HIGH PRESSURE PROPERTIES OF METALS FROM FIRST PRINCIPLE CALCULATIONS: GOLD AS AN EXAMPLE

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INTRODUCTION

- Importance of Gold as a Calibration Standard
- Calculation Techniques
- Equation of State of Au
- Elastic Properties
- Phonon Dispersion Relations
- Conclusion

Gold as a Calibration Standard

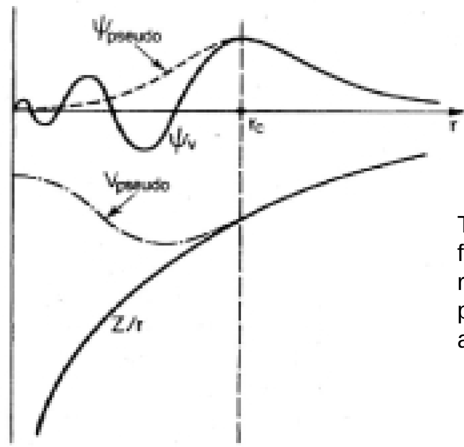
- Gold is often used as a calibration standard in high pressure experiments due to:
  - Low strength and rigidity
  - Chemical inertness
  - High structural stability (stable fcc structure up to 100 GPa)

⇒ The physical and chemical properties of Au have to be known

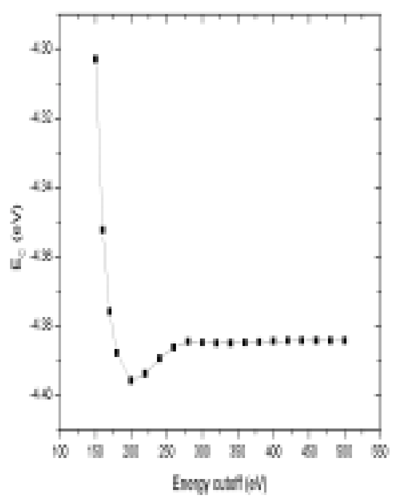
Calculation Method

- Density Functional Theory (DFT)
- First principles calculations (*ab-initio*) Calculations
- Plane wave basis sets (E_{cutoff}=400 eV)
- Pseudopotential approximation (Ultrasoft Vanderbilt Pseudopotentials)
- Special k-point mesh (Monkhorst-Pack)

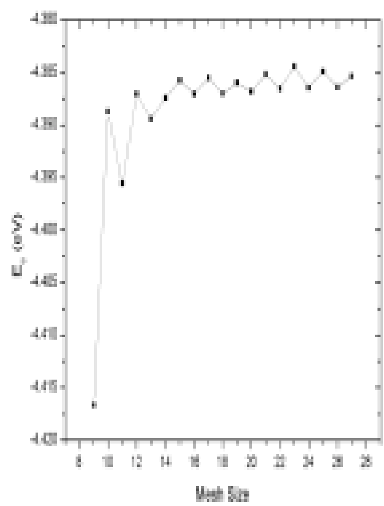
Pseudopotential Approximation



The valence electrons wave functions are oscillating rapidly due to high core potential, which is replaced by a pseudopotential.



Energy cutoff test



k-point test

Local Denstiy Approximation (LDA)

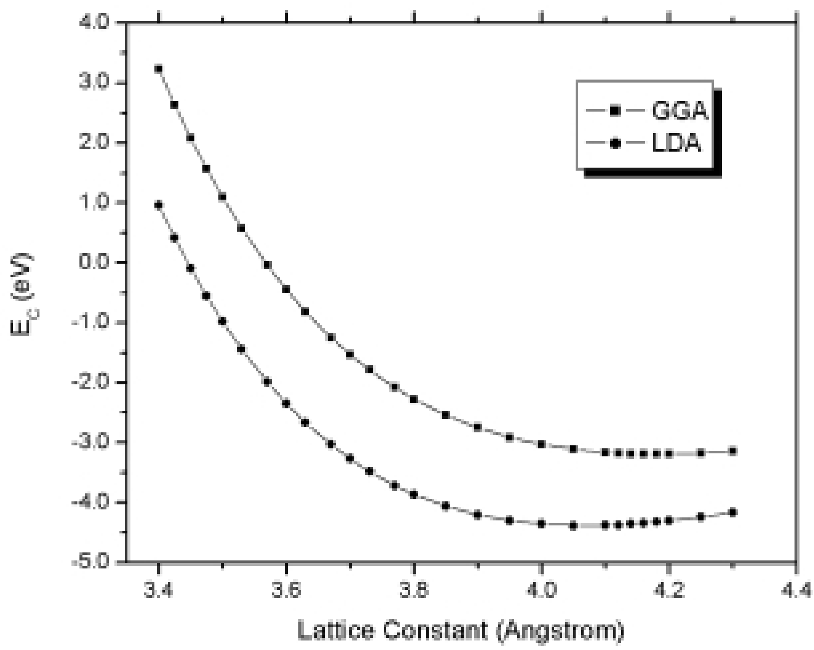
- **Overestimates bulk modulus, cohesive energy**
- **Underestimates lattice constant and thus cell volume**
- **Lower bound to the pressure for a given volume**

Generalized Gradient Approximation (GGA)

- **Underestimates bulk modulus, cohesive energy**
- **Overestimates lattice constant and thus cell volume**
- **Upper bound to the pressure for a given volume**

Equation of State of Gold

- Ab-initio calculations were performed for fcc Au at various pressures
- Cohesive energies were calculated for both LDA and GGA
- Spin-unpolarized calculations
- Spin-orbit coupling (SOC) effects was also neglected
- Energy versus lattice parameter curve was obtained



Vinet EOS

$$E(V,T) = E_0(T) + \frac{9B_0(T)V_0(T)}{\xi^2}\{1 + \{\xi(1-x) - 1\}\exp\{\xi(1-x)\}\}$$

$$P(V,T) = \left\{\frac{3B_0(T)(1-x)}{x^2}\right\}\exp\{\xi(1-x)\}$$

$$x = (V/V_0)^{1/3}$$

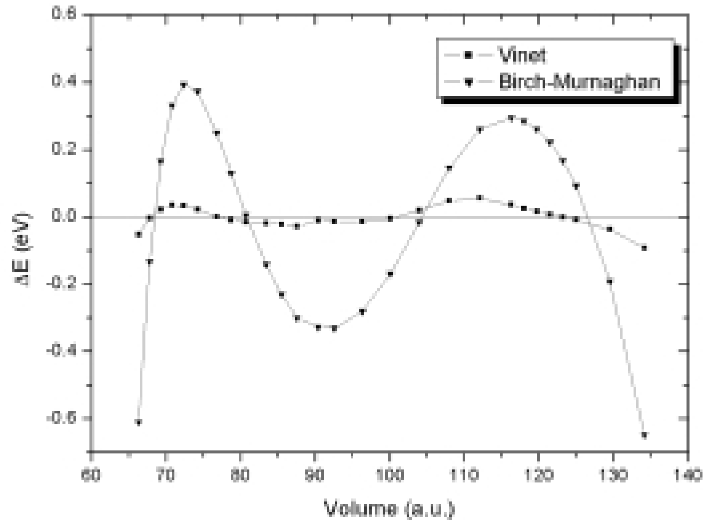
$$\xi = \frac{3}{2}(B_0' - 1)$$

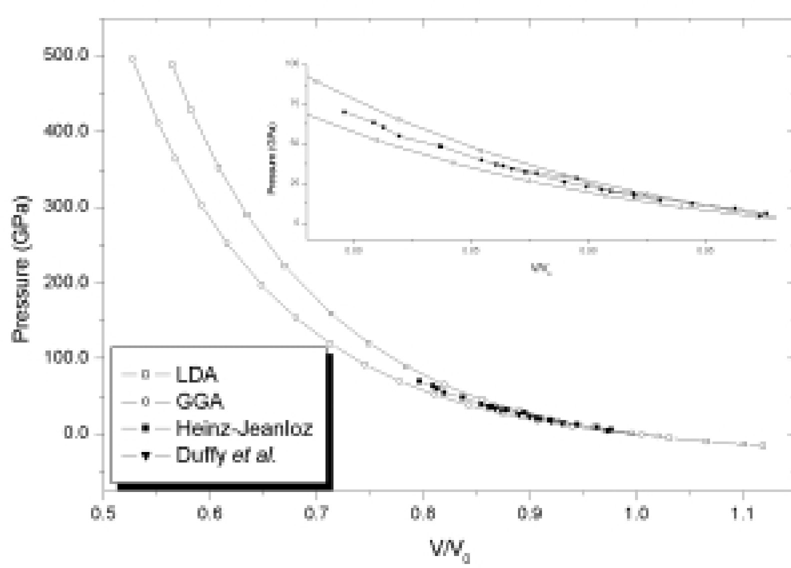
Birch-Murnaghan EOS

$$E(V,T) = E_0(T) + \frac{9B_0(T)V_0(T)}{8}\left\{1 + \frac{\kappa}{2}(x^{-2} - 1)\right\}(x^{-2} - 1)$$

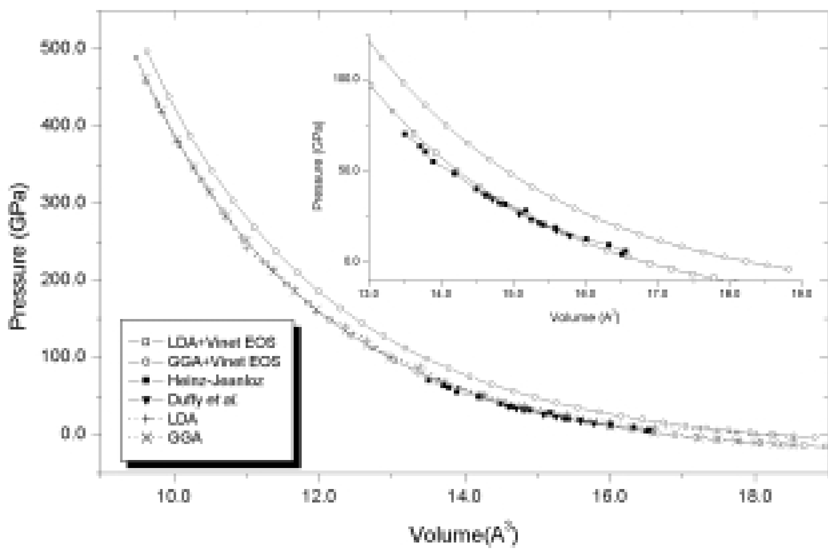
$$P(V,T) = \frac{3}{2}B_0(T)\{x^{-7} - x^{-5}\}\left\{1 + \frac{3}{4}\kappa(x^{-2} - 1)\right\}$$

$$\kappa = B_0' - 4$$


Vinet
Birch-Murnaghan
ΔE (eV)
Volume (a.u.)


Pressure (GPa)
LDA
GGA
Heinz-Jeanloz
Duffy et al.
V/V0

Equation of state of Au



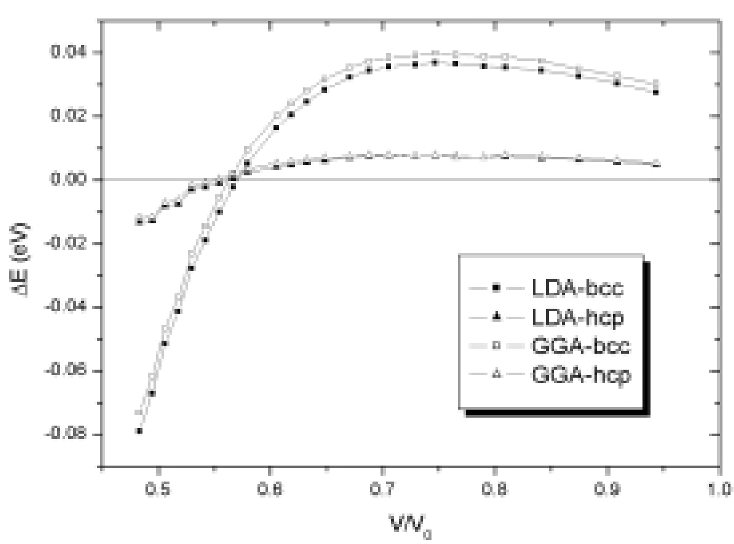
Zero-pressure volume, cohesive energy, bulk modulus and pressure derivetive of bulk modulus

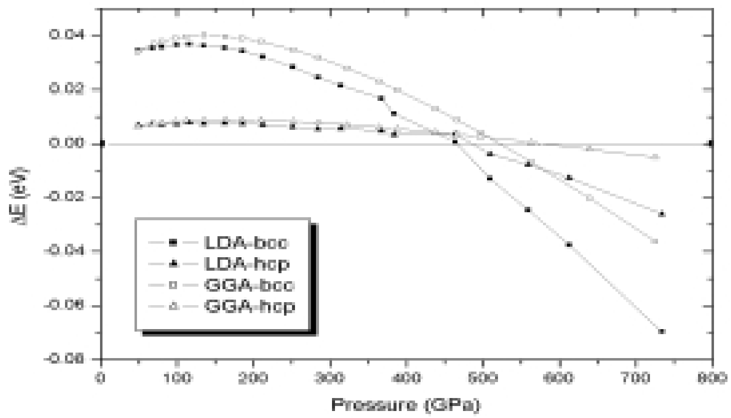
V_0 (Å^3)	E_0 (eV)	B (GPa)	$\partial B/\partial P$	ref
18.29 (7.8)	-3.19 (16)	134.16 (19.5)	5.97 (8.5)	GGA
16.82 (0.8)	-4.39 (15.6)	186.76 (12.1)	5.73 (4.18)	LDA
16.96	-3.796	166.65	5.5	Heinz-Jeanloz
16.95	...	170.65	4.72	Duffy

LDA predicts the physical properties of fcc Au better than GGA.

Structural Phase Transition of Au

- First principle calculations were performed for bcc and hcp structures of Au.
- In order to perform BZ integrations for bcc phase, k increment is set equal to the one of fcc calculation.
- For hcp, c/a ratios were not taken as ideal but optimized before calculations

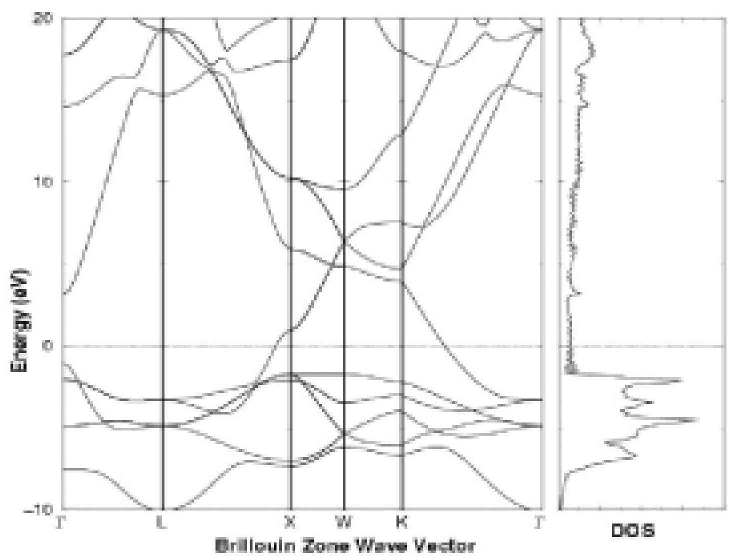


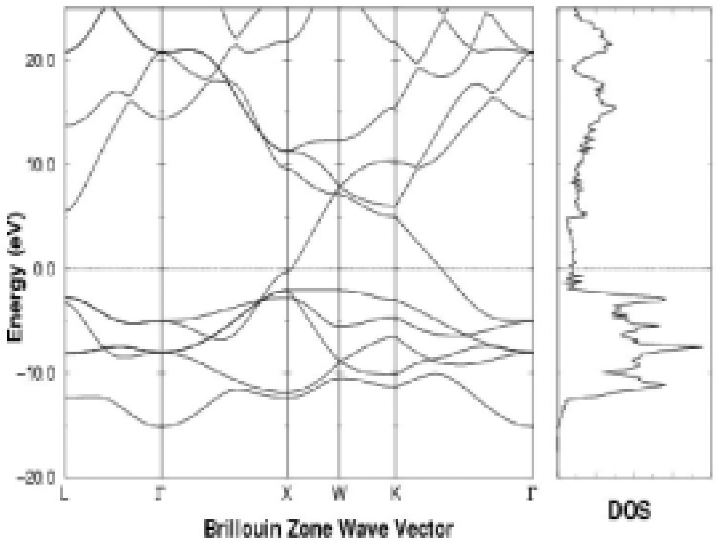


Transition pressures are:

455 GPa (fcc to bcc) and 457 GPa (fcc to hcp) using LDA

534 GPa (fcc to bcc) and 590 GPa (fcc to hcp) using GGA





Calculation of Elastic constants

In any cubic crystals there are three independent stiffness constants (c_{11}, c_{12} and c_{44}).

Tetragonal Deformation

$$\epsilon = \begin{pmatrix} \delta & 0 & 0 \\ 0 & \delta & 0 \\ 0 & 0 & (1+\delta)^{-2}-1 \end{pmatrix}$$

$$E(\delta) = E(0) + 6c_s V\delta^2 + O(\delta^3)$$

Orthorhombic Deformation

$$\epsilon = \begin{pmatrix} 0 & \delta & 0 \\ \delta & 0 & 0 \\ 0 & 0 & \delta^2/(1-\delta^2) \end{pmatrix}$$

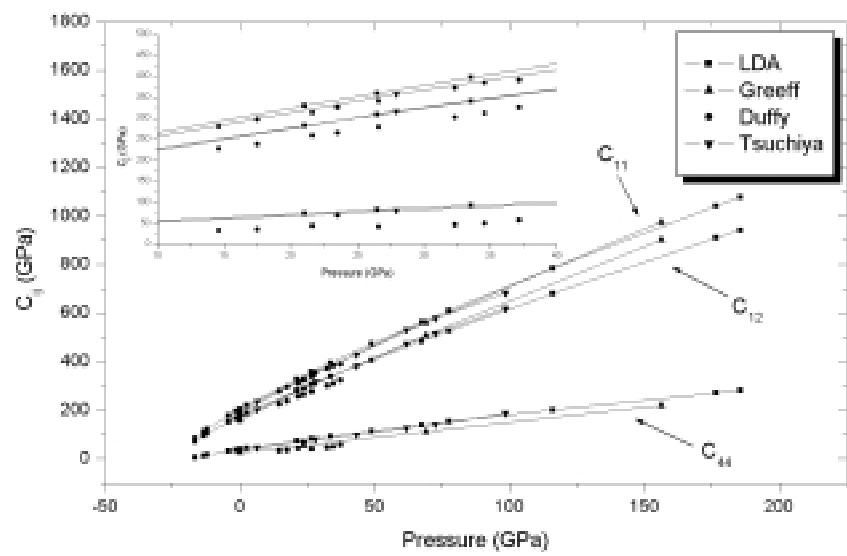
$$E(\delta) = E(0) + 2c_{44} V\delta^2 + O(\delta^4)$$

$$B = (c_{11} + 2c_{12})/3$$

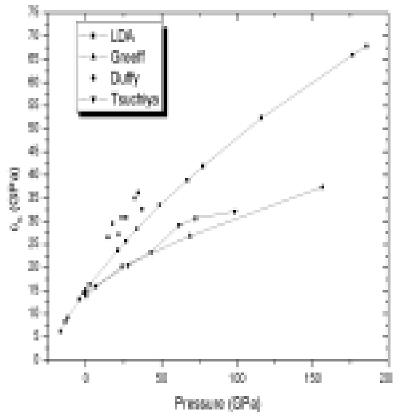
$$c_s = (c_{11} - c_{12})/2$$

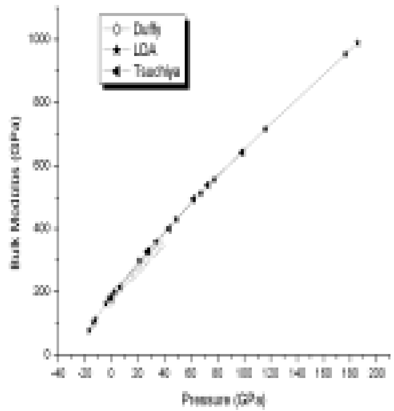
The zero-pressure elastic constants and pressure derivatives of elastic stiffness constants. The references with asterisk are experimental studies

ref	B	C_s	c_{11}	c_{12}	c_{44}	$\partial c_{11}/\partial P$	$\partial c_{12}/\partial P$	$\partial c_{44}/\partial P$
LDA	186.8	15.2	207.0	176.6	39.9	6.30	5.41	1.81
GGA	135.5	11.3	150.6	127.9	26.9	6.47	5.74	1.86
Daniels*	172.6	14.7	192.2	162.8	42.0	7.01	6.14	1.79
Hiki*	173.5	14.6	192.9	163.8	41.5	5.71	4.95	1.52
Golding*	172.8	14.7	192.4	163.0	42.0	6.73	5.86	1.84
Tsuchiya	184.5	12.6	201.3	176.1	36.9	5.97	5.38	1.43
Greeff	172.0	13.8	190.4	162.8	27.4	...	...	...
Duffy*	168.5	14.5	187.8	158.8	33.5	6.0	4.3	0.9
Biswas(79K)*	179.8	15.5	200.4	169.5	44.5	6.49	5.66	1.79
Biswas(298K)*	173.0	14.4	192.2	163.4	41.8	6.71	5.85	1.83
Anderson(0K)	180.3	16.0	201.6	169.7	45.4	...	...	...
Anderson(298K)	172.9	14.6	192.3	163.1	42.0	...	...	...
LDA @ exp	178.0	14.5	197.2	168.3	37.1	...	...	...



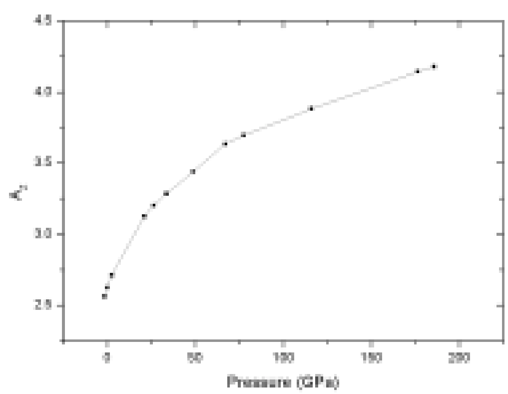
The tetragonal shear modulus and bulk modulus as a function of pressure





The Zener Anisotropy defined as;

$$A_Z = 2c_{44}/(c_{11} - c_{12}) = c_{44}/c_S$$



Aggregate Properties:

Voigt averaged and Reuss averaged shear modulus are given as;

$$G_V = (c_{11} - c_{12} + 3c_{44})/5$$

$$G_R = 5(c_{11} - c_{12})c_{44}/[4c_{44} + 3(c_{11} - c_{12})]$$

ref	G_V	G_R	G_{VRH}
LDA	30.0	24.2	27.1
GGA	20.8	17.6	19.1
Daniels*	31.1	24.1	27.6
Hiki*	30.7	23.8	27.3
Golding*	31.1	24.1	27.6
Tsuchiya	27.2	20.8	24.0
Greeff	22.0	19.7	20.8
Duffy*	25.9	21.9	23.9
Biswas(79K)*	32.9	25.4	29.1
Biswas(298K)*	30.8	23.7	27.3
Anderson(0K)	33.6	26.1	29.9
Anderson(298K)	31.0	24.0	27.5
LDA @ exp	28.1	22.9	25.5

Sound velocities can be determined by solving Cristoffel equation;

$$(c_{ijkl} n_j n_k - \rho v^2 \delta_{ij}) u_i = 0$$

For cubic crystals the solution of the above secular equation for [110 direction] gives;

$$\rho v^2 = (c_{11} + c_{12} + 2c_{44})/2 \qquad \textbf{Longitudinal}$$

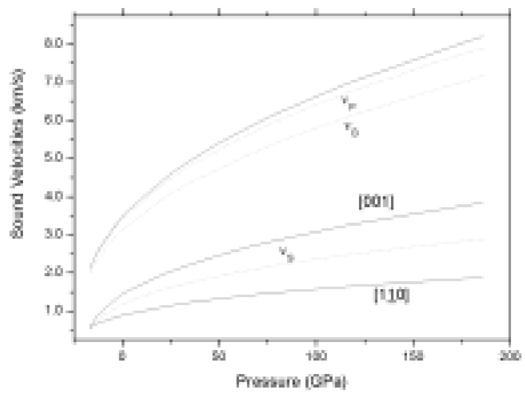
$$\rho v^2 = c_{44}$$

$$\rho v^2 = (c_{11} - c_{12})/2$$

Transverse

The compressional, shear and bulk sound velocities defined as;

$$
\begin{aligned}
\nu_P &= [(B + 4/3G)/\rho]^{1/2} \\
\nu_S &= (G_{VRH}/\rho)^{1/2} \\
\nu_B &= (B/\rho)^{1/2}
\end{aligned}
$$



Phonon Dispersion Relations

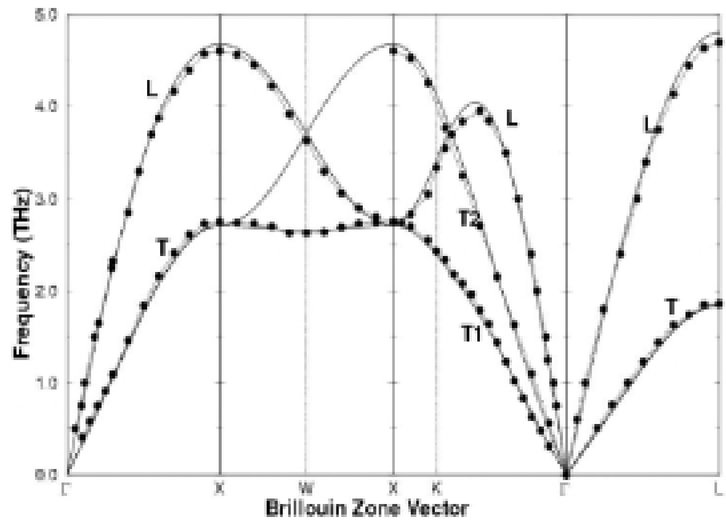
The phonon frequencies calculated using dynamical matrix

$$U = \frac{1}{2}\sum_{\mathbf{RR}'} \phi(\mathbf{R} - \mathbf{R}' + \mathbf{u}(\mathbf{R}) - \mathbf{u}(\mathbf{R}) - \mathbf{u}(\mathbf{R}'))$$

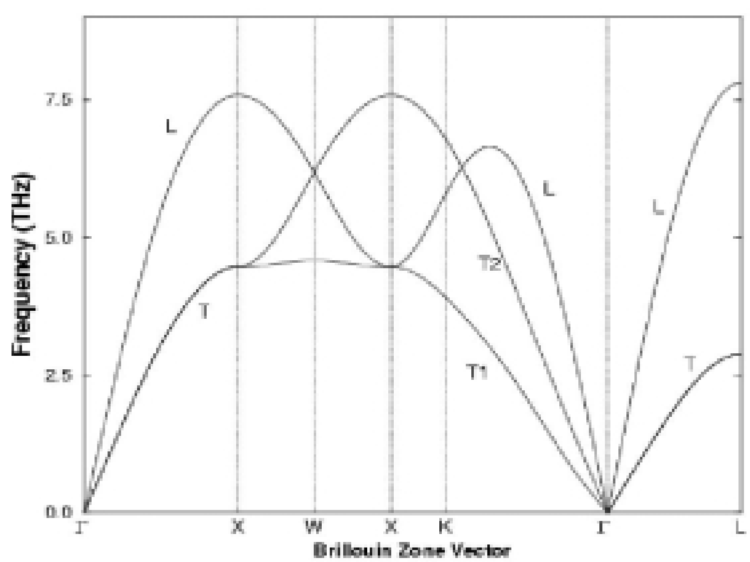
$$\mathbf{D}(\mathbf{k}) = \sum_{\mathbf{R}} \mathbf{D}(\mathbf{R}) exp(-i\mathbf{k}.\mathbf{R}) \qquad \phi_{\mu\nu} = \frac{\partial^2 \phi(\bar{r})}{\partial r_\mu \partial r_\nu}$$

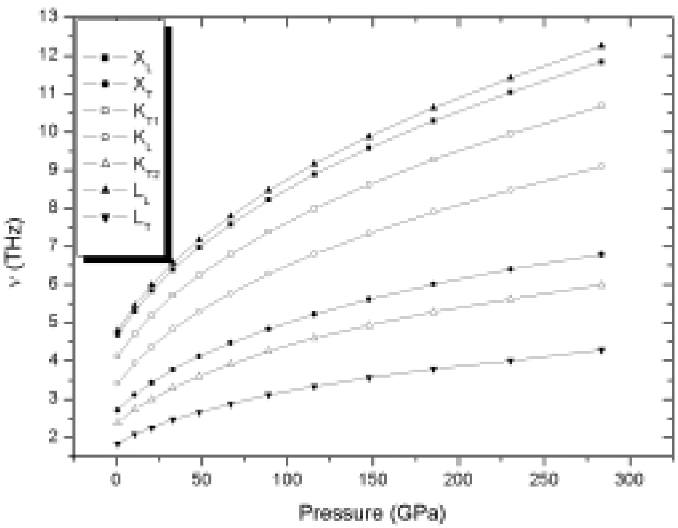
$$M\omega^2\epsilon = \mathbf{D}(\mathbf{k})\epsilon$$

Phonon dispersion at 0 GPa

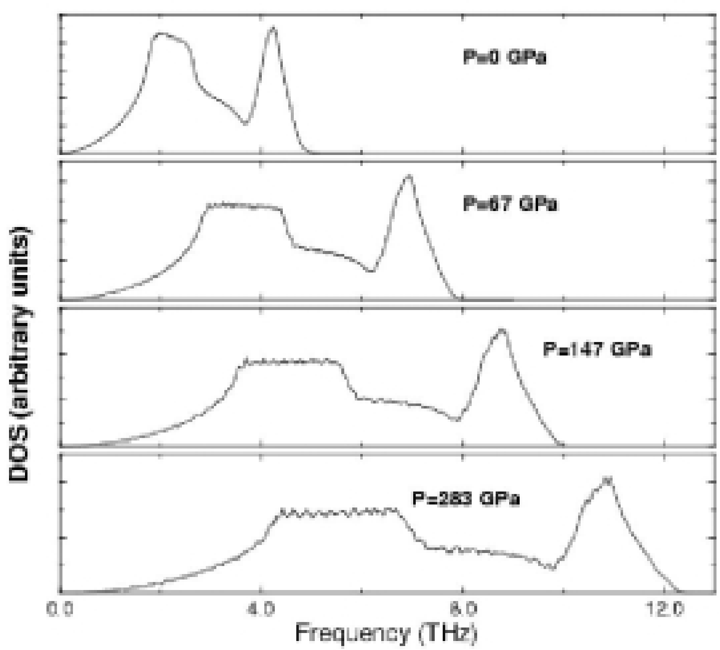


Phonon dispersion at 67 GPa





X_L
X_T
K_{T1}
K_L
K_{T2}
L_L
L_T
ν (THz)
Pressure (GPa)



P=0 GPa
P=67 GPa
P=147 GPa
P=283 GPa
DOS (arbitrary units)
Frequency (THz)

CONCLUSION

- Physical properties of gold is calculated up to 500 GPa
- Equation of state of Au is obtained
- LDA approximates the physical properties of Au better than GGA at the 0-500 GPa pressure range
- Vinet type equation of state is better describe the EOS of Au
- Fcc phase to bcc phase structural transition is observed at ultra-high pressure regime
- Fcc phase stability is observed up to 455 GPa
- Calculated elastic constants of gold at ambient pressure is in good agreement with experimental data
- With increasing pressure all elastic constants increase almost linearly
- At ambient pressure calculated vibrational spectra is in perfect agreement with neutron scattering data
- With increasing pressure phonon frequencies shift upward, after 100 GPa is almost linearly.