The Equation of State of Diamond

Andrea Ma

26th July 2006

with R. Maezono, N.D. Drummond, M. Towler and R. J. Needs

Contents

Introduction

- Aims – with DFT and QMC, determine:
  - EOS parameters: the lattice constant, bulk modulus and the pressure derivative of the bulk modulus of diamond
  - Zone-centre optical phonon frequency (Raman frequency) of diamond
- Why?
  - Experimental disagreement in B_0'
  - Raman frequency has a possible role in pressure calibration in diamond anvil cells
- Study carried out up to 500 GPa. Pressure currently achieved in diamond anvil cells is around 350 GPa.

Equation of state (EOS)

- Pressure-volume or energy-volume relationship
- Useful in geo, planetary, solar and stellar physics
- Data consisting of pressure, temperature and volume are parameterized as a functional form.
- A correct form helps us predict the high-pressure properties of solids
- Many different proposed forms of EOSs:
  - Birch, Murnaghan, Dodson, Holzapfel, Vinet, Kumari-Dass, Parsafar-Mason...

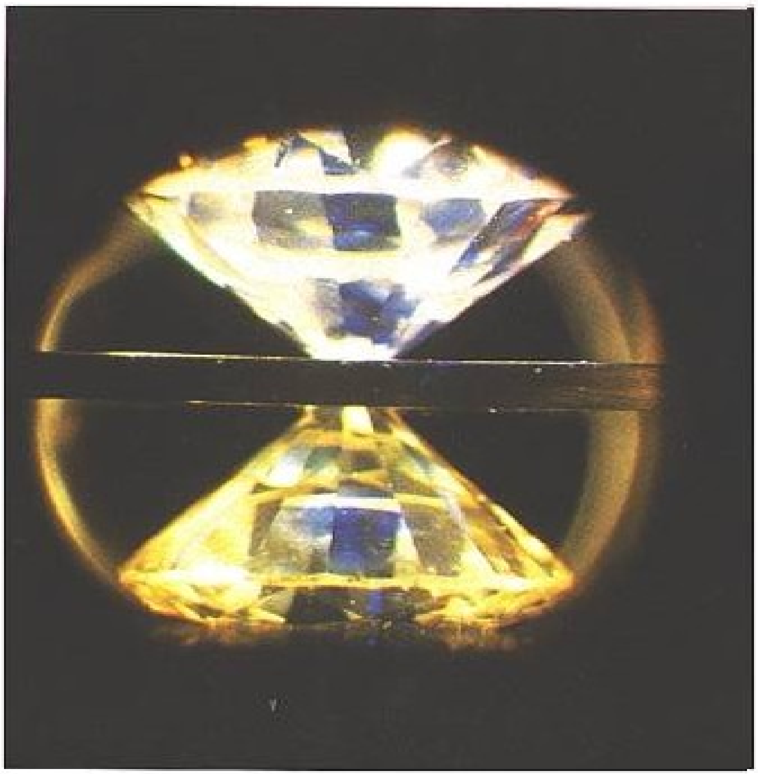
The Vinet EOS (1987)

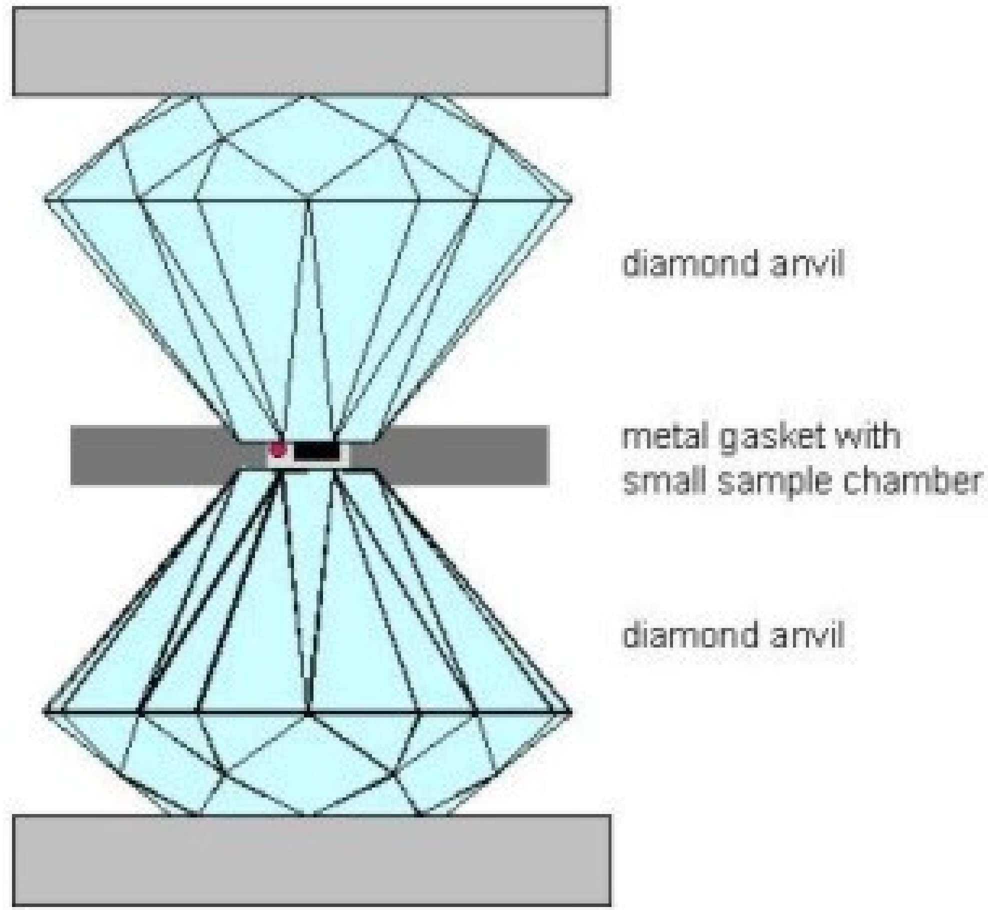
$$E(V)=\frac{-4B_0V_0}{(B_0'-1)^2}\left[1-\frac{3}{2}(B_0'-1)\left(1-\left(\frac{V}{V_0}\right)^{1/3}\right)\right]\times\exp\left[\frac{3}{2}(B_0'-1)\left(1-\left(\frac{V}{V_0}\right)^{1/3}\right)\right]+E_0$$

- Parameters for an energy-volume EOS are
  - V_0, B_0, B_0', E_{offset}
- The Vinet EOS gave the best fit to our data and yielded EOS parameters closest to experimental values.
- How accurate?
  - Vinet up to $V/V_0=0.2\text{-}0.3$ (or 10 Tpa)[1]
  - Dodson, KD and Murnaghan up to $V/V_0=0.7$

(1) Hama et al., J. Phys.: Condens. Matter 8 67, (1996)

The Diamond Anvil Cell (DAC)





The Diamond Anvil Cell

Top view onto an open Mao-Bell type DAC. The main components of the DAC are a long piston-cylinder assembly loaded with a lever arm.

- Typical sample size 10-30 μm
- Fluid rare gas loaded as pressure-transmitting medium
- < 5 μm size ruby sphere (calibration)
- Pressures up to 350GPa reached

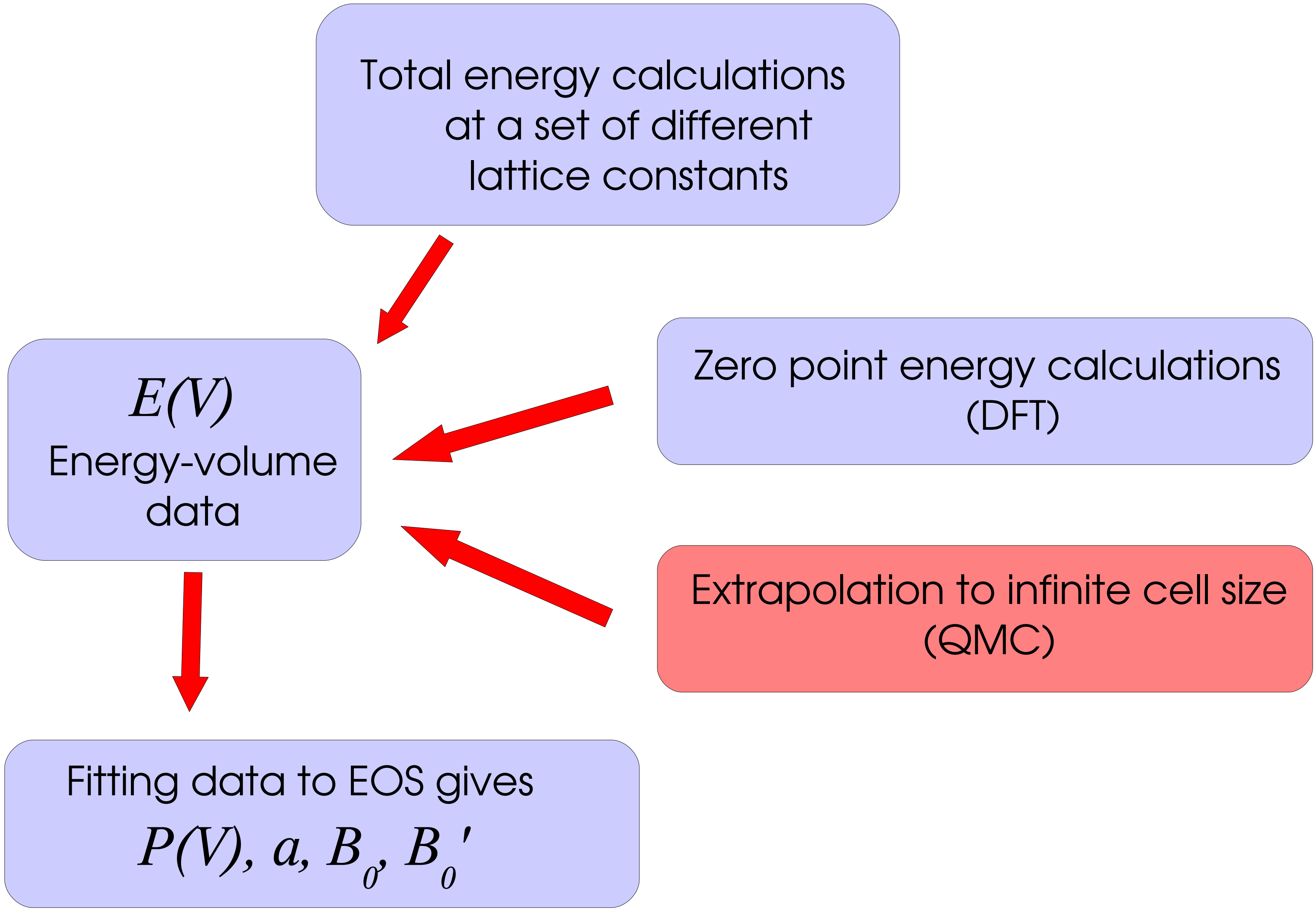
Difficulties in experiments

- Sample chamber becomes very thin (<10μm)
- Separation of diffraction signal of diamond from diamond anvils
- Pressure above 140GPa leads to breakage of diamond anvils in Occelli's experiment
- Calibration of the pressure (underestimates pressure by 11% in ruby calibration?)

Pressure derivative of the bulk modulus

Method	B_0'
Ultrasonic, up to 0.2GPa, McSkimin and Andreatch (1972)	4.0(5)
X-ray diffraction and Raman scattering, up to 140GPa, F. Occelli, P. Loubeyre, and R. LeToullec (2003)	3.0(1)
LDA Fahy et al, Chelikowsky et al, Pavone et al, Kunc et al, Crain et al	3.5, 3.54, 3.5, 3.63(3), 4.22
GGA Kunc et al, Ziambaras et al (4^{th} order polynomial, Murnaghan, Birch)	3.67(3), 3.71, 3.72, 3.70

Overview of EOS calculations

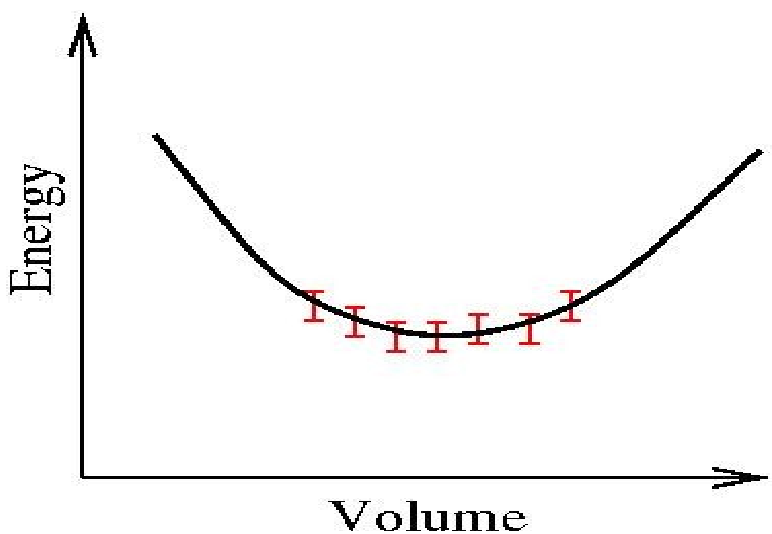


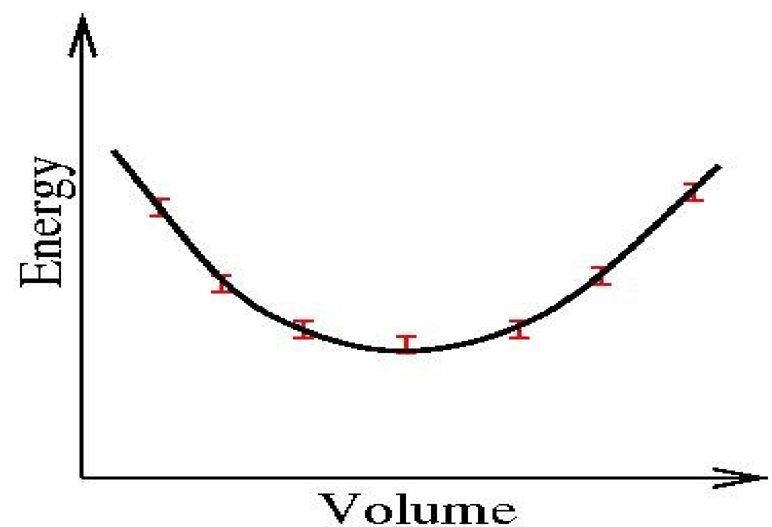
DFT calculations for EOS

- Computational details:
  - Code: CASTEP (plane waves)
  - GGA (PBE) and LDA
  - Ultrasoft pseudopotentials
  - Energy cutoff 100 a.u. (converged to 5×10^{-5} a.u./atom)
  - 8x8x8 MP k-point grid (converged to within 1×10^{-5} a.u./atom)
- Calculate E(V) for pressures up to 500GPa

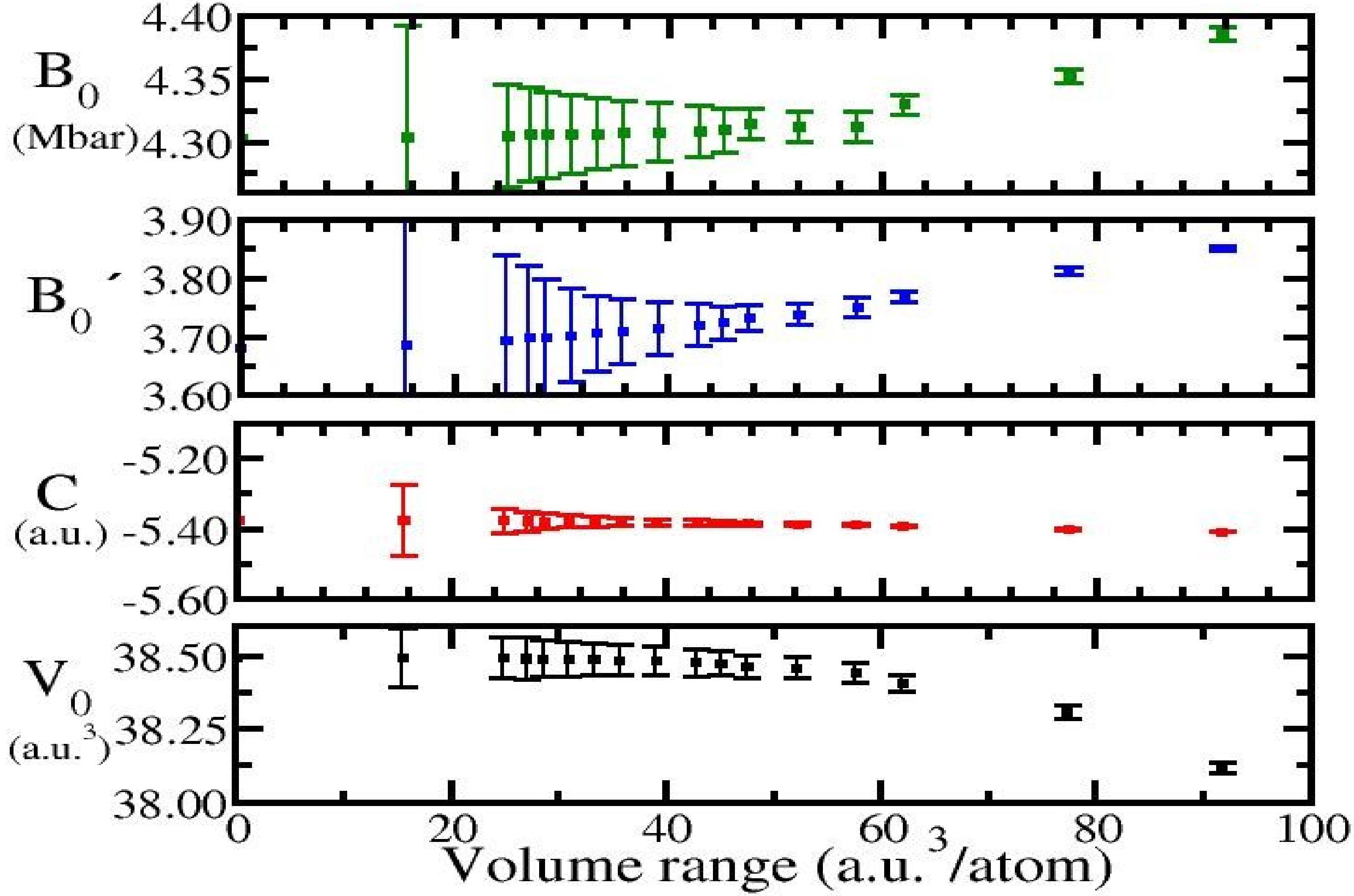
Choosing volume range for QMC

- Assume the energy-volume from PBE and QMC are similar
- In QMC we aim for a statistical error bar of 0.0001 a.u. per atom
- Add statistical noise to DFT data to study the effect of statistical noise on the EOS fitting parameters





Choosing volume range for QMC



QMC calculations for EOS (I)

- We expect our QMC calculations to give accurate results because:
  - Diamond is a material with a large band gap (5.47 eV), so a single Slater-determinant is expected to give a good nodal surface
  - Carbon has small non-polarisable core, therefore the pseudopotential approximation works well
  - HF pseudopotentials designed for QMC calculations

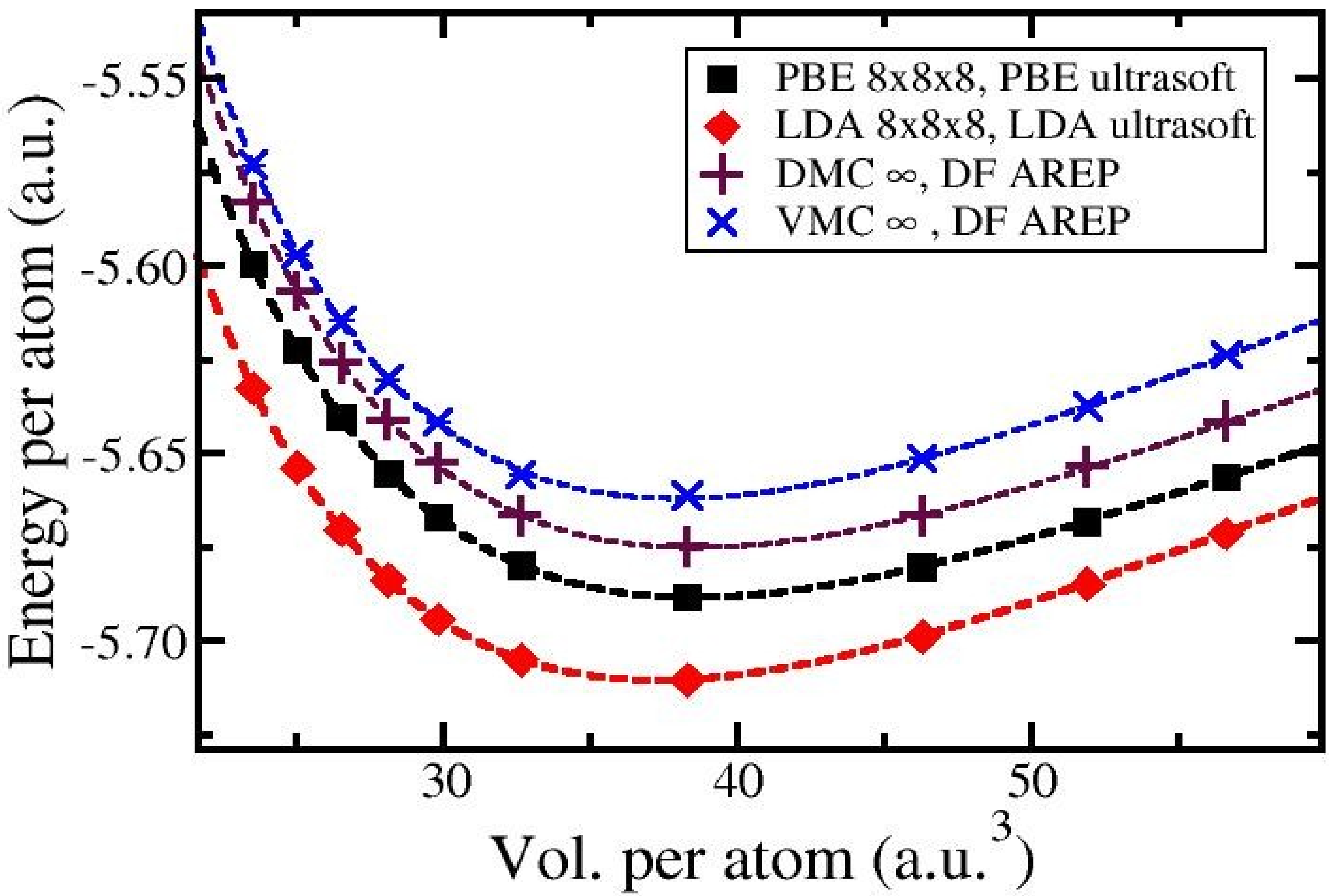
QMC calculations for EOS (II)

- Computational details:
  - calculations at 7 lattice constants around equilibrium, plus 3 lattice constants up to 500 GPa
  - 4x4x4 and 5x5x5 supercells (128 atoms and 250 atoms)
  - blip basis set[(1)]
  - HF pseudopotentials[(2)]
- Results corrected for finite-size effects and zero-point motion (from DFT-PBE calculations)

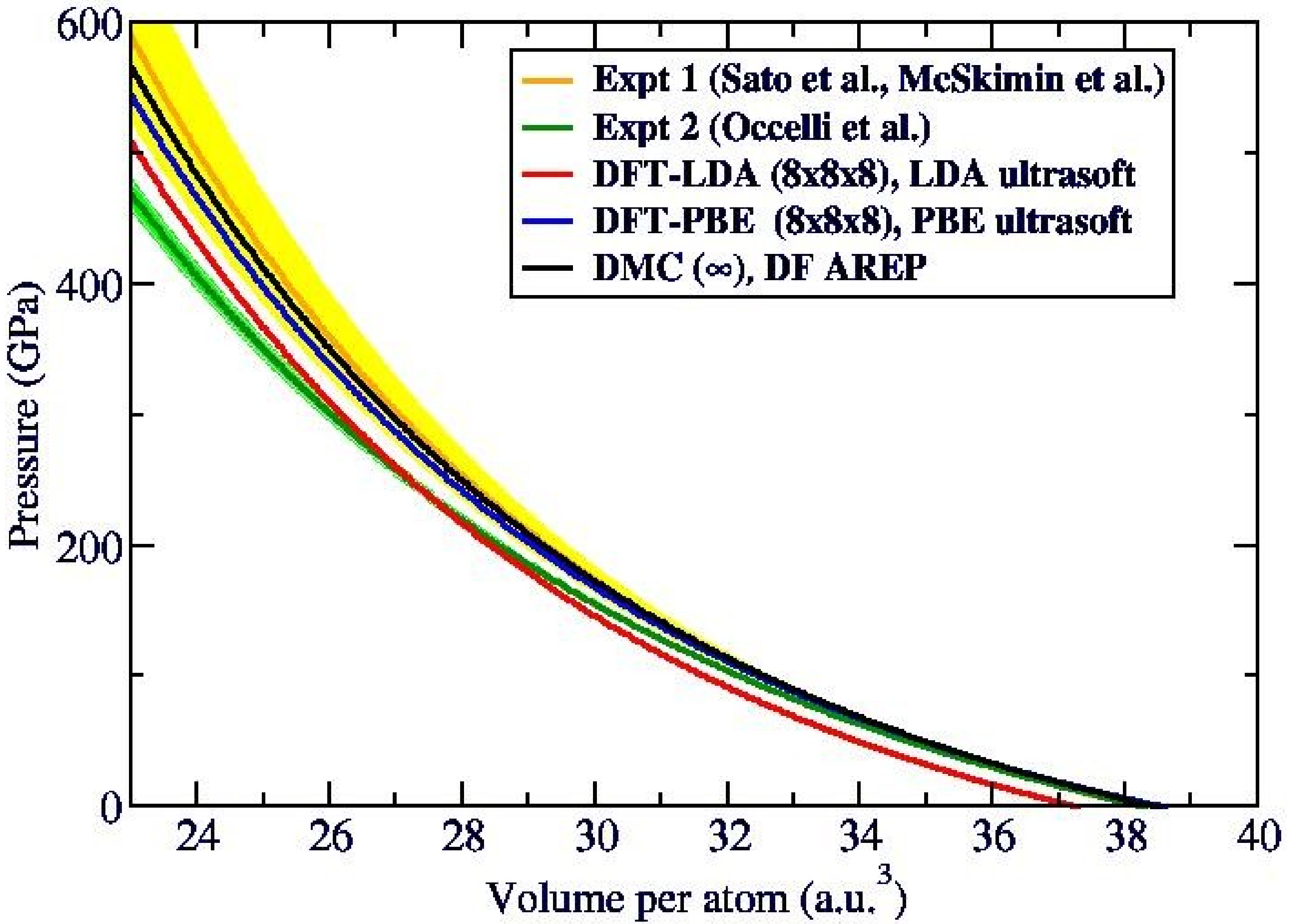
(1) Alfè et al, PRB 70, 161101 (2004)

(2) Trail and Needs, JCP 122 014112 (2005), JCP 122, 174109 (2005)

Energy-volume EOS



Pressure-volume EOS



EOS parameters

	DFT GGA (from lit.)	PBE	LDA	VMC	DMC	Expt
Lattice constant (Å)	3.55, 3.568, 3.565	3.577	3.536	3.555(1)	3.5737(8)	3.567, 3.5668
Bulk Modulus (Mbar)	4.33(2), 4.32, 4.22, 4.36, 4.32, 4.35	4.22	4.55	4.69(2)	4.38(1)	4.42, 4.43, 4.52, 4.448(8), 4.46(1), 4.45, 4.69 (at 0K)
Pressure deriv. of the bulk modulus	3.67(3), 3.71, 3.72, 3.70	3.75	3.68	4.38(1)	3.79(3)	4.0(5), 3.0(1)

Overview of phonon frequency calculations

Total energy calculations at a particular lattice constant, with the carbon atoms displaced in the (111) direction

$E(0), E(u_1), E(u_2)$

3 energies

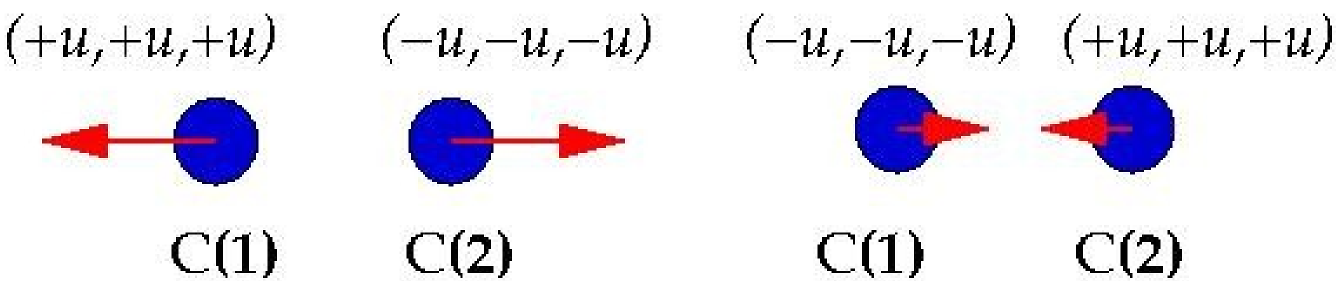
Fitting data to third order polynomial $E(u)$

Account for up to 4th order terms with DFT

Frozen phonon frequency

Frozen phonon frequencies (I)

- Frozen phonon method



- Energy $E(u)$ taken as a 3rd order polynomial:

$$E(u) = E(0) + A\,u^2 + B\,u^3$$

harmonic phonon frequency

$$\omega_0 = \sqrt{\frac{A}{3\mathrm{M}}}$$

3rd order term

Calculations at $E(0)$, $E(u_1)$ and $E(u_2)$

Frozen phonon frequencies (II)

- Calculated of 2^{nd} and 3^{rd} order coefficients (*A* and *B*) with PBE, LDA and QMC
- 4^{th} order coefficients with PBE (involves displacements of the carbon atoms in the [100] and [110] directions)
- Vanderbilt(1) showed with perturbation theory:

$$\Delta E_{[100]}(u) = \kappa u^2 + \alpha u^4$$

$$\Delta E_{[110]}(u) = \kappa u^2 + \frac{1}{2}(\alpha + 3\beta) u^4$$

$$\Delta E_{[111]}(u) = \kappa u^2 + \frac{2\gamma}{\sqrt{3}} u^3 + \frac{1}{3}(\alpha + 6\beta) u^4$$

(1) Vanderbilt et l, PRL 53(15) 1477 (1984)

Frozen phonon frequencies (III)

- anharmonic term in the phonon frequency is given approximately by

$$\Delta\omega \approx \frac{3\hbar}{4M^2\omega_0^2}(\alpha + 2\beta - \gamma^2/2\kappa)$$

κ	2nd order coeff.
γ	3rd order coeff.
α, β	4th order coeff.
M	Mass of carbon atom
ω_0	Harmonic phonon frequency

$$\omega = \omega_0 + \Delta\omega$$

Frozen phonon frequencies (IV)

- To deduce coefficients up to 4th order:

$$\Delta E_{[100]}(u)=\kappa u^2+\alpha u^4$$

$$\Delta E_{[110]}(u)=\kappa u^2+\frac{1}{2}(\alpha+3\beta)u^4$$

$$\Delta E_{[111]}(u)=\kappa u^2+\frac{2\gamma}{\sqrt{3}}u^3+\frac{1}{3}(\alpha+6\beta)u^4$$

$$\frac{\Delta E_{[100]}(u)}{u^2}=\kappa+\alpha u^2$$

$$\kappa,\alpha$$

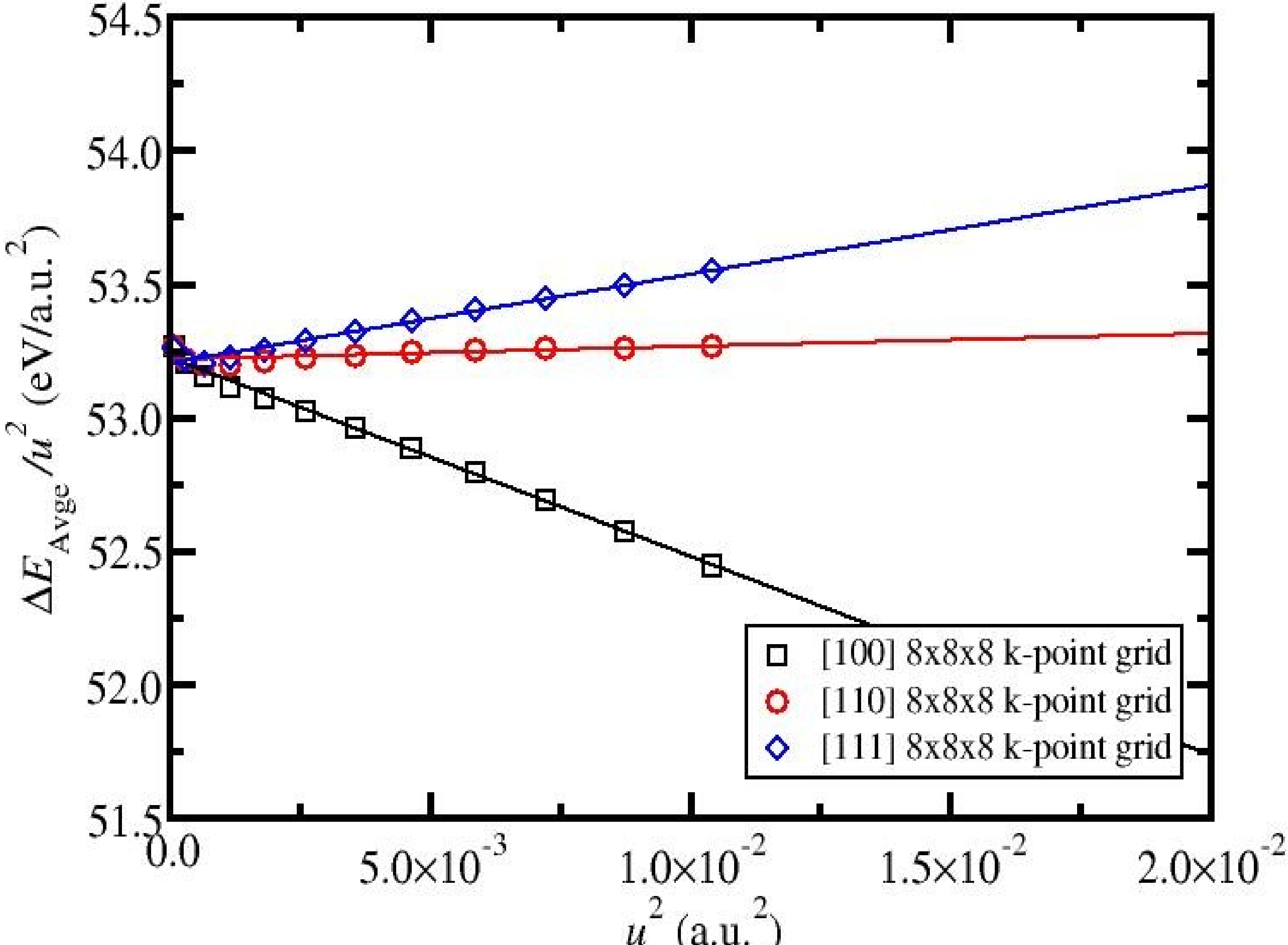
$$\frac{\Delta E_{[110]}(u)}{u^2}=\kappa+\frac{1}{2}(\alpha+3\beta)u^2$$

$$\kappa,(\alpha+3\beta)$$

$$\Delta E_{[111]}(u)-\Delta E_{[111]}(-u)=\frac{4\gamma}{\sqrt{3}}u^3$$

$$\gamma$$

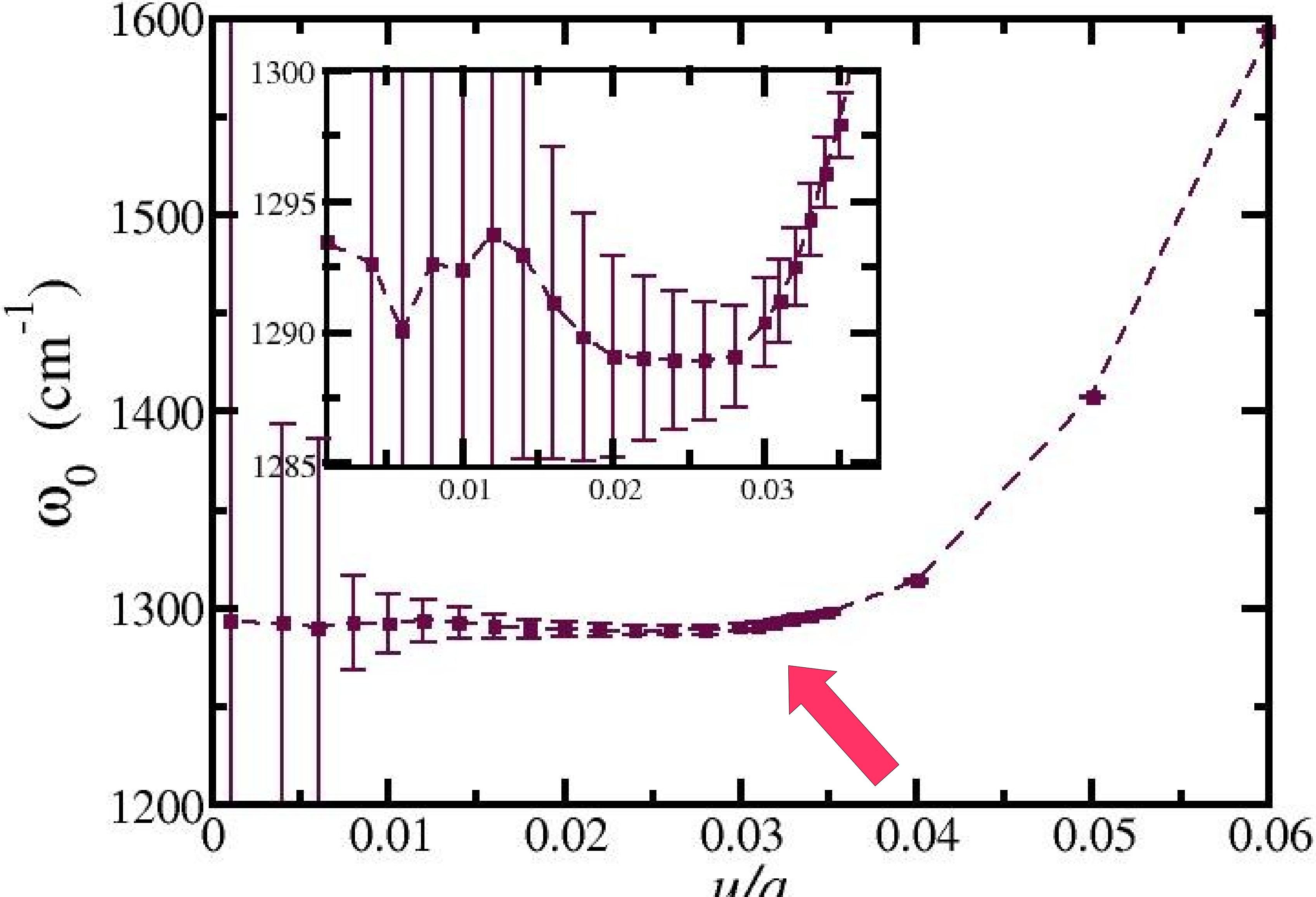
Determining coefficients (500 GPa)



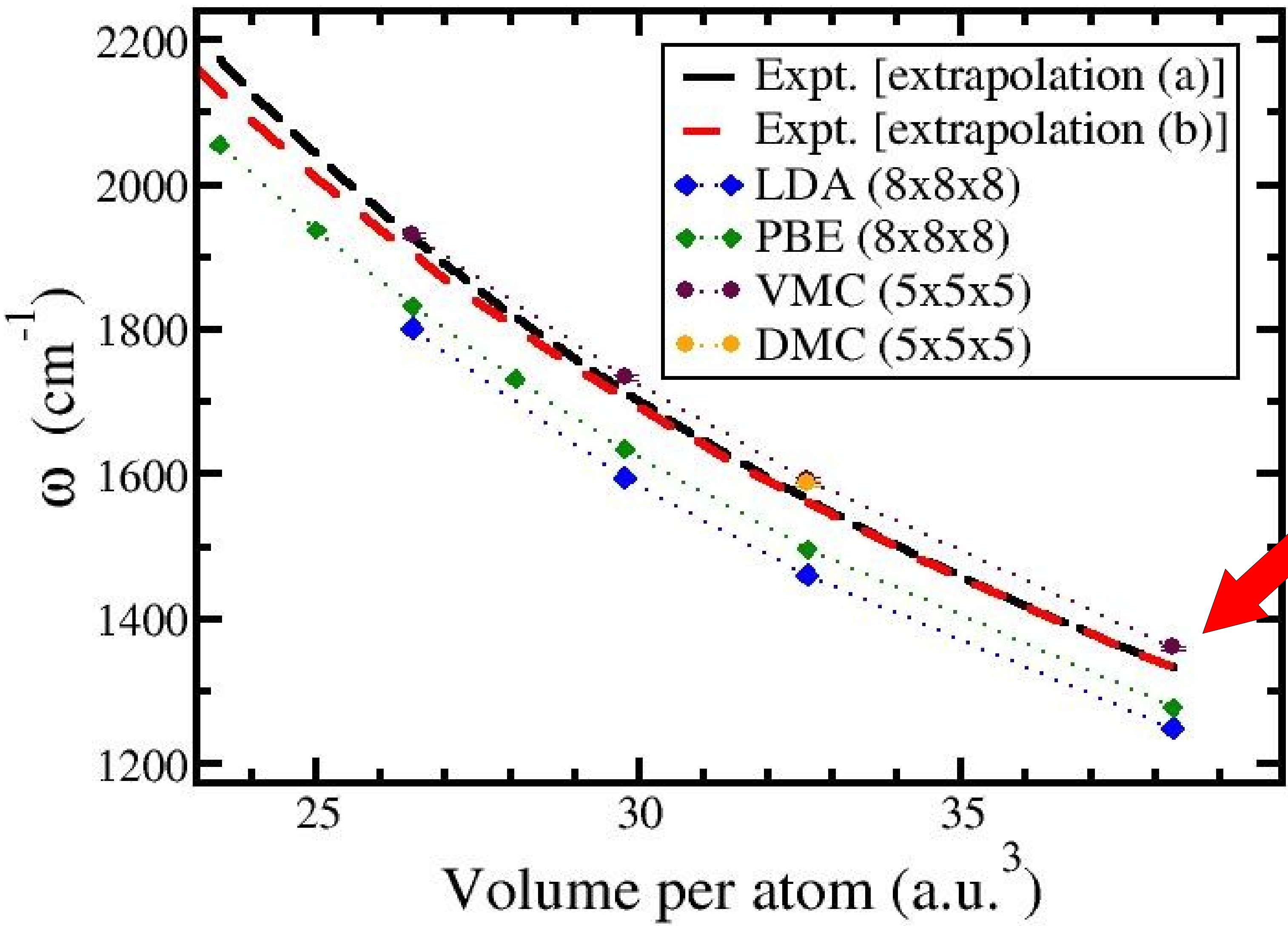
Atomic displacements (I)

- Small atomic displacements in DFT
  - $U = 0.001a$, $a =$ lattice constant:
  - Stretch and compress the carbon-carbon bond by the same amount
- How about atomic displacements in QMC?
  - Have to consider effects of statistical noise on QMC data (0.0001 a.u./atom)
  - Stretch and compress the carbon-carbon bond by the same amount, or not?
  - Aim for an error bar of $<5\text{cm}^{-1}$, and an anharmonicity of <1% of the phonon frequency

Atomic displacements (II)



Final phonon frequencies



Experimental value
$\omega = 1333\mathrm{cm}^{-1}$

Extrapolation of experimental values

- Extrapolation *(a)*

$$\omega(V)=\omega(V_{expt})\left(\frac{V_{expt}}{V}\right)^{\gamma}$$

$$\gamma=1$$

- Extrapolation *(b)*

$$\omega(V)=\omega(V_{expt})\frac{\gamma}{\gamma'}\left[\left(\frac{V}{V_{expt}}\right)^{-\gamma'}-1\right]+\omega(V_{expt})$$

$$\gamma=1.000(5),\ \gamma'=0.80$$

Comparison with experiments

Equation of State
(DFT, QMC)
500 GPa

Frozen phonon frequency
(DFT, QMC)
300 GPa

DFT(PBE)
a ~ +0.2%
B ~ -3%
B_0'=3.75

DMC
a ~ +0.2%
B ~ -2%
B_0'=3.79(3)

PBE
ω ~ -5%

VMC
ω ~ +2%

Conclusions

- Performed DFT and QMC calculations on carbon diamond to determine
  - EOS parameters *a*, B_0 and B_0' up to 500 GPa
  - Zone-center frozen phonon frequencies up to 300 Gpa
- DMC results for *a* and B_0 agree within 0.2% and 2% of the experimental values respectively
- DMC determined value of $B_0' = 3.79(3)$ agrees with the earlier experimental result of $B_0' = 4.0(5)$ (McSkimin *et al.*)

Extras

- QMC finite size effects (I)
- QMC finite size effects (II)
- Parameters in anharmonic term
- DMC EOS parameters

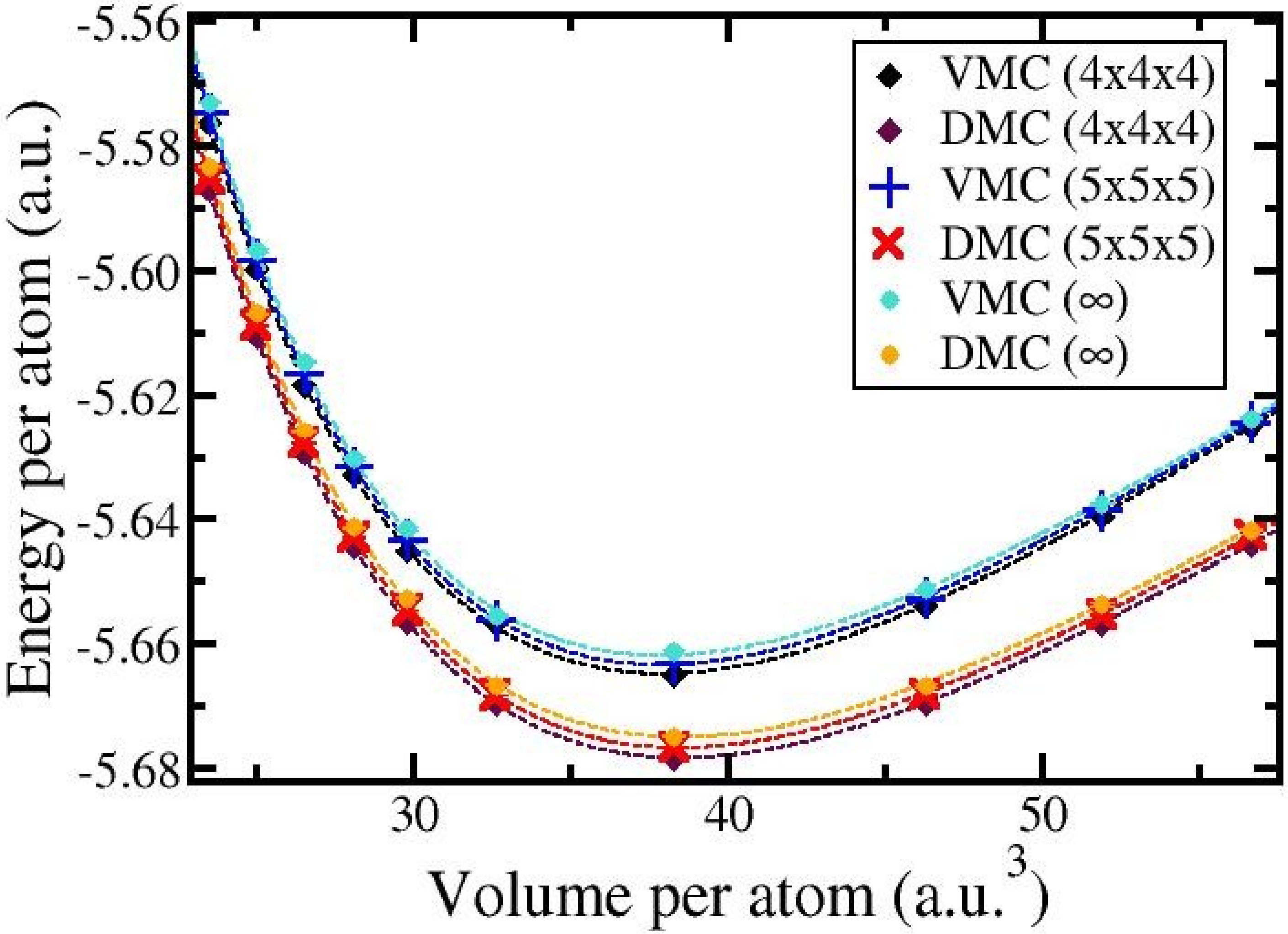
QMC finite size effects (I)

- Coulomb finite size bias
- The static energy in the infinite system limit is given by: $$E_{\infty}^{SL}(V) = E_N^{SL}(V) + \frac{b(V)}{N}$$

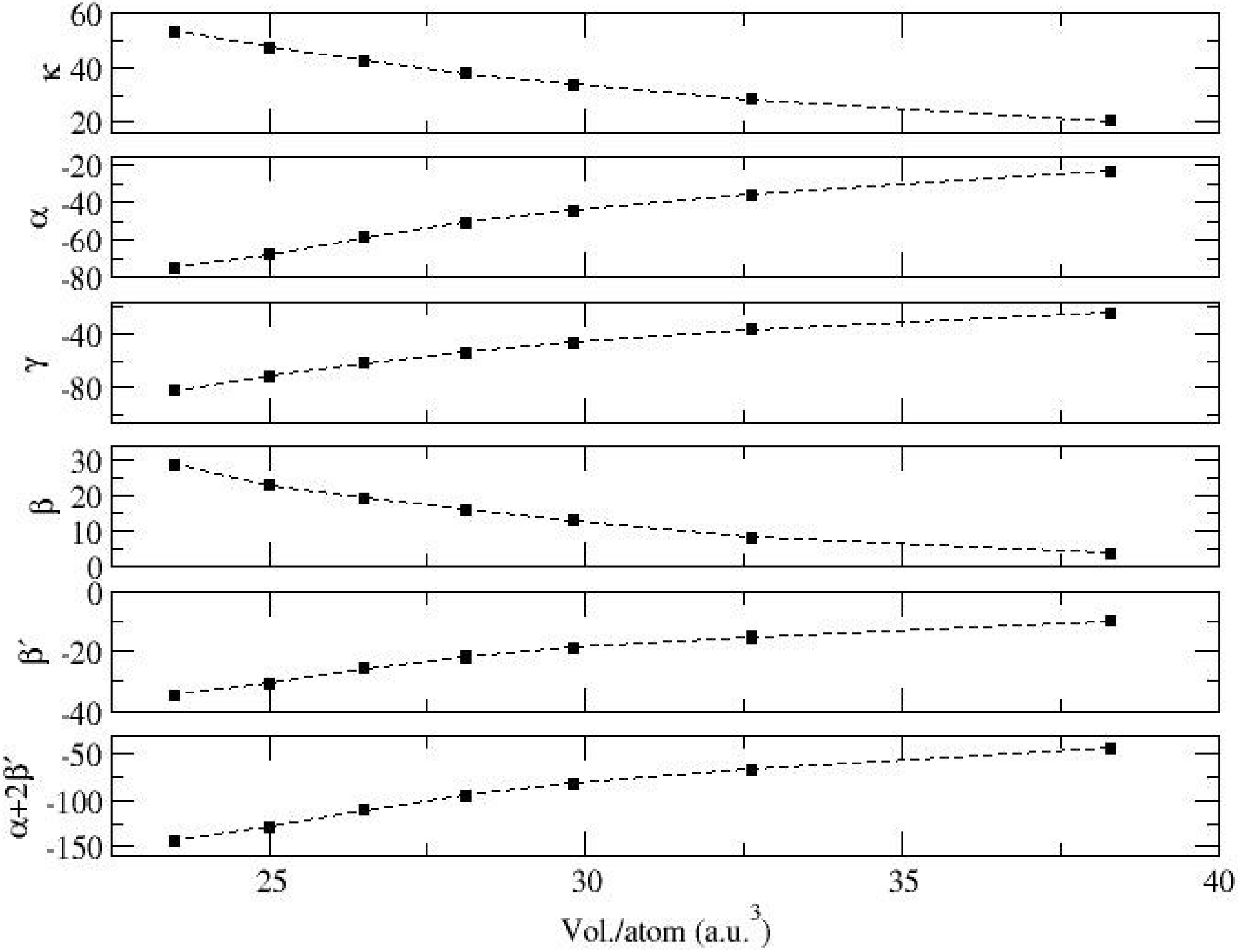
- For two system sizes, we can eliminate *b(V)*:

$$E_{\infty}^{SL}(V) = \frac{N\,E_N^{SL}(V) - M\,E_M^{SL}(V)}{N-M}$$

QMC finite size effects (II)



Parameters in anharmonic term



DMC EOS parameters

	4x4x4 supercell	5x5x5 supercell	Infinite cell size without ZPE	Infinite cell size	Expt
Lattice constant (Å)	3.5620(4)	3.5620(4)	3.5622(8)	3.5737(8)	3.567, 3.5668
Bulk Modulus (Mbar)	4.546(8)	3.522(8)	4.50(1)	4.38(1)	4.42, 4.43, 4.52, 4.448(8), 4.46(1), 4.45, 4.69 (at 0K)
Pressure deriv. of the bulk modulus	3.68(1)	3.73(2)	3.77(3)	3.79(3)	4.0(5), 3.0(1)