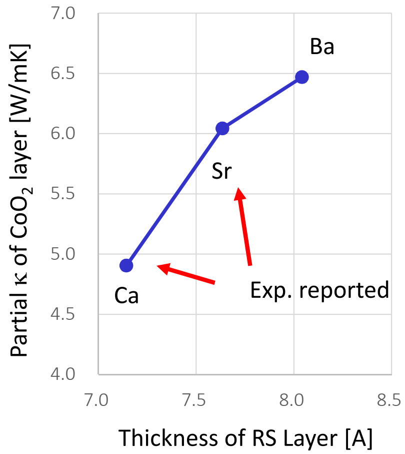
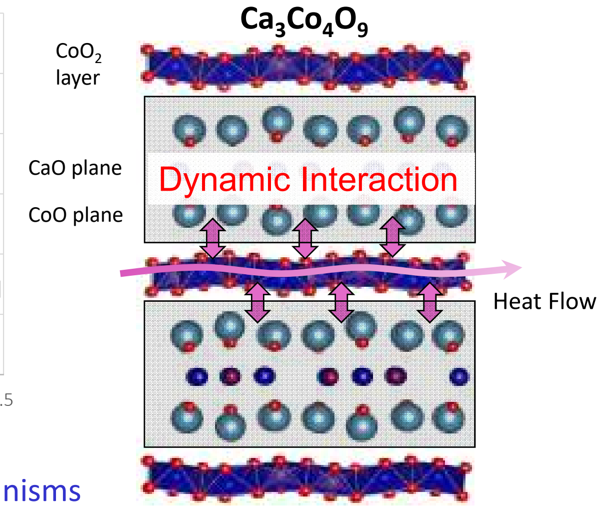
Exp. Observation Understood





Elucidated unsolved mechanisms
（Increased κ with Larger Misfit）

S.F, MY, J. Electron. Mater., (2016)

SF, MY, J. Electron. Mater., (2014)

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Anharmonicity

Anharmonicity: Origin of Phonon Scattering

$$U = U_0 + \frac{1}{1!}\frac{\partial U}{\partial \mathbf{r}} + \frac{1}{2!}\frac{\partial^2 U}{\partial \mathbf{r}^2} + \frac{1}{3!}\frac{\partial^3 U}{\partial \mathbf{r}^3} + \frac{1}{4!}\frac{\partial^4 U}{\partial \mathbf{r}^4} + \cdots$$

$$\frac{\partial U}{\partial \mathbf{r}} = -\boldsymbol{F}$$

Harmonic

$$U = U_0 + \frac{1}{2}\frac{\partial^2 U}{\partial \mathbf{r}^2} + \frac{1}{6}\frac{\partial^3 U}{\partial \mathbf{r}^3} + \frac{1}{24}\frac{\partial^4 U}{\partial \mathbf{r}^4} + \cdots$$

EVERYTHING ELSE is categorized as “anharmonicity”

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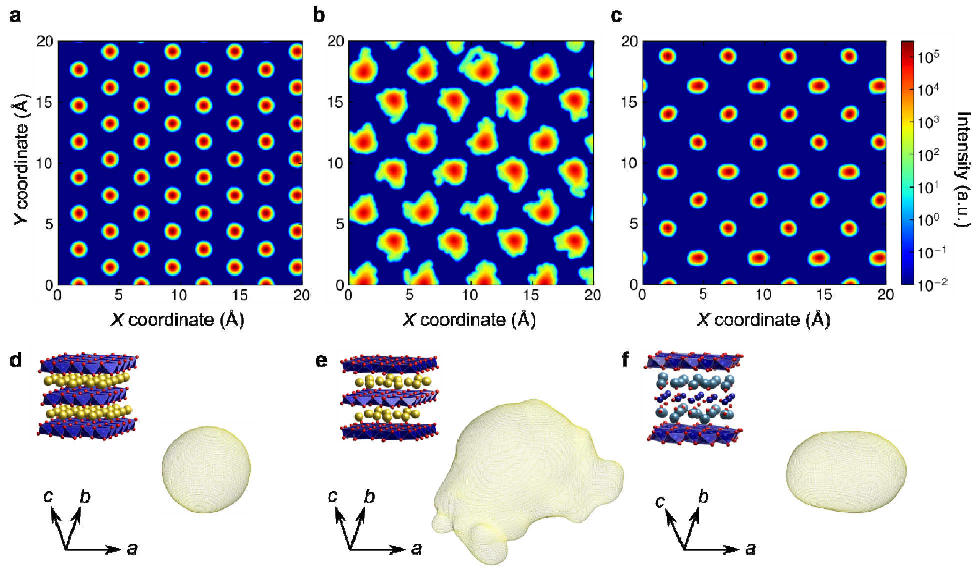
Variety of “Anharmonicity”



個々の原子振動が非調和的　　集団で非調和的

SF, MY, CAJF, Sci. Rep. (2018)

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CTE: Coeff. Thermal Expansion

✓Introduction to Computation (ab initio and beyond)

✓Thermal Conductivity

✓Thermal Expansion

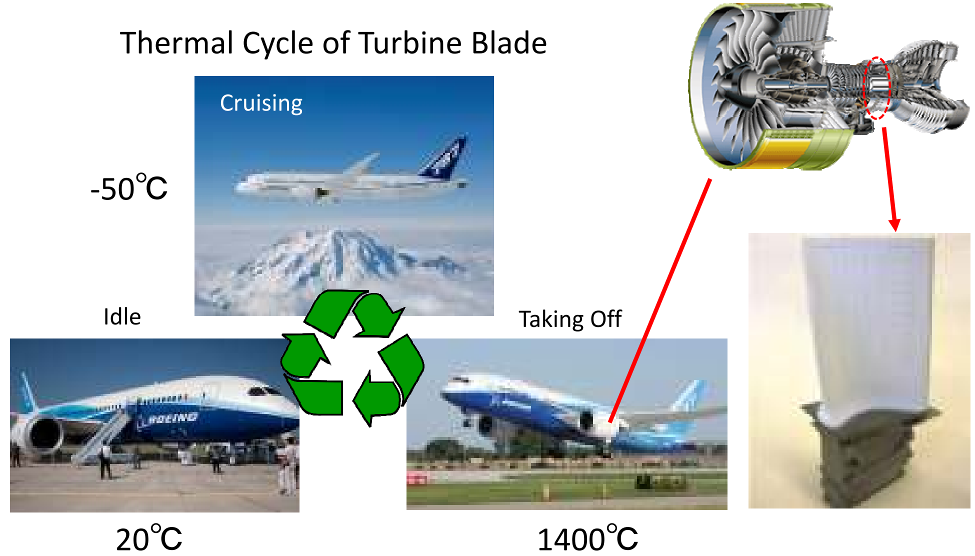
✓Conclusions

Masato Yoshiya : yoshiya@ams.eng.osaka-u.ac.jp, http://www.cmdc.ams.eng.osaka-u.ac.jp

Thermal Expansion : EBC

SIP-SM^4I Structural Materials for Innovation

EBC: Environmental Barrier Coatings



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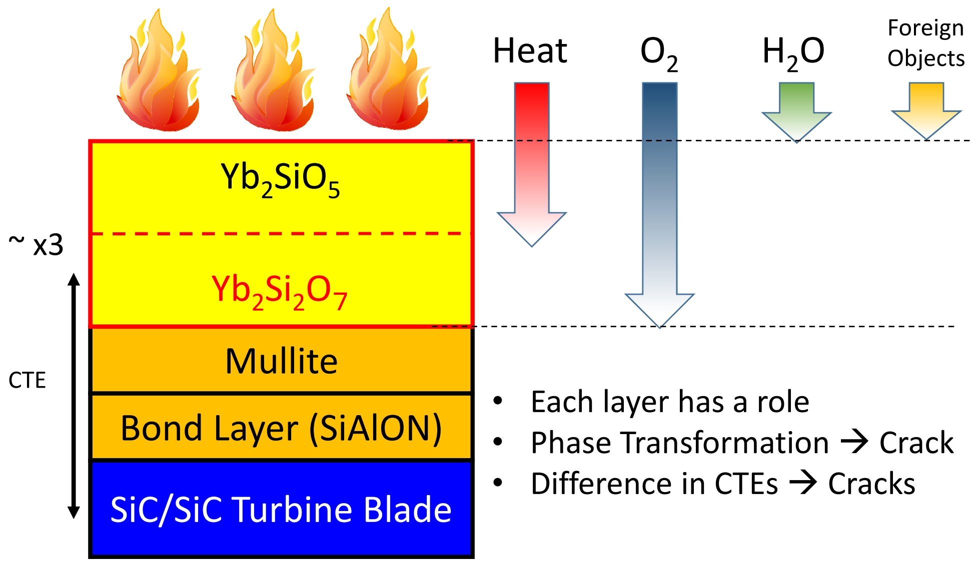
Multilayers of EBC



- Each layer has a role
- Phase Transformation → Crack
- Difference in CTEs → Cracks

The most serious concern is lifetime.

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Mitigate Thermal Fatigue and Fracture

1. Suppress Phase Transformation: Gibbs Free Energy (at high T &P)
2. Control CTE : Anharmonicity?

J. Eur. Ceram. Soc, (2019)

Grüneisen parameter (anharmonicity)
Differences attributed to γ (Conventional)

$$\alpha = \frac{\rho\, C_V\, \gamma}{K_T}$$

α : Coeff. Thermal Expansion
ρ : Density (Mass)
C_V: Specific Heat
K_T: Elastic Constant
γ : Grüneisen parameter

Questions left:

- How to change anharmonicity of phonons?
- Wther thermal conductivity is sacrificed or not?
- Can we use the equation above?

→Directly calculate equilibrium volume at each T having minimum Gibbs free energy

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Approaches to Thermal Expansion

1. CTE～10^{-6}/K： *ab initio* Calc.
2. Phonons： Lattice Dynamics（not MD）
3. T dependence： "Quasi-"harmonic Approx.
4. *f* -electrons： Almost frozen（pseudized）
5. Crystal Symmetry： Not fixed（exp. at high T）
6. Preliminary： Machine Learning

Validity of these assumption verified before main calc.
（Vol.: -0.5% underestimated, CTEs are good agreements with exp.）

Conclusions #1

For computational studies to do some role,
It is critically important

- To fully understand advantages and limitations of each method
- To carefully set a problem (What to understand)
- To discuss experimentalist beforehand

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Conclusions #2

It is probably a good idea

For Experiments

To talk with computer guys
not for ideal values or theoretical values
but to sort out complexity of reality
and to find out mechanism behind phenomena

For computer guys

To go out to find that world is wider

To talk with your colleague to find out what to calculate

For Theorist (Analytical)

To let computers help you to solve your problem
while sleeping