First-principles study of the lattice dielectric function in rutile TiO_2

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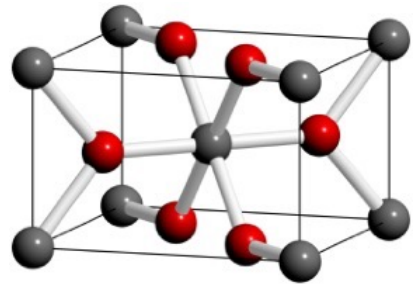


- Lattice dielectric properties
- Anharmonic phonon theory
- Applied to strongly anharmonic rutile TiO_2

TA et al. *arXiv preprint arXiv:2210.15873* (2022).

YITP Workshop Fundamentals in density functional theory (DFT2022)
@ Y306, Yukawa Hall, YITP, Kyoto University

Dielectric function : 5G・6G materials

5G:30–60GHz

6G:100–300GHz

- dielectric loss is important in higher frequency region (~THz)

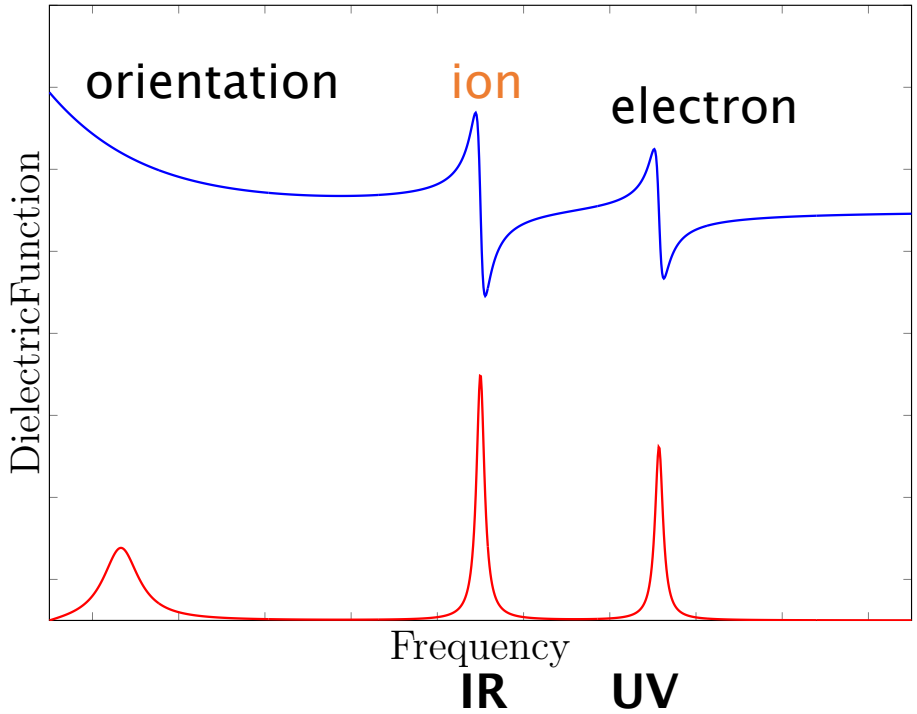
Dielectric loss

$$\tan\theta = \epsilon''/\epsilon'$$

Dielectric function

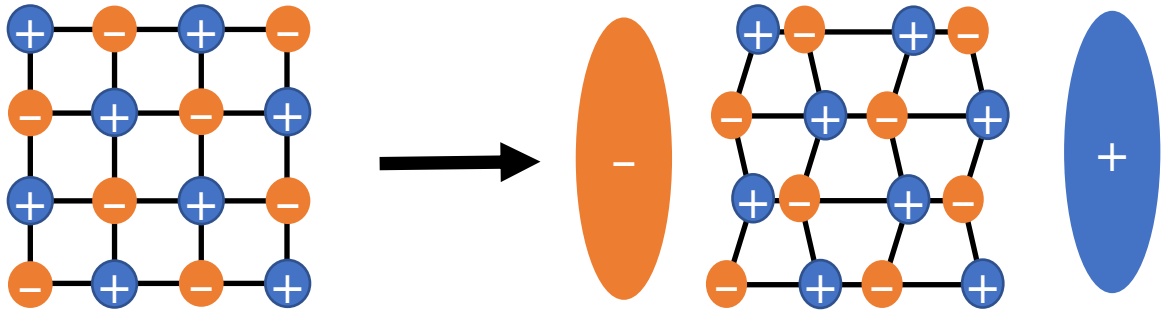
$$\epsilon(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$$

- Ionic polarization is dominant in THz region



Ionic polarization (IR-active phonon)

$$\boldsymbol{P} = \sum_{\kappa} Z_{\kappa} r_{\kappa}$$



(+ and – move oppositely)

Lattice dielectric function by phonons

➢ **Dielectric function of phonons[1]**

$$\epsilon_{\alpha\beta}(\omega) = \epsilon^{\infty}_{\alpha\beta} + \frac{1}{V_0}\sum_{(\mathbf{0},j)} \frac{S^j_{\alpha\beta}}{\omega^2_{\mathbf{0}j} - \omega^2 + 2\omega_{\mathbf{0}j}\Sigma_{\mathbf{0}j}(\omega)}$$

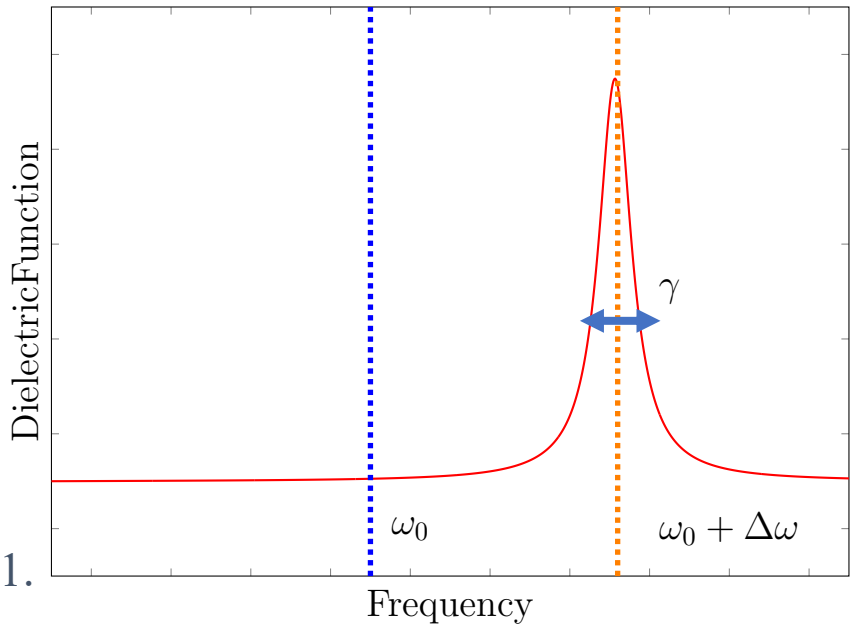
S :: mode oscillator strength

ω_0 :: phonon frequency

Σ :: phonon self energy
(real: frequency shift, imaginary: linewidth)

Lorentz model

$$\epsilon(\omega) = \epsilon^{\infty} + \sum_{(\mathbf{0}j)} \frac{\Delta\epsilon_{\mathbf{0}j}\Omega^2_{\mathbf{0}j}}{\Omega^2_{\mathbf{0}j} - \omega^2 + i\gamma_{\mathbf{0}j}\omega}$$



➢ Anharmonic phonon calculation

T. Tadano et al. 2014. J. Phys. : Cond. Mat. 26.22 (2014): 225402.

Hellman Olle et el. *Phys. Rev. B* 84.18 (2011): 180301.

Monacelli, Lorenzo, et al. J. Phys.: Cond. Mat. 33.36 (2021): 363001.

Phono anharmonic effect is essential for dielectric function

[1] R.A. Cowley. Advances in Physics 12(48):421–480, 10 1, 1963.

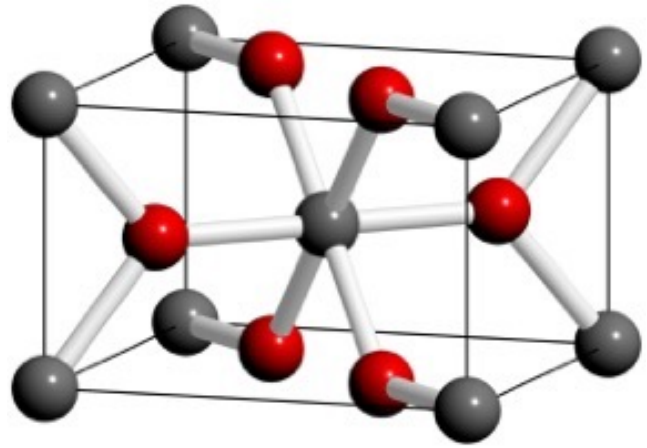
ab-initio calculation on Dielectric properties

DFT calculation on Dielectric properties from anharmonic-phonon theory

- anharmonic phonon calculations
  - Thermal Conductivity
  - Structure phase transition
  - NOT so many optical properties…

- Objective :: ab-initio dielectric function on rutile TiO_2
  - Self-consistent approach for Strongly Anharmonic materials
  - Frequency-dependence of self-energy

Rutile TiO_2



O Ti

- Strong Anharmonicity
- gigantic dielectric constant (incipient ferroelectric)

[1] Fugallo, Giorgia, Benoit Rousseau, and Michele Lazzeri *Physical Review B* 98.18 (2018): 184307.
[2] Tong, Zhen, et al *Physical Review B* 101.12 (2020): 125416

Harmonic Phonon Theory

Lattice energy expansion (with atomic displacements)

$$\delta U = U_2 + U_3 + U_4 + \cdots$$

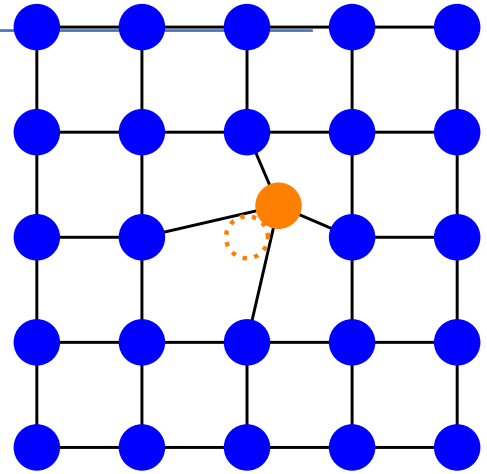
Harmonic Hamiltonian (ω :: harmonic phonon frequency)

$$H_0 = \sum_{\mathbf{q}j} \omega_{\mathbf{q}j} A^{\dagger}_{\mathbf{q}j} A_{\mathbf{q}j}$$

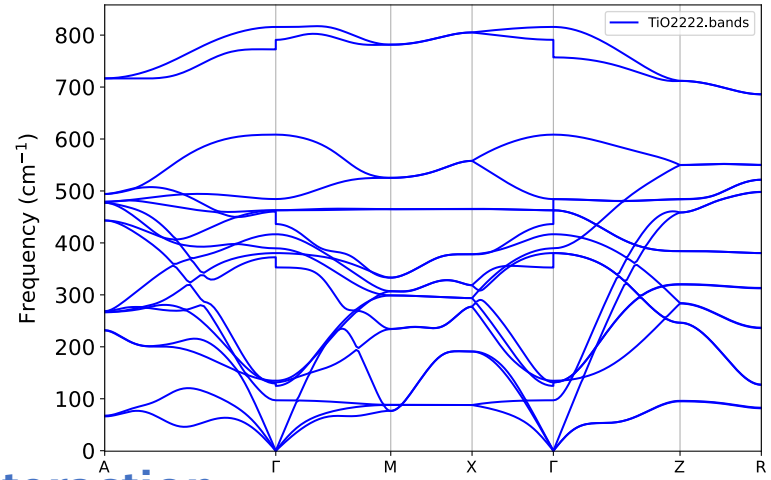
Green's function

$$G_{\mathbf{q},jj'}(\omega) = \frac{2\omega_{qj}\delta_{jj'}}{\omega_{qj}^2 - \omega^2}$$

Atomic displacement



Phonon Band structure



✗ NO phonon-phonon interaction

→ NO phonon linewidth

→ impossible to calculate dielectric properties

We need higher order terms to include phonon-phonon interaction

Anharmonic Phonon Theory[1]

Lattice energy expansion (with atomic displacement)

$$\delta U = \boldsymbol{U}_2 + \underline{\boldsymbol{U}_3 + \boldsymbol{U}_4 + \cdots}$$

anharmonic terms (3rd,4th,,,)

Hamiltonian

$$H = H_0 + U_3 + U_4 + \cdots$$

harmonic 3phonon 4phonon

Green's function

$$G_{\mathbf{q},jj'}(\omega) = \frac{2\omega_{qj}\delta_{jj'}}{\omega_{qj}^2 - \omega^2 - 2\omega_{qj}\Sigma_{\mathbf{q},jj'}(\omega)}$$

O Include phonon-phonon interaction

① Frequency shift $\Delta\omega(q,\omega,T) = -\operatorname{Re}\Sigma_q(\omega_q)$

② linewidth $\Gamma(q,\omega,T) = \operatorname{Im}\Sigma_q(\omega_q)$

Anharmonic effect give rise to phonon frequency-shift & linewidth

[1] T. Tadano, Y. Gohda, & S. Tsuneyuki. (2014). *Journal of Physics: Condensed Matter*, *26*(22), 225402

Estimate phonon properties from DFT[1]

- Lattice energy expansion (with atomic displacement)

Interatomic force constant (parameter)

$$\delta U = U_2 + U_3 + U_4 + \cdots$$
$$= \frac{1}{2}\sum_{i,j} \Psi_{i,j} u_i u_j + \frac{1}{3!}\sum_{i,j} \Psi_{i,j,k} u_i u_j u_k + \frac{1}{3!}\sum_{i,j} \Psi_{i,j,k,l} u_i u_j u_k u_l + \cdots$$
$$= \boldsymbol{b} \cdot \boldsymbol{\Psi}$$

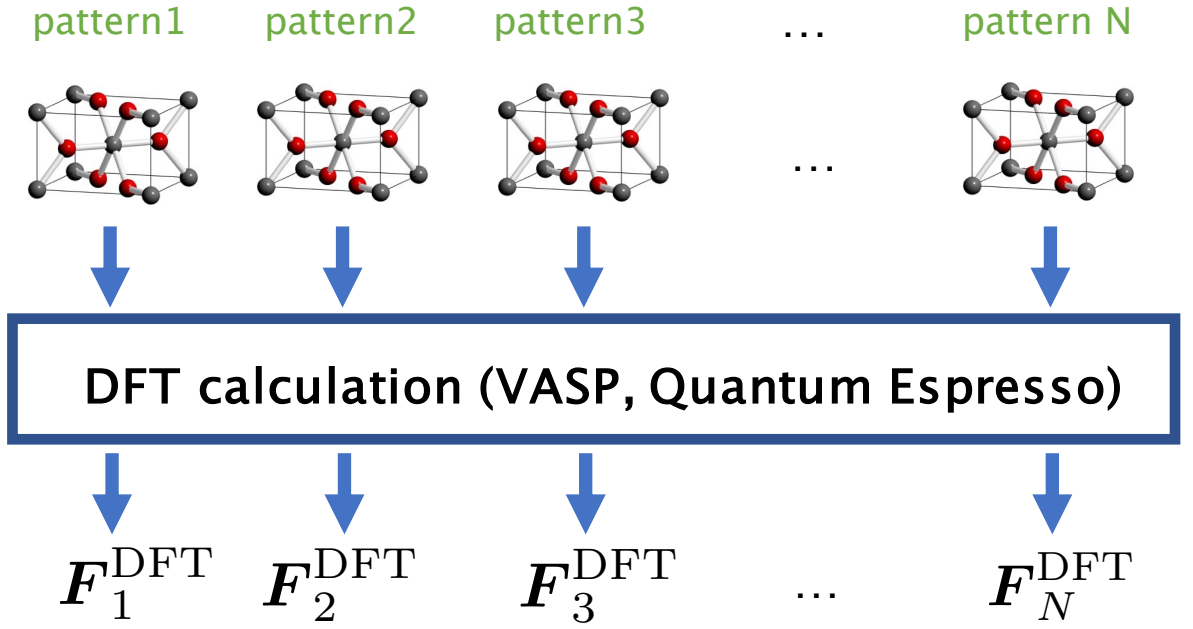
Atomic displacement (descripter)

- Force acting on atoms

$$F = -\frac{\partial U}{\partial u} \equiv A\boldsymbol{\Psi}$$

- Least square fitting for IFCs

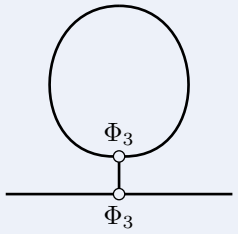
$$\tilde{\boldsymbol{\Psi}} = \arg\min_{\Psi} |A\boldsymbol{\Psi} - \boldsymbol{F}^{\mathrm{DFT}}|^2$$



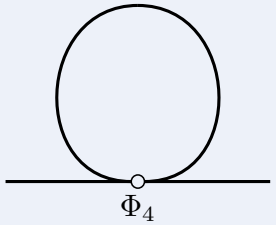
[1] T. Tadano, Y. Gohda, & S. Tsuneyuki. (2014). *Journal of Physics: Condensed Matter*, *26*(22), 225402

Self-energy of phonon

Tadpole Σ^T

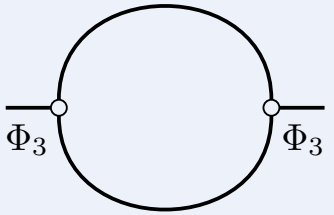


Loop Σ^L



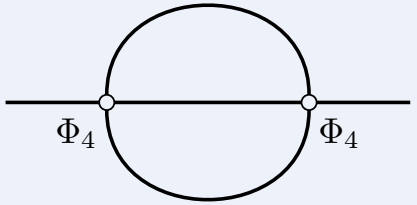
ω-independent, real

Bubble $\Sigma^B(\omega)$



2/3phonon-scattering

4ph $\Sigma^{4ph}(\omega)$



4phonon-scattering

ω-dependent, complex

Calculate phonon frequencies self-consistently, not perturbatively

	ω-dependent	Real/Complex	Real	Imaginary
Tadpole	×	Real	SCPH	-
Loop	×	Real	SCPH	-
Bubble	○	Complex	SCPH+B	One-shot
4ph	○	Complex	One-shot	One-shot

Self-Consistent-PHonon (SCPH)

Calculate renormalized phonon frequencies including Tadpole&Loop

SCPH equation [1] : Tadpole&Loop

- Self consistent equation for ω and G^S

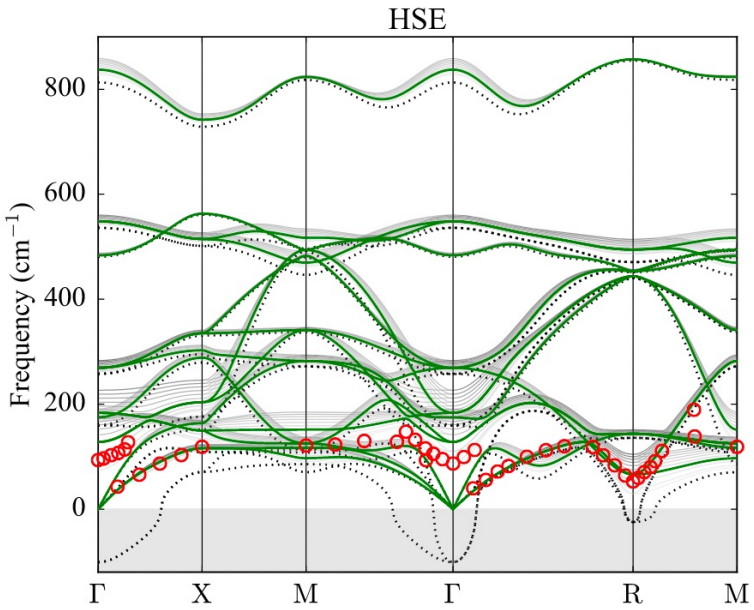
$$\left[G_q^S(\omega)\right]^{-1} = \left[G_q^0(\omega)\right]^{-1} - \Sigma^{\mathrm{T}}[G^S] - \Sigma^{\mathrm{L}}[G^S]$$

$$G^{\mathrm{S}}_{\mathbf{q},jj'}(\omega) = \frac{2\omega^{\mathrm{S}}_{qj}\delta_{jj'}}{(\omega^{\mathrm{S}}_{qj})^2 - \omega^2}$$

SCPH+bubble equation[2] : Bubble (real part)

- Self consistent equation for Ω. G^S is fixed during calculation

$$\Omega_q^2 = \left(\omega_q^S\right)^2 - 2\omega_q^S \,\mathrm{Re}\,\Sigma_q^{\mathrm{B}}[G^S, \Phi_3](\omega = \Omega_q)$$

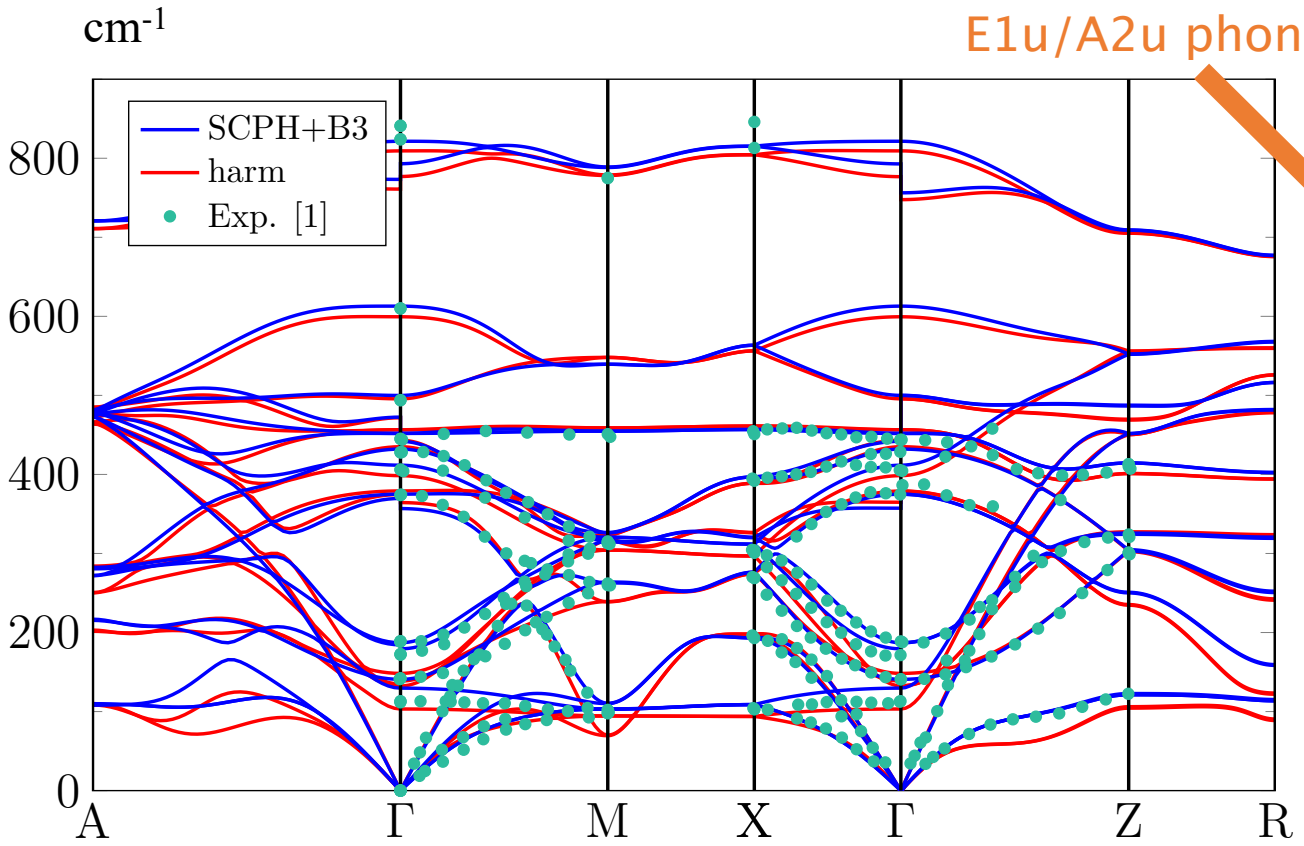


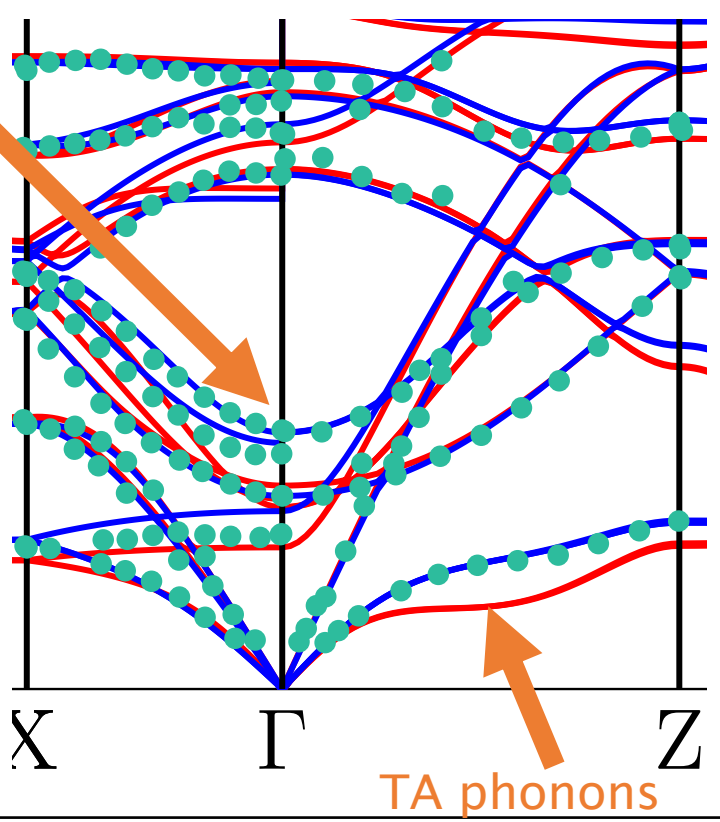
$$\omega_{\mathrm{harm}} \longrightarrow \omega^{\mathrm{S}} \longrightarrow \Omega^{\mathrm{SCPH+B}}$$

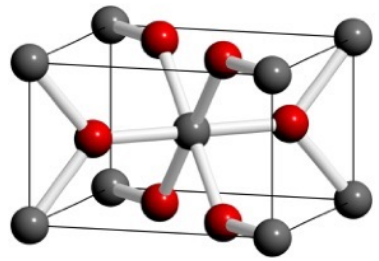
[1] T. Tadano, S. Tsuneyki Phys. Rev. B .92.054301
[2] Tadano, Terumasa, and Wissam A. Saidi. *Physical Review Letters* 129.18 (2022): 185901.
[3] Tadano, Terumasa, and Shinji Tsuneyuki. *Journal of the Physical Society of Japan* 87.4 (2018): 041015.

Band：harmonic vs SCPH+B (r²SCAN)

SCPH+B well describes TA-phonons & Γ-point optical phonons.





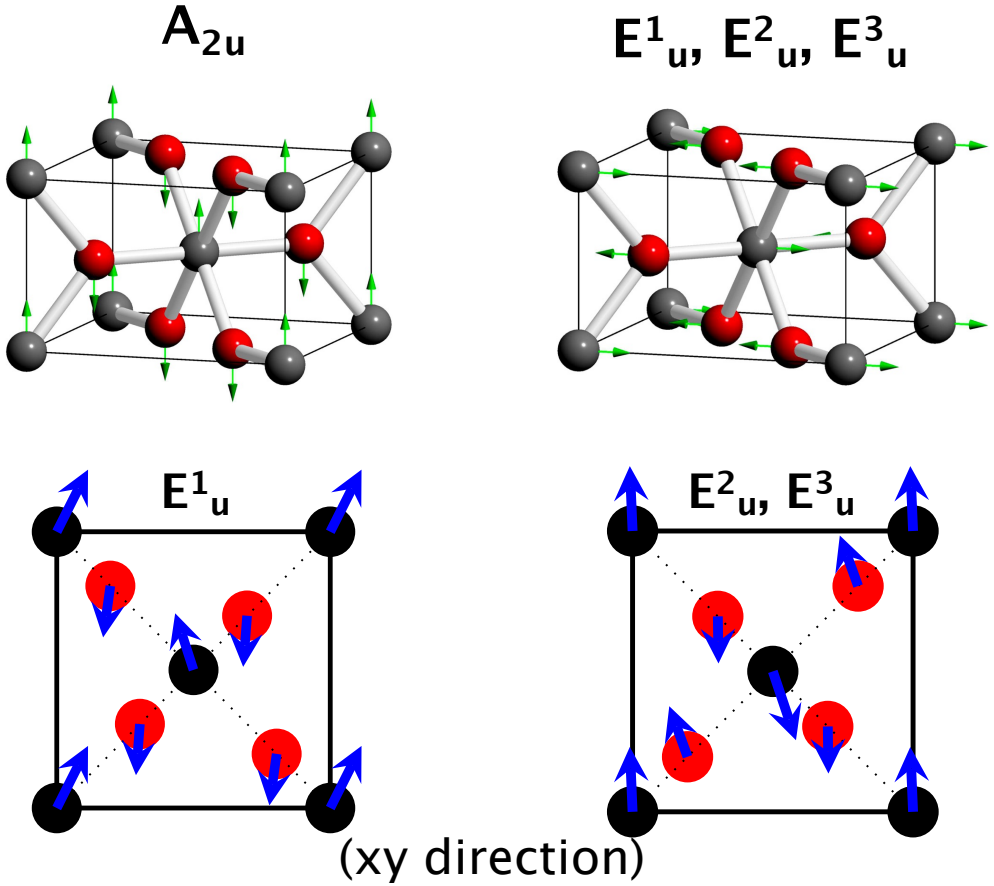


DFT	VASP
Supercell	2×2×4 supercell
Functional	r2SCAN
K-points	3×3×3
Phonon	ALAMODE
Temperature	300 [K]

[1]Traylor, Joseph Gibson, et al. *Physical Review B* 3.10 (1971): 3457.

IR active phonons : harmonic vs SCPH+B

SCPH+B well describes strongly anharmonic A2u & E1u



IR active phonon frequency

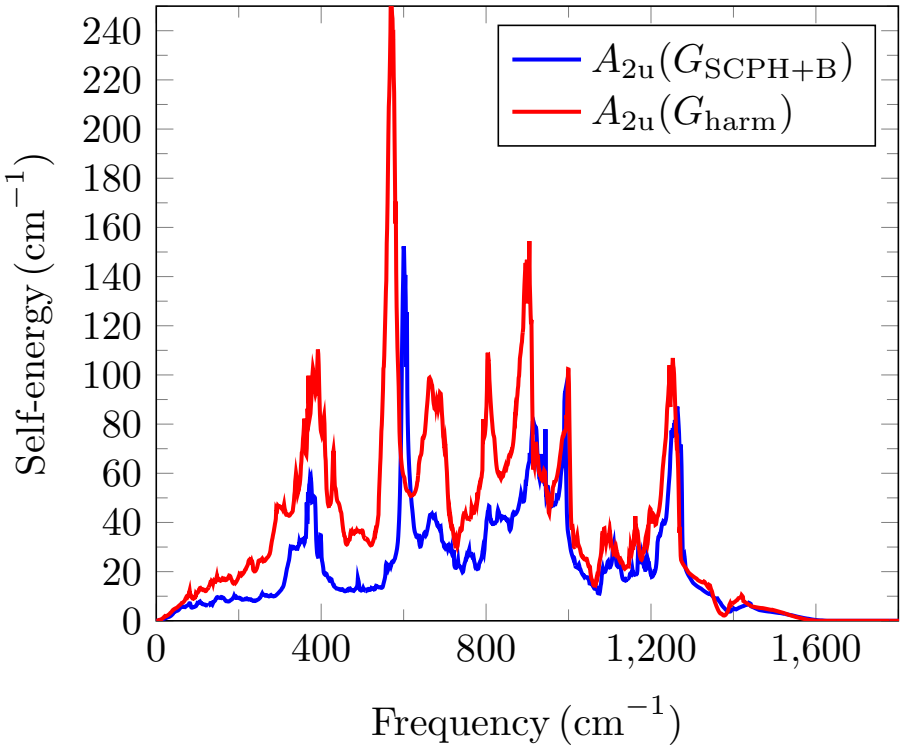
	R2SCAN		neutron [1]
	harm	SCPH+B3	
A_{2u}	138.5	179.4	172.6
E^1_u	132.7	186.9	189
E^2_u	378.8	374.9	374
E^3_u	495.7	500.1	494

[1]Traylor, Joseph Gibson, et al. *Physical Review B* 3.10 (1971): 3457.

Linewidth (non-SC vs SCPH+B)

Perturbative calculation Overestimates linewidth

Imaginary part of Bubble self-energy



ω-independent linewidth

$$\gamma^{\mathrm{SCPH+B}} = 2\,\mathrm{Im}\,\Gamma[G_{\mathrm{SCPH+B}}](\omega = \omega_{\mathrm{SCPH+B}})$$
$$\gamma^{\mathrm{non-SC}} = 2\,\mathrm{Im}\,\Gamma[G_{\mathrm{harm}}](\omega = \omega_{\mathrm{harm}})$$

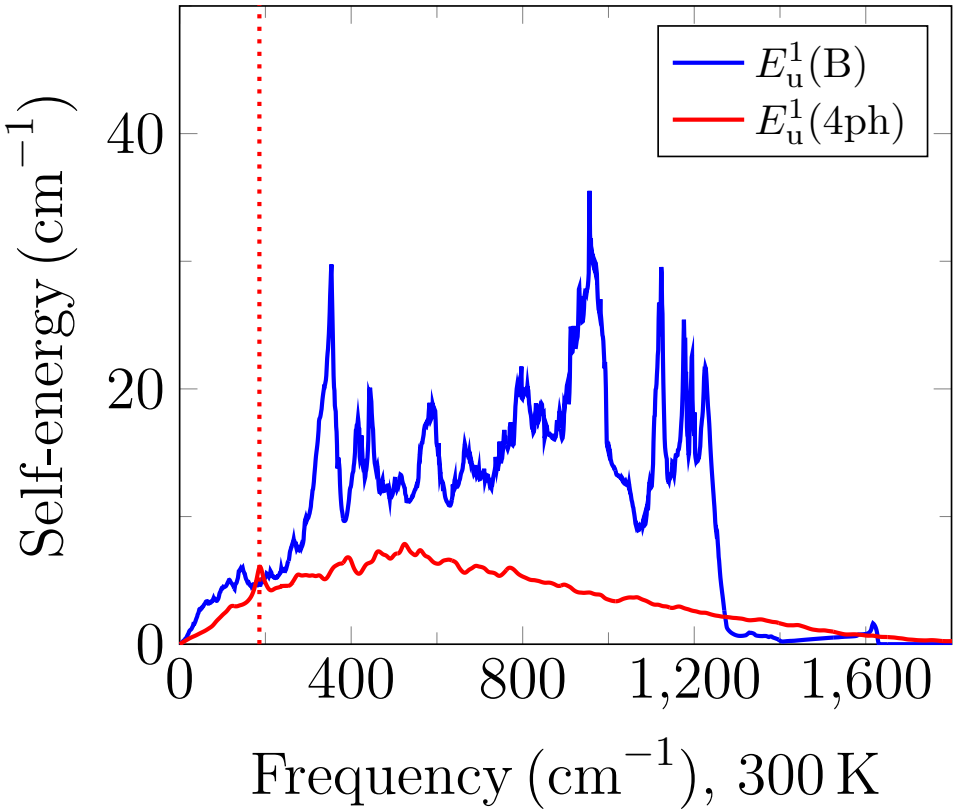
	non-SC			SCPH+B			FPSQ [1]
	bubble	4ph	total	bubble	4ph	total	
E_u^1	21	70	91	8.5	8.0	16	14.7
E_u^2	41	7.1	48	15	1.8	16	19.3
E_u^3	28	12	40	13	3.5	16	22.4
A_{2u}	29	52	81	16	9.6	26	20.0

[1] Schöche, S., et al. *Journal of Applied Physics* 113.16 (2013): 164102.

Linewidth (bubble vs 4ph)

4ph is as large as bubble linewidth

Self energy (E1u phonon)



ω-independent linewidth

$$\gamma^{\mathrm{SCPH+B}} = 2\,\mathrm{Im}\,\Gamma[G_{\mathrm{SCPH+B}}](\omega = \omega_{\mathrm{SCPH+B}})$$

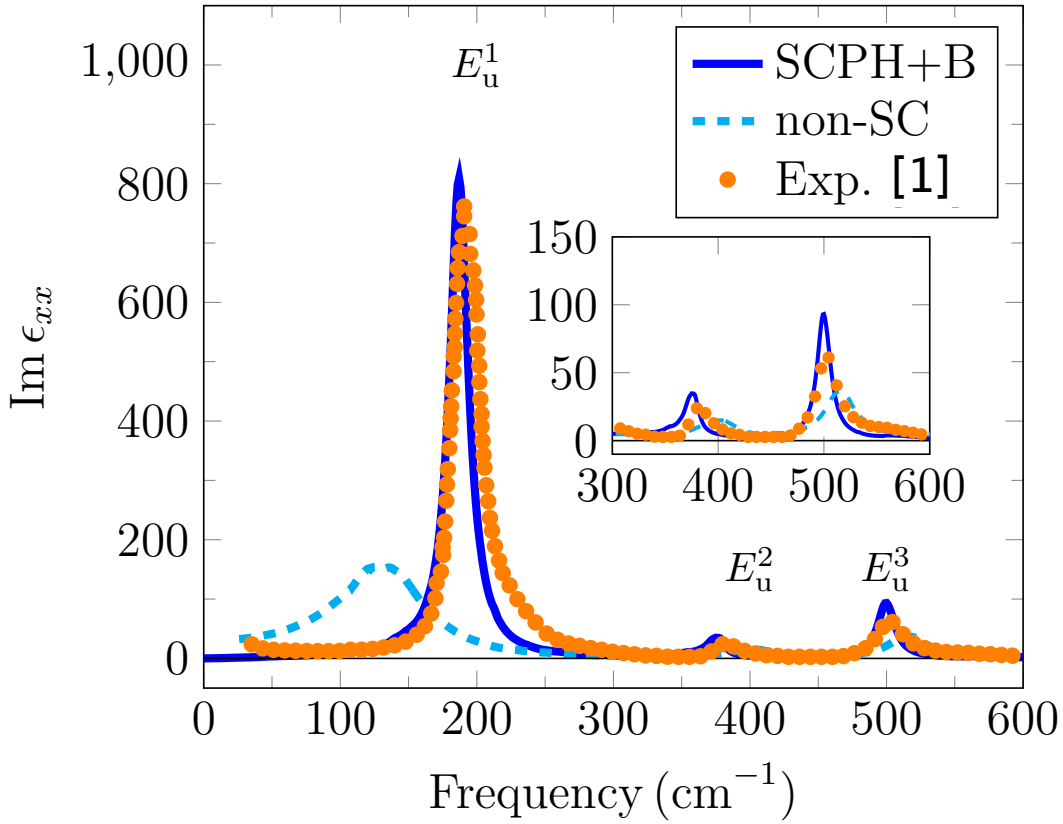
Calculated linewidth [cm-1]@300K

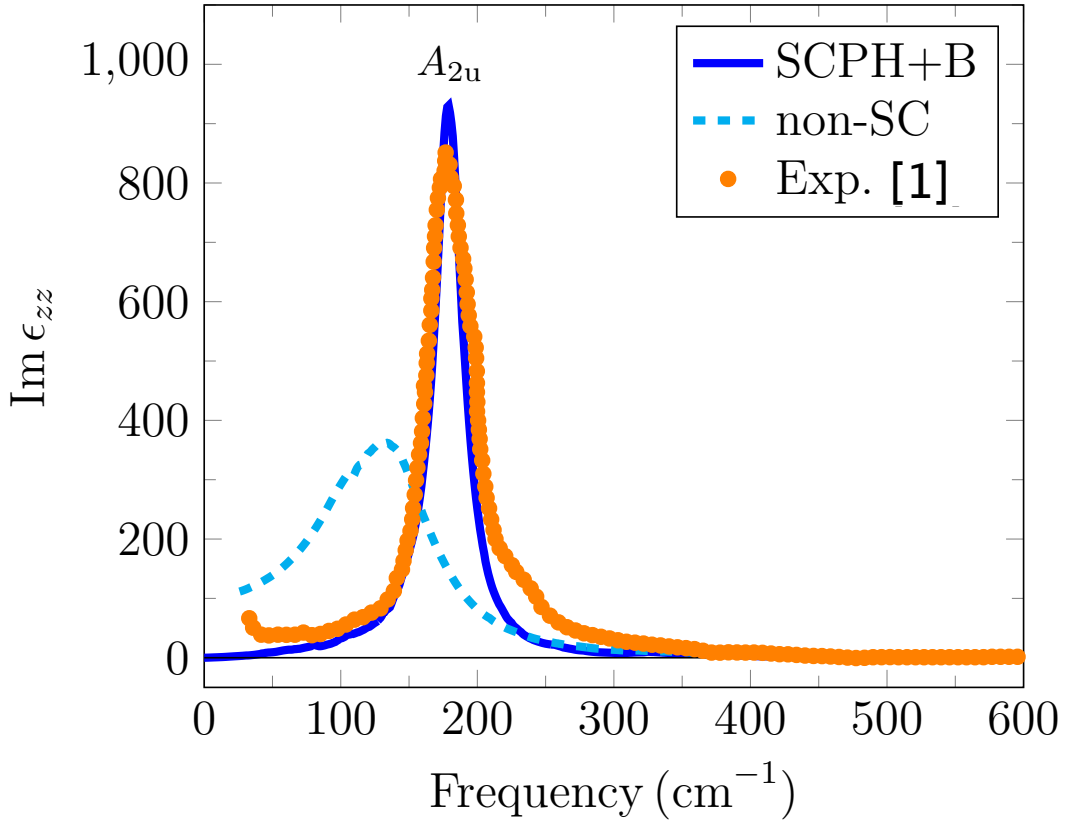
	SCPH+B3			Exp. [1]
	bubble	4 ph	total	
E1u	8.54	7.95	16.4	14.7 ± 8.0
E2u	14.5	1.81	16.2	19.3 ± 2.8
E3u	12.6	3.47	16.0	22.4 ± 3.1
A2u	16.3	9.57	25.7	20.0 ± 10.2

[1] Schöche, S., et al. *Journal of Applied Physics* 113.16 (2013): 164102.

Dielectric function

SCPH+B very well agree with experimental data



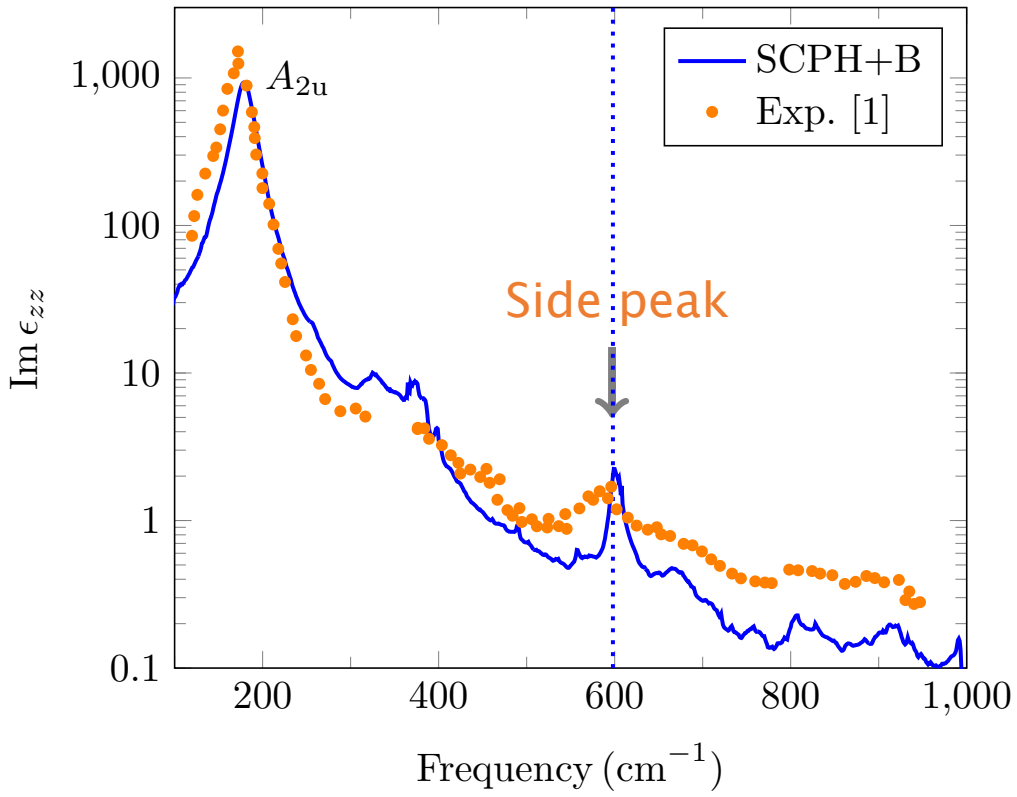


[1] Kanehara, Kazuki, et al. *Journal of the Ceramic Society of Japan* 123.1437 (2015): 303-306

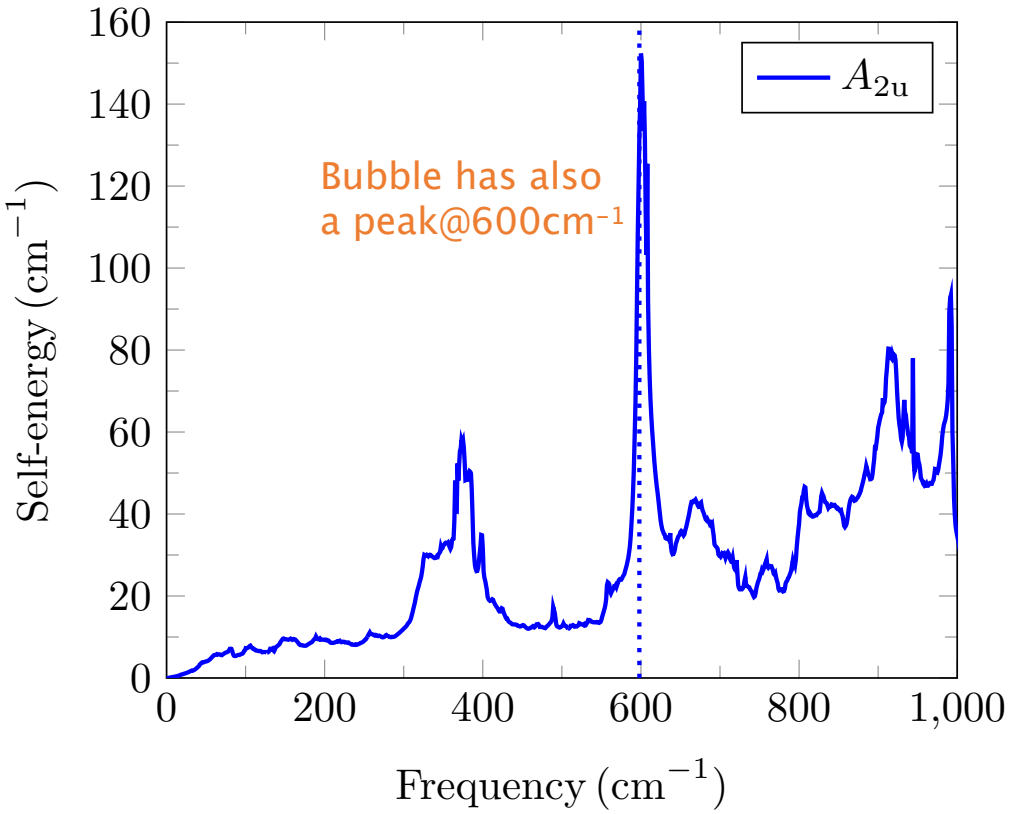
Dielectric function : Side peak@600cm^{-1}

Bubble-selfenergy describes the side peak

Imaginary part of ε_{zz}



Imaginary part of bubble (A2u)



[1] Schöche, S., et al. *Journal of Applied Physics* 113.16 (2013): 164102.

Conclusion

SCPH+B & frequency-dependent self-energy is important for dielectric property

- **Self-Consistent Phonon approach (SCPH+B) for strongly anharmonic material**

  ※ SCPH+B well describe phonon frequencies of rutile TiO_2

  ※ Phonon frequencies renormalization by SCPH+B is important for phonon linewidths

  ※ 4ph linewidth is as large as bubble linewidth @ 300K

- **Cowley's theory to use frequency-dependent self-energy**

  ※ Bubble self-energy can describe side-peak of dielectric function

  ※ 4ph self-energy do not so frequency-dependent