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Lattice Dynamics, Thermal Properties, and Density Functional Perturbation Theory

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Lattice Dynamics, Thermal Properties, and Density Functional Perturbation Theory

- Why you need estimates of thermal corrections
- Thermodynamics of collection of oscillators
- Mathematical description of crystals (review)
- Atomic displacement waves (phonons)
- Dynamical matrix
- Secular equation (equations of motion)
- Densities of states
- Kieffer models
- Examples
- Ionic systems—non-analyticity
- Born effective charges
- Linear response
- Density functional perturbation theory
- Process for DFPT computations

Lattice Vibrations and Thermodynamics

Helmholtz free energy:

$$F = E - TS = -kT \ln Z$$

Partition function

$$Z = \sum e^{-\epsilon_i / kT}$$

Harmonic oscillator eigenvalues ϵ_i

$$\epsilon_i = \tfrac{1}{2} h\nu_i, \tfrac{3}{2} h\nu_i, \tfrac{5}{2} h\nu_i$$

for each frequency ν_i.

(Note $2\pi\nu = \omega$ $\quad h\nu = \hbar\omega$)

Thus we get

$$Z_i = e^{-\frac{1}{2} h\nu_i / kT} \sum_{s=0}^{\infty} e^{-sh\nu_i / kT} = \frac{e^{-\frac{1}{2} h\nu_i / kT}}{1 - e^{-h\nu_i / kT}}$$

$$F_i = \tfrac{1}{2} h\nu_i + kT \ln \left(1 - e^{-h\nu_i / kT}\right)$$

$$F = E_0 + \sum_i F_i$$

Mathematical Description of Crystals

Lattice:

$$x(\ell) = \ell^1 \vec{a}_1 + \ell^2 \vec{a}_2 + \ell^3 \vec{a}_3$$

ℓ^1, ℓ^2, ℓ^3 integers
$\vec{a}_1, \vec{a}_2, \vec{a}_3$ lattice vectors

In general atoms are displaced from the lattice points and there can be multiple atoms (say n) per unit cell:

$$x\begin{pmatrix}\ell \\ k\end{pmatrix} = x(\ell) + x(k)$$

$x(k)$ can be represented as

$$x(k) = \lambda^1 \vec{a}_1 + \lambda^2 \vec{a}_2 + \lambda^3 \vec{a}_3$$

$\lambda^1, \lambda^2, \lambda^3$ fractional, say $0 \le \lambda^i < 1$

Reciprocal lattice:

$$Q(G) = G_1 \vec{Q}^1 + G_2 \vec{Q}^2 + G_3 \vec{Q}^3$$

$$Q^\alpha \cdot a_\beta = \delta_{\alpha\beta}$$

G_1, G_2, G_3 integers
$\vec{Q}^1, \vec{Q}^2, \vec{Q}^3$ reciprocal lattice vectors

Mathematical Description of Crystals (contd)

$$\vec{Q}^1 = \frac{a_2 \times a_3}{a_1 \cdot a_2 \times a_3} \qquad \vec{Q}^2 = \frac{a_3 \times a_1}{a_2 \cdot a_3 \times a_1} \qquad \vec{Q}^3 = \frac{a_1 \times a_2}{a_3 \cdot a_1 \times a_2}$$

Note: $\vec{a}_1, \vec{a}_2, \vec{a}_3$ covariant basis
$\vec{Q}^1, \vec{Q}^2, \vec{Q}^3$ contravariant basis

Any position vector $r(x) = x^1 \vec{a}_1 + x^2 \vec{a}_2 + x^3 \vec{a}_3$

Any reciprocal vector $b(\xi) = b_1 \vec{\xi}^1 + b_2 \vec{\xi}^2 + b_3 \vec{\xi}^3$

x^1, x^2, x^3 contravariant components
b_1, b_2, b_3 covariant components

Note: $\vec{r} \cdot \vec{b} = 2\pi (x^1 b_1 + x^2 b_2 + x^3 b_3) = (x b \pi)$

Metric tensor (real space) $g_{\alpha\beta} = a_\alpha \cdot a_\beta$

$$r(x) \cdot r(x') = \sum g_{\alpha\beta} x^\alpha x'^\beta$$

Periodic crystal $\exp(iQ \cdot r)$ is periodic in $\vec{r}$ w.r.t. $\vec{a}_\alpha$

More notation:

$$x\begin{pmatrix} l & 0 \\ k & k' \end{pmatrix} = x\begin{pmatrix} l \\ k \end{pmatrix} - x\begin{pmatrix} 0 \\ k' \end{pmatrix}$$

$$\left(\frac{\partial^2 E}{\partial r_\alpha(k)\, \partial r_\beta(k')}\right)_0 = E_{\alpha\beta}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix} \qquad \left(\frac{\partial E}{\partial r_\alpha(k)}\right)_0 = E_\alpha\begin{pmatrix} l \\ k \end{pmatrix}$$

Lattice Waves

Consider a lattice at static mechanical equilibrium:

atoms at $x\left(\begin{smallmatrix} l \\ k \end{smallmatrix}\right)$

Now let them be displaced from their equilibrium positions to $r\left(\begin{smallmatrix} l \\ k \end{smallmatrix}\right)$

$$r\left(\begin{smallmatrix} l \\ k \end{smallmatrix}\right) = x\left(\begin{smallmatrix} l \\ k \end{smallmatrix}\right) + u\left(\begin{smallmatrix} l \\ k \end{smallmatrix}\right)$$

where $u\left(\begin{smallmatrix} l \\ \alpha \end{smallmatrix}\right)$ are the displacements.

Equations of motion: $ma = F$

$$m_k \ddot{u}_\alpha\left(\begin{smallmatrix} l \\ k \end{smallmatrix}\right) = -\frac{\partial E}{\partial u}\left(\begin{smallmatrix} l \\ k \end{smallmatrix}\right)$$

(note we use cartesian coordinates for the dynamics)

Consider a Taylor series for the energy E:

$$E = E_0 + \sum_{\substack{\alpha l k}} E_\alpha\left(\begin{smallmatrix} l \\ k \end{smallmatrix}\right) u_\alpha\left(\begin{smallmatrix} l \\ k \end{smallmatrix}\right) + \frac{1}{2}\sum_{\substack{\alpha l k \\ \beta l' k'}} E_{\alpha\beta}\left(\begin{smallmatrix} l\,l' \\ k\,k' \end{smallmatrix}\right) u_\alpha\left(\begin{smallmatrix} l \\ k \end{smallmatrix}\right) u_\beta\left(\begin{smallmatrix} l' \\ k' \end{smallmatrix}\right) + \cdots$$

Harmonic approximation: truncate after 2nd order term (small displacements)

$$\frac{\partial E}{\partial u_\alpha\left(\begin{smallmatrix} l \\ k \end{smallmatrix}\right)} = E_\alpha\left(\begin{smallmatrix} l \\ k \end{smallmatrix}\right) + \sum_{l' k' \beta} E_{\alpha\beta}\left(\begin{smallmatrix} l\,l' \\ k\,k' \end{smallmatrix}\right) u_\beta\left(\begin{smallmatrix} l' \\ k' \end{smallmatrix}\right)$$

Lattice Waves (Continued)

For a lattice in static mechanical equilibrium:

$$E_\alpha\begin{pmatrix}\ell\\ \kappa\end{pmatrix} = 0$$ (forces on atoms are zero at equilibrium positions)

So we have for the equations of motion:

$$m_\kappa \ddot{u}_\alpha\begin{pmatrix}\ell\\ \kappa\end{pmatrix} = -\sum_{\ell'\kappa'\beta} E_{\alpha\beta}\begin{pmatrix}\ell\,\ell'\\ \kappa\,\kappa'\end{pmatrix} u_\beta\begin{pmatrix}\ell'\\ \kappa'\end{pmatrix}$$

Infinite number of 2nd order differential equations.

Consider waves $$u_\alpha\begin{pmatrix}\ell\\ \kappa\end{pmatrix} = \frac{1}{\sqrt{m_\kappa}} w_\alpha(\kappa)\exp\left[i\vec{q}\cdot\vec{x} - i\omega t\right]$$ (with $\vec{q}$ in units of 2π)

substitute into eq. of motion:

$$\boxed{\omega^2 w_\alpha(\kappa) = \sum_{\kappa'\beta} D_{\alpha\beta}\begin{pmatrix}q\\ \kappa\kappa'\end{pmatrix} w_\beta(\kappa')}$$

where the Dynamical matrix D is given by:

$$D_{\alpha\beta}\begin{pmatrix}q\\ \kappa\kappa'\end{pmatrix} = \frac{1}{\sqrt{m_\kappa m_{\kappa'}}} \sum_{\ell'} E_{\alpha\beta}\begin{pmatrix}\ell-\ell'\\ \kappa\kappa'\end{pmatrix}\exp\left\{-i\vec{q}\cdot x\begin{pmatrix}\ell\,\ell'\\ \kappa\kappa'\end{pmatrix}\right\}$$

$$D_{\alpha\beta}\begin{pmatrix}q\\ \kappa\kappa'\end{pmatrix} = \frac{\exp\left\{-i\vec{q}\cdot x(\kappa\kappa')\right\}}{\sqrt{m_\kappa m_{\kappa'}}} \sum_{\ell} E_{\alpha\beta}\begin{pmatrix}\ell\\ \kappa\,\kappa'\end{pmatrix} e^{-i\vec{q}\cdot x(\ell)}$$

Note: this is from $E_{\alpha\beta}\begin{pmatrix}\ell\,\ell'\\ \kappa\,\kappa'\end{pmatrix}$ depends on $\ell-\ell'$, not ℓ,ℓ'.

Dynamical Matrix + Secular Equation

We have

$$D_{\alpha\beta}\begin{pmatrix} q \\ \kappa\kappa' \end{pmatrix} = \frac{e^{-i\frac{2\pi}{a}q\cdot x(\kappa\kappa')}}{\sqrt{m_\kappa m_{\kappa'}}} \sum_\ell E_{\alpha\beta}\begin{pmatrix} \ell \\ \kappa\kappa' \end{pmatrix} e^{-i\frac{2\pi}{a}q\cdot x(\ell)}$$

$$\omega^2 w_\alpha(\kappa) = \sum_{\kappa'\beta} D_{\alpha\beta}\begin{pmatrix} q \\ \kappa\kappa' \end{pmatrix} w_\beta(\kappa')$$

Solution:

$$\left| \omega^2 \delta_{\alpha\beta}\delta_{\kappa\kappa'} - D_{\alpha\beta}\begin{pmatrix} q \\ \kappa\kappa' \end{pmatrix} \right| = 0$$

3n solutions for each q.

ω^2 eigenvalues w_α eigenvectors of D

Note: D is Hermitian

$$D^*_{\alpha\beta}\begin{pmatrix} q \\ \kappa\kappa' \end{pmatrix} = D_{\beta\alpha}\begin{pmatrix} q \\ \kappa'\kappa \end{pmatrix}$$

ω^2 is real, so ω is real or imaginary.

Also: note $D^*_{\alpha\beta}\begin{pmatrix} q \\ \kappa\kappa' \end{pmatrix} = D_{\alpha\beta}\begin{pmatrix} -q \\ \kappa\kappa' \end{pmatrix}$

$$\omega\begin{pmatrix} -q \\ j \end{pmatrix} = \omega\begin{pmatrix} q \\ j \end{pmatrix} \qquad w_\alpha\left(\kappa \middle| \begin{matrix} -q \\ j \end{matrix}\right) = w^*_\alpha\left(\kappa \middle| \begin{matrix} q \\ j \end{matrix}\right)$$

for each j.

The Dynamical Matrix

$$D_{11}\binom{g}{11} \quad D_{12}\binom{g}{11} \quad D_{13}\binom{g}{11} \cdots D_{11}\binom{g}{1n} \quad D_{12}\binom{g}{1n} \quad D_{13}\binom{g}{1n}$$

$$D_{21}\binom{g}{11} \quad D_{22}\binom{g}{11} \quad D_{23}\binom{g}{11}$$

$$D_{31}\binom{g}{11}$$

$$\vdots$$

$$D_{31}\binom{g}{n1} \qquad\qquad D_{33}\binom{g}{nn}$$

Density of states: $g(\omega)$

$$\int g(\omega)\, d\omega = 3N \qquad g(\omega) = \sum_i \delta(\omega - \omega_i)$$

$$C_V^{\text{Einstein}} = \frac{\left(\frac{\hbar\omega}{kT}\right)^2 e^{\hbar\omega/kT}}{\left[e^{\hbar\omega/kT} - 1\right]^2}$$

Einstein model $g(\omega) = \delta(\omega - \omega_i)$

Debye model $g(\omega) \sim \omega^2$

$$C_V^{QH} = \int_0^\infty g(\omega)\, C_V^{\text{Einstein}}\, d\omega$$

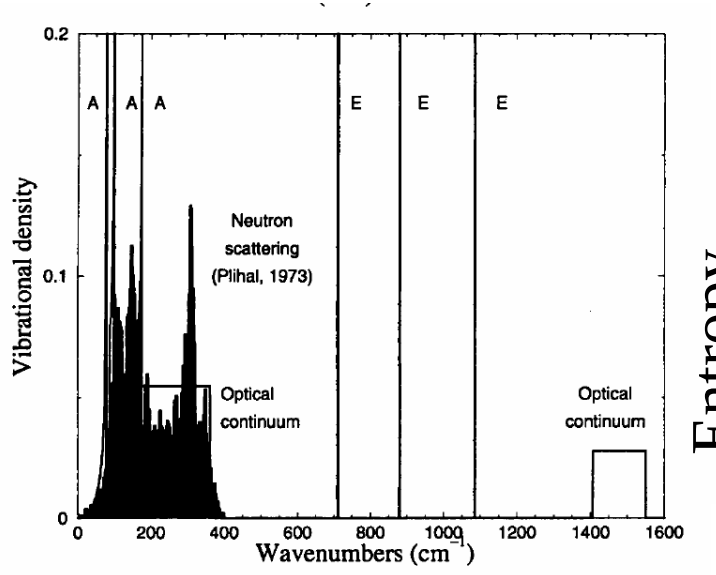
Actually $g(\omega) \to 0$ at ω_{cut}

In practice, except for analytic models of $g(\omega)$, or models such as Keitter models, which are models of $g(\omega)$ pieced together from experimental data, it is more efficient to just sample the integrand of interest at a set of q vectors, weighted by the weight in the full BZ of each vector from symmetry.

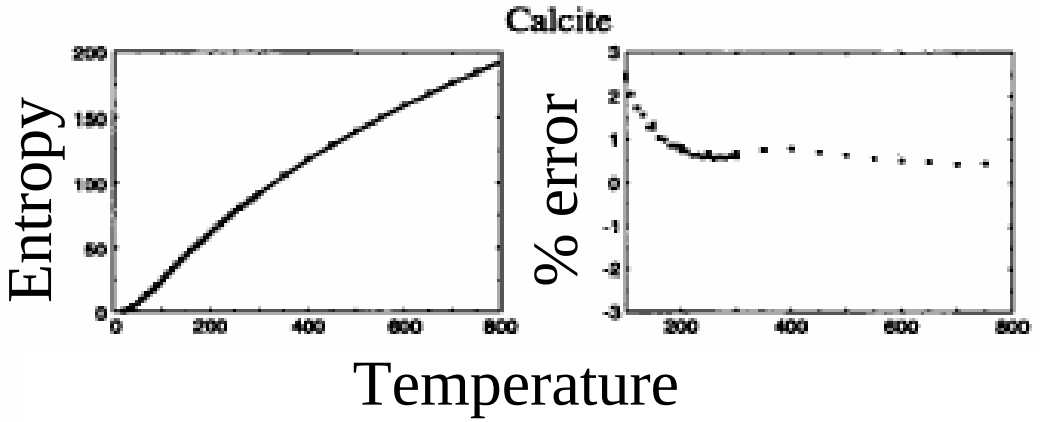
$$F(V,T) = \frac{1}{N_q} \sum_i \left[\frac{1}{2}\hbar\nu_i + kT \ln\left(1 - e^{-\hbar\nu_i/kT}\right)\right]$$

Kieffer models

1. Kieffer, S.W., *Thermodynamics and lattice vibrations of minerals: 1. Mineral heat capcities and their relationships to simple lattice vibrational models.* Reviews of Geophysics and Space Physics, 1979. **17**: p. 1-19.
2. Kieffer, S.W., *Thermodynamics and lattice vibrations of minerals: 2. Vibrational characteristics of silicates.* Reviews of Geophysics and Space Physics, 1979. **17**: p. 20-34.
3. Kieffer, S.W., *Thermodynamics and lattice vibrations of minerals:3. Lattice dynamics and an approximation for minerals with application to simple substances and framework silicates.* Reviews of Geophysics and Space Physics, 1979. **17**: p. 35-59.
4. Kieffer, S.W., *Thermodynamics and lattice vibrations of minerals:4. Application to chain and sheet silicates and orthosilicates.* Reviews of Geophysics and Space Physics, 1980. **18**: p. 862-886.
5. Kieffer, S.W., *Thermodynamics and lattice vibrations of minerals:5. Applications to phase equilibria, itostopic fractionation, and high-pressure thermodynamic properties.* Reviews of Geophysics and Space Physics, 1982. **20**: p. 827-849.

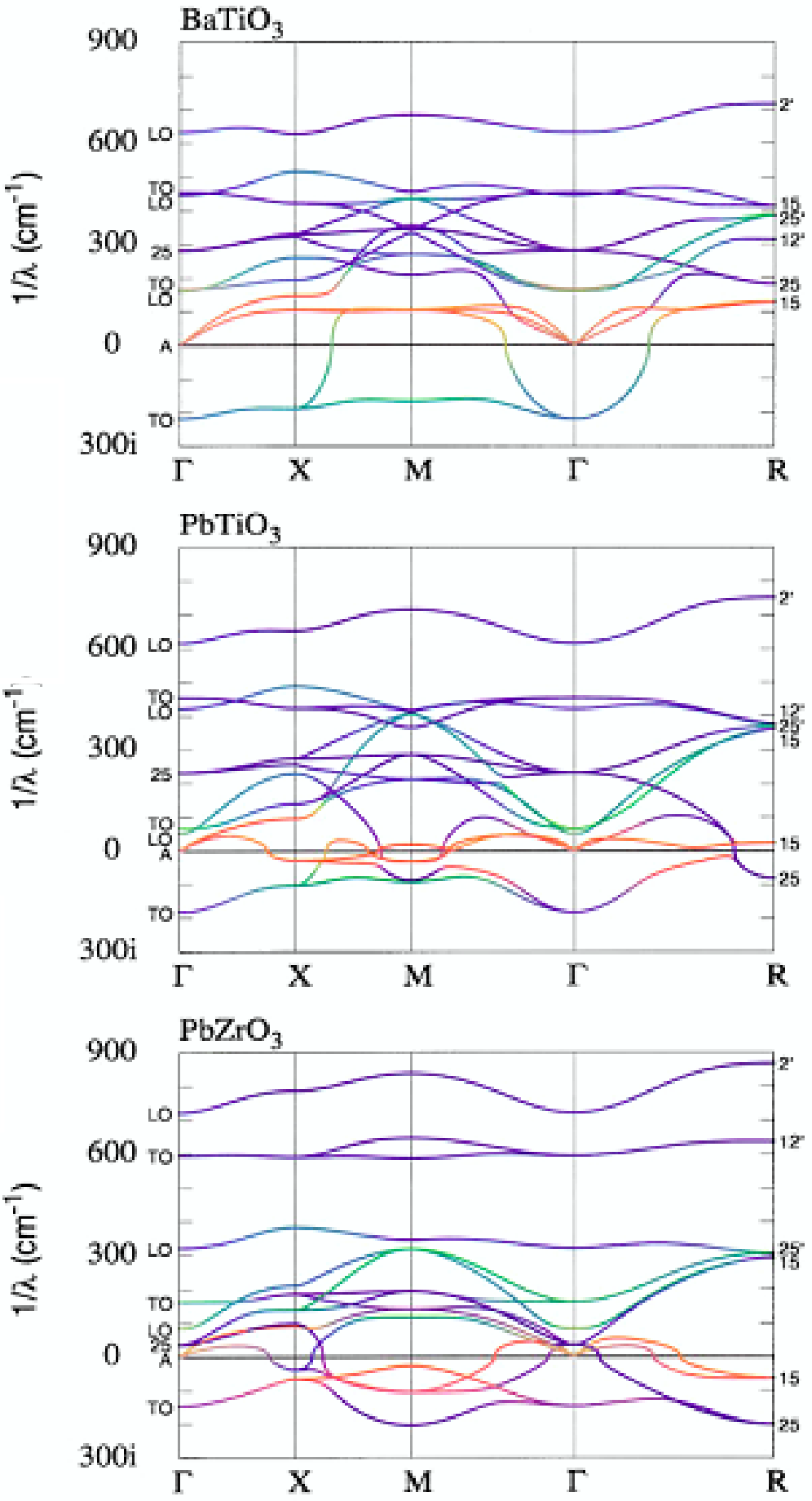


Matas, J., et al., *Thermodynamic properties of carbonates at high pressures from vibrational modelling.* Eur J Mineral, 2000. 12(4): p. 703-720.

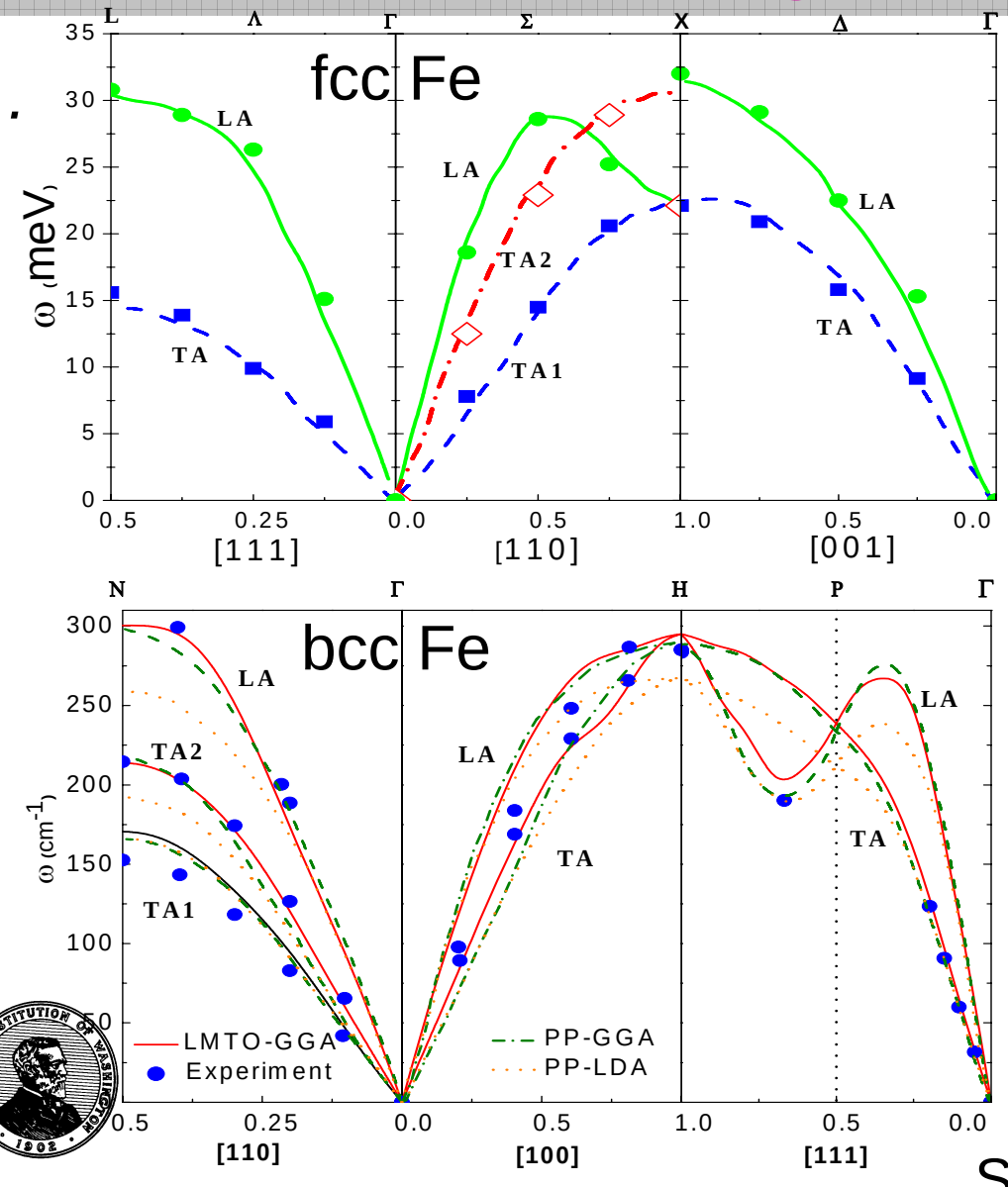


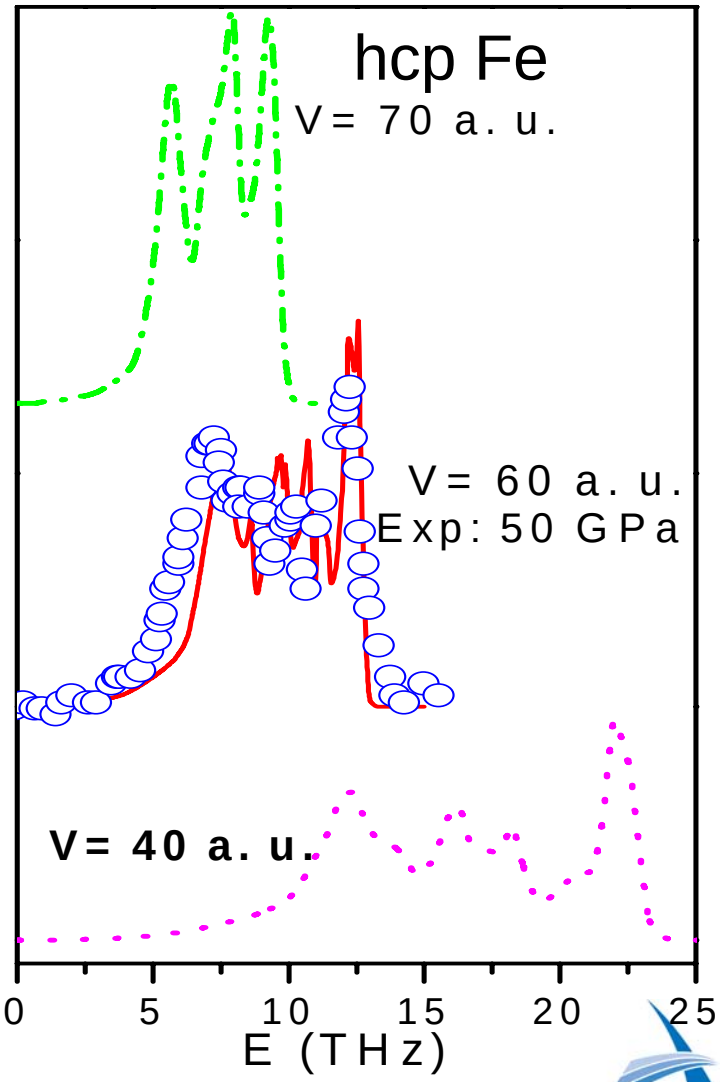
Ghosez et al.
Phys. Rev. B,
1999. **60,** 836

Squares of harmonic frequencies
are the curvatures of the potential surface.



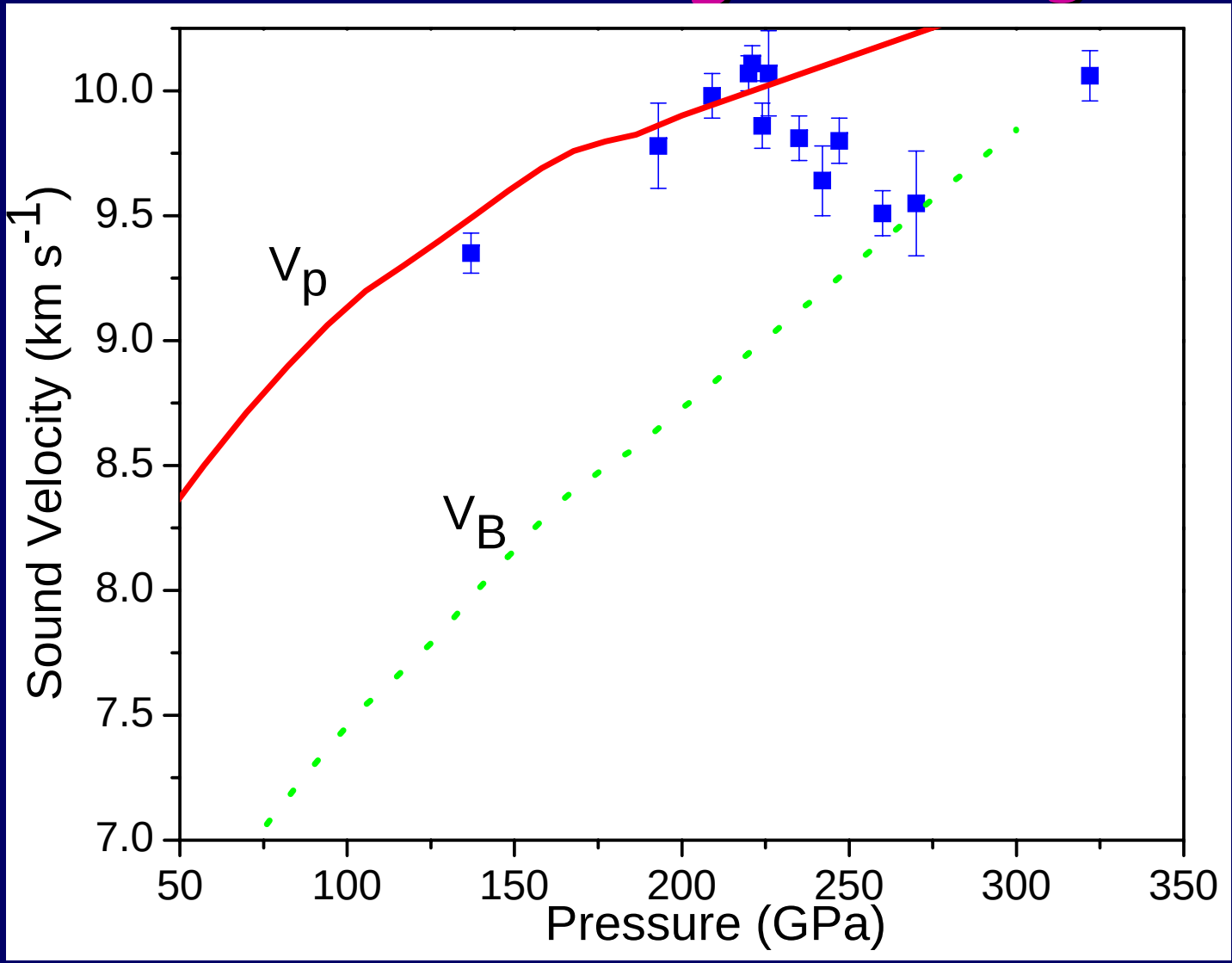
Calculated phonon frequencies of bcc, fcc and hcp Fe all show excellent agreements with experiment





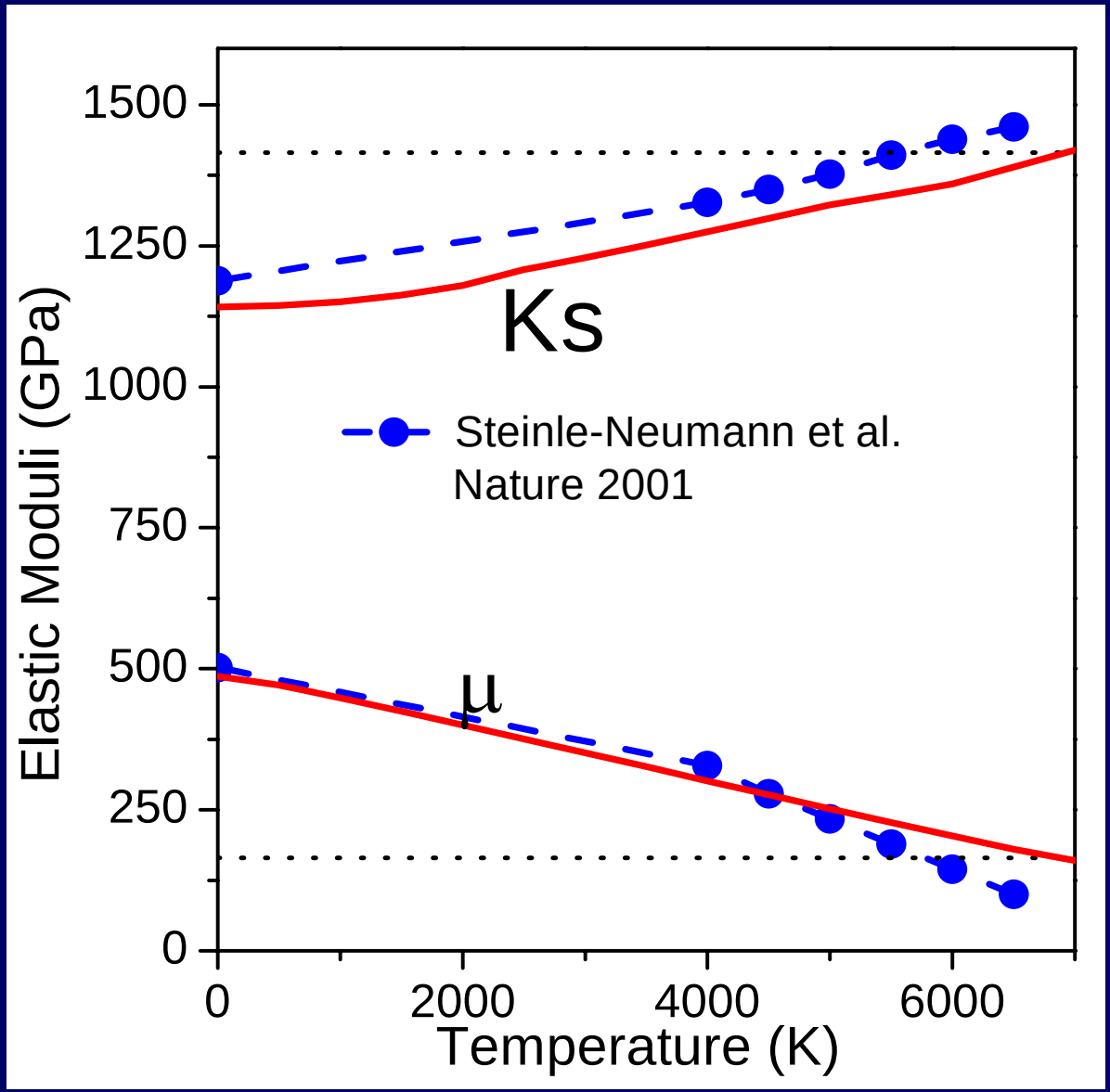
Sha and Cohen

sound velocities along the Hugoniot



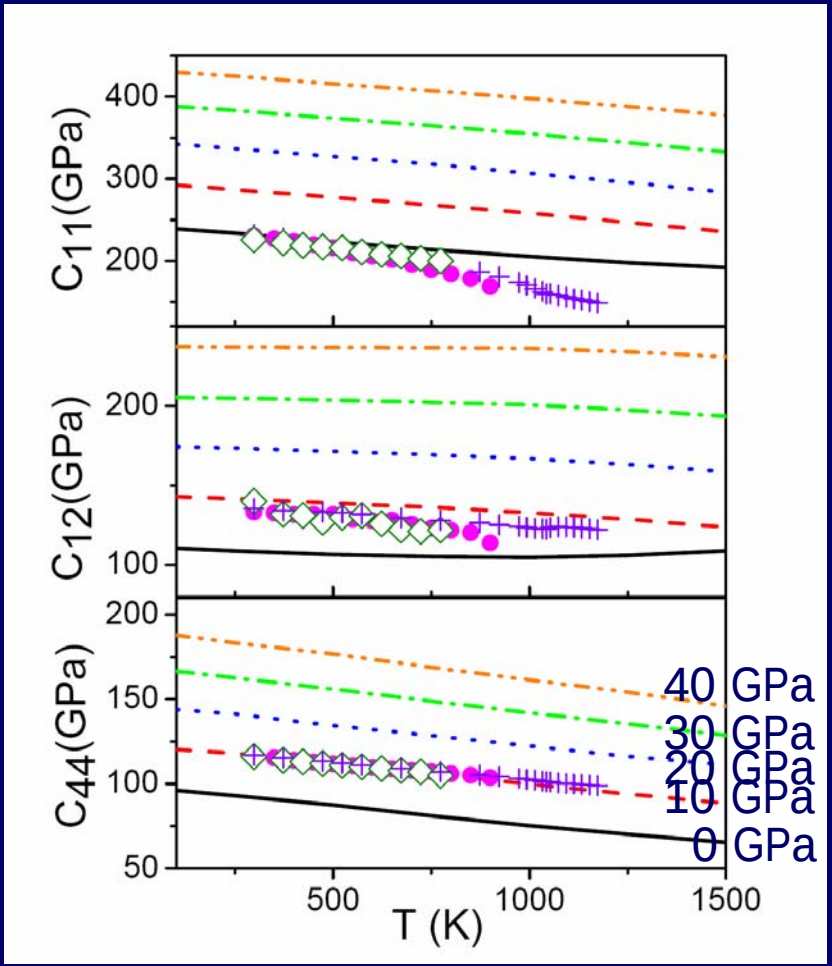
Experiments: Nguyen and Holmes, Nature 2004 Theory: Sha and Cohen

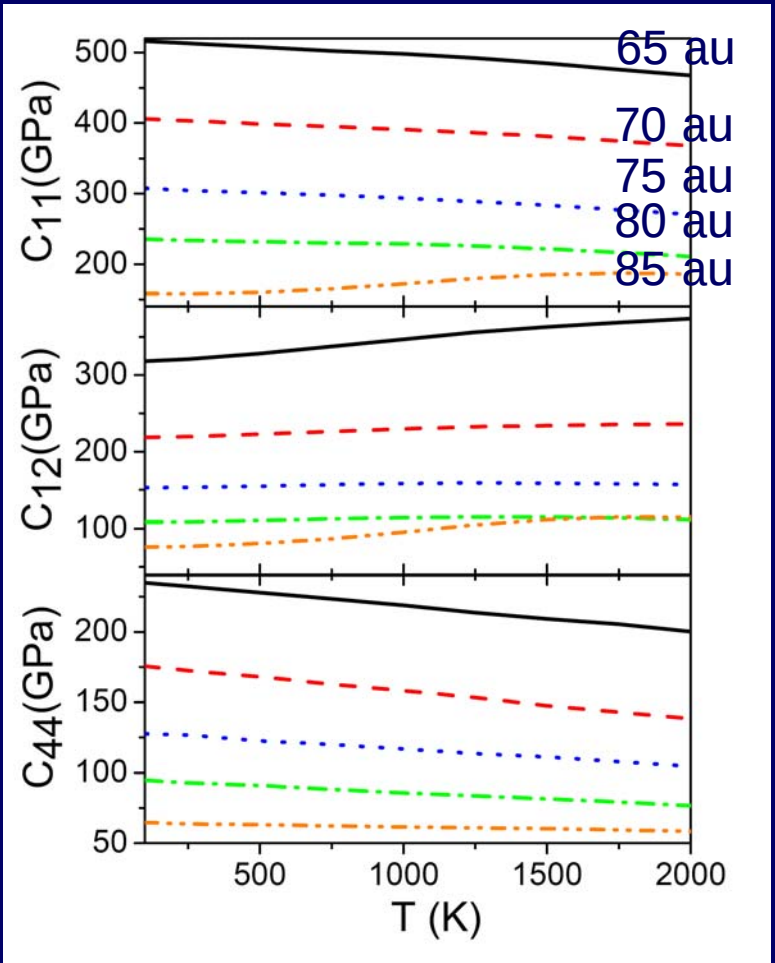
Temperature in Earth's inner Core



Sha and Cohen

Thermoelasticity of bcc Fe



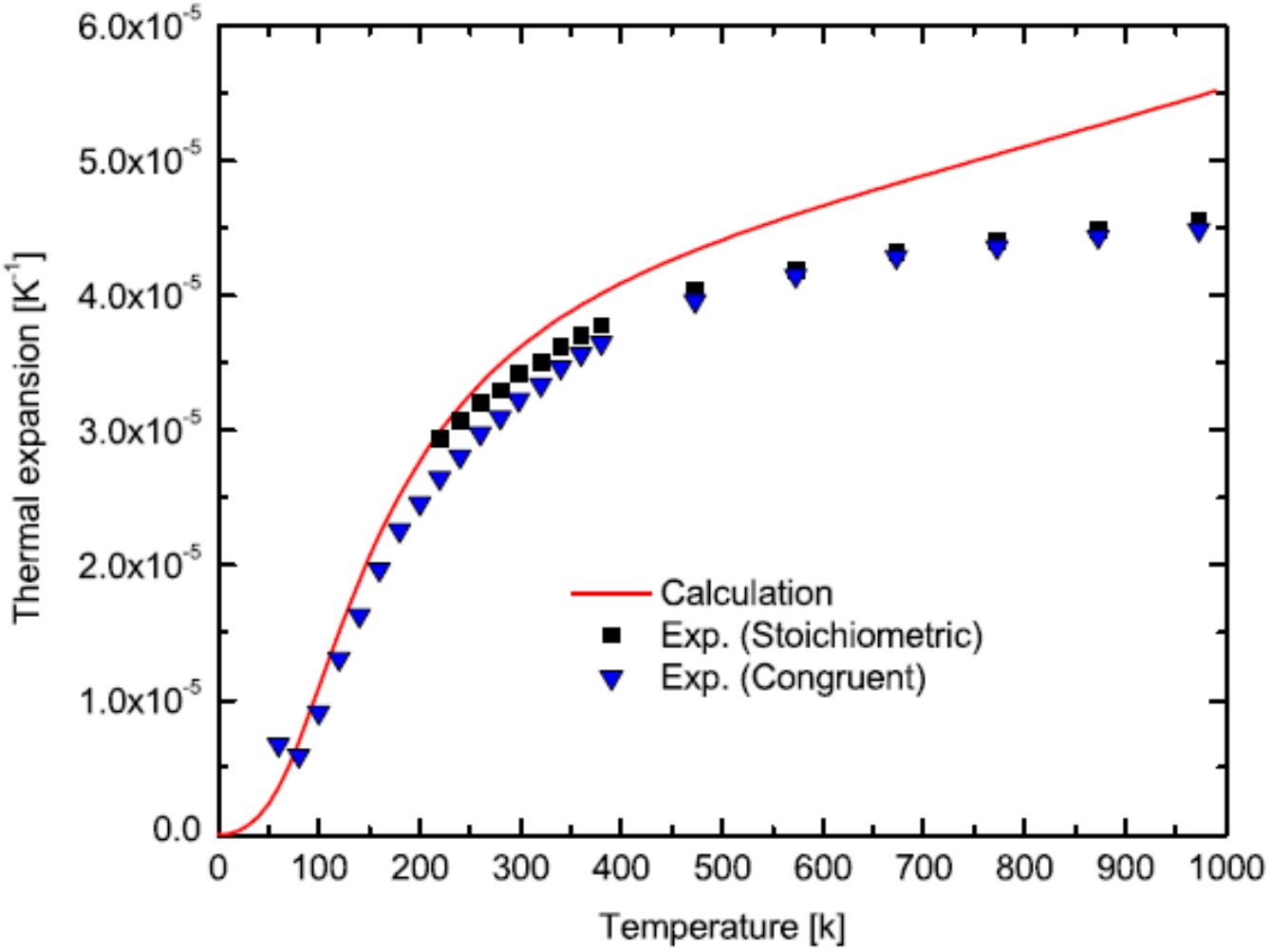


Exp: Dever (1972) J. Appl. Phys. 43: 3293; Isaak and Masuda (1995) JGR 100(B9): 17689.

Sha and Cohen

Change in elastic constants with temperature at constant V (beyond normal quasiharmonic approximation)

$LiNbO_3$ Thermal Expansivity from Linear Response (LDA) vs. Experiment



Dynamical Matrix

Separation of non-analytic part

(ionic insulators D is non-analytic as $q \to 0$)

$$D^{\kappa\kappa'}_{\alpha\beta}(q) = {}^{an}D + \tilde{D}$$

Non-analytic part:

$$\tilde{D}^{\kappa\kappa'}_{\alpha\beta}(q) = \frac{4\pi}{V} e^2 \frac{(q \cdot Z^*_\kappa)_\alpha (q \cdot Z^*_{\kappa'})_\beta}{q \cdot \epsilon^\infty \cdot q}$$

Long-wavelength limit of lattice dynamics

Hardy et al., 1981 AFOSR-TR-71-2138

Miller + Axe 1967

Born + Huang

ionic displacements: $u_\alpha\begin{pmatrix}\ell\\ \kappa\end{pmatrix} = \frac{1}{\sqrt{m_\kappa}} W_{\alpha j}(\kappa)(q)\exp\left[2\pi i\, q\cdot x\begin{pmatrix}\ell\\ \kappa\end{pmatrix} - i\omega_j(q)t\right]$

Expand everything in powers of ϵ, where $q = \epsilon\hat{q}$ ($\hat{q}$ direction of q)

Dynamical matrix: separate out irregular part

$$D_{\alpha\beta}\begin{pmatrix}q\\ \kappa\kappa'\end{pmatrix} = \bar{D}_{\alpha\beta}\begin{pmatrix}q\\ \kappa\kappa'\end{pmatrix} + \frac{4\pi}{v}\frac{z_\kappa z_{\kappa'}}{\sqrt{m_\kappa m_{\kappa'}}}\frac{q_\alpha q_\beta}{q^2}$$

Macroscopic electric field:

$$E_{\alpha j}(q) = -\frac{4\pi}{v}\sum_{\kappa'\beta}\frac{q_\alpha q_\beta}{q^2}\frac{z_{\kappa'}}{\sqrt{m_{\kappa'}}} W_{\beta j}(\kappa')(q)$$

Secular equation:

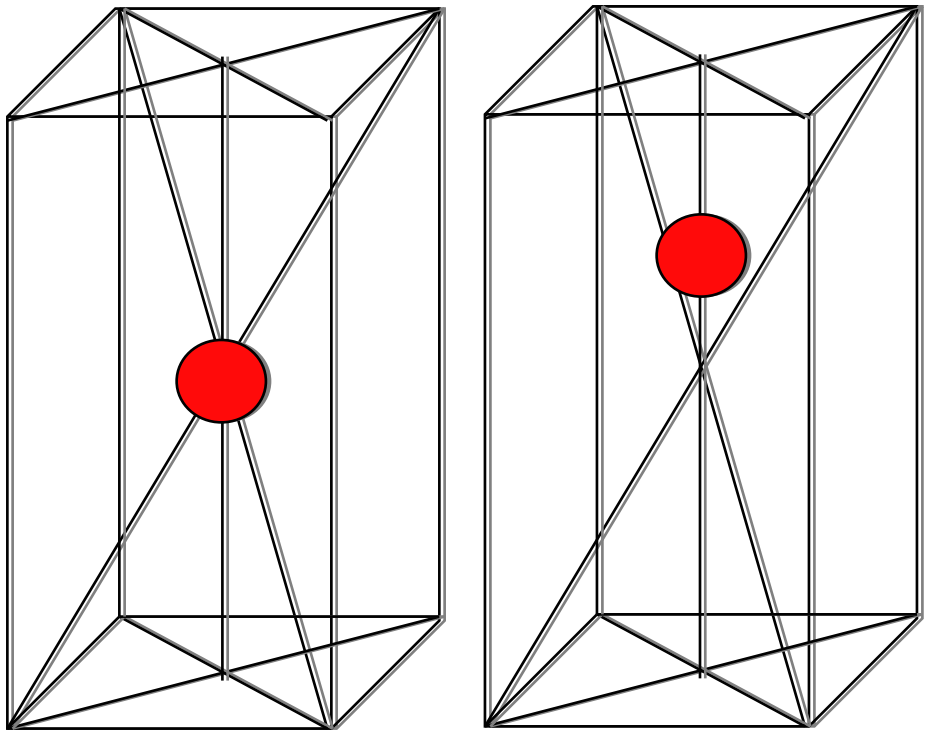
$$\sum_{\kappa'\beta}\bar{D}_{\alpha\beta}\begin{pmatrix}q\\ \kappa\kappa'\end{pmatrix} W_{\beta j}(\kappa')(q) - \frac{z_\kappa}{\sqrt{m_\kappa}} E_{\alpha j}(q) = \omega_j^2(q)\, W_{\alpha j}(\kappa)(q)$$

Born Effective Charges

$$Z^* = \frac{\Omega}{e}\frac{\partial P_3}{\partial z} = \frac{\Omega}{e}\frac{P_3(2) - P_3(1)}{z(2) - z(1)}$$

displacements=0.3%

$P_3(1)$, $z(1)$ $P_3(2)$, $z(2)$



Born effective charge tensors for tetragonal $PbTiO_3$

Effective charges are tensors

Ti

6.2	**0**	**0**
0	**6.2**	**0**
0	**0**	**5.2**

(1/2 1/2 0.530)

O_1

$-2.61_{\perp}$	**0**	**0**
0	**$-5.18_{\parallel}$**	**0**
0	**0**	**-2.16**

(1/2 0 0.610)

Pb

3.74	**0**	**0**
0	**3.74**	**0**
0	**0**	**3.52**

(0 0 0)

O_3

-2.15	**0**	**0**
0	**-2.15**	**0**
0	**0**	**-4.38**

(1/2 1/2 0.105)

Effective charges

Effective charges can be greatly enhanced compared to nominal charges.

Ph. GHOSEZ, J.-P. MICHENAUD, AND X. GONZE

PRB, 58, 6224, 1998

TABLE II. Born effective charges of $BaTiO_3$ in the cubic structure.

		$Z^{*(T)}_{Ba}$	$Z^{*(T)}_{Ti}$	$Z^{*(T)}_{O_\perp}$	$Z^{*(T)}_{O_\parallel}$
Nominal		+2	+4	−2	−2
Experiment		+2.9	+6.7	−2.4	−4.8
Models	(shell model)	+1.63	+7.51	−2.71	−3.72
	(SCAD model)	+2.9	+7.3	−2.2	−5.8
First-principles	(linear response)	+2.77	+7.25	−2.15	−5.71
	(Berry phase)	+2.75	+7.16	−2.11	−5.69

Experimental determination of effective charges

Reflectivity (oscillator strength)

$$R = \left| \frac{1-\sqrt{\varepsilon}}{1+\sqrt{\varepsilon}} \right|^2$$ Reflectivity

$$\vec{\vec{\varepsilon}}(\nu) - \vec{\vec{\varepsilon}}(\nu)^{\infty} = \sum_j \frac{f_{j\alpha}\omega_j^2}{\left(\omega_j^2 - \nu^2\right)}$$

$$f_{j\alpha} = \left(\frac{4\pi}{NV\nu^2}\right)\left|\Delta P_{j\alpha}\right|^2$$ oscillator strength

$$\Delta P_{j\alpha} = \sum_{\kappa\beta} Z^*_{\kappa,\alpha\beta} u_{\kappa,j\beta}$$

LO-TO splitting

For example

for cubic diatomic compound:

$$\omega_{LO}^2 - \omega_{TO}^2 = \frac{4\pi Z^{*2} e^2}{MV\,\mathrm{Re}(\varepsilon)}$$

Or in general:

$$\sum\left(\omega_{LO,j}^2 - \omega_{TO,j}^2\right) = \frac{4\pi}{V}\sum\frac{Z_k^{*2}}{m_k}$$

Linear Response Theory

$$\left.\frac{\partial E_\lambda}{\partial \lambda}\right|_{\lambda=0} = \langle \psi_0 | \frac{\partial H}{\partial \lambda} | \psi_0 \rangle$$

Force on an atom i:

$$F_i = -\frac{\partial E}{\partial R_i} = -\langle \psi | \frac{\partial H}{\partial R_i} | \psi \rangle$$

$$= -\int n(r) \frac{\partial V}{\partial R_i} dr - \frac{\partial E_c}{\partial R_i}$$

Force constants, Dynamical matrix elements:

$$\frac{\partial^2 E}{\partial R_i \partial R_j} = -\frac{\partial F_i}{\partial R_j} = \int \frac{\partial n}{\partial R_j} \frac{\partial V}{\partial R_i} d^3r + \int n(r) \frac{\partial^2 V}{\partial R_i \partial R_j} d^3r + \frac{\partial^2 E_c}{\partial R_i \partial R_j}$$

↑ linear response

Density Functional Perturbation Theory

Gonze, Phys. Rev. A 52, 1096, 1995

small parameter λ

$$E(\lambda) = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \lambda^3 E^{(3)} + \dots \quad (1)$$

$$E^{(n)} = \frac{1}{n!} \frac{d^n E}{d\lambda^n}\bigg|_{\lambda=0} \quad (2)$$

Consider moving one atom (nucleus, ion core) ℓ along direction $\vec{e}$

$$\Delta V(r) = -\frac{Z_\ell}{|\vec{r} - (\vec{R}_\ell + \lambda_\ell \vec{e})|} + \frac{Z_\ell}{|\vec{r} - \vec{R}_\ell|} \quad (3)$$

$$V^{(1)}(r) = \frac{-[\vec{e} \cdot (\vec{r} - \vec{R}_\ell)] Z_\ell}{|\vec{r} - \vec{R}_\ell|^3} \quad (4)$$

Single Particle Schrödinger Equation

$$[H(\lambda) - E_\alpha(\lambda)]\,|\phi_\alpha(\lambda)\rangle = 0 \qquad (11)$$

$$\langle \phi(\lambda) | \phi(\lambda) \rangle = 1 \qquad (12)$$

Expand to first order:

Sternheimer Equation

$$(H - E_\alpha)^{(0)} |\phi_\alpha^{(1)}\rangle = -(H - E_\alpha)^{(1)} |\phi_\alpha^{(0)}\rangle \qquad (13)$$

$$\langle \phi_\alpha^{(0)} | \phi_\alpha^{(1)} \rangle = 0 \quad \text{(By chosing phase of } \phi\text{)} \qquad (16)$$

Multiply (13) on left by $\langle \phi_\alpha^{(0)}|$ we get

$$E_\alpha^{(1)} = \langle \phi_\alpha^{(0)} | H^{(1)} | \phi_\alpha^{(0)} \rangle \qquad (17)$$

Hellmann-Feynman Theorem

can plug into R.H.S. of (13) so Sternheimer eq. becomes a nonhomogeneous linear differential equation for $\phi^{(1)}$

2n+1 Theorem

Gonze PRA 52 1086 1995

Expansion of E up to order $2n+1$, $E^{(2n+1)}$

requires ϕ only up to order n, $\phi^{(n)}$

$$E^{(2n+1)} = \left\{ \hat{E}_{(\lambda)} \left[\sum_{i=0}^{n} \lambda^i \phi^{(i)} \right] \right\}^{(2n+1)} \quad (23)$$

$\hat{E}_{(\lambda)}$ energy operator

Minimum Principle

$E^{(2n)}$ is a minimum for $\phi^{(n)}$

$$E^{(2n)} = \min_{\phi^{(n)}} \left\{ \left(\hat{E}_{(\lambda)} \left[\sum_{i=0}^{n} \lambda^i \phi^{(i)} \right] \right)^{(2n)} \right\} \quad (24)$$

Not typo in Gonze

Gonze, Phys. Rev. A 52, 1096, 1995

$$E^{(m)} = \sum_{\alpha=1}^{N}\sum_{j=0}^{n}\sum_{k=0}^{m}\sum_{l=0}^{n}\delta(m-j-k-l)\langle\Phi_\alpha^{(j)}|(T+v)^{(k)}|\Phi_\alpha^{(l)}\rangle$$
$$+\frac{1}{m!}\frac{d^m}{d\lambda^m}E_{\rm Hxc}\left[\sum_{\alpha=1}^{N}\left(\sum_{j=0}^{n}\lambda^j\Phi_\alpha^{(j)*}(\mathbf{r})\right)\left(\sum_{k=0}^{n}\lambda^k\Phi_\alpha^{(k)}(\mathbf{r})\right)\right]\Bigg|_{\lambda=0}$$
$$-\sum_{\alpha,\beta=1}^{N}\sum_{j=0}^{n}\sum_{k=0}^{m}\sum_{l=0}^{n}\delta(m-j-k-l)\Lambda_{\beta\alpha}^{(k)}\langle\Phi_\alpha^{(j)}|\Phi_\beta^{(l)}\rangle+\sum_{\alpha,\beta=1}^{N}\Lambda_{\beta\alpha}^{(m)}\delta_{\alpha\beta}\ .$$

$$E^{(m)} = \sum_{\alpha=1}^{N}\sum_{j=0}^{n}\sum_{k=0}^{m-n-1}\sum_{l=0}^{n}\delta(m-j-k-l)\langle\Phi_\alpha^{(j)}|H^{(k)}|\Phi_\alpha^{(l)}\rangle-\sum_{\alpha,\beta=1}^{N}\sum_{j=0}^{n}\sum_{k=0}^{m-n-1}\sum_{l=0}^{n}\delta(2n-j-k-l)\Lambda_{\beta\alpha}^{(k)}\langle\Phi_\alpha^{(j)}|\Phi_\beta^{(l)}\rangle$$
$$+\sum_{\alpha=1}^{N}\sum_{j=0}^{n}\sum_{k=m-n}^{m}\sum_{l=0}^{n}\delta(m-j-k-l)\langle\Phi_\alpha^{(j)}|(T+v)^{(k)}|\Phi_\alpha^{(l)}\rangle+\frac{1}{m!}\frac{d^m}{d\lambda^m}E_{\rm Hxc}\left[\sum_{j=0}^{n}\lambda^j n^{(j)}\right]\Bigg|_{\lambda=0}\ . \qquad (51)$$

$$n^{(i)}(\mathbf{r}) = \sum_{j=0}^{i}\sum_{\alpha=1}^{N}\Phi_\alpha^{(j)*}(\mathbf{r})\Phi_\alpha^{(i-j)}(\mathbf{r})\ . \qquad (43)$$

$$\sum_{j=0}^{i}\langle\Phi_\alpha^{(j)}|\Phi_\beta^{(i-j)}\rangle = 0 \quad \text{for } i\geq 1\ .$$

$$\sum_{j=0}^{i}H^{(j)}|\Phi_\alpha^{(i-j)}\rangle = \sum_{j=0}^{i}\sum_{\beta=0}^{N}\Lambda_{\beta\alpha}^{(j)}|\Phi_\beta^{(i-j)}\rangle\ . \qquad (45)$$

$$H^{(i)} = T^{(i)} + v_{\rm KS}^{(i)} = T^{(i)} + v^{(i)} + v_{\rm Hxc}^{(i)}$$

$$v_{\rm Hxc}^{(i)}(\mathbf{r}) = \frac{1}{i!}\frac{d^i}{d\lambda^i}\left[\frac{\delta E_{\rm Hxc}\left[\sum_{j=0}^{i}\lambda^j n^{(j)}\right]}{\delta n(\mathbf{r})}\right]\Bigg|_{\lambda=0}\ .\quad \Lambda_{\beta\alpha}^{(i)} = \sum_{j=0}^{i}\sum_{k=0}^{i}\langle\Phi_\beta^{(j)}|H^{(i-j-k)}|\Phi_\alpha^{(k)}\rangle\ .$$

Perturbation Theory for DFT Kohn-Sham

Review of DFT:

Minimize $E[n] = E[\phi_\alpha] = \sum_{\alpha=1}^{N} \langle \phi_\alpha | T + v | \phi_\alpha \rangle + E_{Hxc}[n]$ (30)

subject to constraint: $\langle \phi_\alpha | \phi_\beta \rangle = \delta_{\alpha\beta}$ (33)

$E_{Hxc} \equiv E_H + E_{xc}$ (31)

$n(r) = \sum \phi_\alpha^* \phi_\alpha$ (32)

So minimize

$$F[\phi_\alpha] = \sum_{\alpha}^{N} \langle \phi_\alpha | T + v | \phi_\alpha \rangle + E_{Hxc} - \sum_{\alpha,\beta=1}^{N} \Lambda_{\beta\alpha} [\langle \phi_\alpha | \phi_\beta \rangle - \delta_{\alpha\beta}] \quad (34)$$

Lagrange-Euler equation:

$$H|\phi_\alpha\rangle = \sum_{\beta=1}^{N} \Lambda_{\beta\alpha} |\phi_\beta\rangle \qquad \Lambda_{\beta\alpha} = \langle \phi_\beta | H | \phi_\alpha \rangle$$

I. Perform converged optimization of structure to zero forces.

II. Compute required derivatives and first order wavefunctions on grid of q points. Each q point can be done in parallel.

III. Transform to obtain real space force constants. after subtracting irregular nonanalytic part. Z^* ϵ^∞ needed

$$C^{\kappa\kappa'}_{\alpha\beta}(R) = \frac{1}{N}\sum_q e^{iq\cdot R}\tilde{C}^{\kappa\kappa'}_{\alpha\beta}(q)$$

IV. Use these to compute phonons on a finer grid.

V. Compute quasiharmonic free energy.