

# **A simple and effective semi-empirical approach to anharmonic corrections**

**Zhongqing Wu**  
**University of Minnesota**

**2008.8.1**

# Computational detail

- *Density Functional Theory* (Hohenberg & Kohn, 1964)
- **LDA or GGA**
- *Plane wave basis – pseudopotential* (Troullier & Martins, 1991, von Bar & Car)
- *Variable Cell Shape MD for structure optimization* (Wentzcovitch et al., 1993)
- *Density Functional Perturbation Theory for phonons* (Baroni et al., 1987)

- VDoS and  $F(T, V)$  within the quasiharmonic approximation (QHA)

$$F(V, T) = U(V) + \sum_{qj} \frac{\hbar\omega_{qj}(V)}{2} + k_B T \sum_{qj} \ln \left( 1 - \exp \left[ -\frac{\hbar\omega_{qj}(V)}{k_B T} \right] \right)$$

N-th (N=3,4,5...) order *isothermal* (eulerian or logarithm) finite strain equation

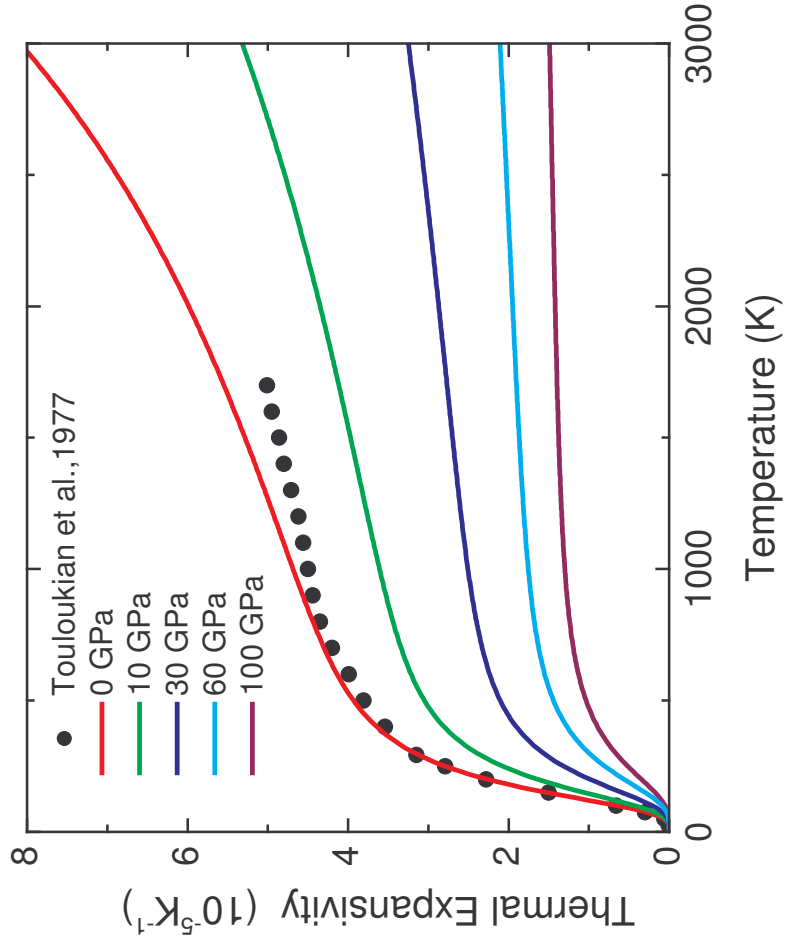
$$P = - \left[ \frac{\partial F}{\partial V} \right]_T$$

$$S = - \left[ \frac{\partial F}{\partial T} \right]_V$$

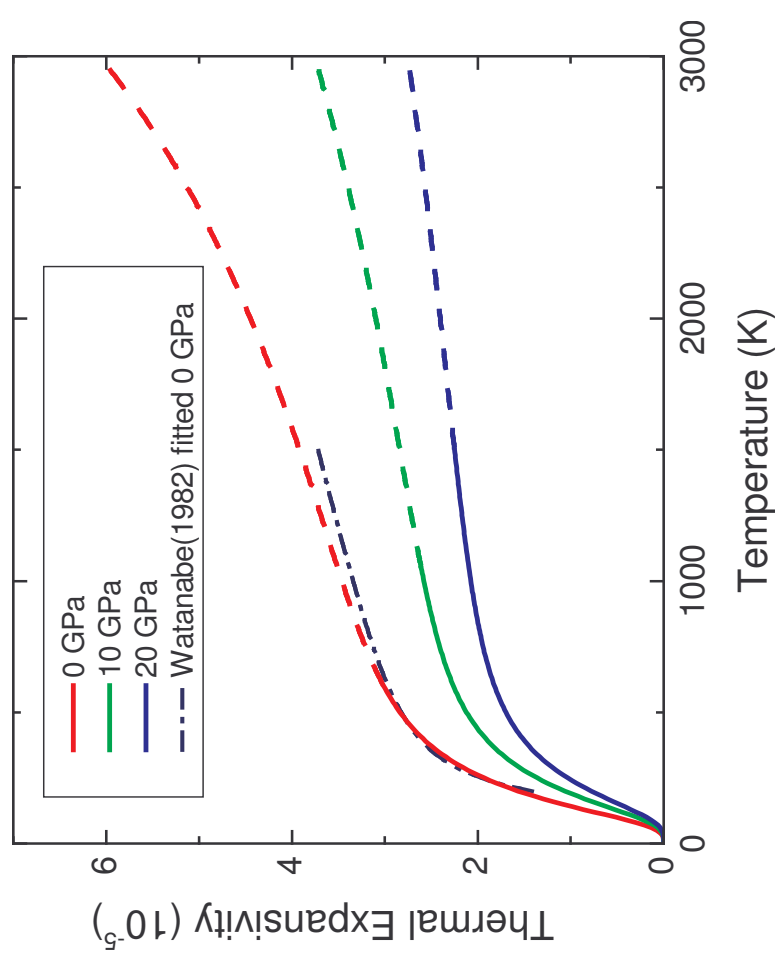
$$G = F - TS + PV$$



# Anharmonicity prominent at high temperature



MgO



$\beta$  phase of  $\text{Mg}_2\text{SiO}_4$

# Quasiharmonic approximation (QHA)

$$F_0(V, T) = U(V) + \sum_{qj} \frac{\hbar \omega_{qj}(V)}{2} + k_B T \sum_{qj} \ln \left( 1 - \exp \left[ -\frac{\hbar \omega_{qj}(V)}{k_B T} \right] \right)$$

Frequencies: depend on **volume** alone !  
independent of temperature

QHA ignores phonon-phonon interactions (anharmonicity) ,  
which cause frequencies depend on temperature at fixed  
volume.

# Traditional approach to anharmonic

- Anharmonic free energy at high temperature is **explicitly** expressed

$$F_{anhc}(V) = \frac{1}{2}A(V)T^2 + \frac{1}{3}B(V)T^3 + \frac{1}{4}C(V)T^4$$

## Drawback:

- too many parameters
- each parameter is volume dependent
- wrong at low temperature

**How do phonon frequencies change with T?**

## How do phonon frequencies change with T?

Two characters of anharmonicity:

- 1) anharmonicity increases with T at fixed V
- 2) anharmonicity decreases with V at fixed T

## How do phonon frequencies change with T?

Two characters of anharmonicity:

- 1) anharmonicity increases with T at fixed V
- 2) anharmonicity decreases with V at fixed T

## Our method

Express the T dependence of renormalized frequencies in **implicit** way:

$$\Omega(V, T) = \omega(V')$$

$$V' = V(P, T) \left( 1 - c \frac{[V(P, T) - V(P, 0)]}{V(P, 0)} \right)$$

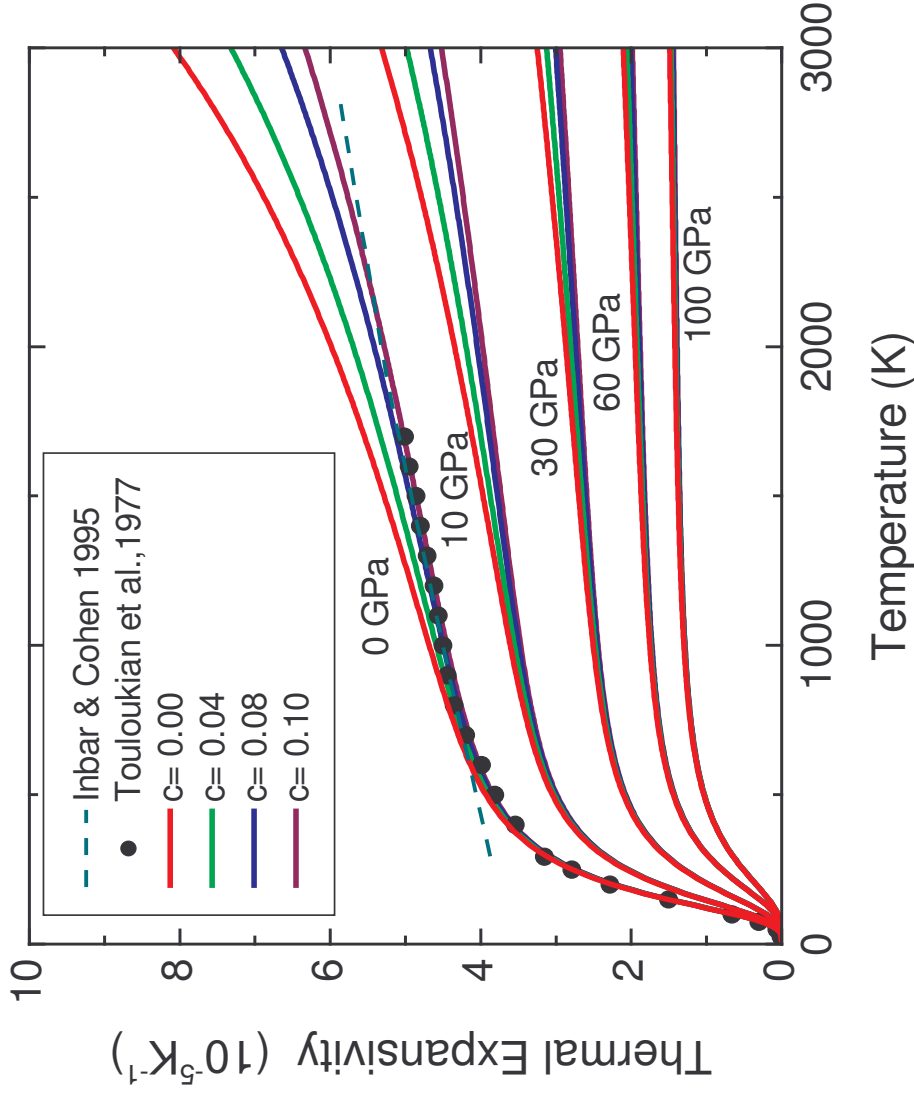


# Free energy with anharmonicity

$$\begin{aligned} F_c(V, T) &= U(V) + \sum_{qj} \frac{\hbar \Omega_{qj}(V, T)}{2} + k_B T \sum_{qj} \ln \left( 1 - \exp \left[ - \frac{\hbar \Omega_{qj}(V, T)}{k_B T} \right] \right) \\ &= U(V) + \sum_{qj} \frac{\hbar \omega_{qj}(V)}{2} + k_B T \sum_{qj} \ln \left( 1 - \exp \left[ - \frac{\hbar \omega_{qj}(V)}{k_B T} \right] \right) \\ &= U(V) + F_0(V, T) - U(V') \end{aligned}$$

$$V' = V(P, T) \left( 1 - c \frac{[V(P, T) - V(P, 0)]}{V(P, 0)} \right)$$

# MgO (rocksalt)

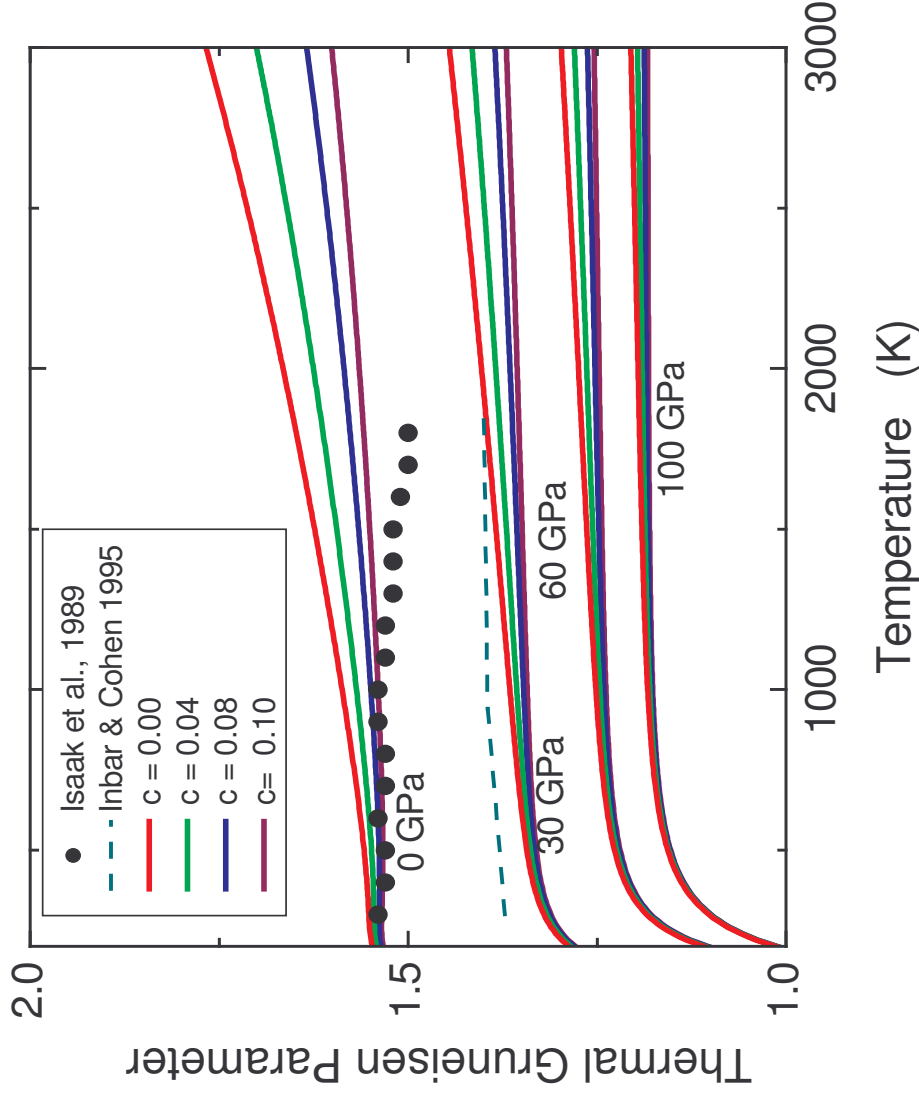


$$\Omega(V, T) = \omega(V')$$

$$V' = V(P, T) \left( 1 - c \frac{[V(P, T) - V(P, 0)]}{V(P, 0)} \right)$$

Correction with **positive c** ( $\sim 0.1$ ) improves thermodynamic properties of MgO very much

# MgO

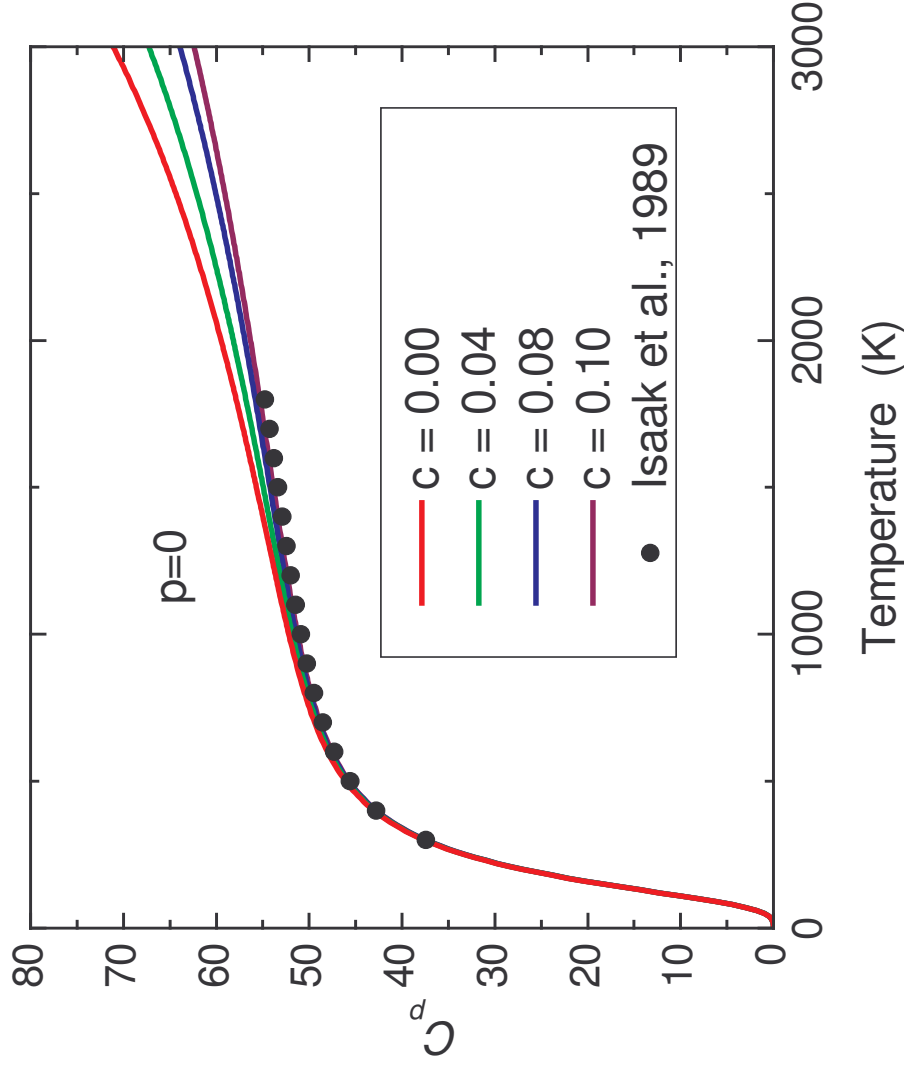


$$\Omega(V, T) = \omega(V')$$

$$V' = V(P, T) \left( 1 - c \frac{[V(P, T) - V(P, 0)]}{V(P, 0)} \right)$$

Correction with **positive c** ( $\sim 0.1$ ) improves thermodynamic properties of MgO very much

# MgO

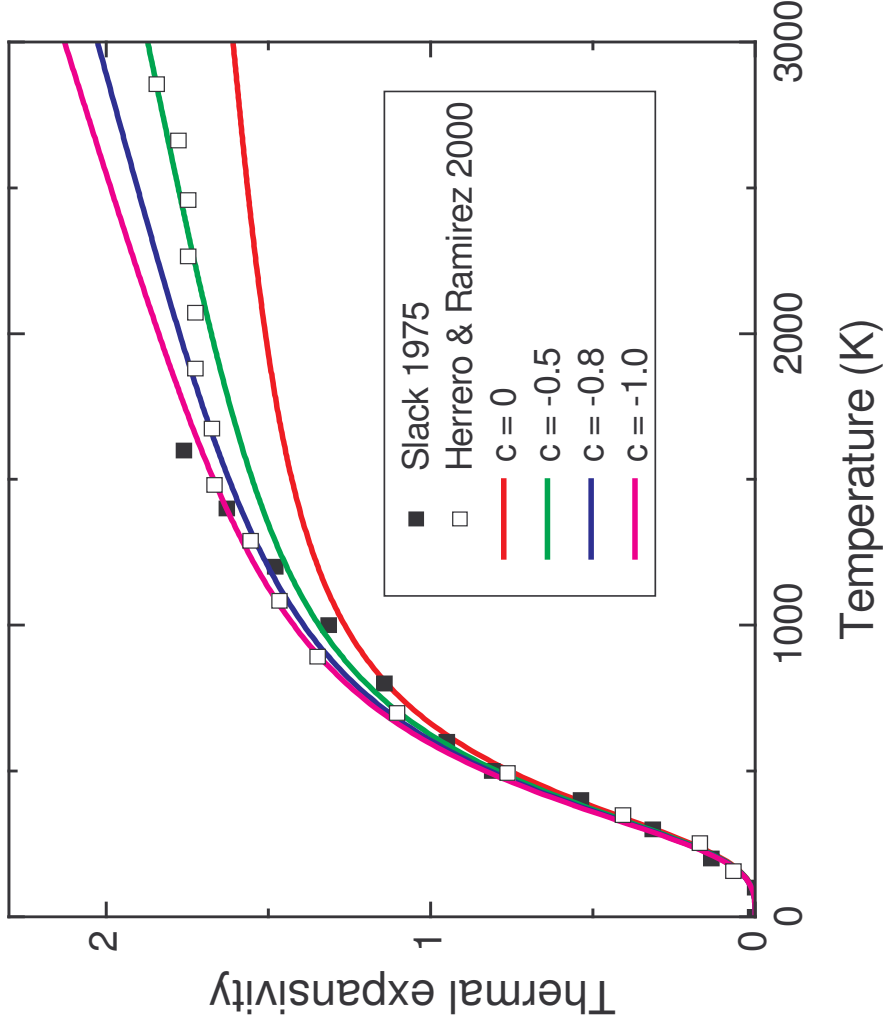


$$\Omega(V, T) = \omega(V')$$

$$V' = V(P, T) \left( 1 - c \frac{[V(P, T) - V(P, 0)]}{V(P, 0)} \right)$$

Correction with **positive  $c$**  ( $\sim 0.1$ ) improves thermodynamic properties of MgO very much

# Diamond

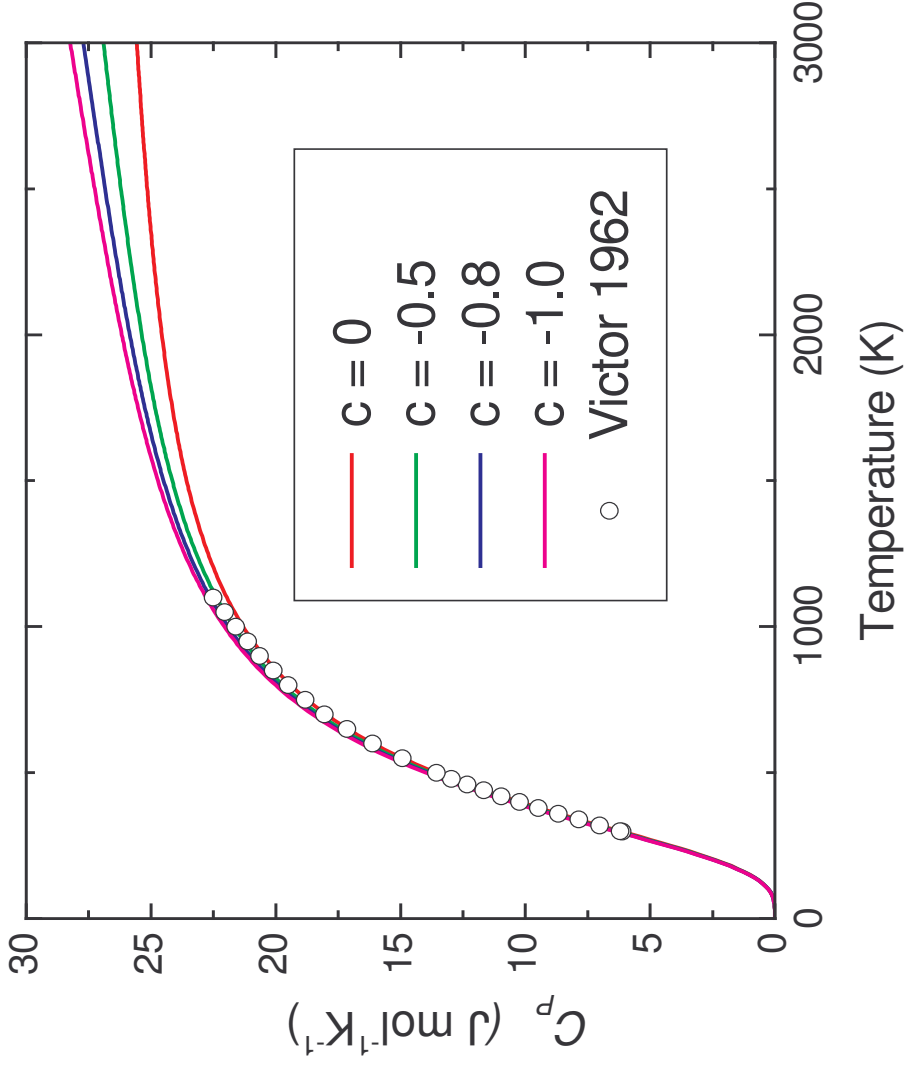


$$\Omega(V, T) = \omega(V')$$

$$V' = V(P, T) \left( 1 - c \frac{[V(P, T) - V(P, 0)]}{V(P, 0)} \right)$$

Correction with **negative c** ( $\sim -0.5$ ) improves thermodynamic properties of diamond very much

# Diamond

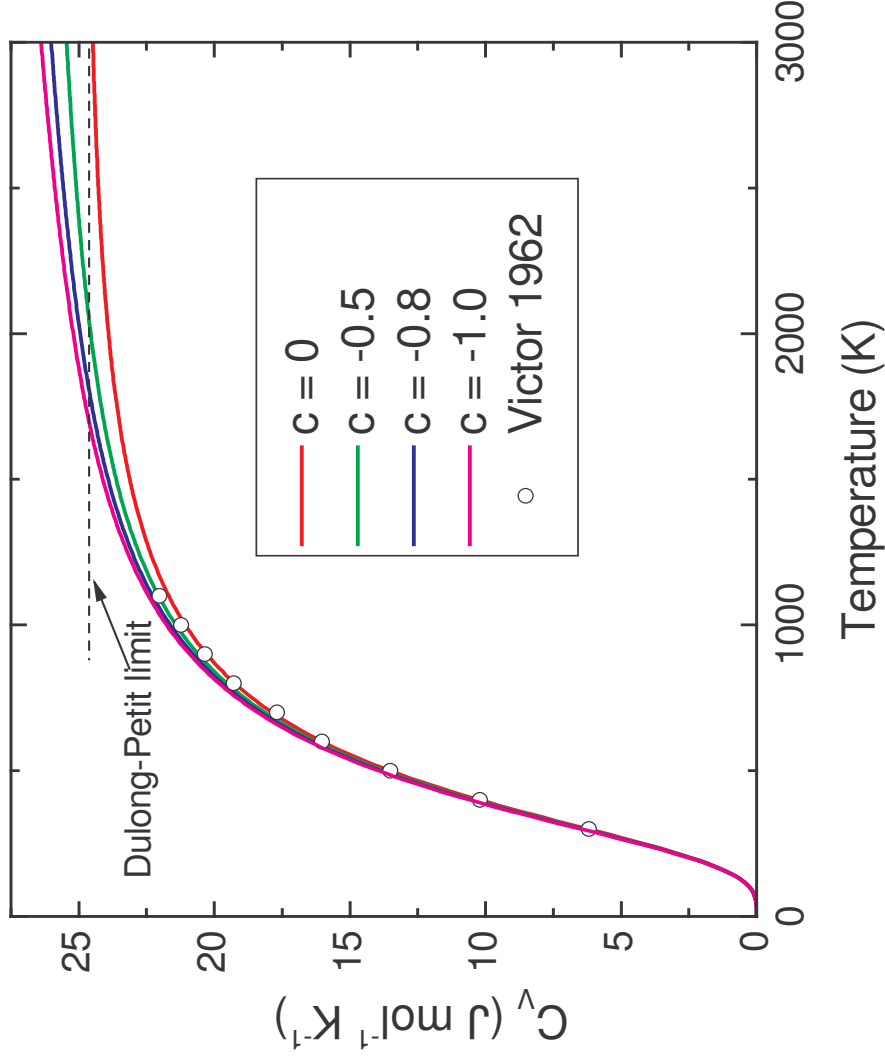


$$\Omega(V, T) = \omega(V')$$

$$V' = V(P, T) \left( 1 - c \frac{[V(P, T) - V(P, 0)]}{V(P, 0)} \right)$$

Correction with **negative  $c$**  ( $\sim -0.5$ ) improves thermodynamic properties of diamond very much

# Diamond



$$\Omega(V, T) = \omega(V')$$

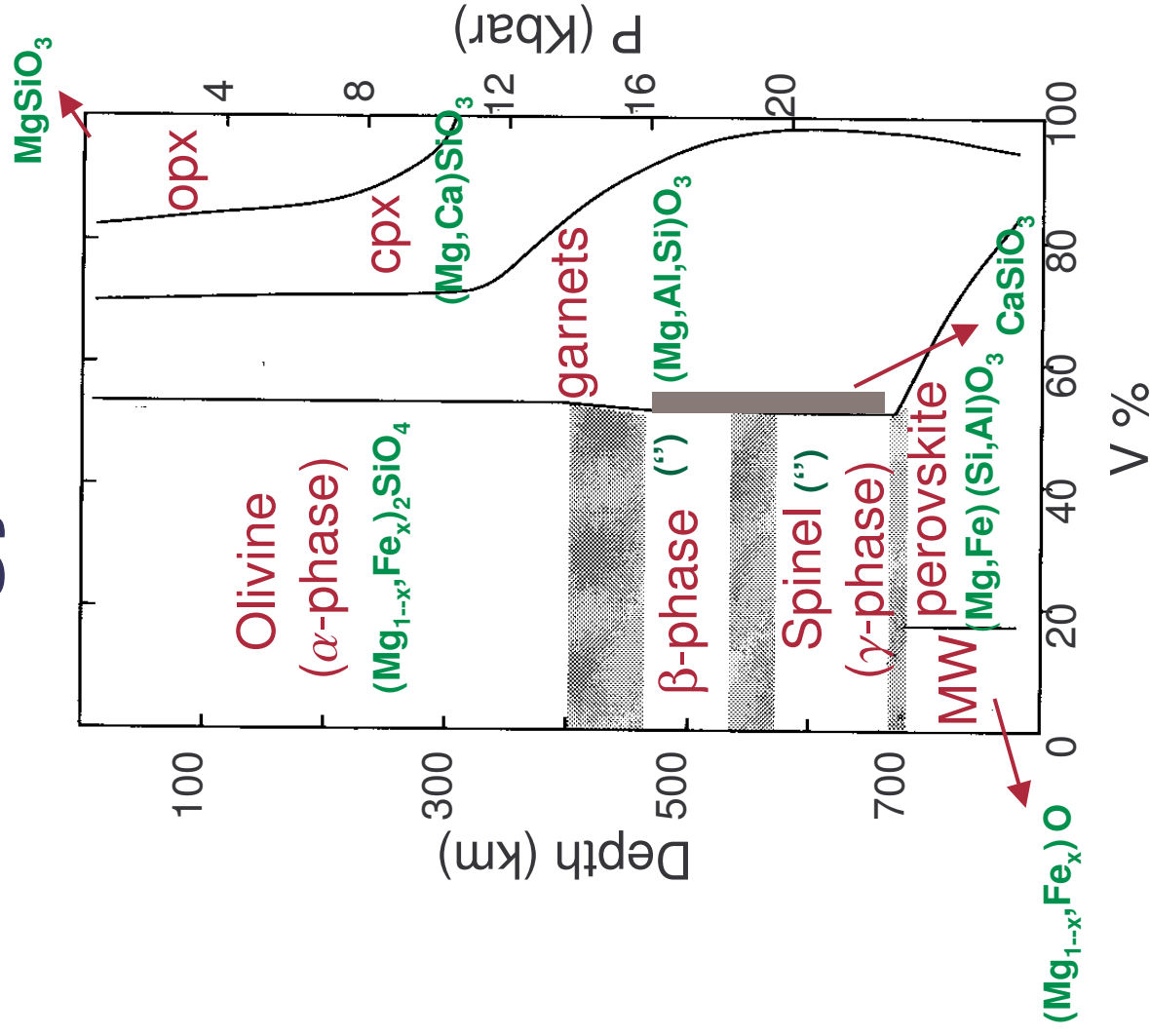
$$V' = V(P, T) \left( 1 - c \frac{[V(P, T) - V(P, 0)]}{V(P, 0)} \right)$$

Correction with **negative c** ( $\sim -0.5$ ) improves thermodynamic properties of diamond very much

# Mantle Mineralogy

Pyrolite model (% weight)

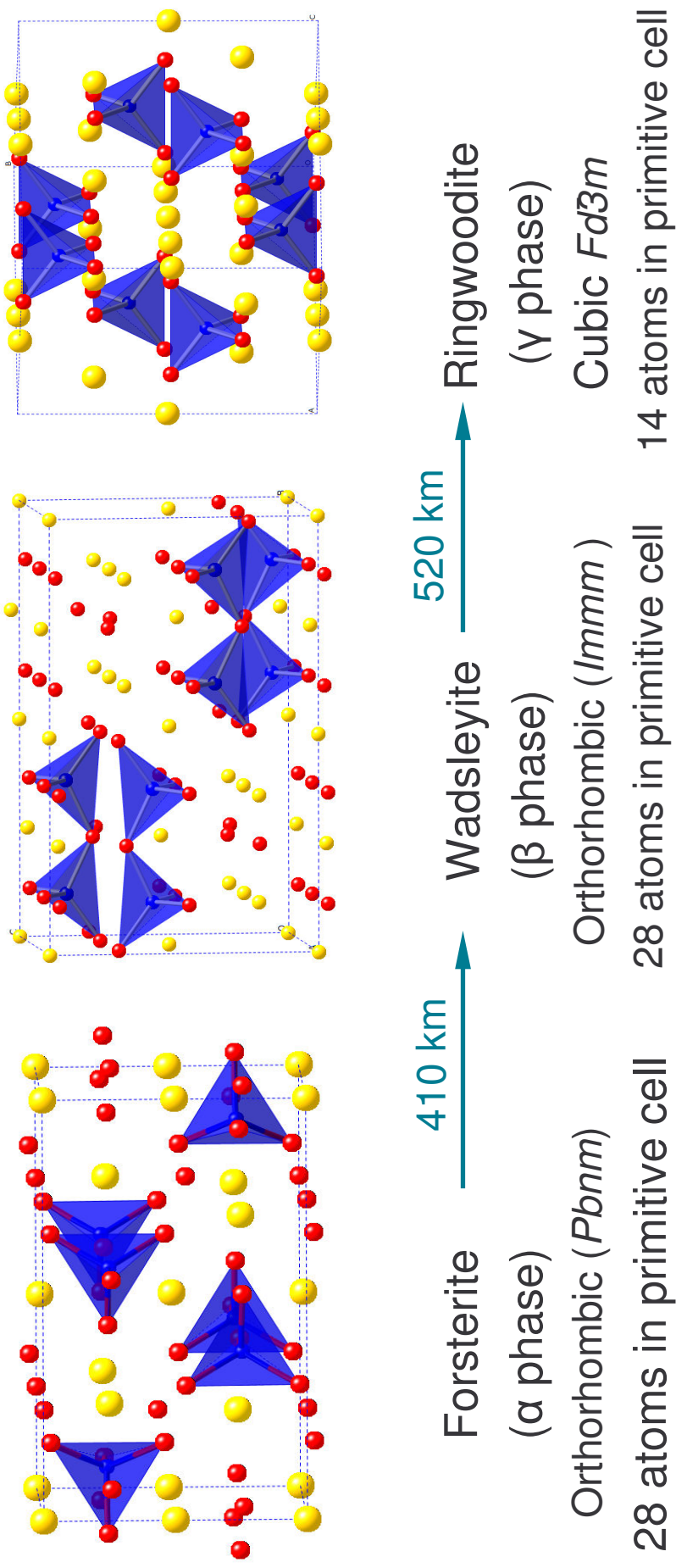
SiO <sub>2</sub>	45.0
MgO	37.8
FeO	8.1
Al <sub>2</sub> O <sub>3</sub>	4.5
CaO	3.6
Cr <sub>2</sub> O <sub>3</sub>	0.4
Na <sub>2</sub> O	0.4
NiO	0.2
TiO <sub>2</sub>	0.2
MnO	0.1



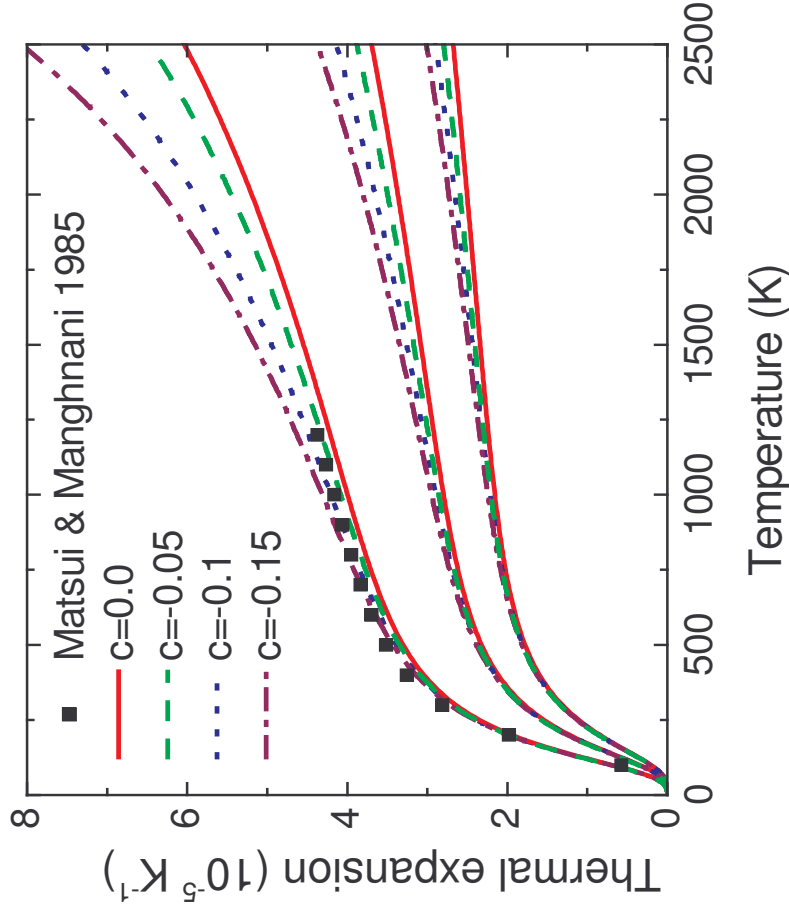
(McDonough and Sun, 1995)



# Structure of $Mg_2SiO_4$

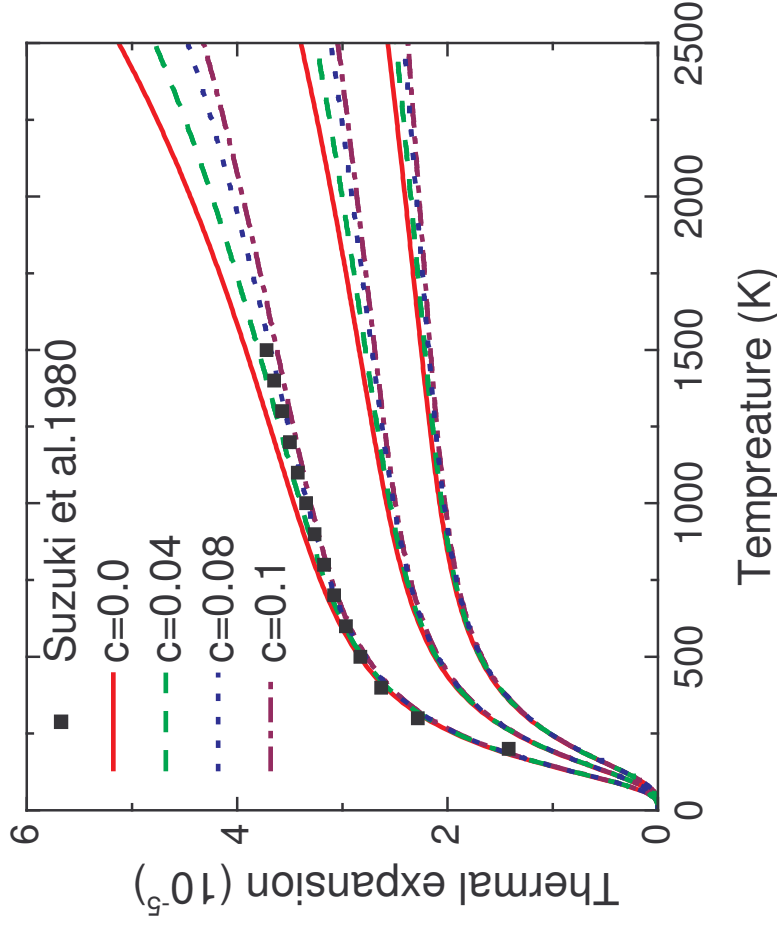


# Mg<sub>2</sub>SiO<sub>4</sub>



$\alpha$  phase (forsterite)

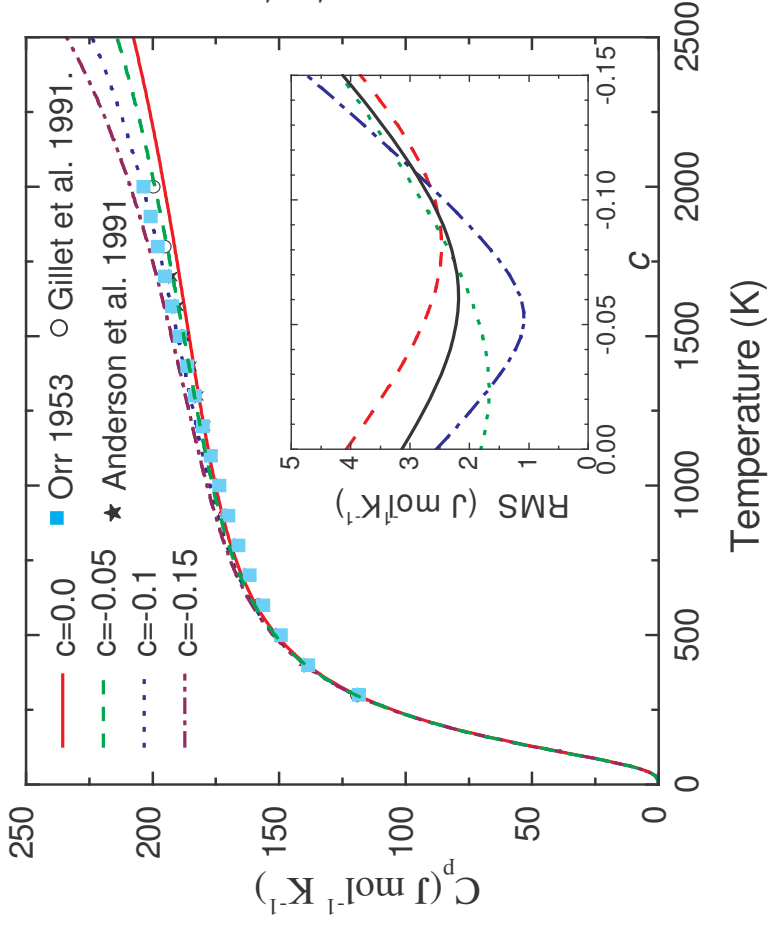
negative  $c$  ( $\sim -0.09$ )



$\beta$  phase (wadsleyite)

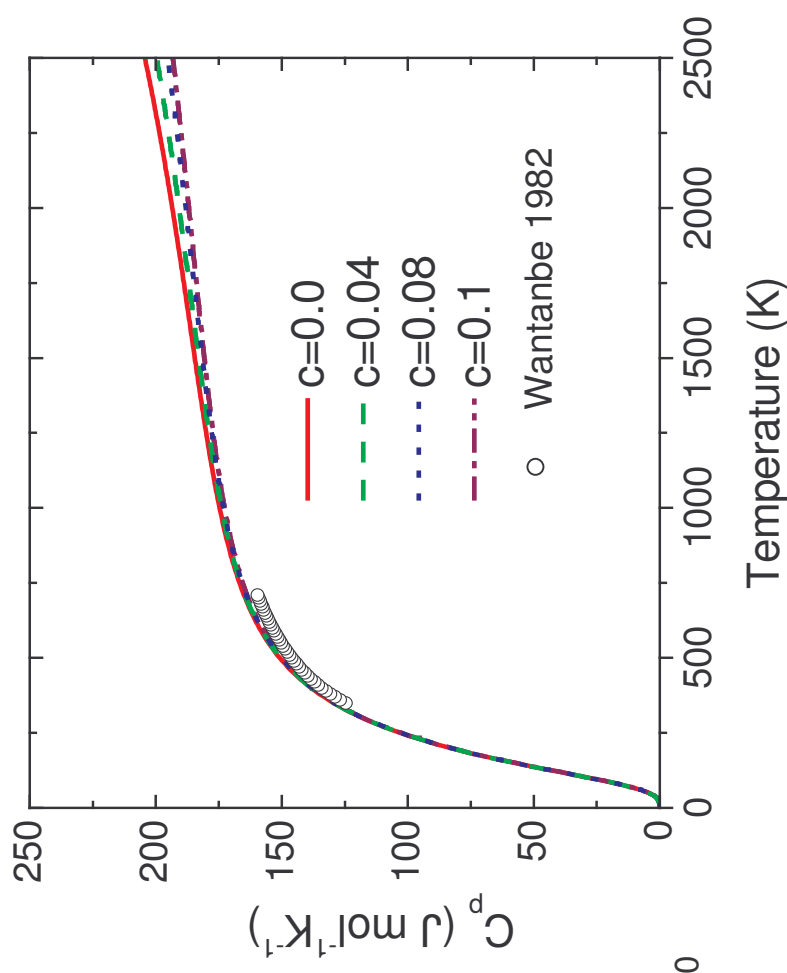
positive  $c$  ( $\sim 0.08$ )

# Mg<sub>2</sub>SiO<sub>4</sub>



$\alpha$  phase (forsterite)

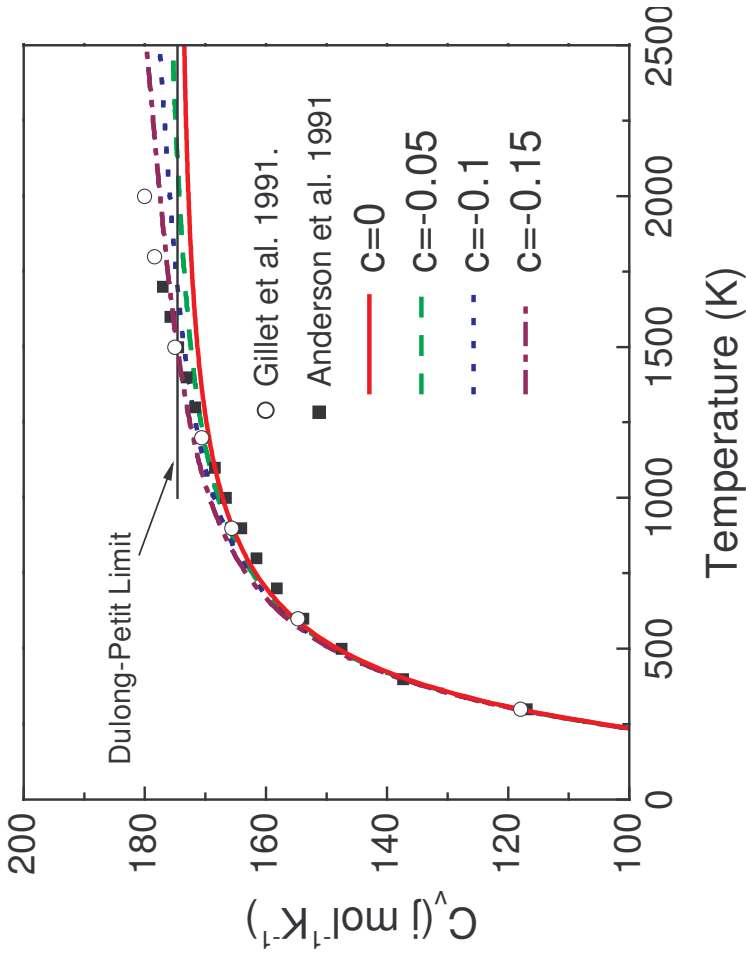
negative  $c$  ( $\sim -0.06$ )



$\beta$  phase (wadsleyite)

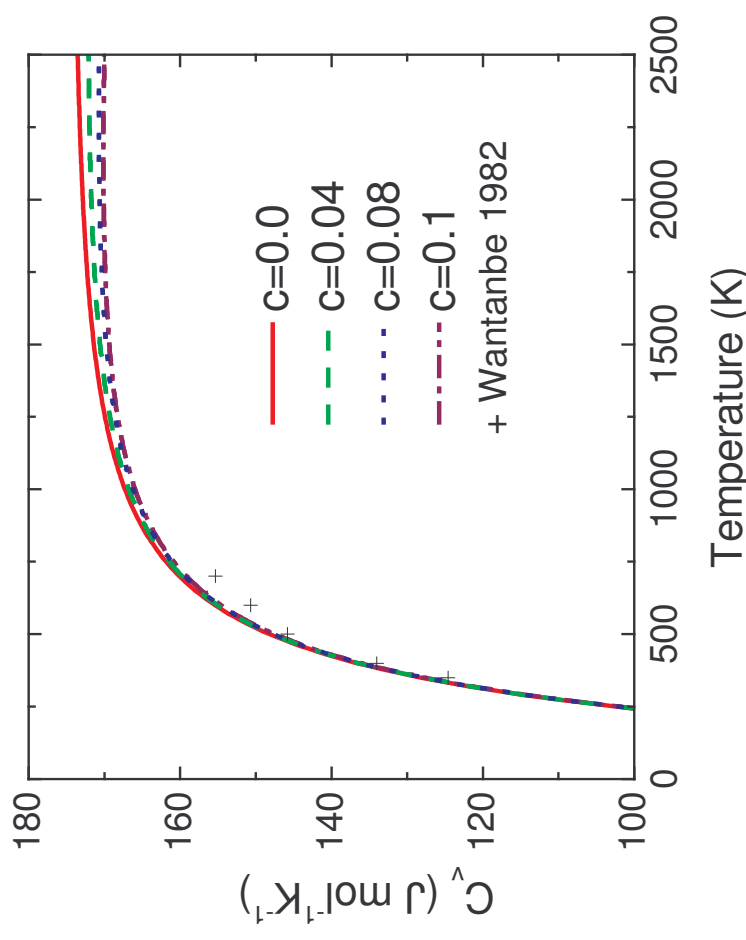
positive  $c$

# Mg<sub>2</sub>SiO<sub>4</sub>



$\alpha$  phase (forsterite)

negative  $c$

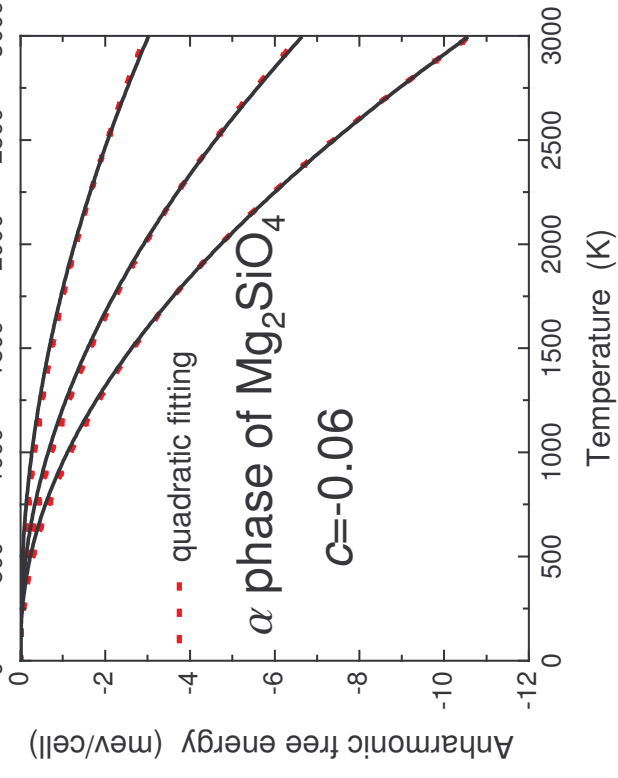
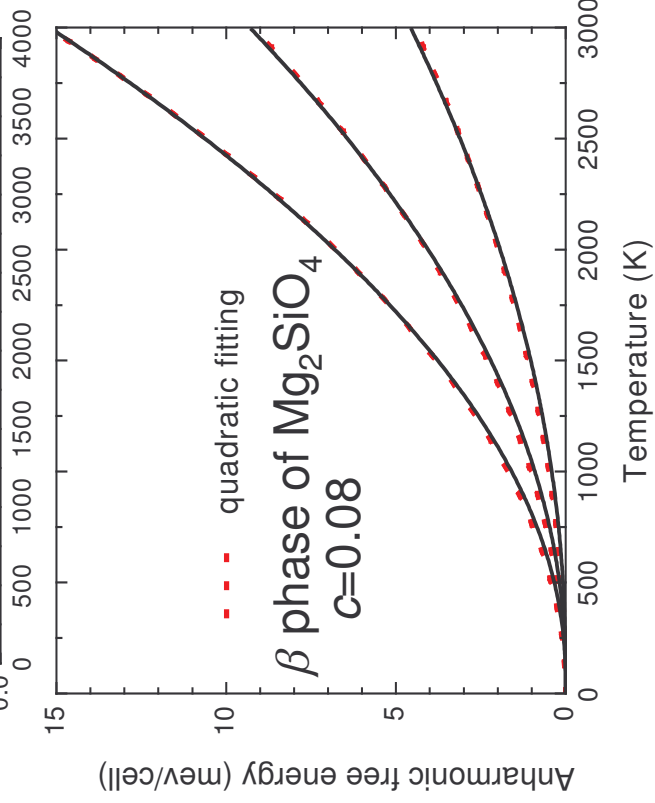
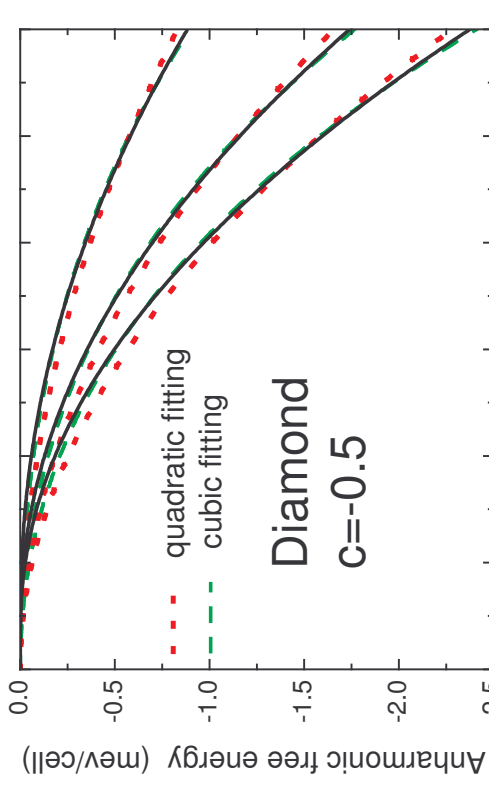
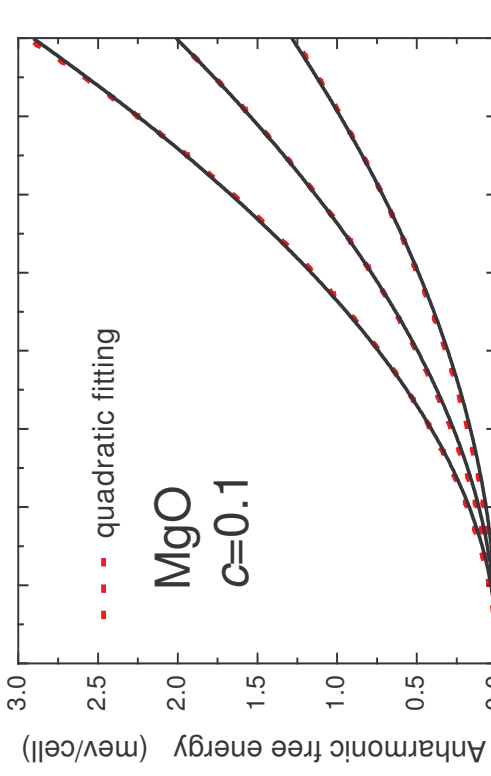


$\beta$  phase (wadsleyite)

positive  $c$

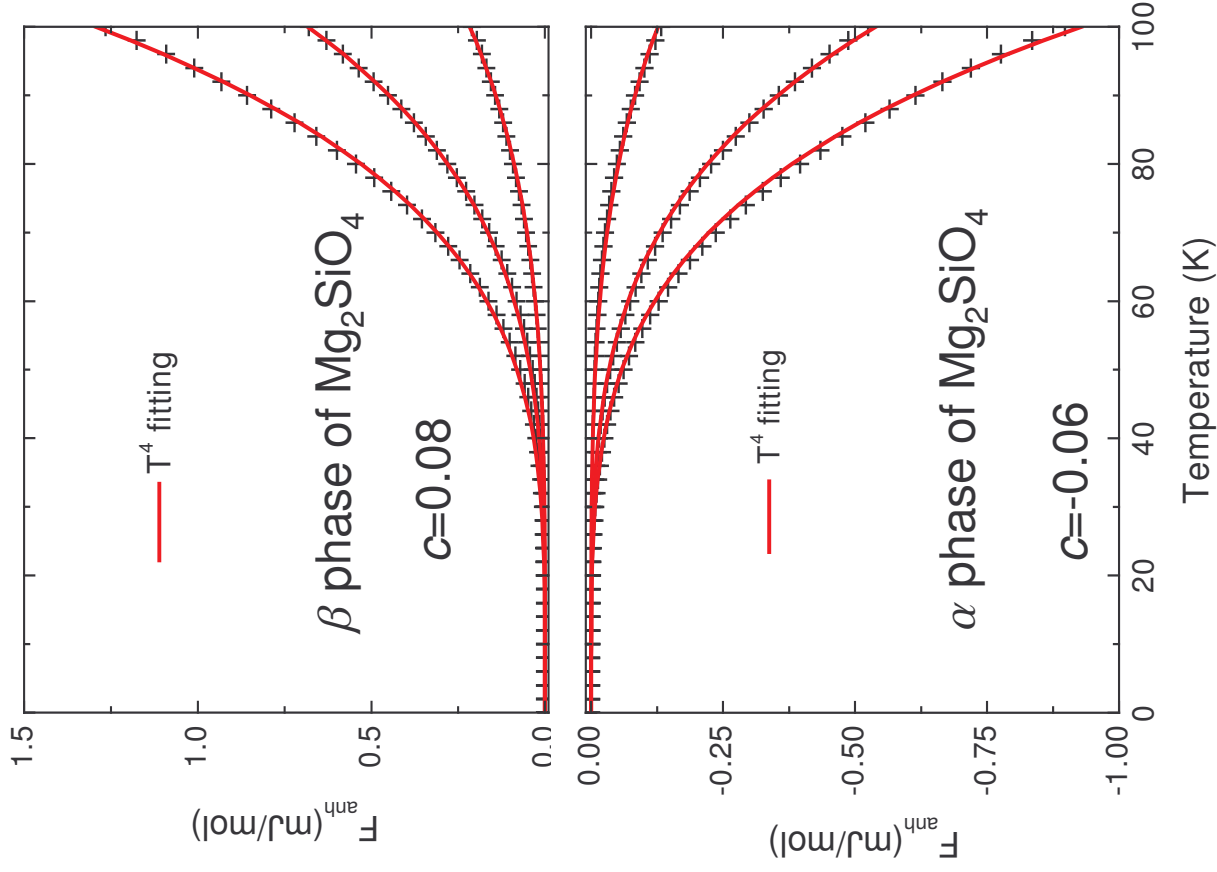
# Anharmonic free energy at high T

$$F_{anhc}(V) = \frac{1}{2}A(V)T^2 + \frac{1}{3}B(V)T^3 + \frac{1}{4}C(V)T^4$$

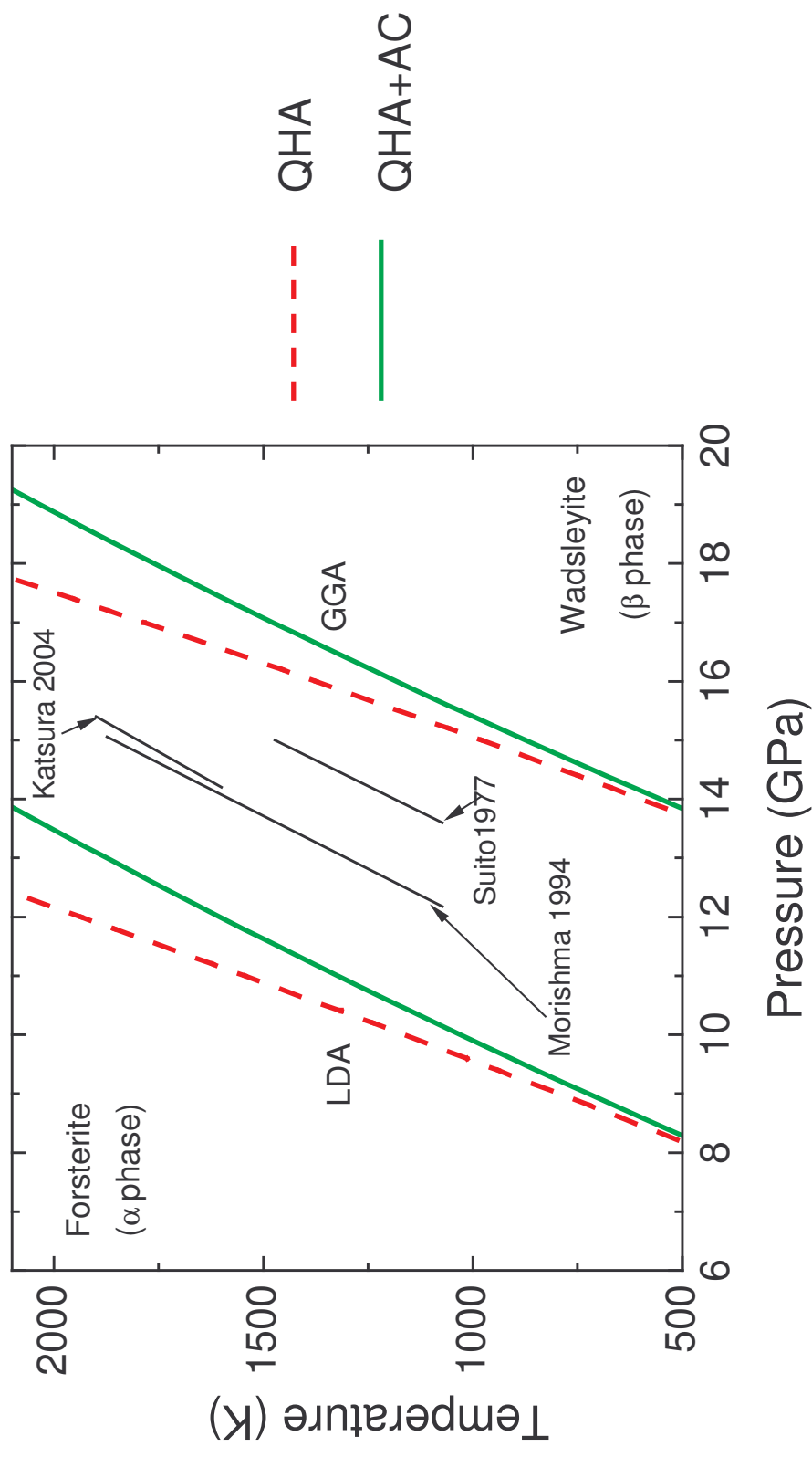


# Anharmonic free energy at low T

$$F_{anhc}(V) \propto T^4$$

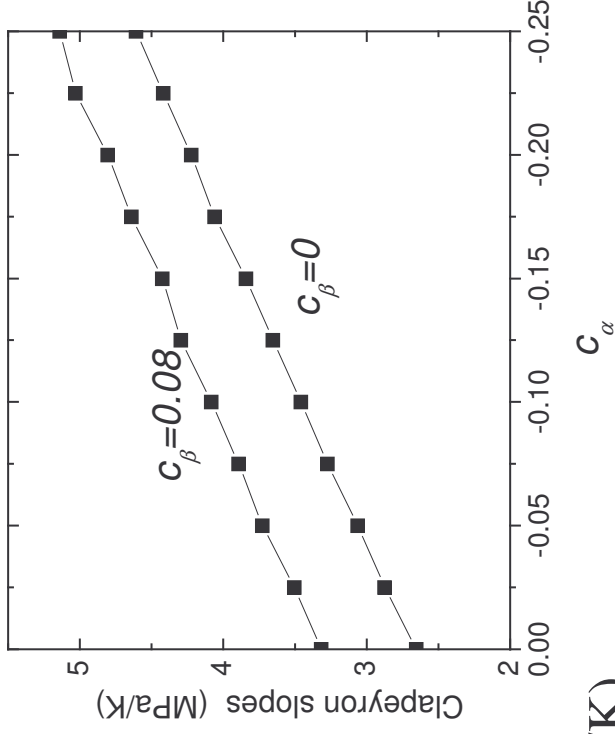


# Anharmonic effect on phase transition between forsterite and wadsleyite



# Clapeyron slopes (dP/dT)

$$S = S_0 + 7.82(c_\beta - c_\alpha)$$

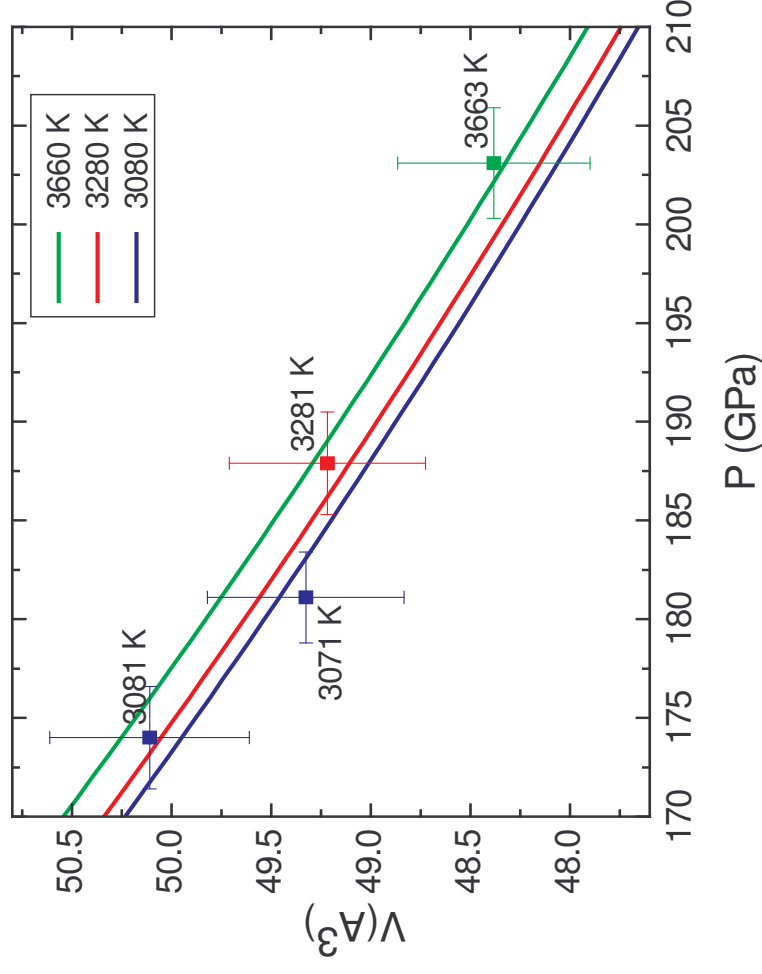


Clapeyron slopes (MPa/K)

High pressure experiment	3.5	Suito, 1977
QHA calculation	3.6	Morishima et al 1994
	4.0	Katsura et al 2004
This study	1.8	Akaogi et al, 1989
	2.7	Our calculation 2007; Price et al 1987; Chopelas 1991
	3.6	$c = -0.06$ (forsterite) and $0.08$ (wadsleyite)



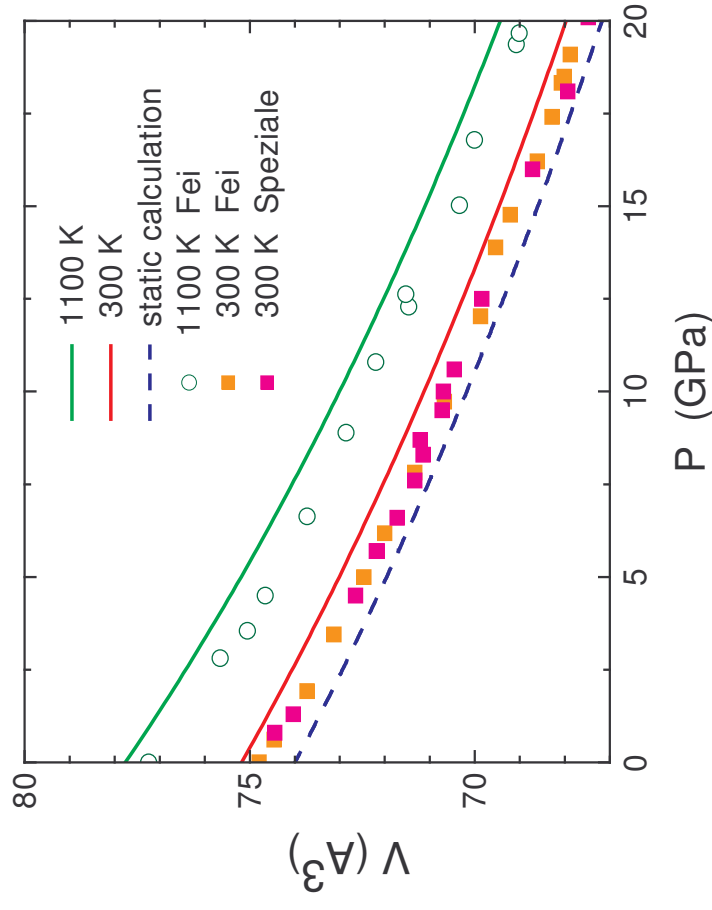
# Equation of state of MgO



**Agree excellently with shock wave data**

**(Svendsen and Ahrens, 1987)**

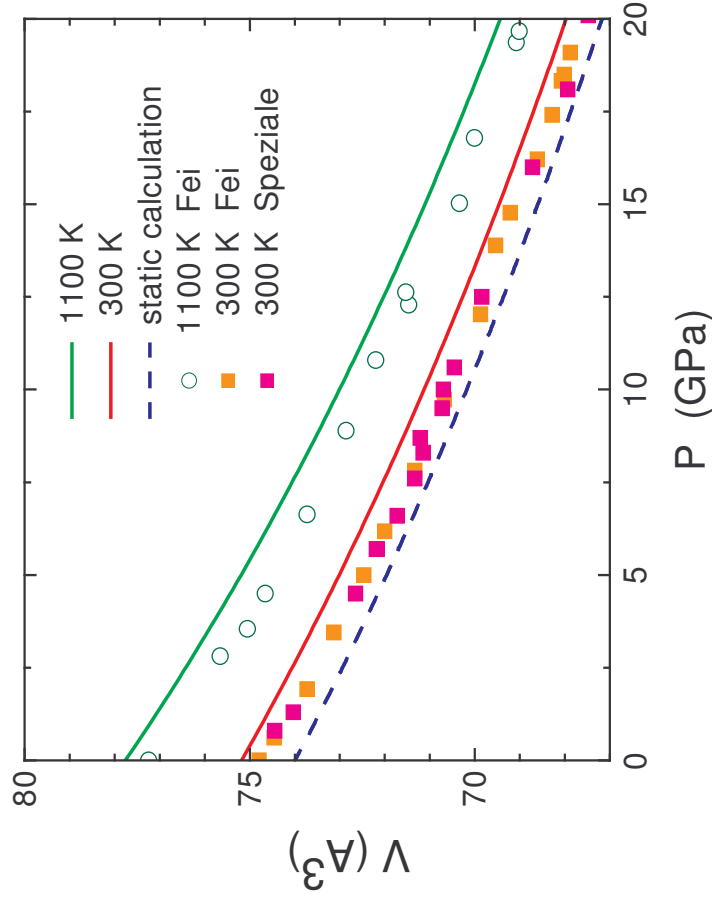
# Equation of state of MgO



Agree well with  
diamond anvil cell data

$$\frac{\Delta V_0}{V_0} \sim 0.6\%$$

# Equation of state of MgO



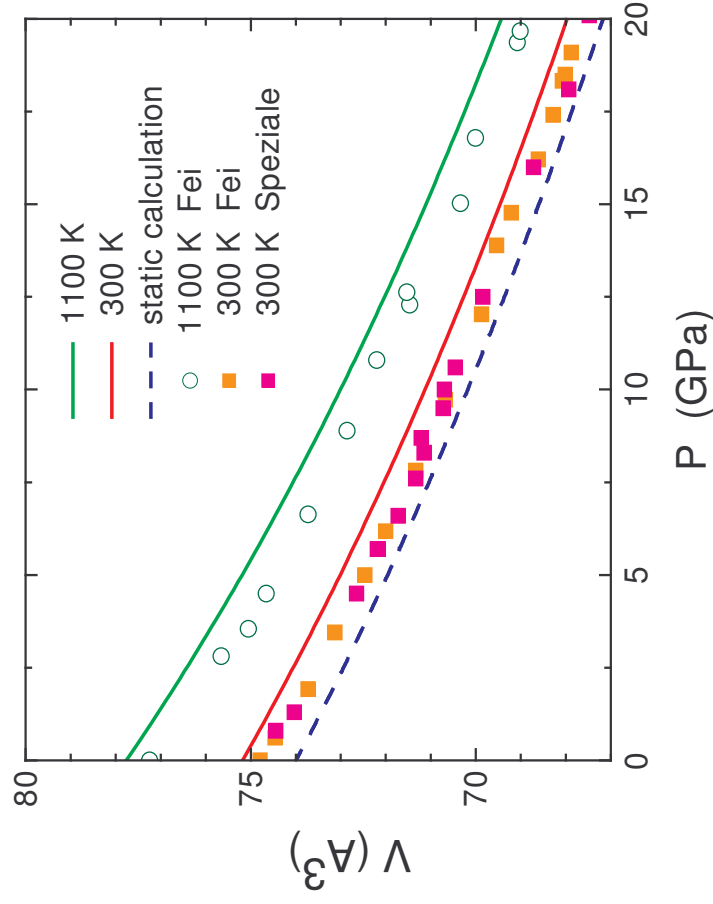
Agree well with  
diamond anvil cell data

$$\frac{\Delta V_0}{V_0} \sim 0.6\%$$

$$\Delta V = \Delta V_0 \exp(-P / P_c)$$

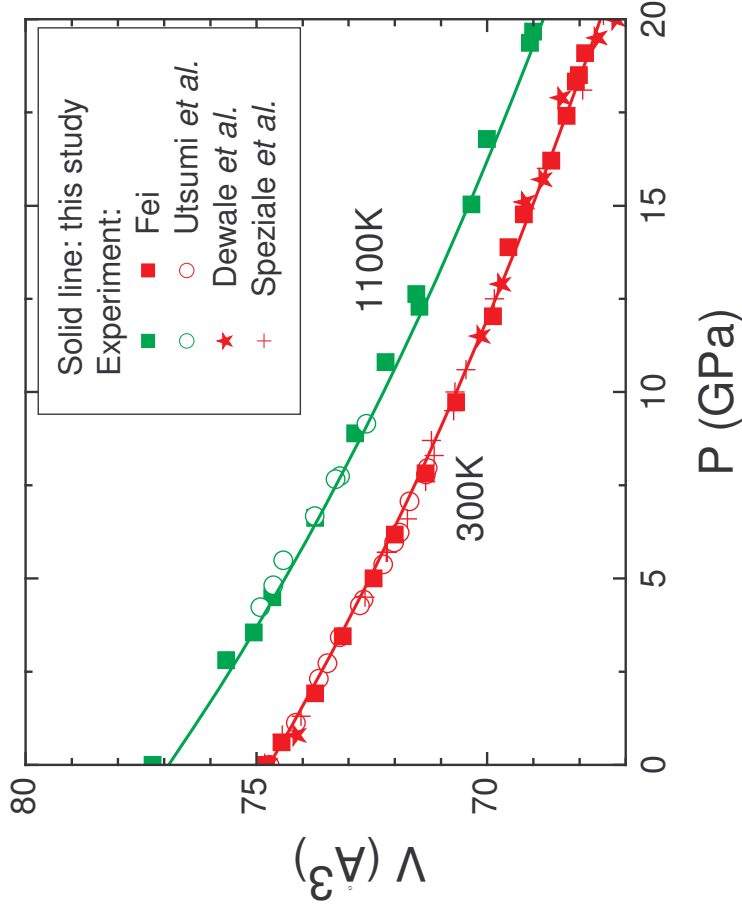
**Empirical correction**

# Equation of state of MgO



Agree well with  
diamond anvil cell data

$$\frac{\Delta V_0}{V_0} \sim 0.6\%$$

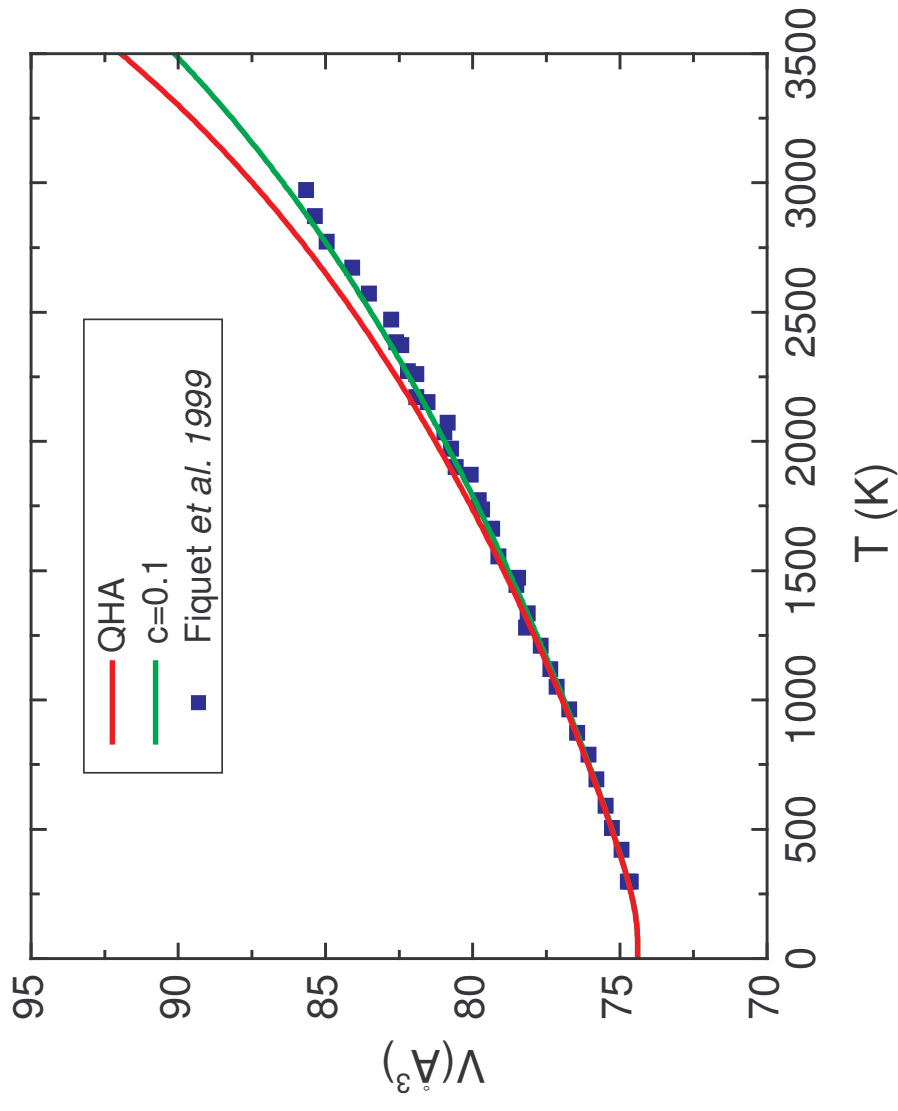


$$P_c = 80 \text{ GPa}$$

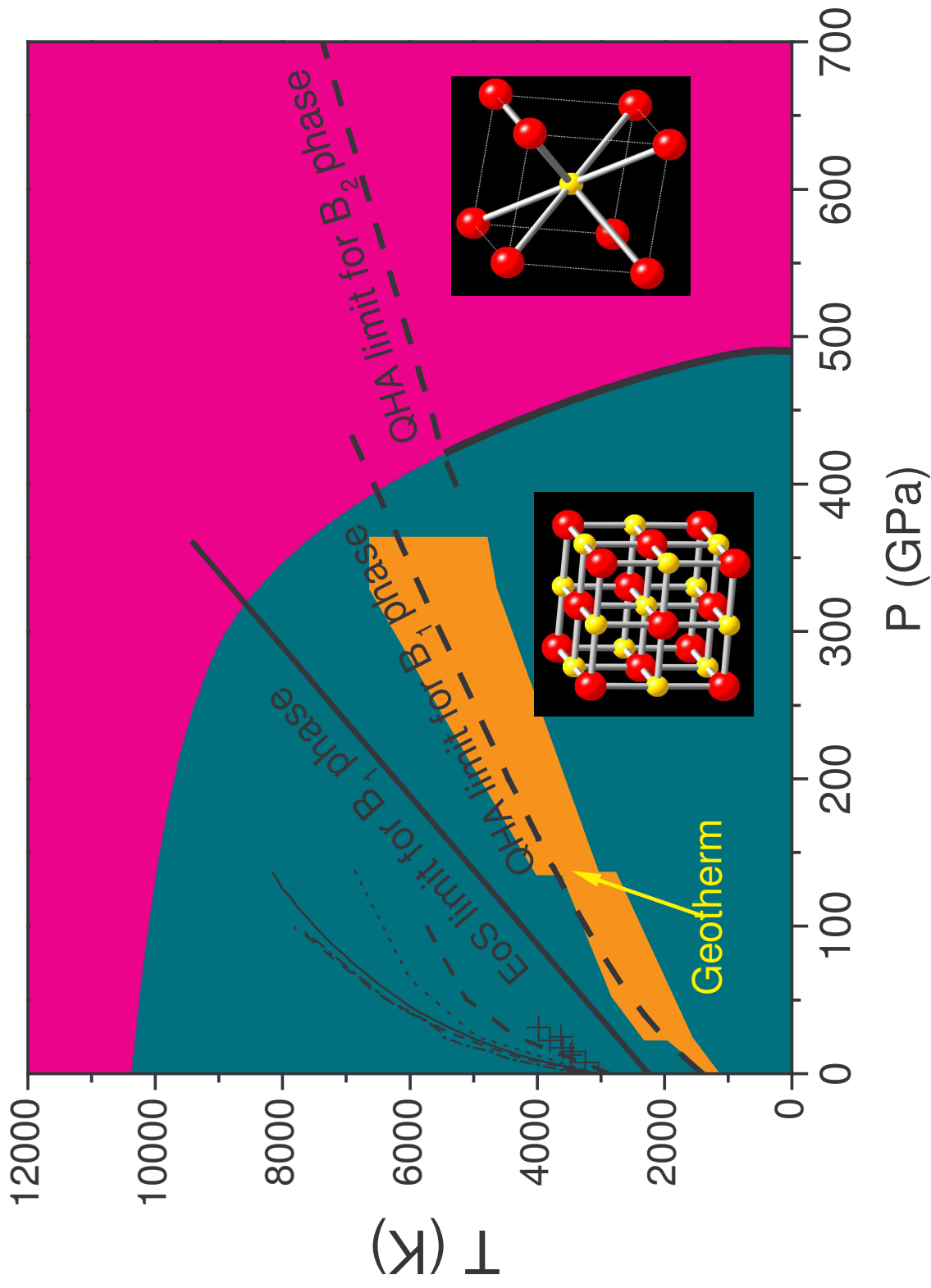
$$\Delta V = \Delta V_0 \exp(-P / P_c)$$

**Empirical correction**

# Anhammonic correction



# Phase diagram of MgO



# Conclusion

- Only one constant,  $c$ , is needed in our new method. QHA becomes a special case ( $c=0$ ).
- The thermodynamic properties of MgO, diamond, wadsleyite, and forsterite improve very much after anharmonic correction.
- Two types of anharmonicity:  $c>0$  or  $c<0$  depending on the structure.
- Anharmonicity changes substantially the phase boundary between wadsleyite and forsterite and reconciles the discrepancy in Clapeyron slopes between the experiment and QHA calculation



# Acknowledge

*Renata M. M. Wentzcovitch*

*Yonggang Yu*

*Koichiro Umemoto*

Research are supported by



UNIVERSITY OF MINNESOTA



599 Walter Library - 117 Pleasant St. SE - Minneapolis, MN 55455  
Phone: (612) 625-1818 - Fax: (612) 624-8861



**Thank you**

**!**