Cij paper on **arXiv**
arxiv.org/abs/2101.12596

Cij code on **GitHub**
github.com/mineralscloud/cij

A Python code for ***thermoelasticity***

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Outline

- Background
- Static elasticity calculation
- Review of the SAM-Cij method
- Usage
- Examples
- Summary

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Background

- **Elasticity at high-PT**
  - Elastic tensor (C_{ij}) vs. *PT* and acoustic velocities can provide geophysical insights (e.g., composition and temperature in the Earth's interior) by helping the ***interpretation of seismological observations.***
  - Despite recent developments, ***measuring C_{ij} at relevant conditions is still extremely challenging.***
- ***Ab initio* high-*PT* C_{ij}**
  - ***Traditional methods*** to compute C_{ij} (P,T) require phonon / MD runs on strained crystal configurations at each *PT* which is ***extremely time consuming.***
  - A ***semi-analytical method (SAM)*** to evaluate the thermal C_{ij} (SAM-Cij) was developed by ***Wu and Wentzcovitch (2011)*** [1,2] as an alternative. Its predictions show ***good agreement with measurements*** on many complex minerals.

1. F. Zou, Z. Wu, W. Wang, R. M. Wentzcovitch, *Journal of Geophysical Research: Solid Earth*. **123**, 7629–7643 (2018).
2. Z. Wu, R. M. Wentzcovitch, *Phys. Rev. B*. **83**, 184115 (2011).

Static elasticity calculation

- Static elastic coefficients are calculated using the stress vs strain method.
- we use Hooke's law to calculate the corresponding elastic tensor coefficient term:

$$\sigma_{ij} = C_{ijkl}\,\epsilon_{kl}$$

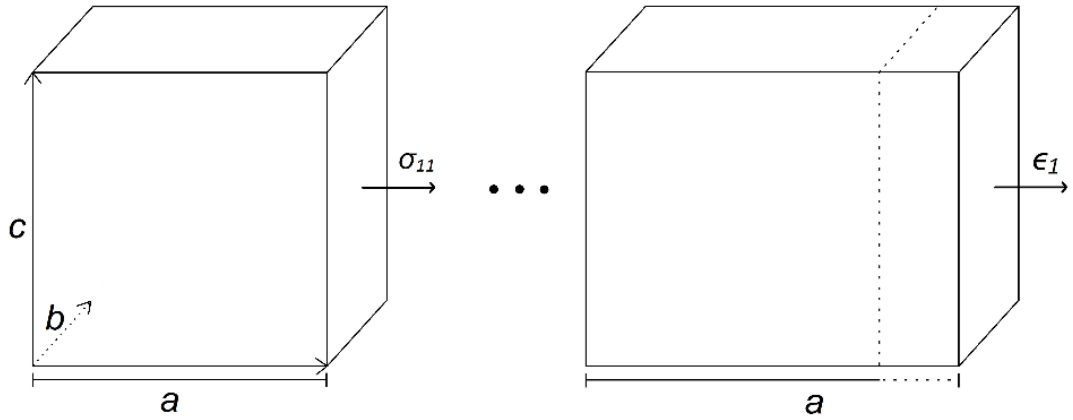

Figure 1. Stress and resulting strain on a cubic lattice.

Static elasticity calculation

If we apply the strain ϵ_1

$$\epsilon_1 = \begin{pmatrix} 0.01 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

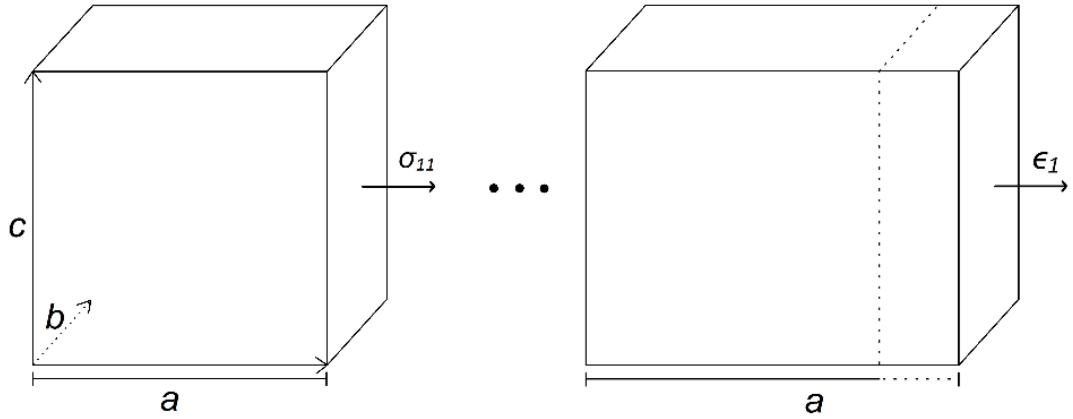

Figure 1. Stress and resulting strain on a cubic lattice.

After the strain, the lattice parameter become

$$\boldsymbol{a} = (I + \epsilon_1)\ \boldsymbol{a^0} = \begin{pmatrix} 1.01 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} a_{11}^0 & 0 & 0 \\ 0 & a_{22}^0 & 0 \\ 0 & 0 & a_{33}^0 \end{pmatrix} = \begin{pmatrix} 1.01\ a_{11}^0 & 0 & 0 \\ 0 & a_{22}^0 & 0 \\ 0 & 0 & a_{33}^0 \end{pmatrix}$$

The stress change $\sigma_{ij}^0 \rightarrow \sigma_{ij}^0 + \sigma_{ij}$

Because of the Hooks law $\sigma_{ij} = C_{ijkl}\ \epsilon_{kl} = C_{ijkl} \begin{pmatrix} 0.01 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}_{kl} = \begin{pmatrix} 0.01\ c_{11} & 0.01\ c_{16} & 0.01\ c_{15} \\ 0.01\ c_{16} & 0.01\ c_{12} & 0.01\ c_{14} \\ 0.01\ c_{15} & 0.01\ c_{14} & 0.01\ c_{13} \end{pmatrix}_{kl}$

We can calculate elastic coefficient terms $c_{11}, c_{12}, c_{33}, \ldots c_{66}$.

In practice, we apply a pair of positive and negative strains.

The SAM-Cij Method (1)

Thermal elastic constants are strain derivative of free energy

$$c_{ijkl}^{T} = \frac{1}{V}\left(\frac{\partial^2 F}{\partial e_{ij}\partial e_{kl}}\right) + \frac{P}{2}\left(2\delta_{ij}\delta_{kl} - \delta_{il}\delta_{kj} - \delta_{ik}\delta_{jl}\right)$$

Under the QHA, the vibrational contribution to the Helmholtz free energy is expressed as a function of phonon frequencies

$$F(V,T) = U^{\mathrm{st}}(V) + \frac{1}{2}\hbar\omega_{qm}(V) + k_B T \sum_{qm} \ln\left[1 - \exp\left[-\frac{\hbar\omega_{qm}(V)}{k_{\mathrm{B}}T}\right]\right]$$

The SAM-Cij Method (1)

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Longitudinal and off-diagonal thermal elastic constants can be expressed as function of strain derivative of phonon frequencies

$$c_{iijj}^{T}(V,T) = c_{iijj}^{\mathrm{st}} + \frac{\hbar}{2V}\sum_{qm}\left(\frac{\partial^2\omega_{qm}(V)}{\partial e_{ii}\partial e_{jj}}\right) + \frac{k_{\mathrm{B}}T}{V}\sum_{qm}\frac{\partial^2\left[\ln\left(1 - e^{-Q_{qm}}\right)\right]}{\partial e_{ii}\partial e_{jj}}$$

where $Q_{qm} = \frac{\hbar\omega_{qm}}{kT}$

The SAM-Cij Method (1)

$$c^{T}_{iijj}(V,T) = c^{\mathrm{st}}_{iijj} + \frac{\hbar}{2V}\sum_{qm}\left(\frac{\partial^2\omega_{qm}(V)}{\partial e_{ii}\partial e_{jj}}\right) + \frac{k_{\mathrm{B}}T}{V}\sum_{qm}\frac{\partial^2\left[\ln\left(1-e^{-Q_{qm}}\right)\right]}{\partial e_{ii}\partial e_{jj}}$$

$$\gamma^{ij}_{qm} = -\frac{\partial \ln \omega_{qm}}{\partial\, e_{ij}}$$

The strain derivative of mode frequency relates to the strain-Grüneisen parameter

$$= c^{\mathrm{st}}_{iijj} + \frac{\hbar}{2V}\sum_{qm}\left(\gamma^{ii}_{qm}\gamma^{jj}_{qm} - \frac{\partial\gamma^{ii}_{qm}}{\partial e_{jj}} + \delta_{ij}\gamma^{ii}_{qm}\right)$$

$$+ \frac{k_{\mathrm{B}}T}{V}\sum_{qm}\left[-Q^2_{qm}\frac{e^{Q_{qm}}}{\left(e^{Q_{qm}}-1\right)^2}\gamma^{ii}_{qm}\gamma^{jj}_{qm} + \frac{Q_{qm}}{\left(e^{Q_{qm}}-1\right)}\left(\gamma^{ii}_{qm}\gamma^{jj}_{qm} - \frac{\partial\gamma^{ii}_{qm}}{\partial e_{jj}} + \gamma^{ii}_{qm}\delta_{ij}\right)\right]$$

where $Q_{qm} = \frac{\hbar\omega_{qm}}{kT}$

The SAM-Cij Method (2)

$$\bar{\gamma} = \frac{1}{3N}\sum_{qm}\gamma_{qm} = \frac{1}{3N}\sum_{qm} -\frac{\partial \ln \omega_{qm}}{\partial V}$$

anisotropic approximation

$$\overline{\gamma^{ii}} = \frac{1}{3N}\sum_{qm}\gamma_{qm}^{ii} = \frac{1}{3N}\sum_{qm} -\frac{\partial \ln \omega_{qm}}{\partial\, e_{ii}} = \frac{1}{3}\frac{e_{11}+e_{22}+e_{33}}{e_{ii}}\overline{\gamma}$$

$$\overline{\gamma^{ii}\gamma^{jj}} = \begin{cases} \frac{1}{5}\frac{(e_{11}+e_{22}+e_{33})^2}{e_{ii}e_{jj}}\overline{(\gamma)^2} & \text{if } i = j \\ \frac{1}{15}\frac{(e_{11}+e_{22}+e_{33})}{e_{ii}e_{jj}}\overline{(\gamma)^2} & \text{if } i \neq j \end{cases}$$

$$\overline{\frac{\partial\gamma^{ii}}{\partial e_{jj}}} = \begin{cases} \frac{1}{5}\frac{(e_{11}+e_{22}+e_{33})^2}{e_{ii}e_{jj}}V\overline{\frac{\partial\gamma}{\partial V}} & \text{if } i = j \\ \frac{1}{15}\frac{(e_{11}+e_{22}+e_{33})^2}{e_{ii}e_{jj}}V\overline{\frac{\partial\gamma}{\partial V}} & \text{if } i \neq j \end{cases}$$

where $$e_{ii,k} = \frac{a_{i,k+1} - a_{i,k-1}}{(a_{i,k+1} + a_{i,k-1})/2} = \frac{\mathrm{d}a_{i,k}}{a_{i,k}} = \ln a_{i,k}$$

Review of the SAM-Cij Method (3)

- Some shear and off-diagonal terms (c_{ijij} and c_{ijkl}) are solvable by applying the constraint of strain energy conservation under axis rotation.
- I will not go into details about this.
- General solution are implemented for all crystal systems.
- Demonstrated with good agreement in three examples in different crystal systems here.

Usage

Installation

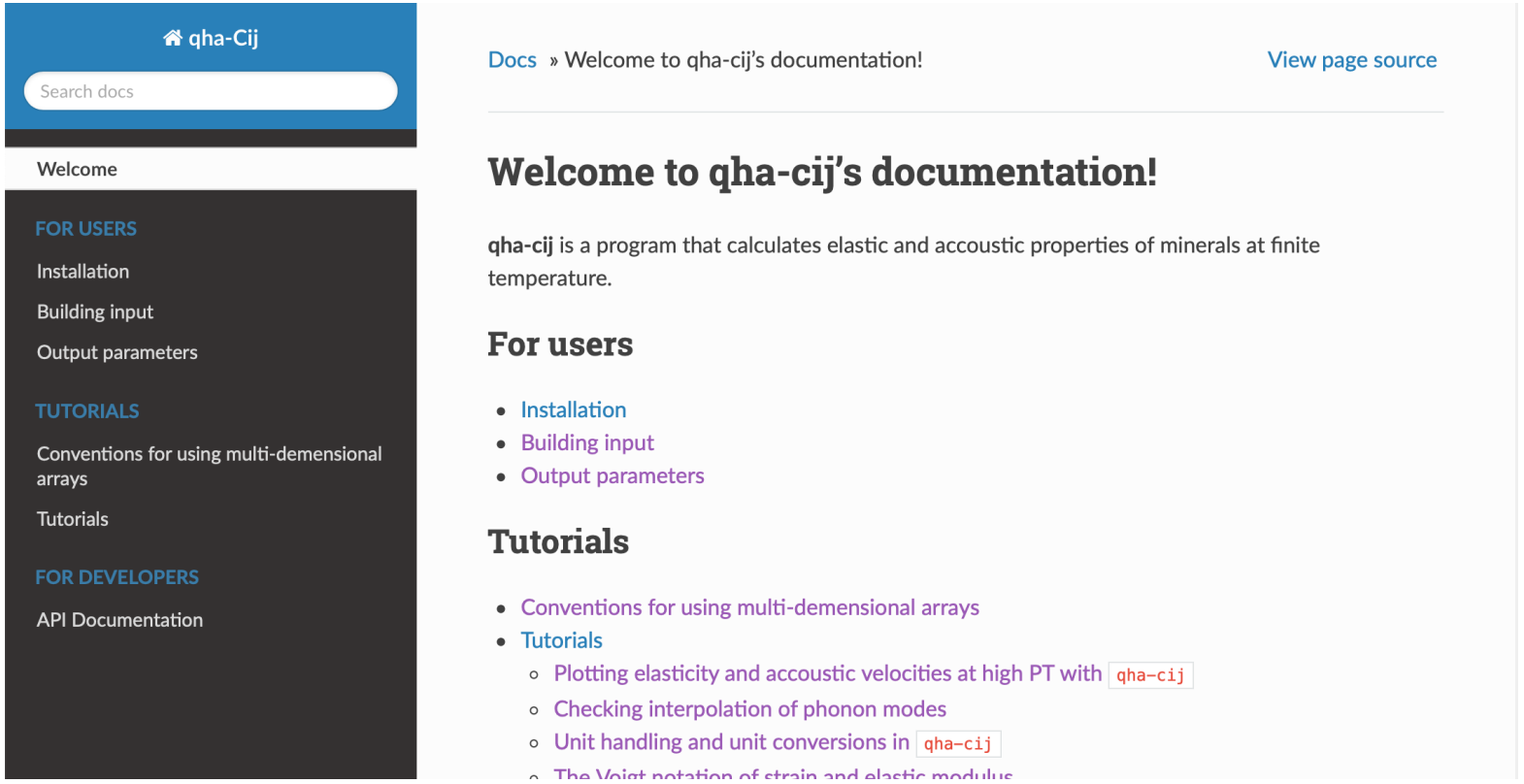
From GitHub

```
$ pip install cij
```

Online documentation

On GitHub Pages

mineralscloud.github.io/cij/

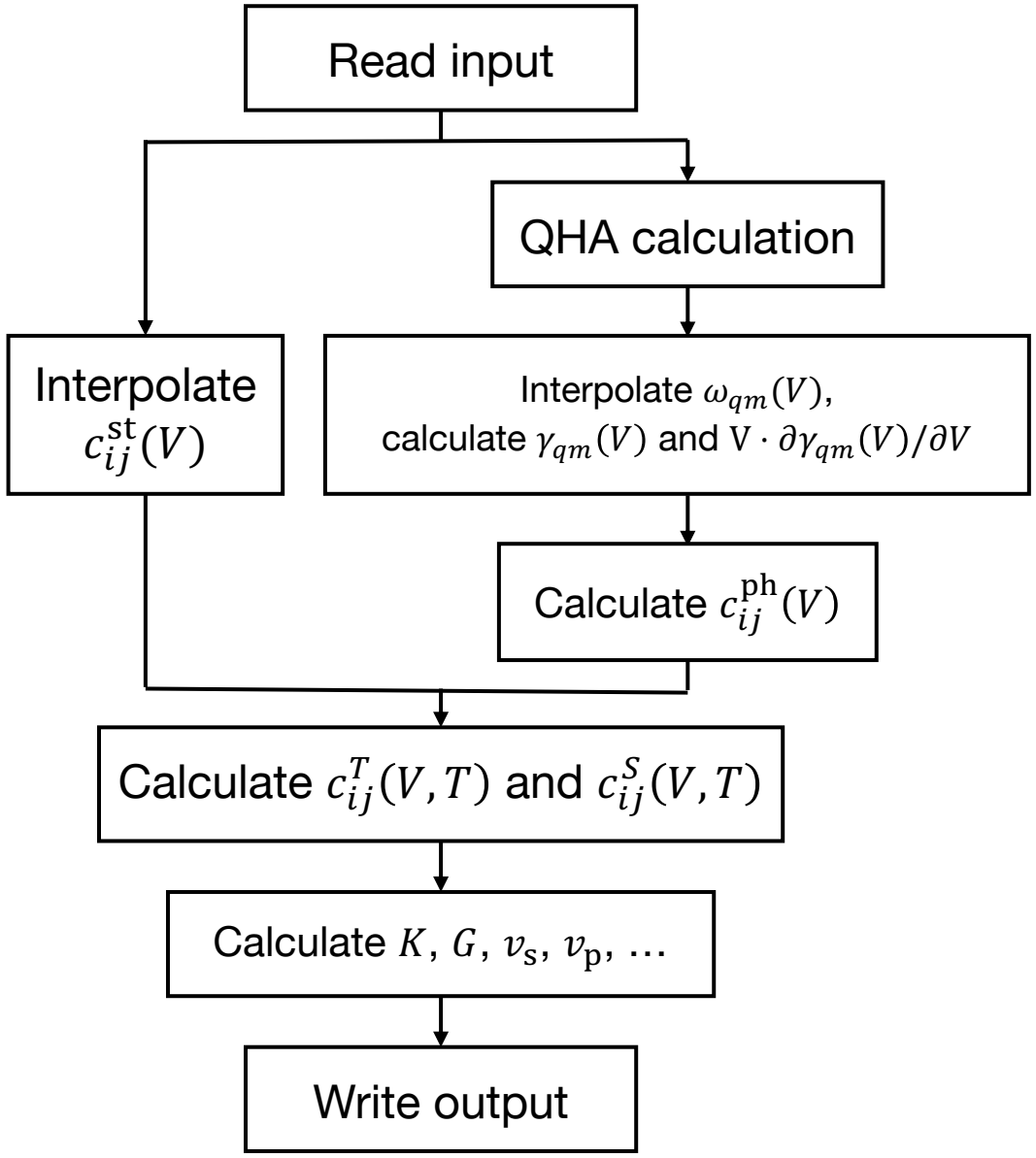


To initiate a SAM-Cij calculation:

```
$ cij run settings.yml
```

```
$ cij run settings.yml
```

Flowchart: SAM-Cij calculation

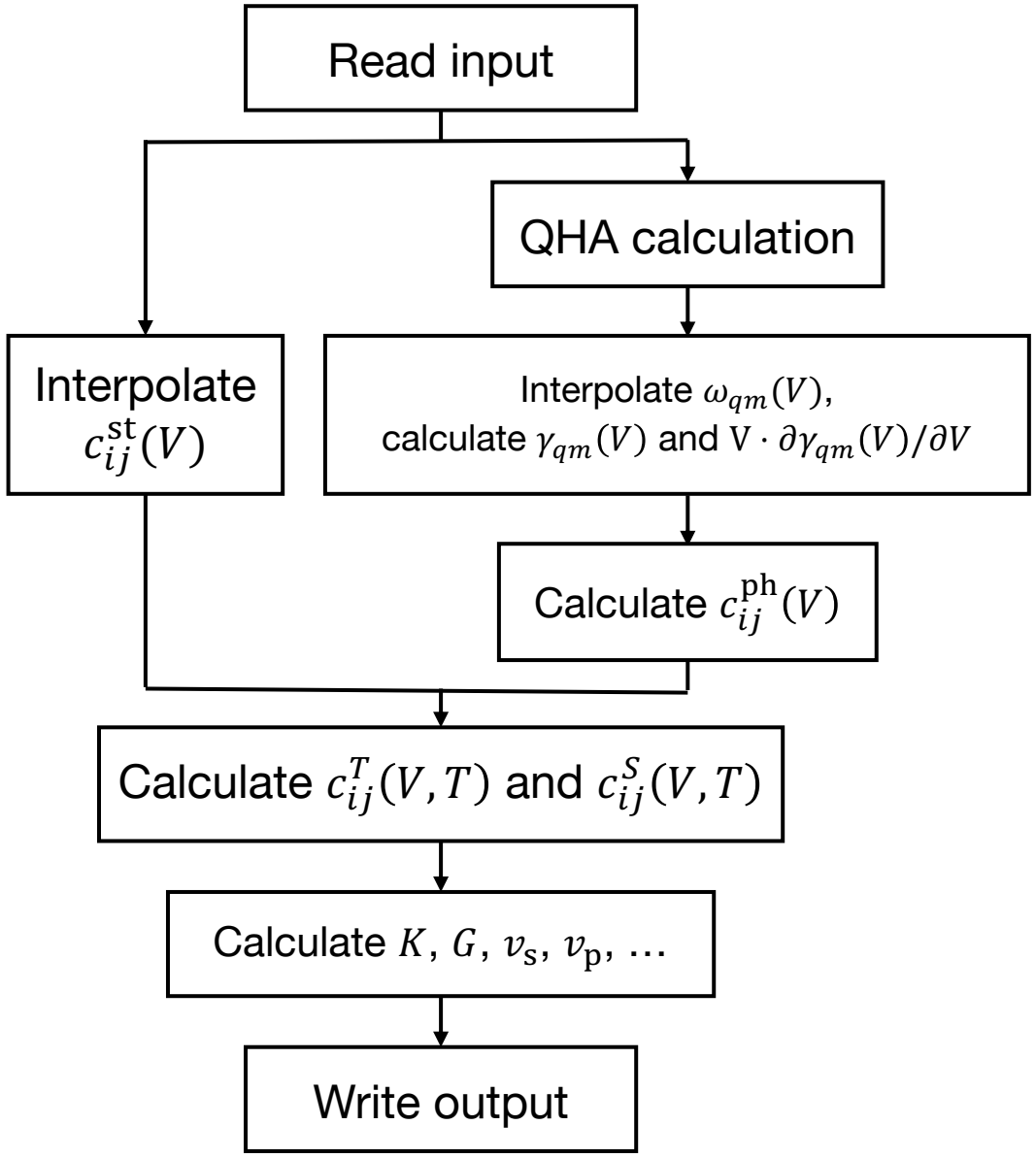


Usage: Building input files

```
$ ls

    settings.yml   # Calculation settings
    input01        # QHA input data
    elast.dat      # Static Cij data

$ cij run settings.yml
```



Usage: Building input files

```
$ ls

    settings.yml    # Calculation settings
    input01         # QHA input data
    elast.dat       # Static Cij data

$ cij run settings.yml
```

Program settings exmaple

```yaml
qha:
  input: input01
  settings:
    T_MIN: 0
    NT: 21
    DT: 100
    P_MIN: -1
    DELTA_P: 1
    NTV: 15
    order: 3
    volume_ratio: 1.2
elast:
  input: input02
  settings:
    system: trigonal8
    mode_gamma:
      interpolator: spline
      order: 3
output:
  pressure_base:
    - cij
    - bm_VRH
    - G_VRH
    - v_s
    - v_p
  volume_base:
    - cij
    - ...
```

Usage: Building input files

```
$ ls

    settings.yml   # Calculation settings
    input01        # QHA input data
    elast.dat      # Static Cij data

$ cij run settings.yml
```

Structure of the QHA input data

```
# title ...
nv   nq   np   nm   na

P= P1    V= V1    E= E1
q1x      q1y      q1z
ωq1,m1
ωq1,m2
...
q2x      q2y      q2z
ωq2,m1
...
P= P2    V= V2    E= E2
q1x      q1y      q1z
ωq1,m1
...

weights
q1x      q1y      q1z      wtq1
q2x      q2y      q2z      wtq2
...
```

Usage: Building input files

```
$ ls

    settings.yml   # Calculation settings
    input01        # QHA input data
    elast.dat      # Static Cij data

$ cij run settings.yml
```

The static Cij input

```
# comment line

V0  N   mcell

V   c11     c22     c33     …

V1  c11[V1] c22[V1] c33[V1]  …

V2  c11[V2] c22[V2] c33[V2]  …

…

VN c11[VN] c22[VN] c33[VN]  …

lattice_a lattice_b lattice_c

a1x[V1]   a2y[V1]   a3z[V1]

a1x[V2]   a2y[V2]   a3z[V2]

…

a1x[VN]   a2y[VN]   a3z[VN]
```

Usage: other tools

$ cij

```
Usage: cij [OPTIONS] COMMAND [ARGS]...
```

Commands:

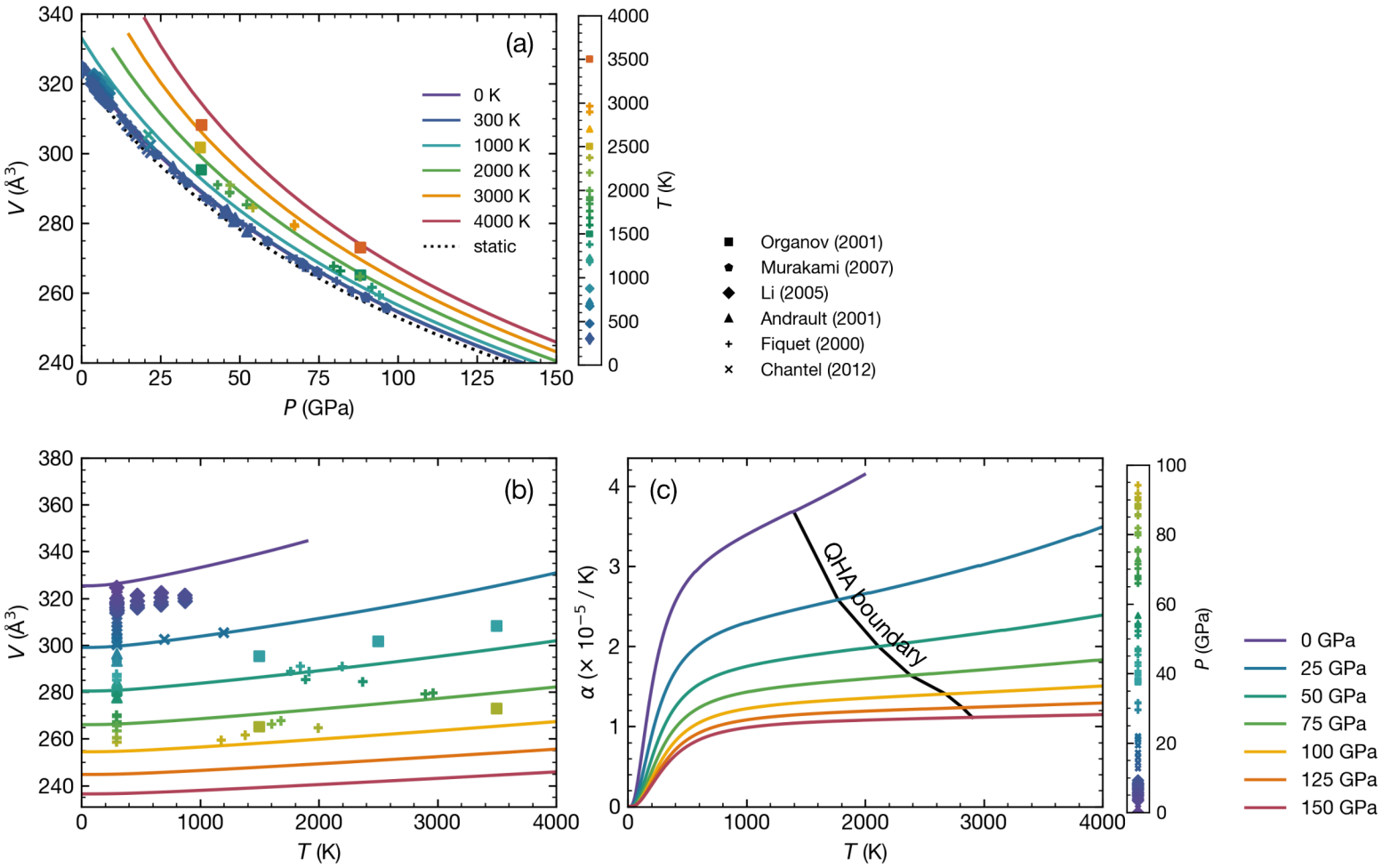
run	Perform SAM-Cij calculation.
run-static	Calculate static elastic moduli and acoustic velocities.
extract	Create data table at specific P or T.
extract-geotherm	Create data table at geotherm PT (require additional geotherm PT table).
fill	Fill non-zero Cij terms based on symmetry.
modes	Plot interpolated mode frequency vs volume.
plot	Plot SAM-Cij calculation results.

Calculation details
LDA + DFPT phonon
Quantum ESPRESSO

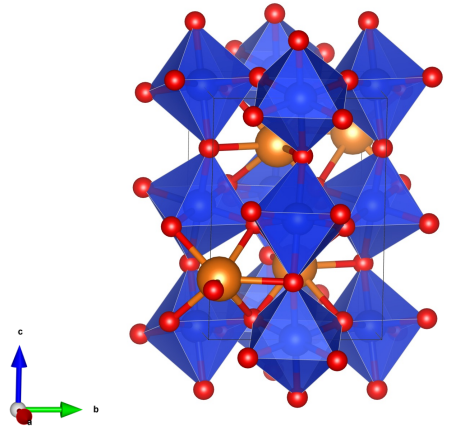
Examples

- $MgSiO_3$ bridgmanite (orthorhombic)
- $MgCaSi_2O_6$ diopside (monoclinic)
- $MgSiO_3$ akimotoite (trigonal)

Example (1): $MgSiO_3$ bridgmanite (orthorhombic)



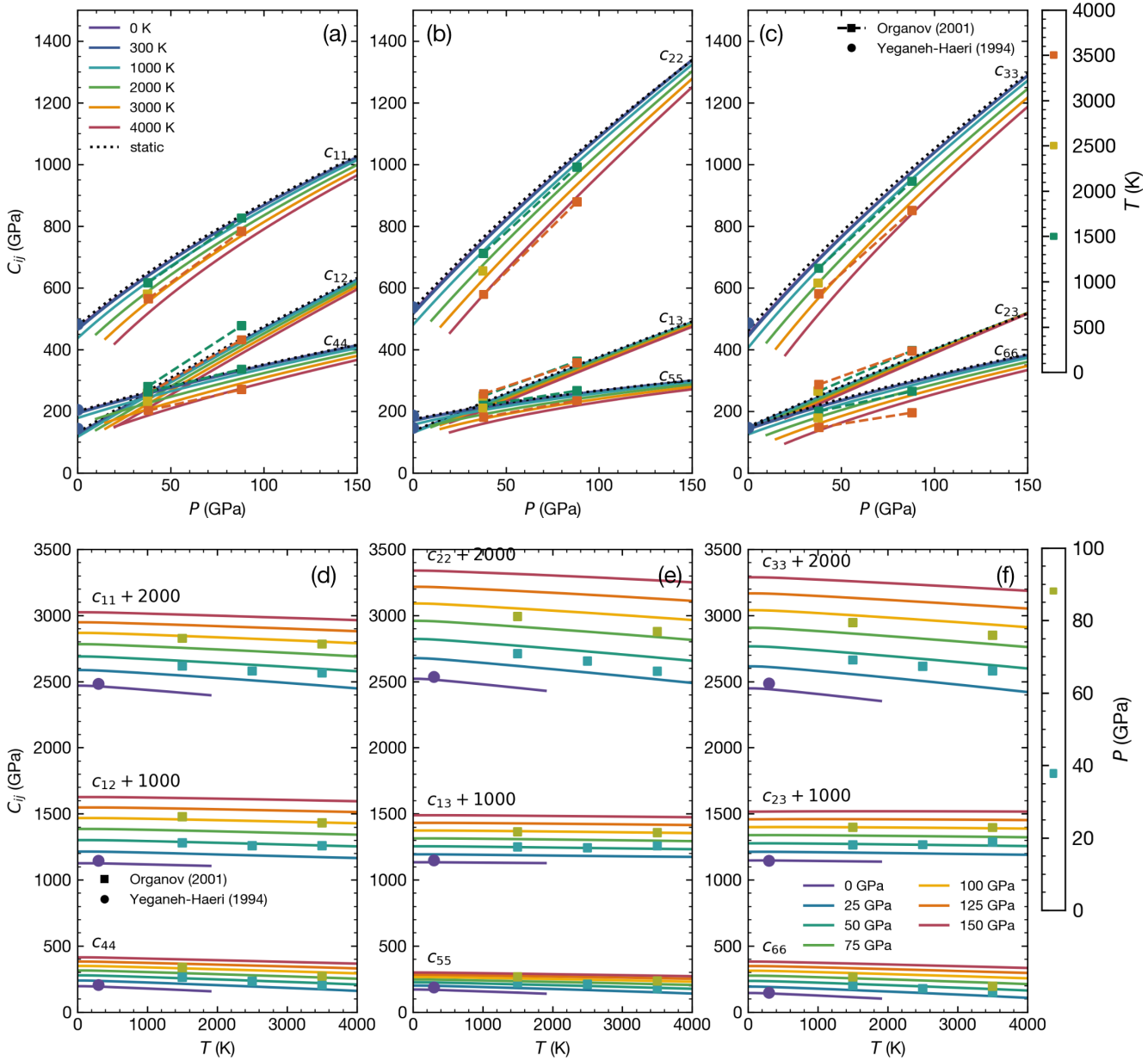
EoS and Thermoexpansivity



Space group: $Pbmn$
Number of atoms: 40 (8 f.u., supercell)
Exchange-correlation functionals: LDA
Pseudopotential:

- Mg: norm-conserving
- Si, O: ultrasoft

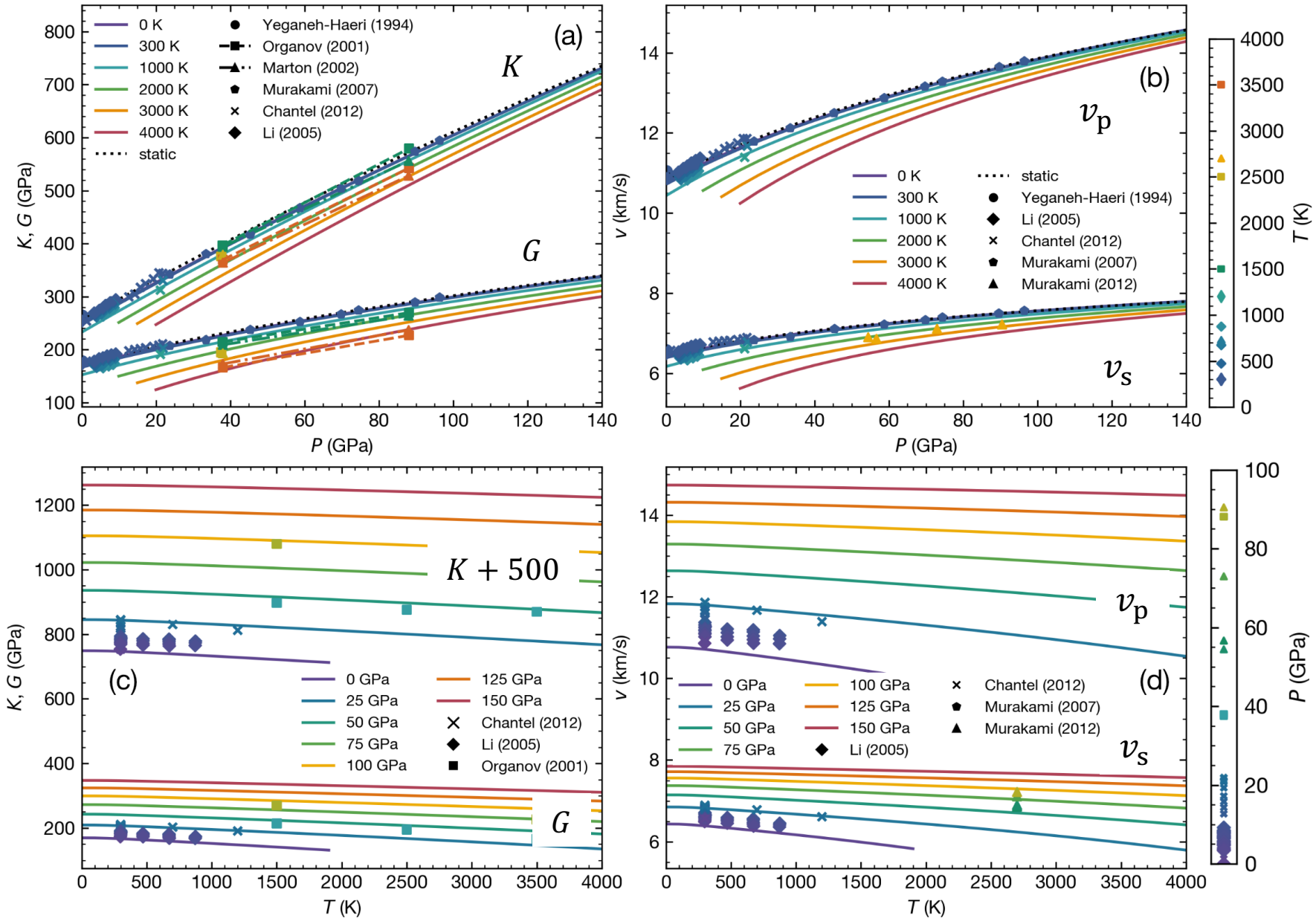
Example (1): $MgSiO_3$ bridgmanite (orthorhombic)



$$\boldsymbol{C}_{\text{ortho}} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & & & \\ . & C_{22} & C_{23} & & & \\ . & . & C_{33} & & & \\ & & & C_{44} & & \\ & & & & C_{55} & \\ & & & & & C_{66} \end{pmatrix}.$$

9 independent c_{ij}

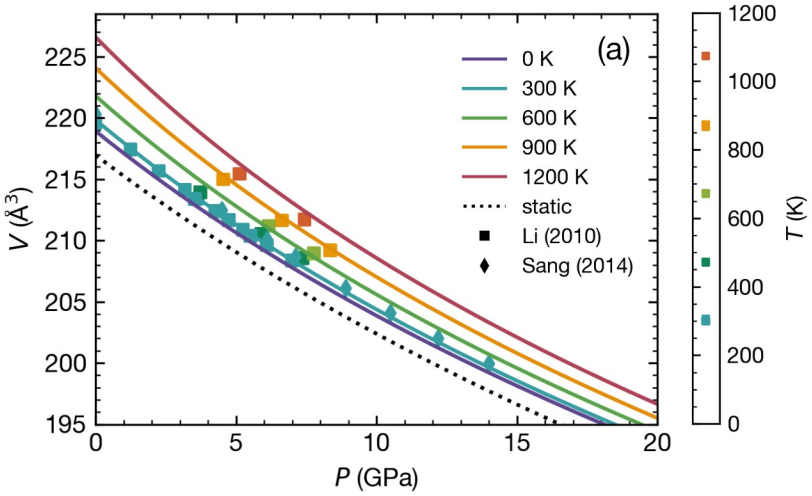
Example (1): $MgSiO_3$ bridgmanite (orthorhombic)

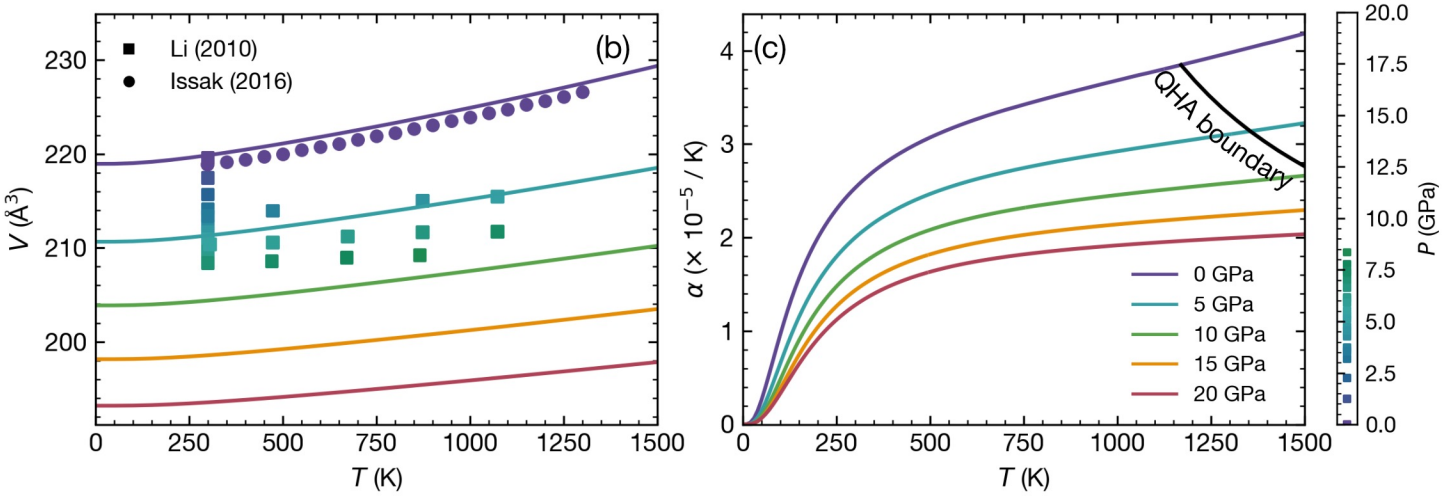


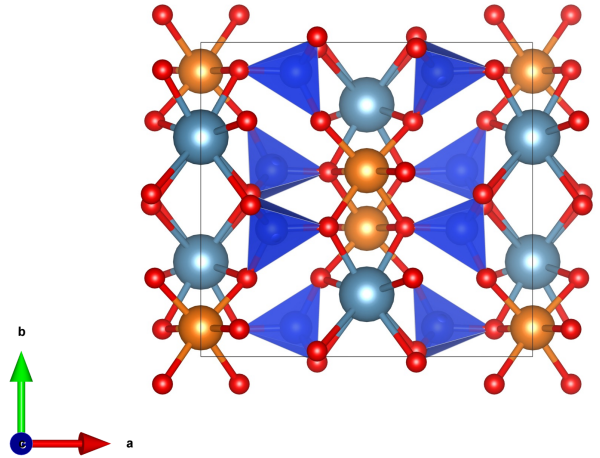
$$v_s = \sqrt{G/\rho}$$

$$v_p = \sqrt{\frac{K + 3/4G}{\rho}}$$

Example (2): $MgCaSi_2O_6$ diopside (monoclinic)



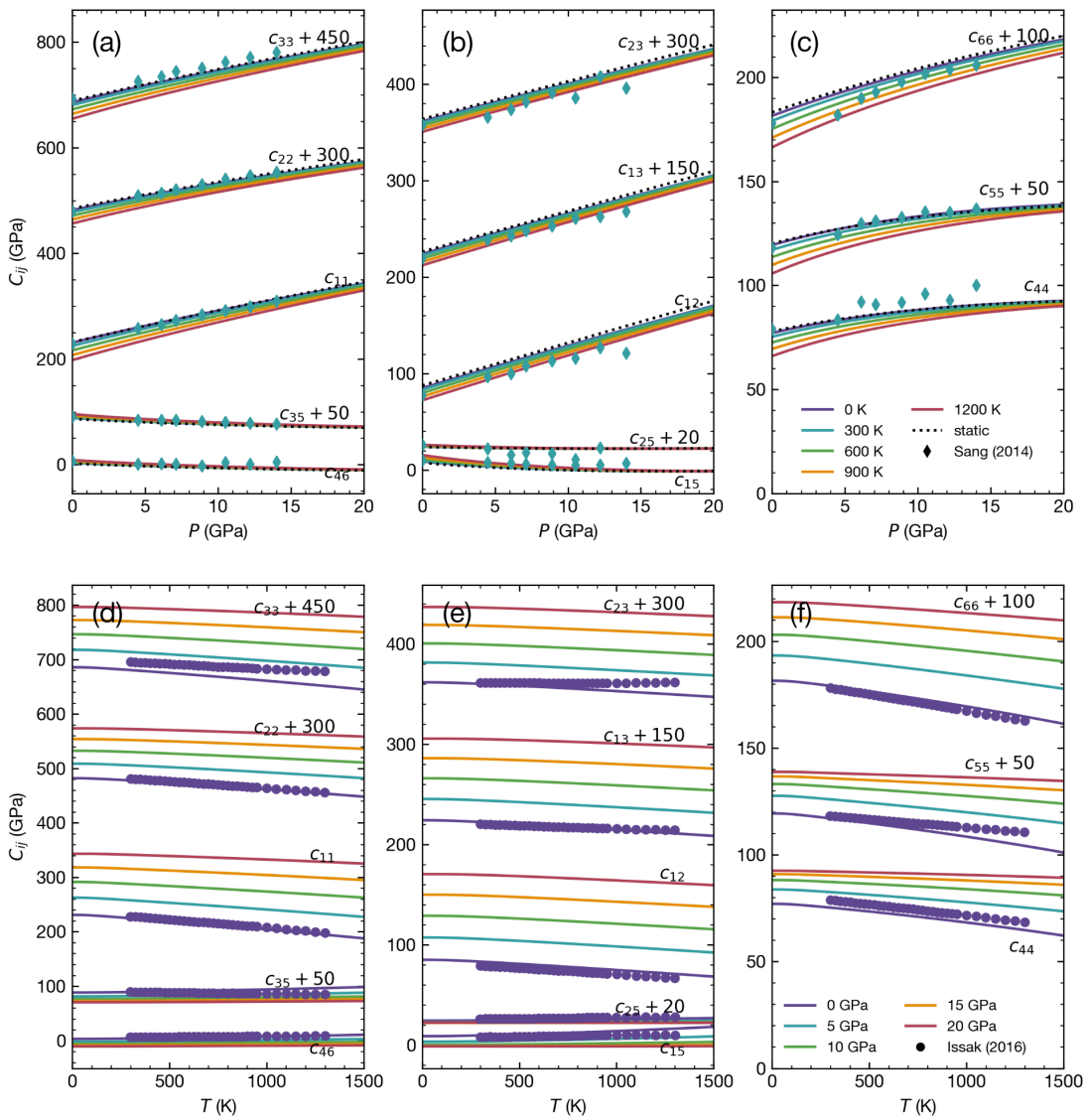




Space group: $C2/c$
Number of atoms: 20 (2 f.u.)
Exchange-correlation functionals: LDA
Pseudopotential:

- Mg, Si, O: norm-conserving
- Ca: ultrasoft

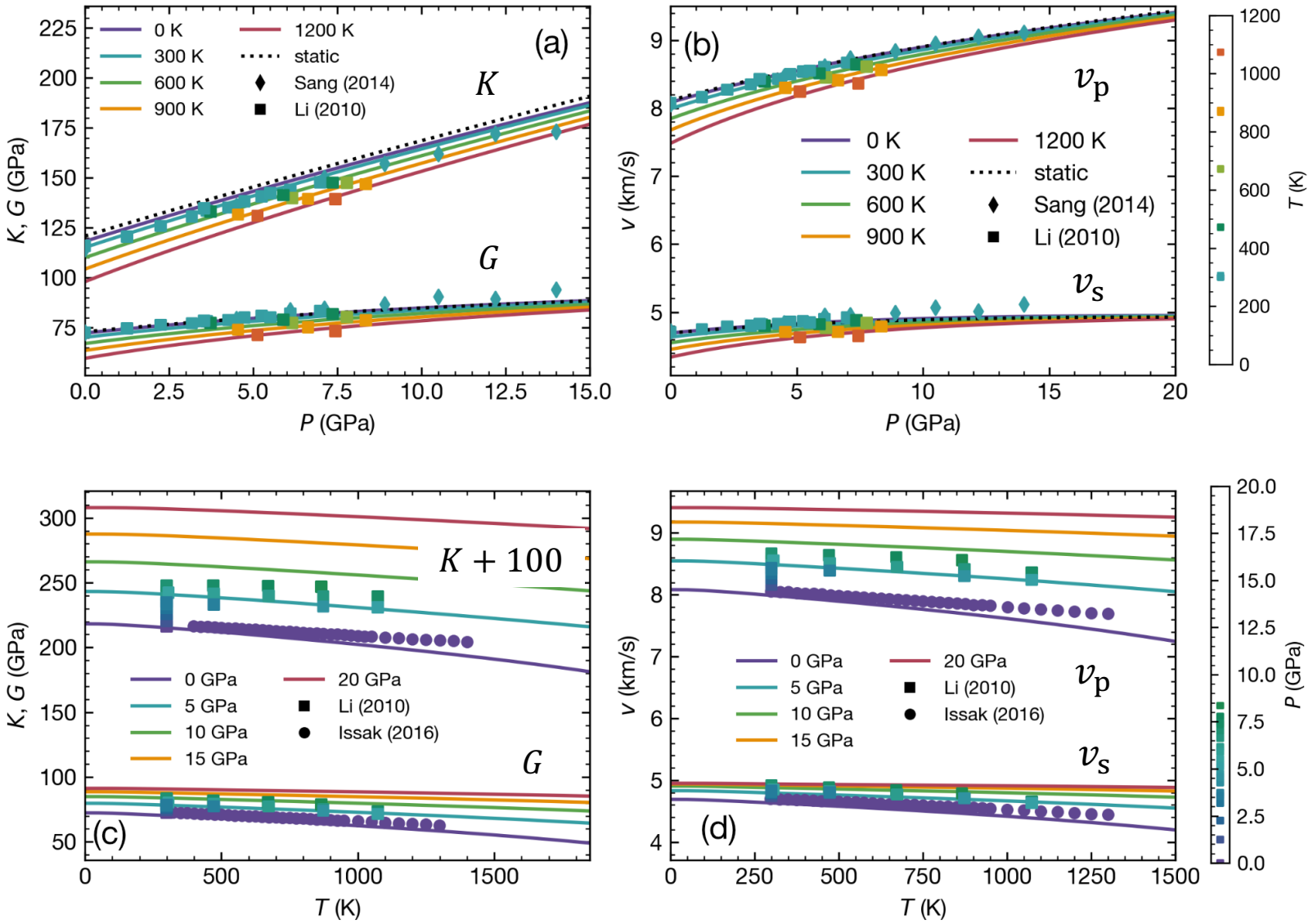
Example (2): $MgCaSi_2O_6$ diopside (monoclinic)



$$C_{ij} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & C_{15} & 0 \\ C_{12} & C_{22} & C_{23} & 0 & C_{25} & 0 \\ C_{13} & C_{23} & C_{33} & 0 & C_{35} & 0 \\ 0 & 0 & 0 & C_{44} & 0 & C_{46} \\ C_{15} & C_{25} & C_{35} & 0 & C_{55} & 0 \\ 0 & 0 & 0 & C_{46} & 0 & C_{66} \end{bmatrix}$$

13 independent c_{ij}

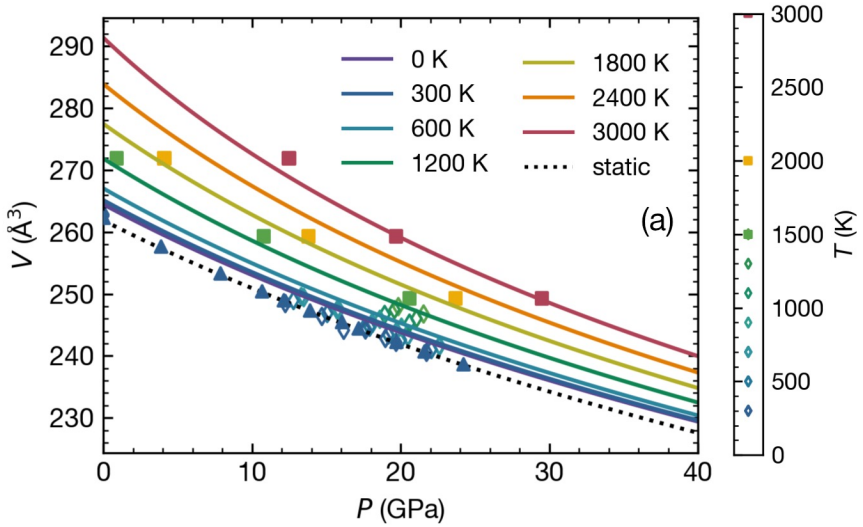
Example (2): $MgCaSi_2O_6$ diopside (monoclinic)

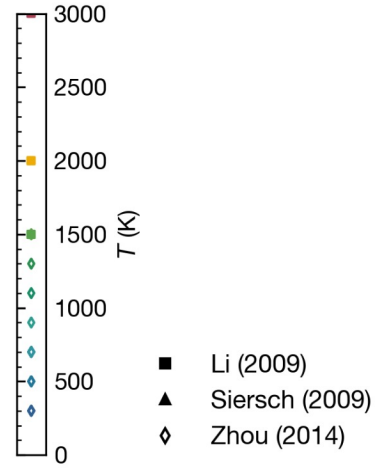


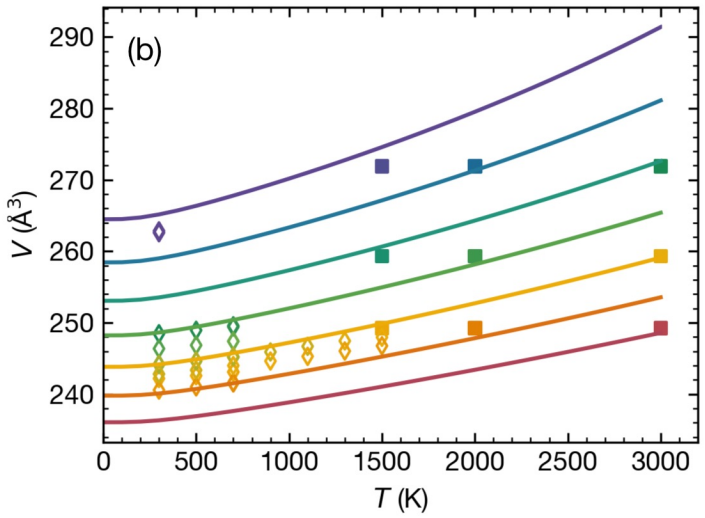
$$v_s = \sqrt{G/\rho}$$

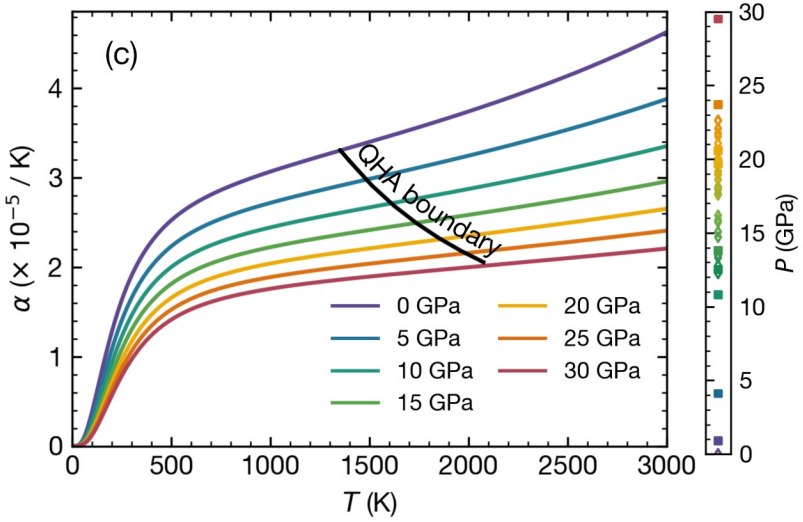
$$v_p = \sqrt{\frac{K + 3/4G}{\rho}}$$

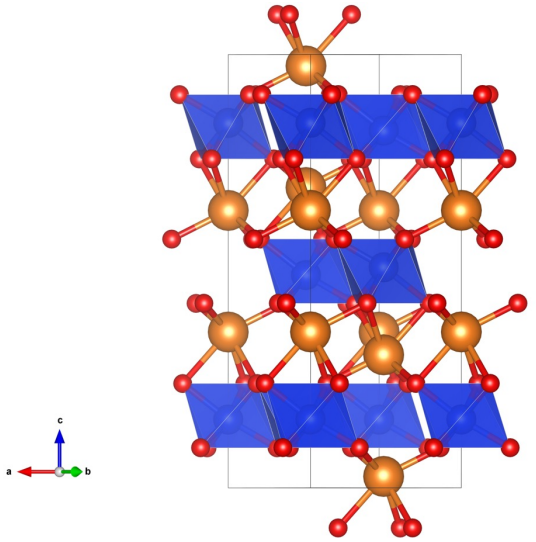
Example (3): $MgSiO_3$ akimotoite (trigonal)











Space group: $R\bar{3}$

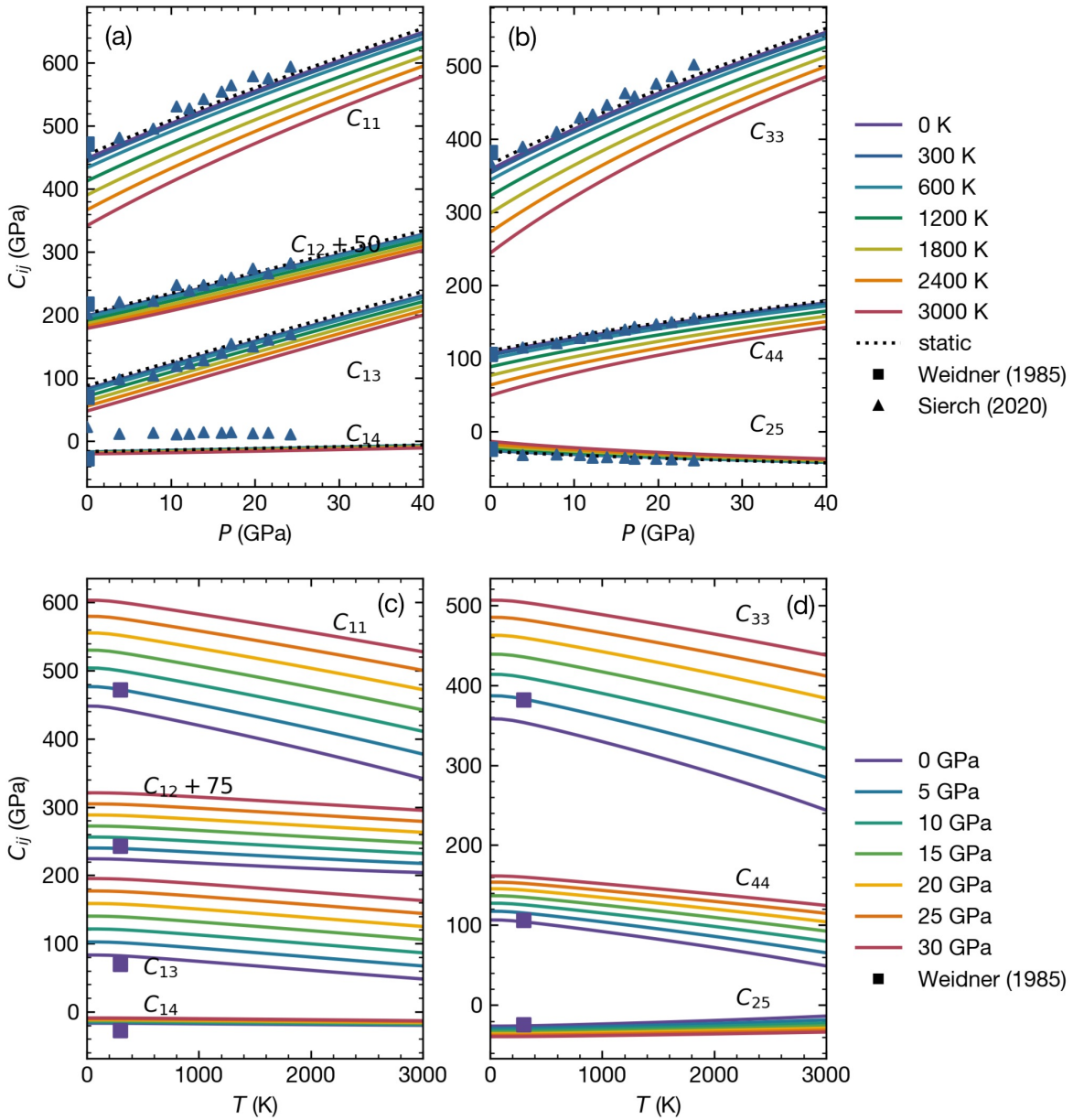
Number of atoms: 30 (6 f.u.)

Exchange-correlation functionals: LDA

Pseudopotential:

- Mg, Si, O: norm-conserving

Example (3): $MgSiO_3$ akimotoite (trigonal)

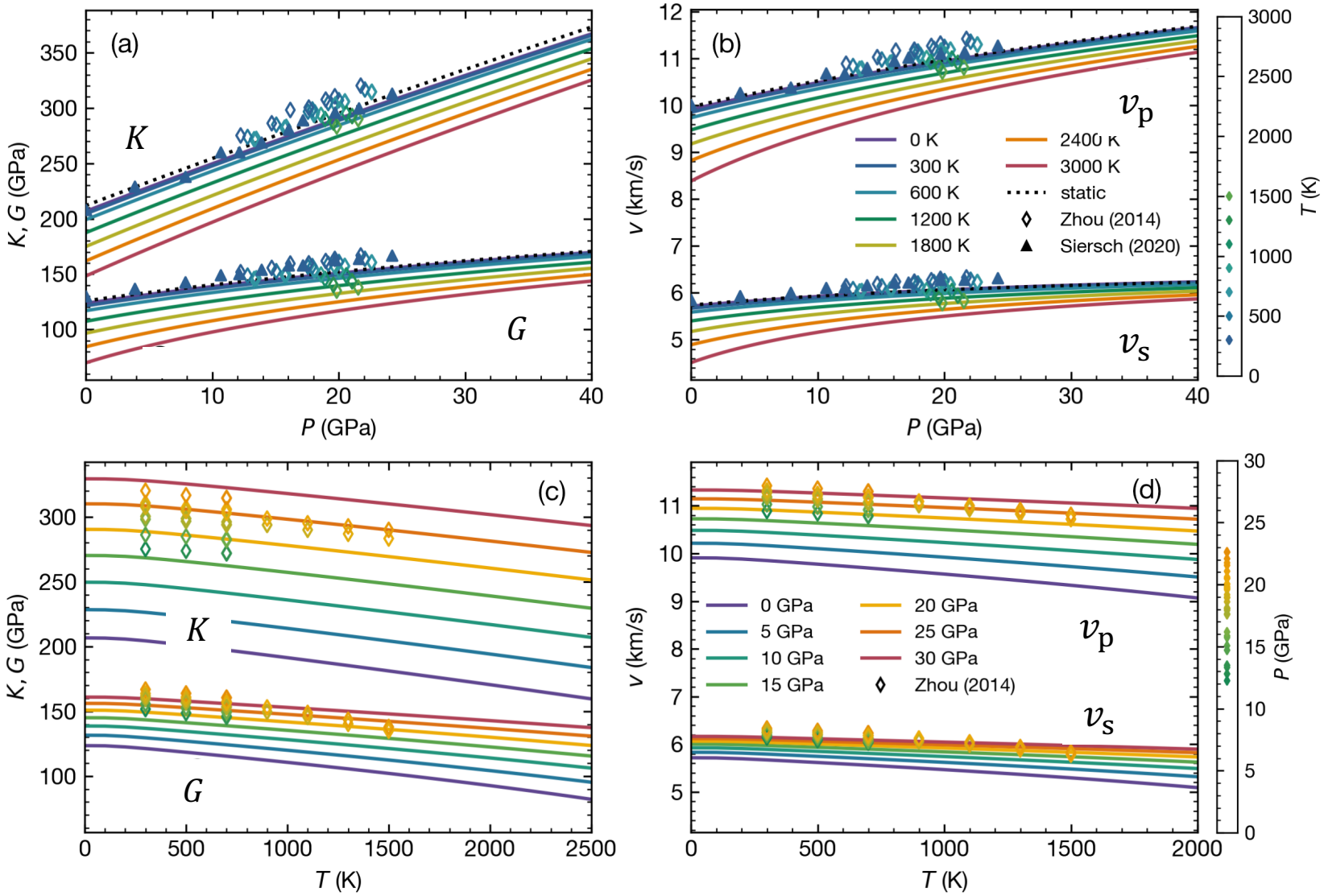


$R\bar{3}$

$$C_{ij} = \begin{bmatrix} c_{11} & c_{12} & c_{13} & c_{14} & -c_{25} & 0 \\ & c_{11} & c_{13} & -c_{14} & c_{25} & 0 \\ & & c_{33} & 0 & 0 & 0 \\ & & & c_{44} & 0 & 2c_{15} \\ & & & & c_{44} & 2c_{14} \\ & & & & & (c_{11}-c_{22})/2 \end{bmatrix}$$

7 independent c_{ij}

Example (3): $MgSiO_3$ akimotoite (trigonal)



$$v_s = \sqrt{G/\rho}$$

$$v_p = \sqrt{\frac{K + 3/4G}{\rho}}$$

Conclusion

We introduce a new Python package, cij, that calculates the thermoelastic tensor and acoustic velocities of solids vs *PT* .

The code implements the SAM-Cij method and has been successfully tested on many systems with different symmetries.

Cij paper on **arXiv**
arxiv.org/abs/
2101.12596

Cij code on **GitHub**
github.com/
mineralscloud/cij

Phonon frequency ordering according to eigenvectors

Assume no degeneracy, at reciprocal coordinate $\mathbf{q}$, $\omega^2_{\mathbf{q}m}$ and $\mathbf{e}_{\mathbf{q}m}$ are the m-th eigenvalue and eigenvector of the dynamical matrix $D(\mathbf{q})$ (Srivastava, 1990),

$$D(\mathbf{q})\,\mathbf{e}_{\mathbf{q}m} = \omega^2_{\mathbf{q}m}\mathbf{e}_{\mathbf{q}m}$$

The orthonormality in the set of normal modes $\mathbf{e}_{\mathbf{q}m}$ is given by

$$\mathbf{e}^{\dagger}_{\mathbf{q}m}\mathbf{e}_{\mathbf{q}m'} = \delta_{mm'} \quad .$$

For crystal under two compression state V and $V + \mathrm{d}V$ ($\mathrm{d}V \ll V$),

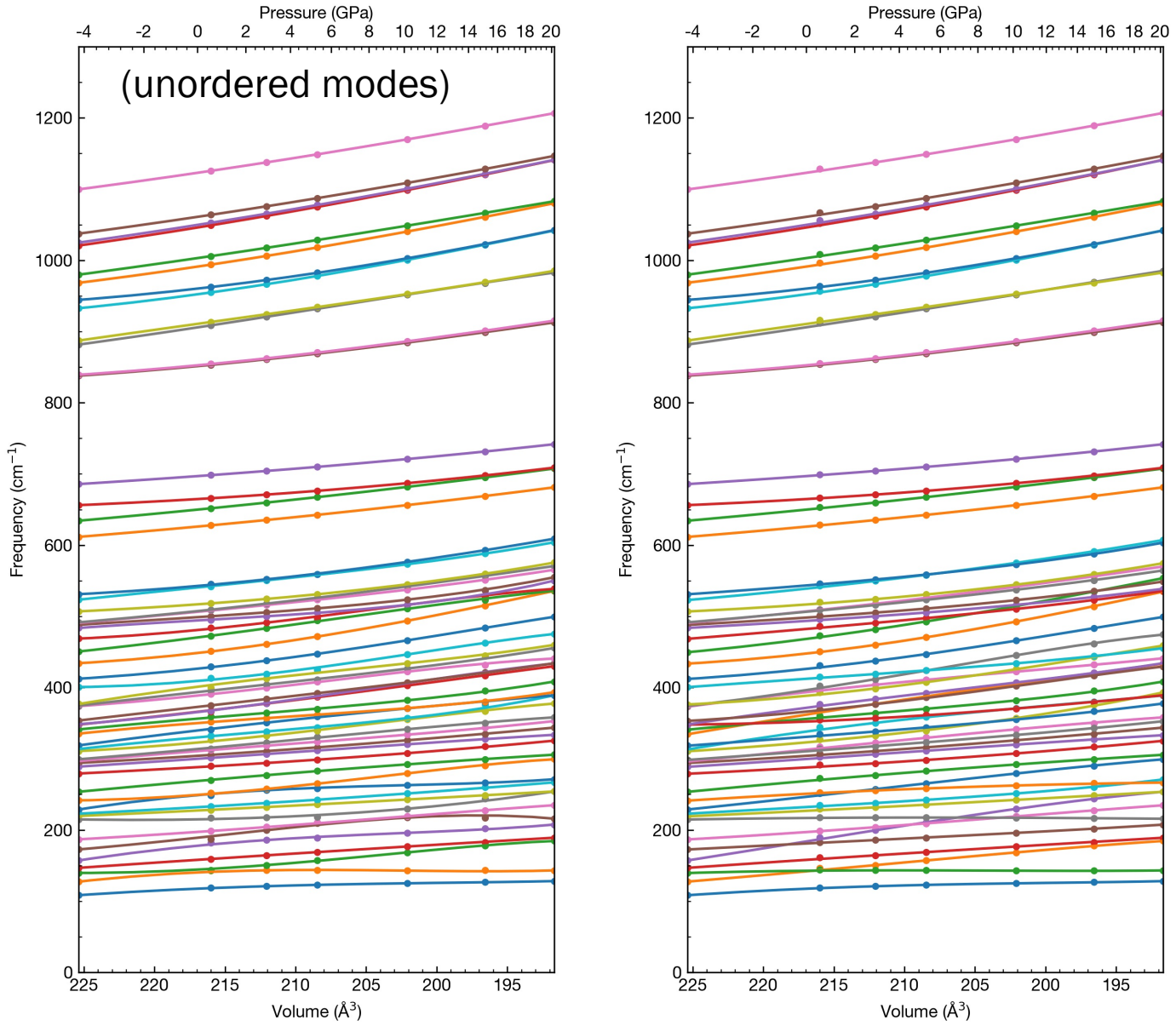
$$\mathbf{e}^{\dagger}_{\mathbf{q}m}(V)\,\mathbf{e}_{\mathbf{q}m'}(V + \mathrm{d}V) = \delta_{mm'} + \epsilon_{mm'}(V, \mathrm{d}V)$$

ϵ is a small number.

In practice, we are able to reorder $\omega_{\mathbf{q}m}$ based on $\mathbf{e}_{\mathbf{q}m}$ by calculating $\mathbf{e}^{\dagger}_{\mathbf{q}m}(V)\,\mathbf{e}_{\mathbf{q}m'}(V + \mathrm{d}V)$ and connect m and m'.

Phonon ω vs V

- Zone center, Γ point
- N = 20 atoms, therefore $3N$ - 3 = 57 modes in total.



Phonon ω vs V