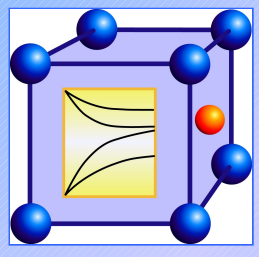
Polish Academy of Sciences

Institute of Nuclear Physics
Polish Academy of Sciences
Cracow, Poland

Material properties studied with PHONON

Krzysztof PARLINSKI



Computing for Materials

Institute of Technics
Pedagogical University
Cracow, Poland

Temperature of materials is determined (maily) by phonons

Strategy of computation

Density Functional Theory codes

VASP **Kresse, Hafner**

Wien2k **Blaha**

Ab initio calculations for supercell
Structure, energy, HF forces
T = 0 K

Phonon **Parlinski**

HF forces
Direct method

Phonons.
Teperature dependences.
Thermodynamics. Spectroscopies.
Phase diagrams. Phase transitions
T > 0 K

Some quantities to be calculated using DFT, and DFT + Phonon

DFT T=0 K, any P

*Lattice parameters
*Atomic positions
*Crystal structure
External stresses and pressure
*HF forces acting on atoms
Charge distribution $\rho(x,y,z)$
Magnetic moments
Electronic states, electronic gap
Electronic structure
Electronic density of states
*Polarization
etc.
* - needed for phonon calculations

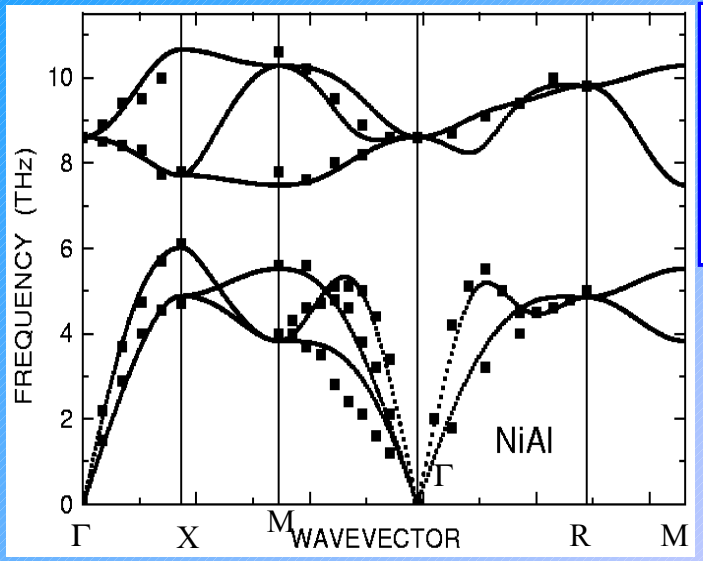
Systems:
Crystals (230 space groups)
Surfaces (on slab)
Multilayers, interfaces
(Point) defects, vacancies
Amorphous
etc. All systems represented by SUPERCELL

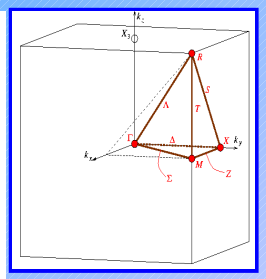
DFT+Phonon T>0 K, any P

Phonon dispersion relations $\omega(\mathbf{k},j)$
Phonon intensities (different filters)
LO/TO splitting from $Z^*(m)$ and ε_{inf}
Irreducible representations of modes
Phonon intensities in many Brillouin Zones
Gruneissen parameters
Atomic displacements involved in a mode
Animate phonon(s) motion
Find electronic state coupled to $\omega(\mathbf{k},j)$
Phonon density of states $g(\omega)$
Partial phonon density of states $g_{\mu,i}(\omega)$
Thermodynamical functions: E, S, F, G, c_V
Debye-Waller factor $\langle u^2(\mu)\rangle$
Thermal expansion
Neutron & x-rays inelastic coherent scattering
Neutron inelastic incoherent scattering
Nuclear inelastic scattering (NIS) with x-rays
Searching for soft modes & phase transitions
Construct (T,P) - phase diagram
Find chemical reactions constant
Diffusion constant
Heat conductivity (?)

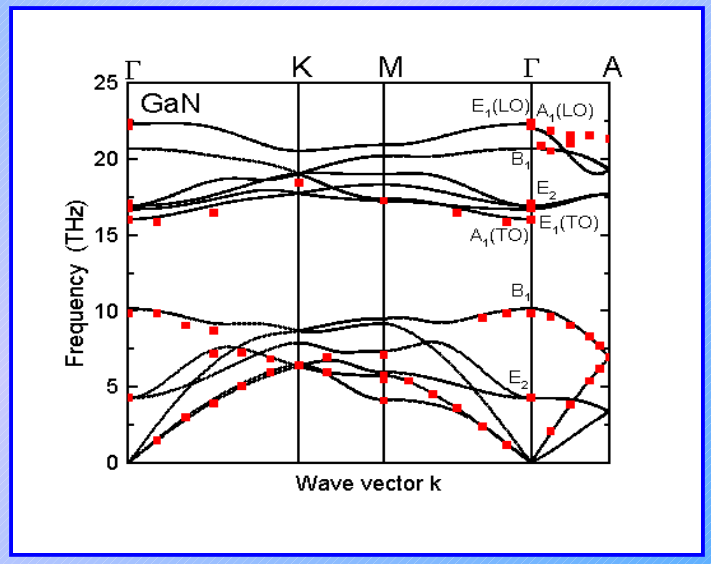
Comparing computed phonon dispersion curves with experiment

NiAl Cubic primitive

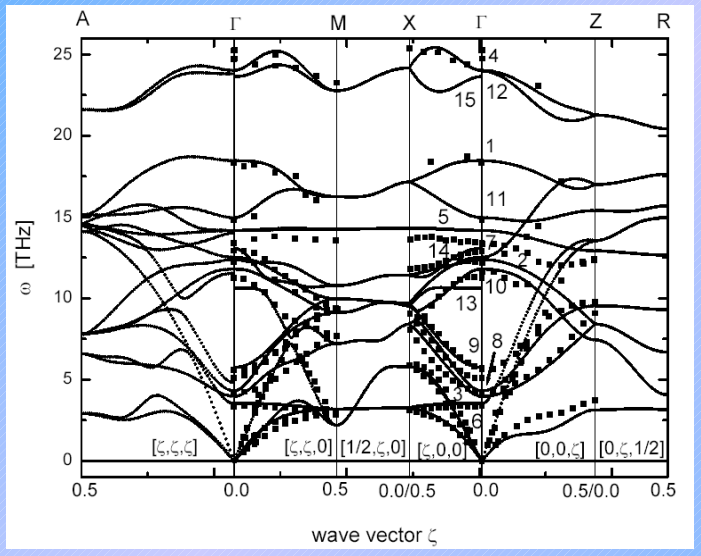


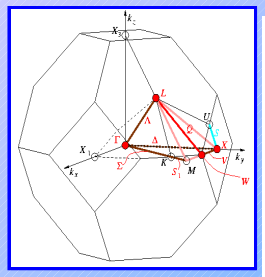


GaN Hexagonal wurzite

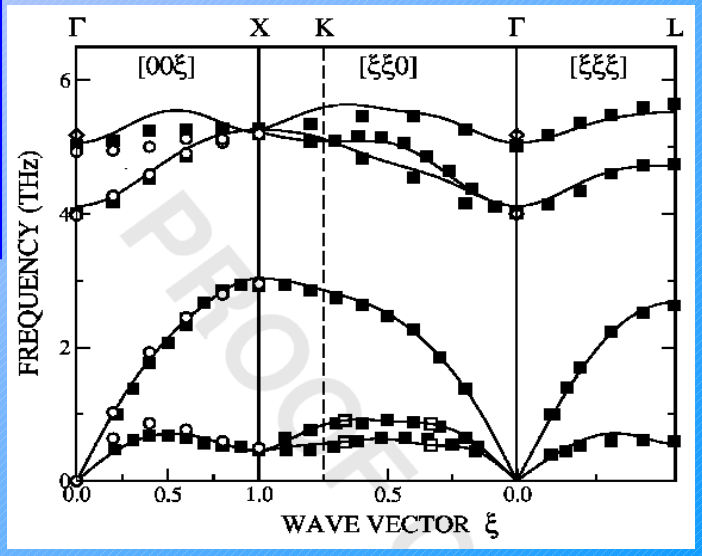


TiO_2 Tetragonal





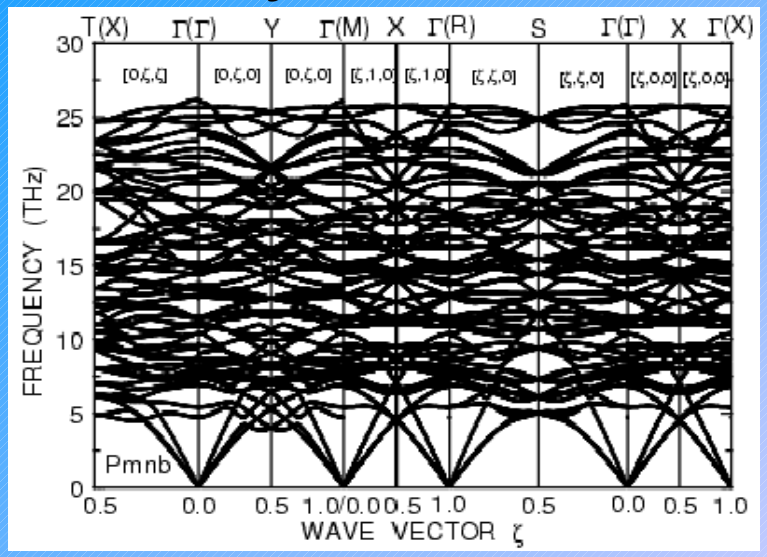
HgSe Cubic face centered



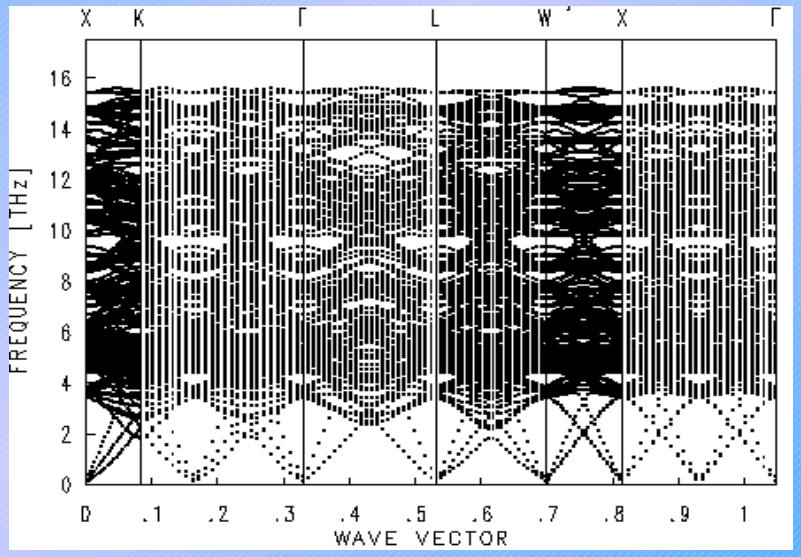
Mercury selenate

Phonon dispersion curves of more complex systems

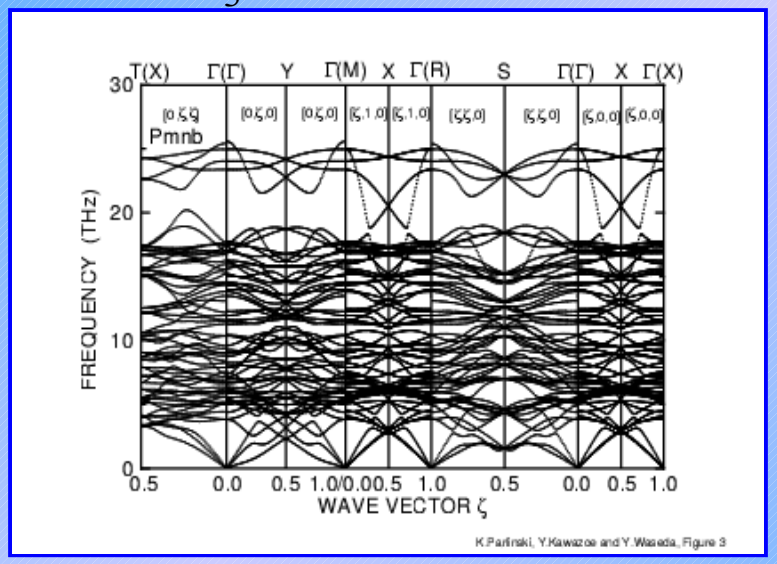
$MgSiO_3$ orthorhombic



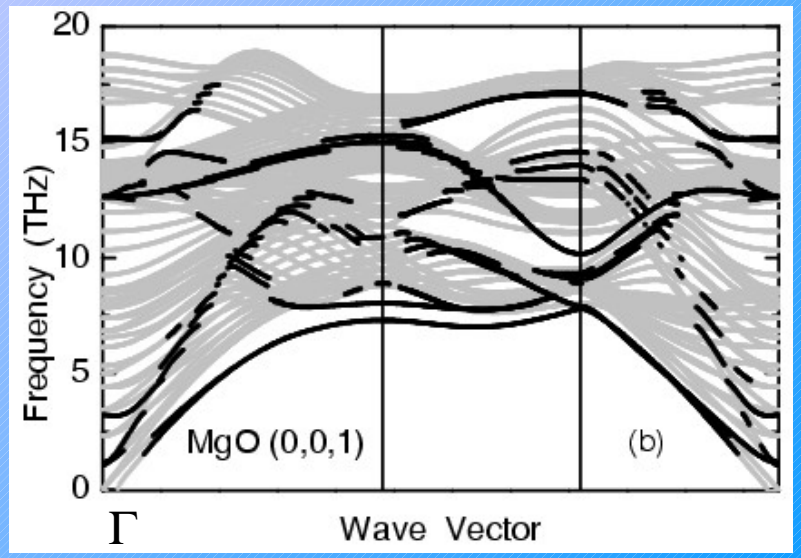
Cubic CoO + one vacancy



$CaTiO_3$ orthorhombic

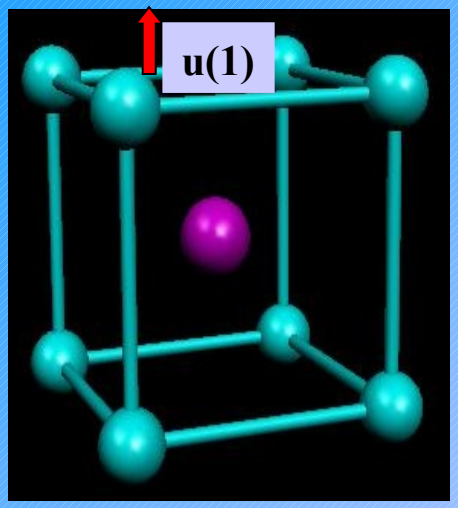


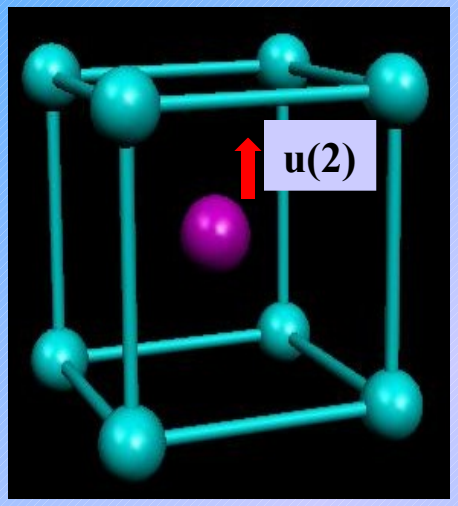
Surface MgO(001) M X Γ



Principle of Direct Method
K.Parlinski

Method to calculate phonons





Potential: $V = \frac{1}{2} \sum_{n,m} \Phi(n, m)\, u(n)\, u(m)$

Force: $F(n) = - \sum_{m} \Phi(n, m)\, u(m)$

$\Phi(n, m)$ – force constant - matrix 3x3 between atom n and m

Dynamical matrix:

$$D(k) = 1/M \sum_{m} \Phi(0, m)\ \exp[-ik(R(0)-R(m))]$$

Phonons: $\omega^2(k)\, e(k) = D(k)\, e(k)$

e(k) – polarization vector, eigenvector

Hellmann-Feynman forces F(n) arise due to displacements of an atom in supercell

$$F(n) \rightarrow \Phi(n, m) \rightarrow \omega(k)$$

Potential: $V = \frac{1}{2} \sum_{k} \omega^2(k)\, |Q(k)|^2$

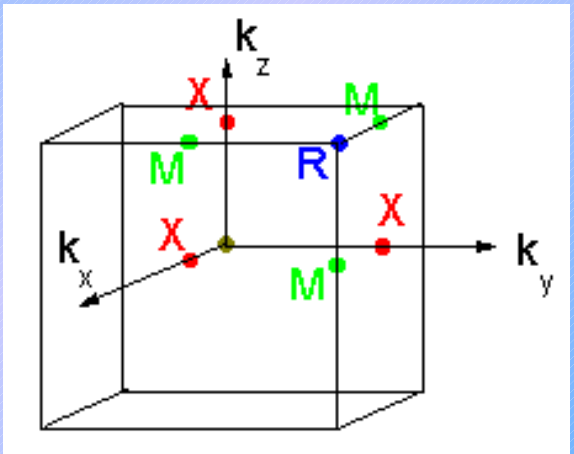
K.Parlinski, Z.Q.Li and Y.Kawazoe, PRL, 78, 4063 (1997)

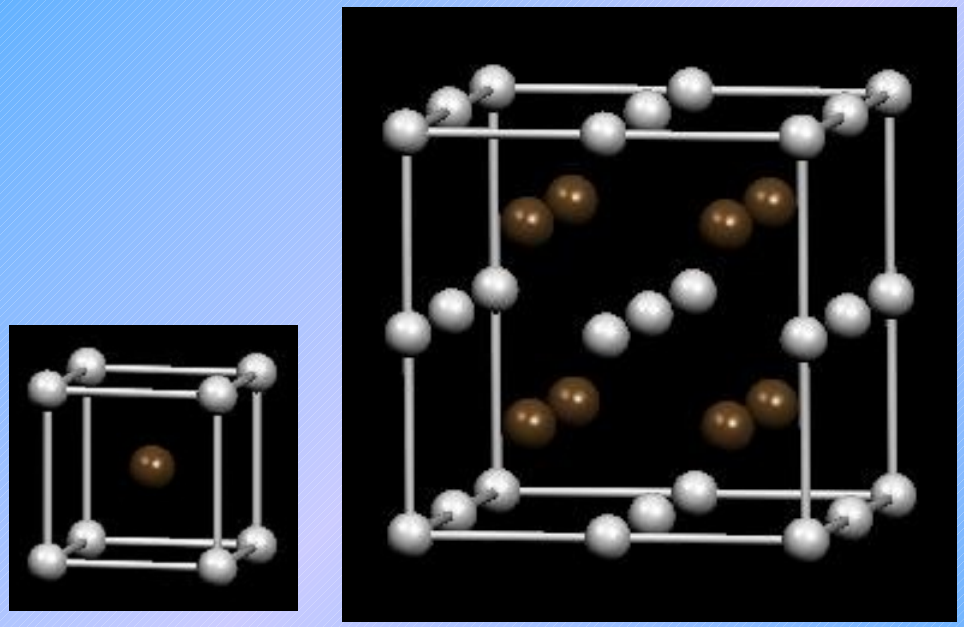
SUPERCELL

Exact wave vectors

Wave vectors, which are commensurate with the size of supercell, provide phonon frequencies being „exact”, independent on the interaction range.

Brillouin zone for simple cubic





Supercell	1x1x1	2x2x2
Exact points	Γ	Γ, X, M, R

Procedure

- Crystals are always treated as **supercell.** Supercell is a fragment of crystal being the multiplication of primitive unit cells. On supercell are imposed **3d** periodic boundary conditions.
- Optimization of crystall supercell by *ab initio* program (VASP, Wien2k)
- Calculation of Hellmann-Feynman atomic forces **F**, created by single atom displacement
- Use of direct method to get from **F** (VASP, Wien2k), force constants **Φ** (Phonon)
- Calculation of dynamical matrix and phonon frequencies

Some results of calculations

Phonons in bulk crystals.

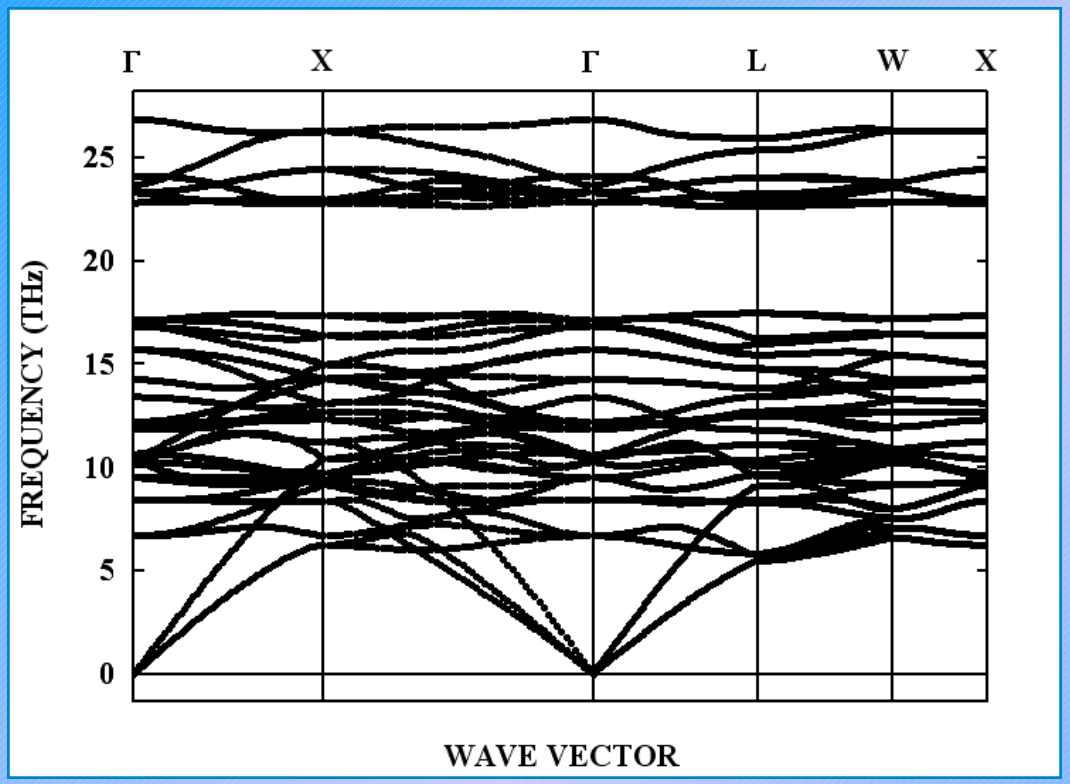
Example: Mg_2SiO_4

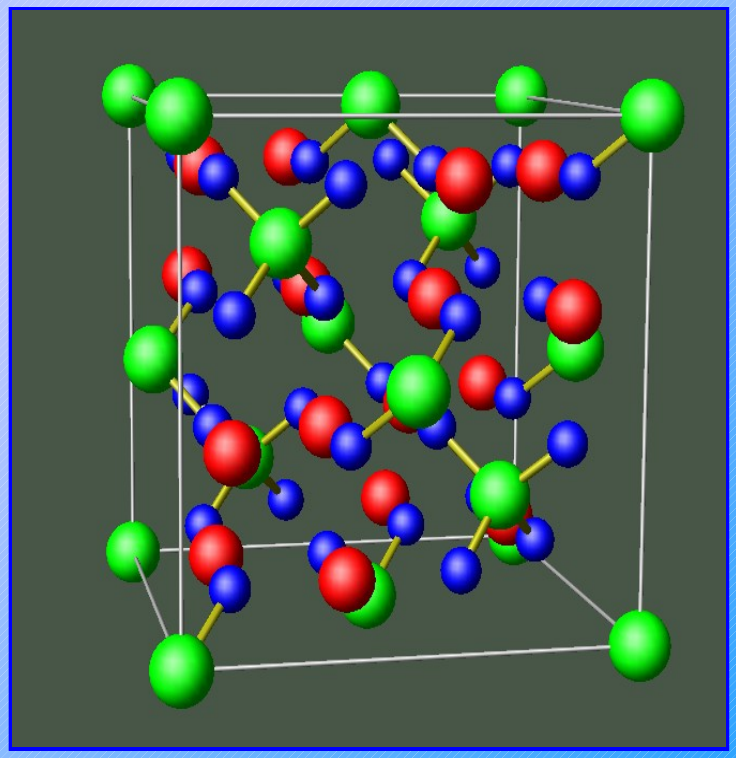
Mg_2SiO_4

Cubic, Fd-3m,

Phonon dispersion relations

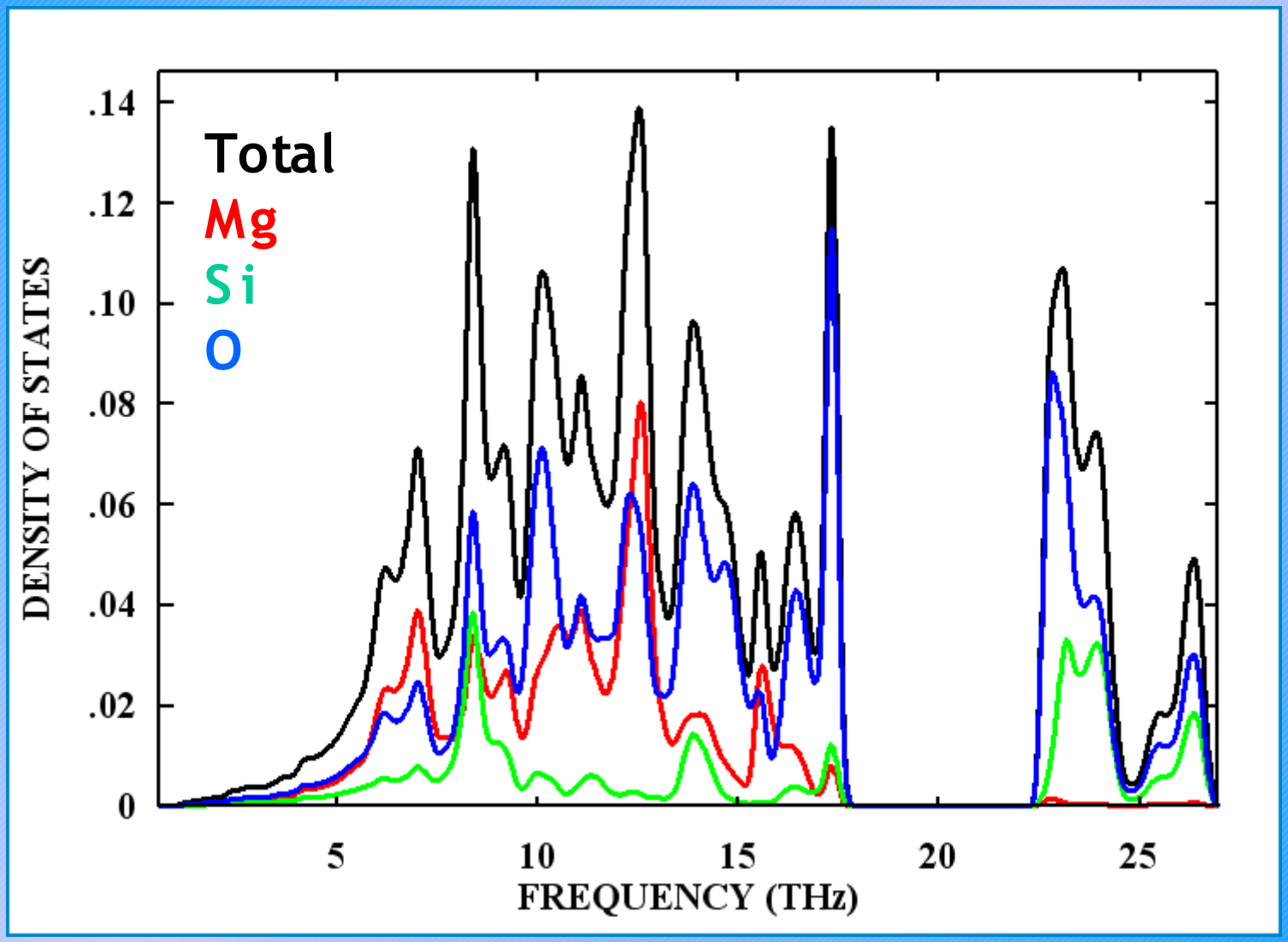
7atoms x 2 x 3 = 42 phonon dispersion curves





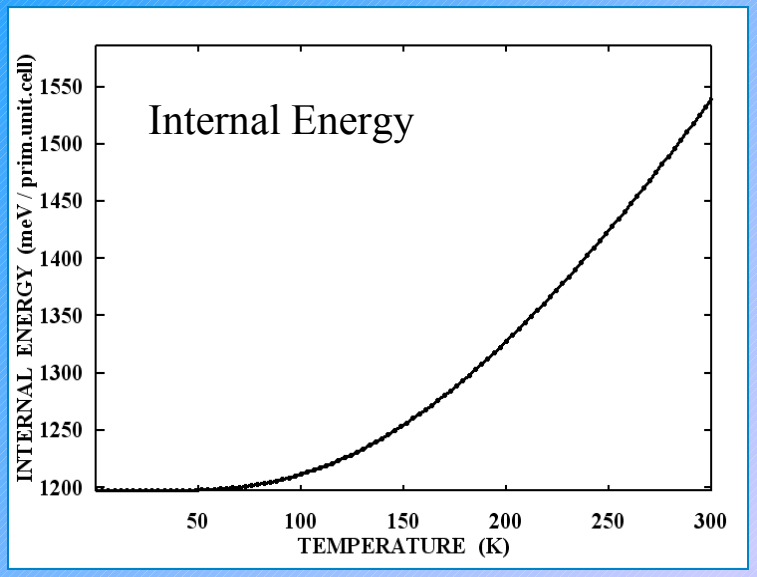
Mg_2SiO_4

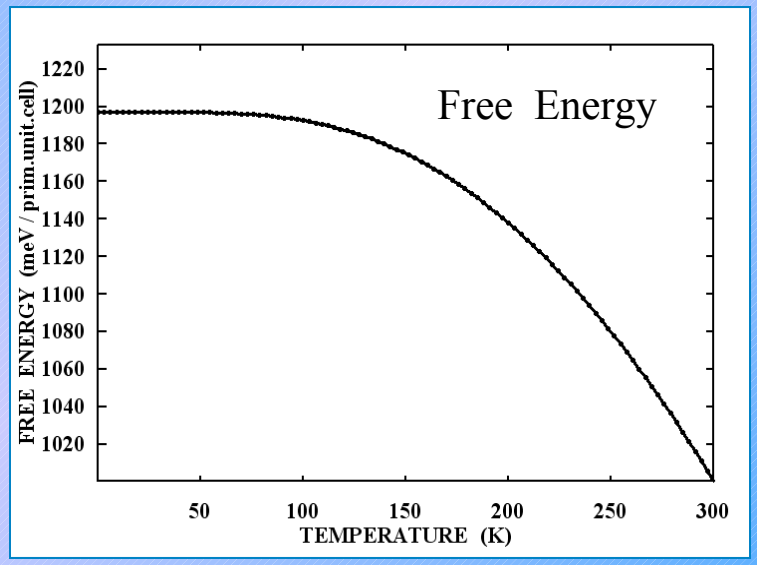
Density of States (DOS)

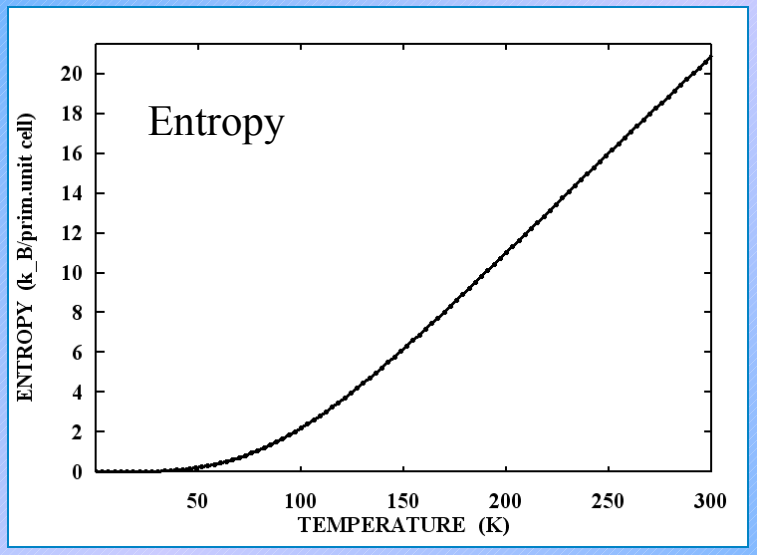


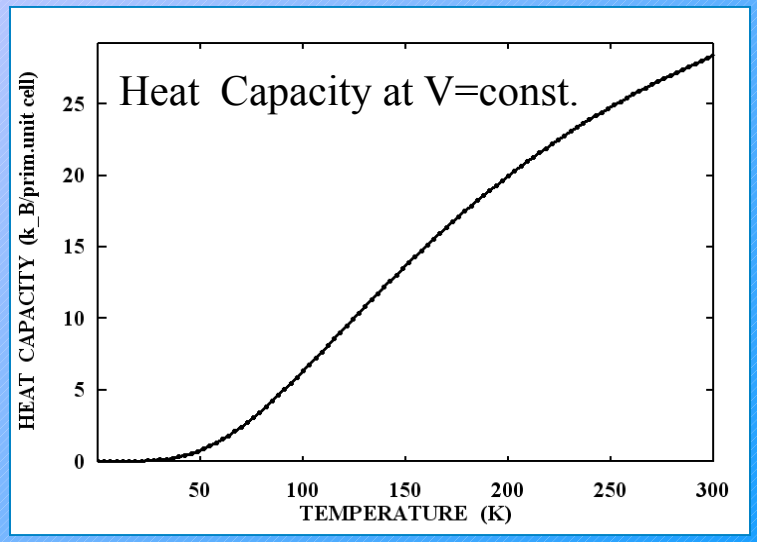
Mg_2SiO_4

Thermodynamical Functions from harmonic phonons



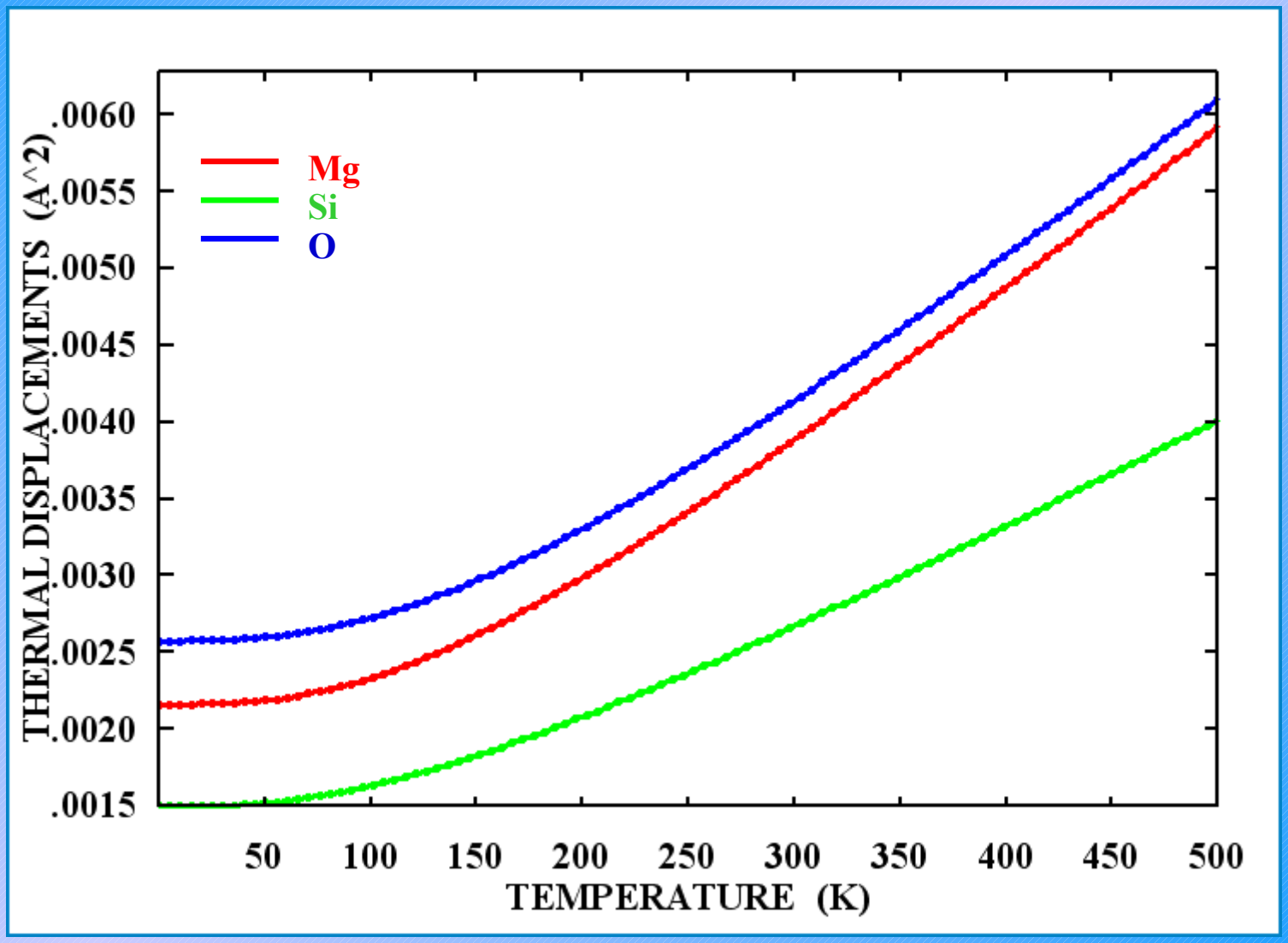






Mg_2SiO_4

Mean square displacements $\langle U^2 \rangle$



Create/Dispersion Curves/Plot for Atoms - filtering of phonon branches

$\mathbf{e_i(k, j; \mu)}$ - i-components (x,y,z) of polarization vector of atom μ, corresponding to phonon wave vector **k** from branch j.

$$\sum_{\mu,i} |e_i(\mathbf{k}, j; \mu)|^2$$

Independent contribution to phonon branch of sum of selected degree of freedom. Intensity does not depend on B.Z.

$$\left| \sum_{\mu,i} \frac{e_i(\mathbf{k}, j; \mu)}{\sqrt{M_\mu}} \right|^2$$

Coherent contribution of degree of freedom. Indicates real occupation of phonon branches. Intensity is independent of selection of unit cell (smaller, larger). Intensity depends on B.Z.

$$\frac{1}{\mathbf{k}^2} \left| \sum_{\mu,i} \frac{\mathbf{k} \cdot e_i(\mathbf{k}, j; \mu)}{\sqrt{M_\mu}} \right|^2$$

Coherent contribution of degree of freedom projected on the transmition wave vectors k as in coherent inelastic neutron scattering. Intensity depends on B.Z.

Filters permit to establish an interpretation of a given phonon mode !!!

$$\omega^2(\mathbf{k})\, e(\mathbf{k}) = D(\mathbf{k})\, e(\mathbf{k})$$

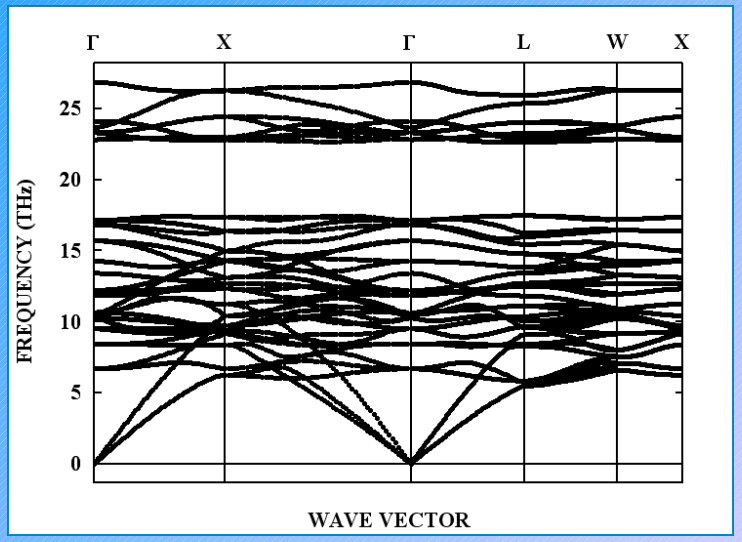
$$\sum_{\mu,i = \text{all}} |e_i(\mathbf{k}, j; \mu)|^2 = 1$$

Normalization condition

Mg_2SiO_4 Participation of atom in phonon dispersion relations:

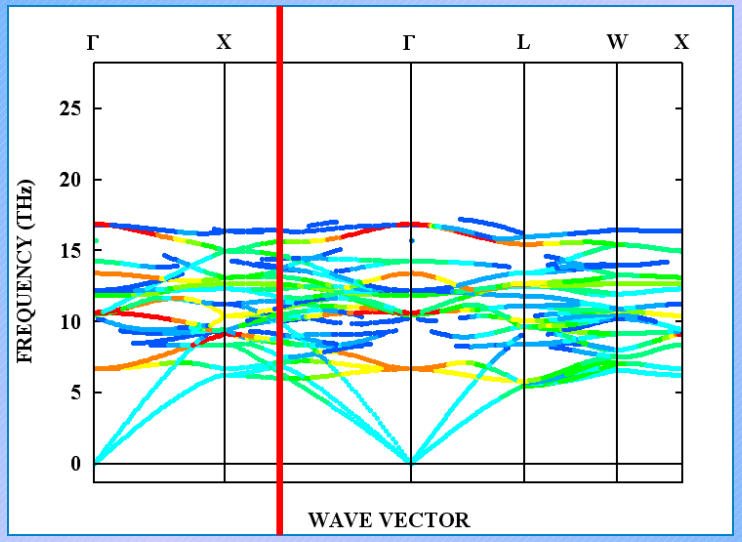
$$\sum_{\mu,i} |e_i(\mathbf{k}, j; \mu)|^2$$

$$\omega^2(k)\, e(k) = D(k)\, e(k)$$

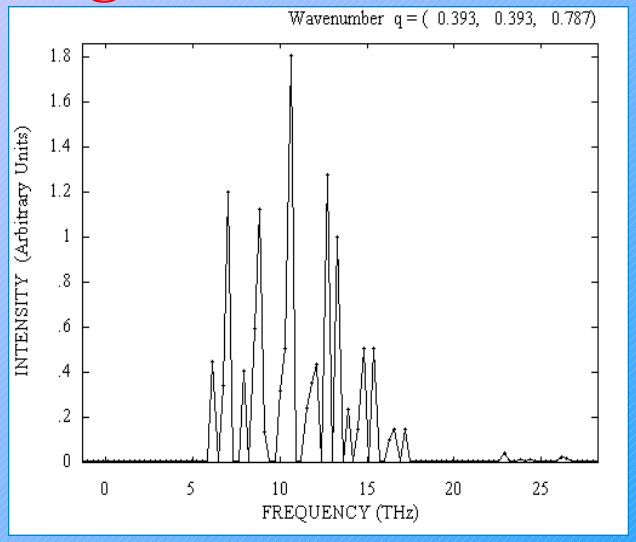


Total - no filter

Intensity scale (%)

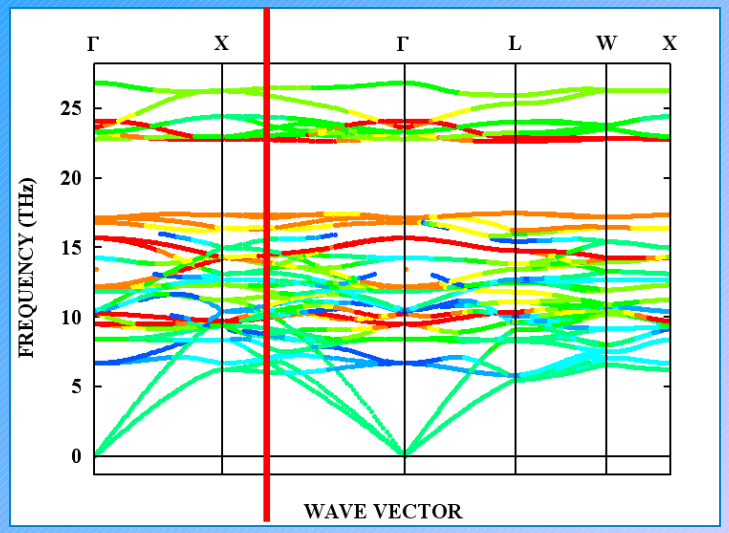


Mg Intensity



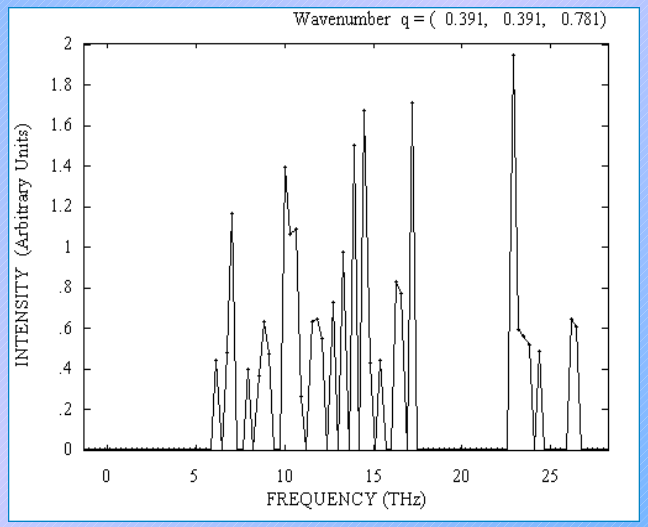
Mg_2SiO_4 Participation of atom in phonon dispersion relations:

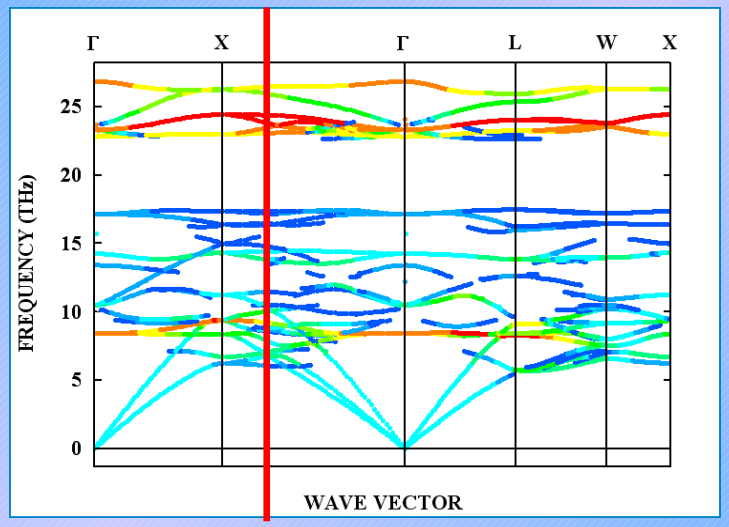
$$\sum_{\mu,i} |\mathbf{e}_i(\mathbf{k}, j; \mu)|^2$$



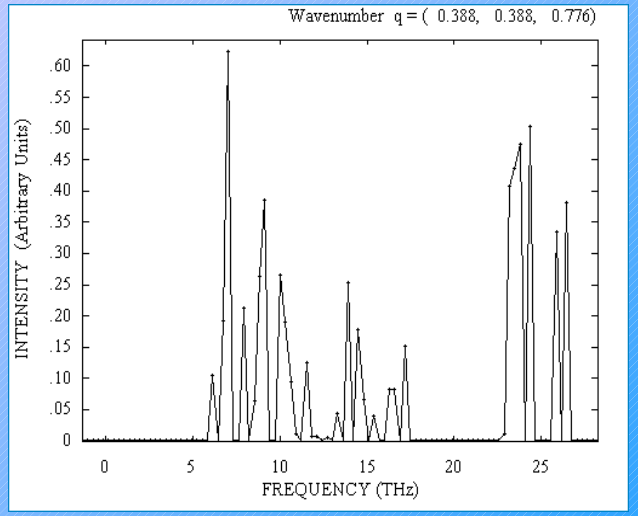
O

Intensity





Si



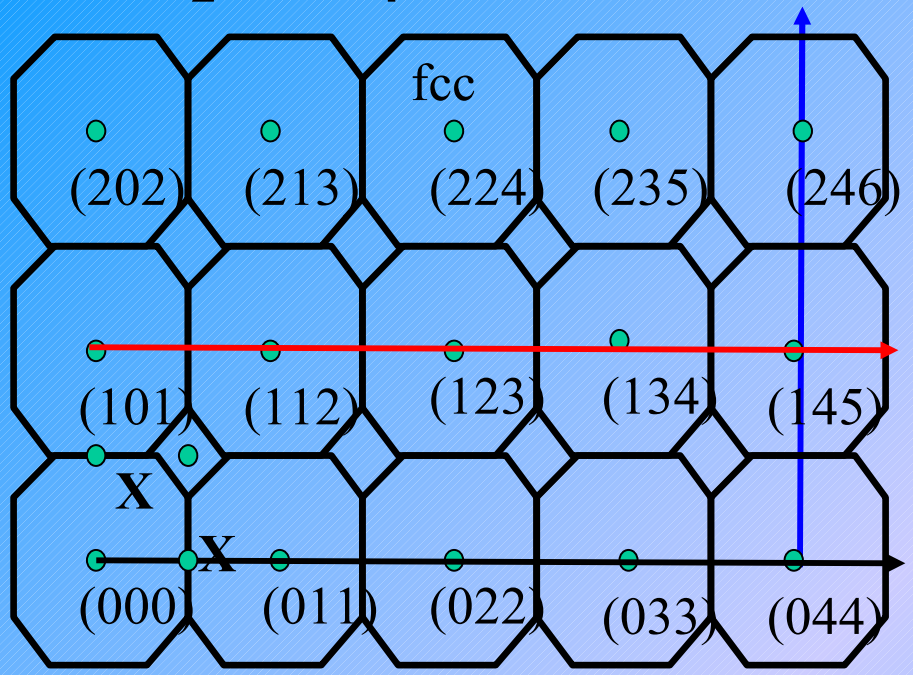
Intensity scale (%)

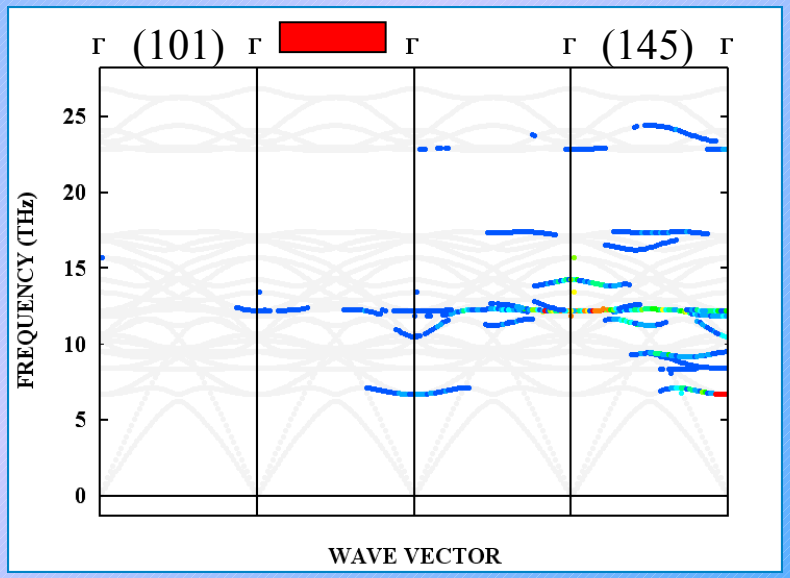
Phonon intensity in inelastic coherent neutron scattering:

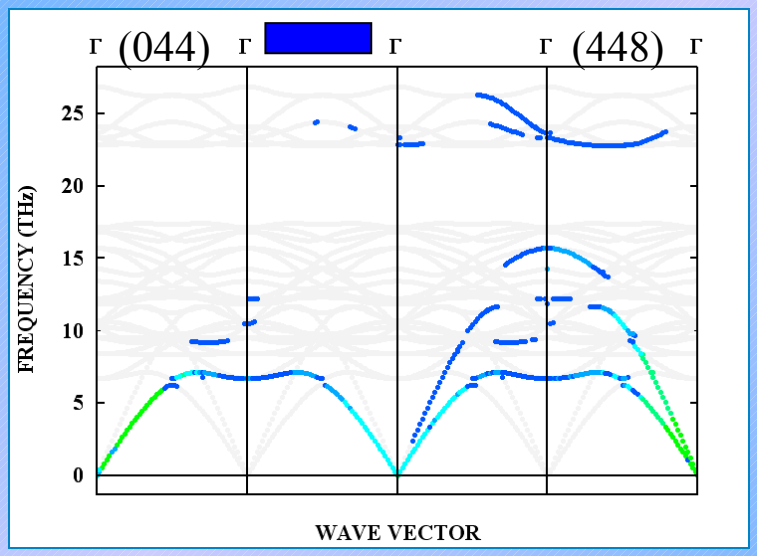
Mg_2SiO_4

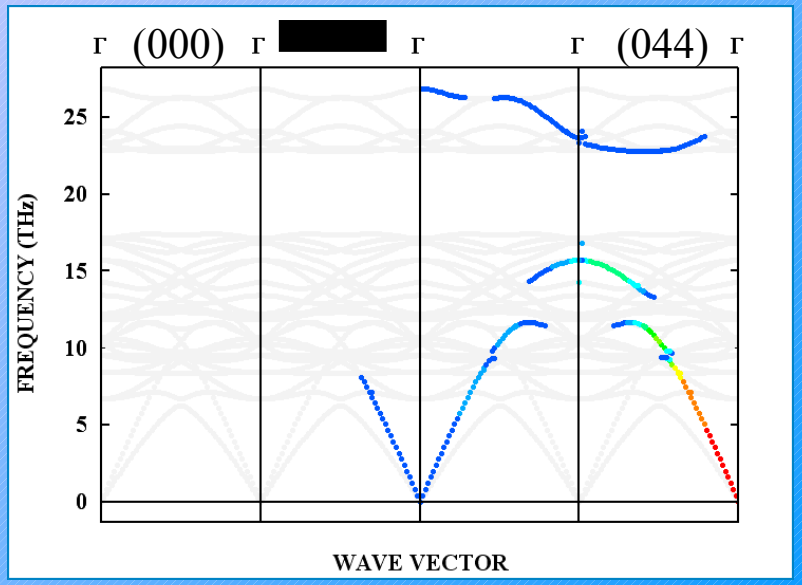
Coherent inelastic neutron scattering:

$$\mathcal{F}(\mathrm{k},j) = \left| \sum_{\mu} a_{coh}(\mu) exp[-W_{\mu}(\mathrm{k})] \frac{2\pi \mathrm{k} \cdot \mathrm{e}(\mathrm{k},j;\mu)}{\sqrt{M_{\mu}}} \right|^2$$

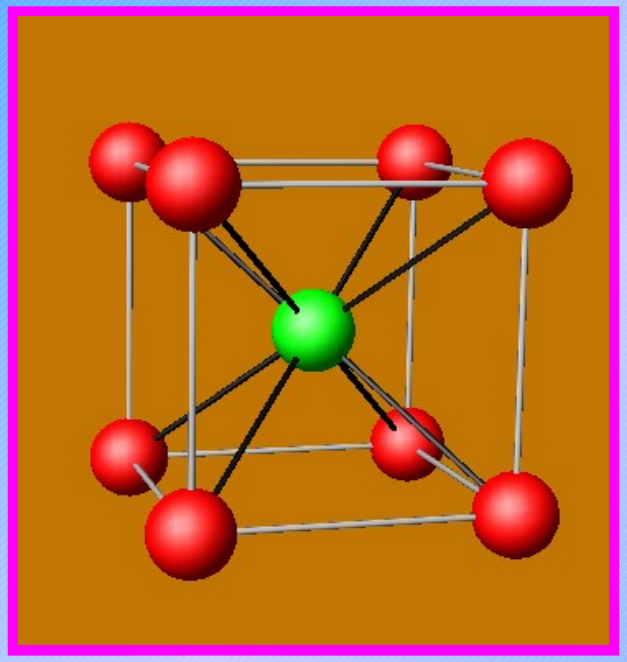








*

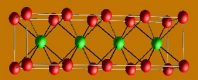


Elongated supercell.

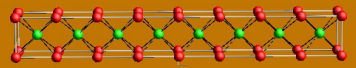
LO / TO splitting. Part 1.
Result of LO mode coupling to induced macroscopic electric field.
Model of simple cubic CsCl

* CsCl

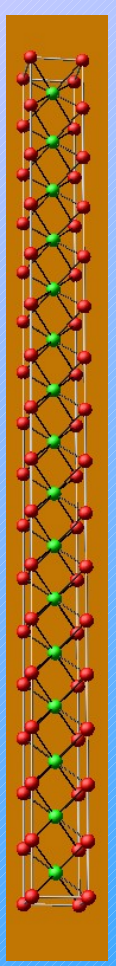
1x1x4

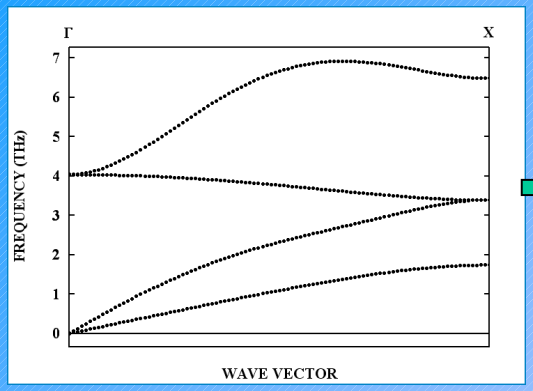


1x1x8

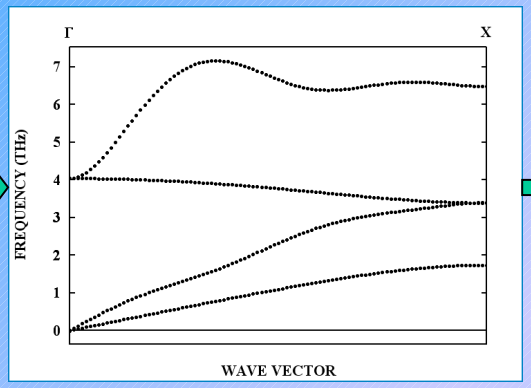


1x1x16

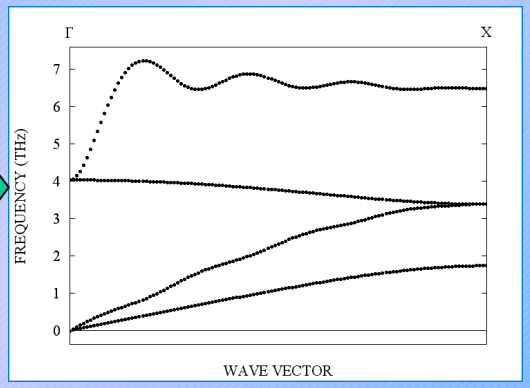




NO non-analytical term

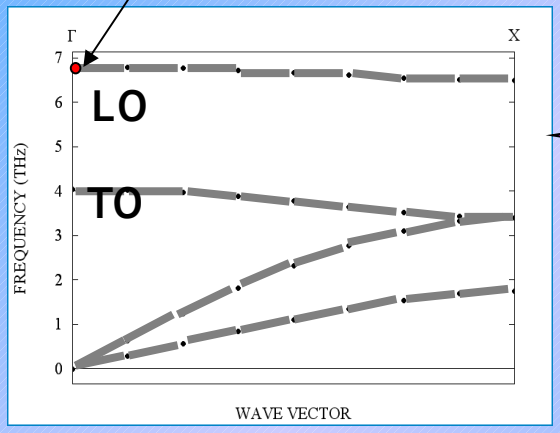


NO non-analytical term



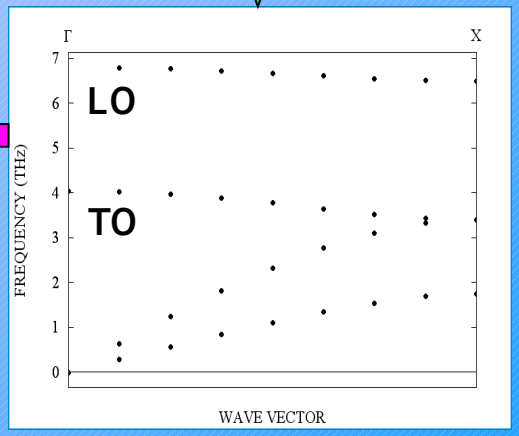
NO non-analytical term

LO from non-analytical term



WITH non-analytical term

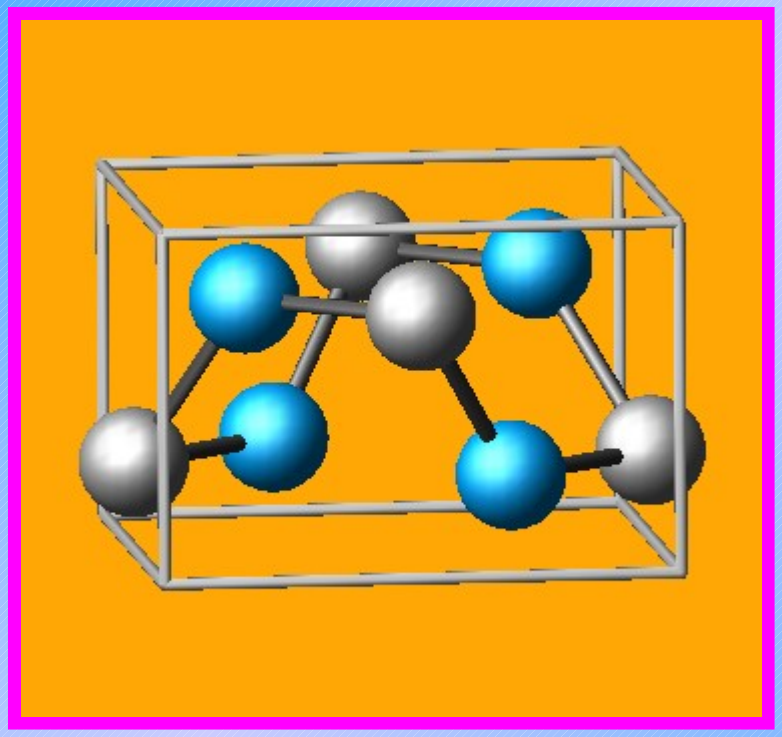
Add non-analytical term to dynamical matrix



NO non-analytical term

*

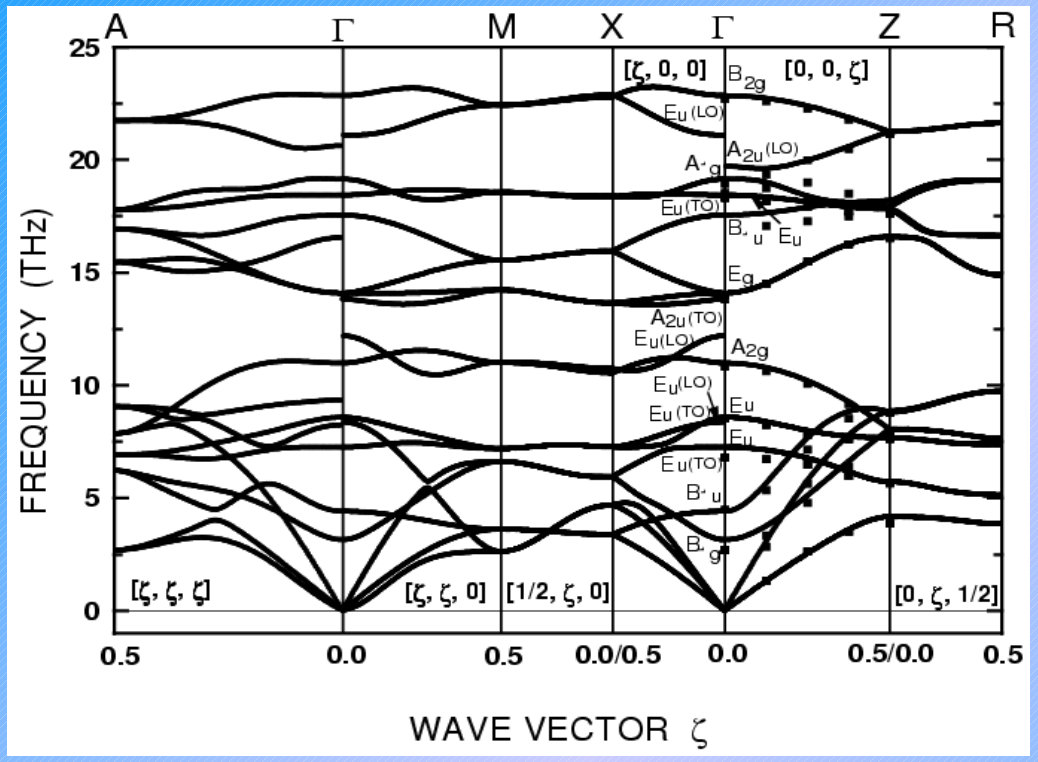
LO / TO splitting. Part 2.
Tetragonal rutile crystal SnO_2



LO/TO splitting from singular term

SnO_2

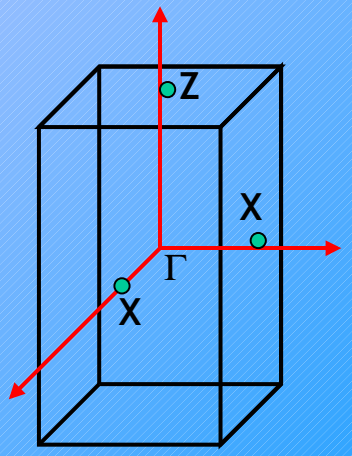
Rutile ($P4_2/mnm$)



Add non-analytical term to classical dynamical matrix

$$\mathbf{D}^{M}_{\alpha,\beta}(\mathbf{k};\mu\nu) = \mathbf{D}_{\alpha,\beta}(\mathbf{k};\mu\nu) + \frac{4\pi e^2}{V\epsilon_\infty\sqrt{M_\mu M_\nu}} \frac{[\mathbf{k}\cdot\mathbf{Z}^*(\mu)]_\alpha[\mathbf{k}\cdot\mathbf{Z}^*(\nu)]_\beta}{|\,\mathbf{k}\,|^2} \times exp[-2\pi i\mathbf{g}\cdot(\mathbf{r}(\mu)-\mathbf{r}(\nu))]$$

$$\times \; d(\mathbf{q})exp\left\{-\pi^2\left[\left(\frac{k_x}{\rho_x}\right)^2+\left(\frac{k_y}{\rho_y}\right)^2+\left(\frac{k_z}{\rho_z}\right)^2\right]\right\}$$



Supercell: 2x2x2, 48 atoms.
Points at Γ – Z are from elongated supercell 1x1x8

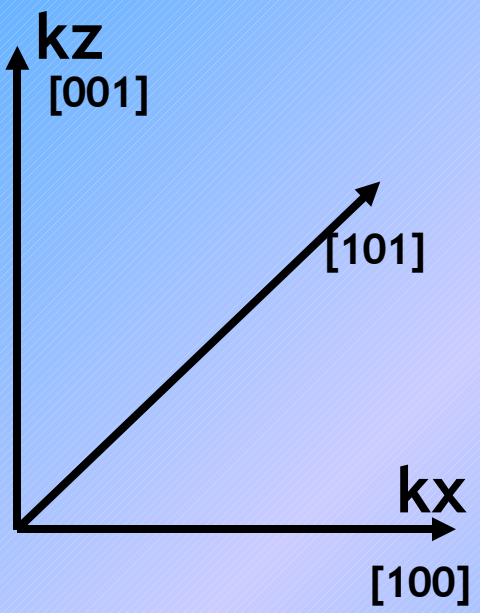
K.Parlinski and Y.Kawazoe, Euro.Phys.J. **B13**, 679 (2000)

Example: SnO_2 S.C.: 1x1x8

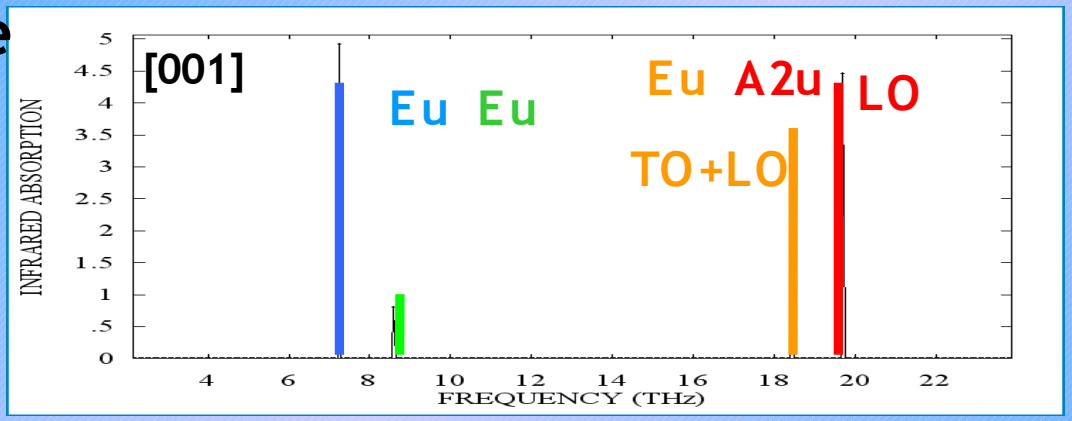
SnO_2

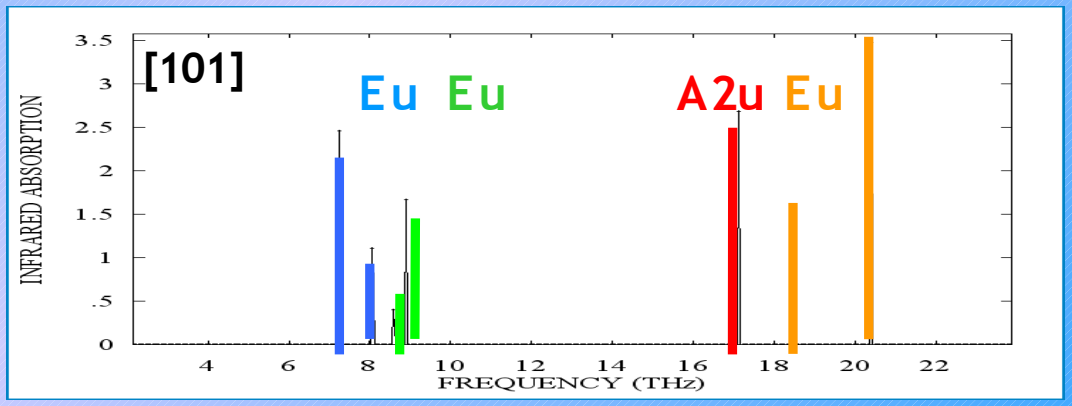
Right movie

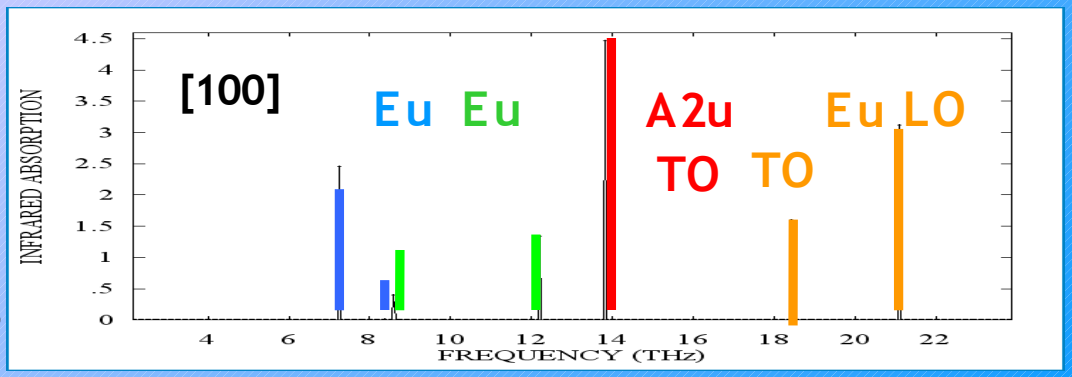
Infrared absorption depends on wavevector orientation



Left movie

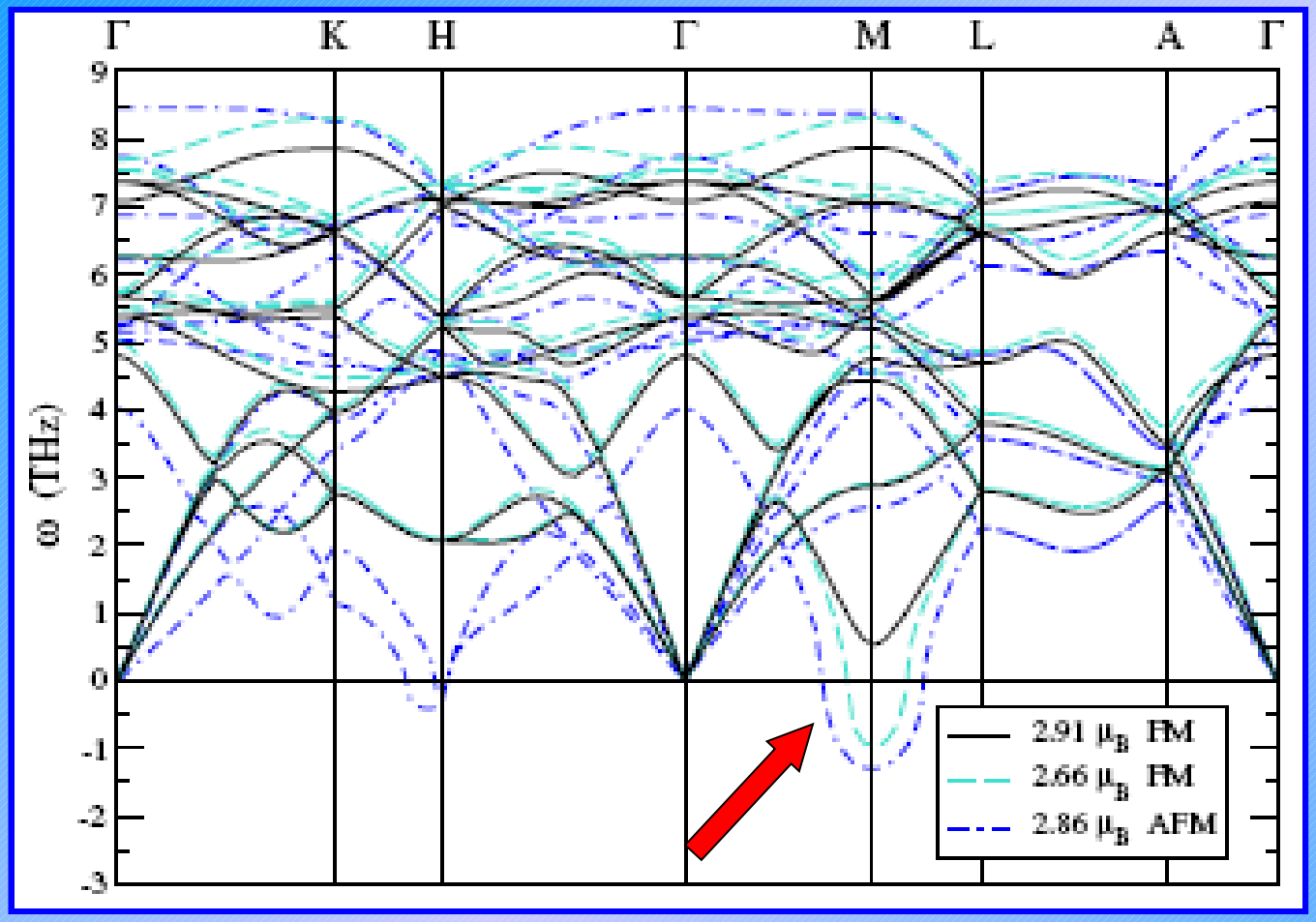






Magnetism and Phonons in MnAs

MnAs



Soft mode at M point depends on
- magnitude of magnetic moment
- FM, or AFM ordering

Calculations performed with fixed value of magnetic moment μ_B

Hexagonal structure, P63/mmc, room temperature.
Supercell 2x2x1 with 16 atoms, VASP.

J.Łażewski, P.Piekarz, J.Toboła, B.Wiendlocha, P.T.Jochym, M.Sternik, and K.Parlinski, Phys.Rev.Lett., 104, 147205 (2010)

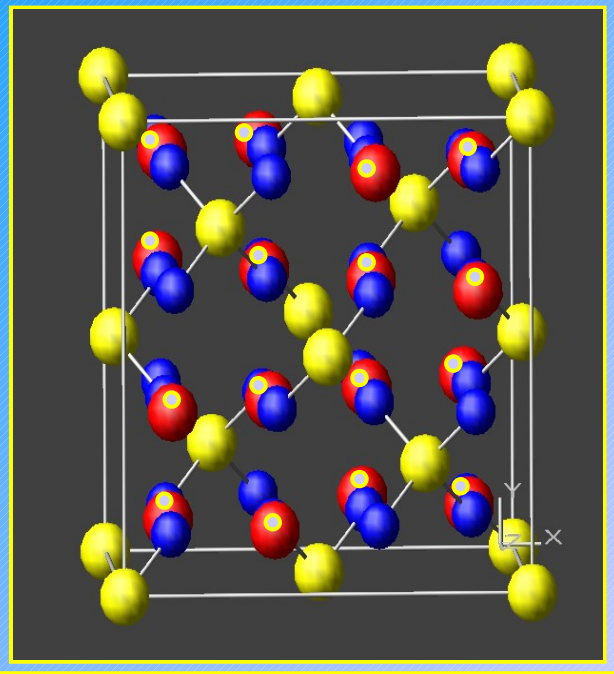
Some reasons why phonon dispersion curves are wrong, i.e. have imaginary (negative) frequencies

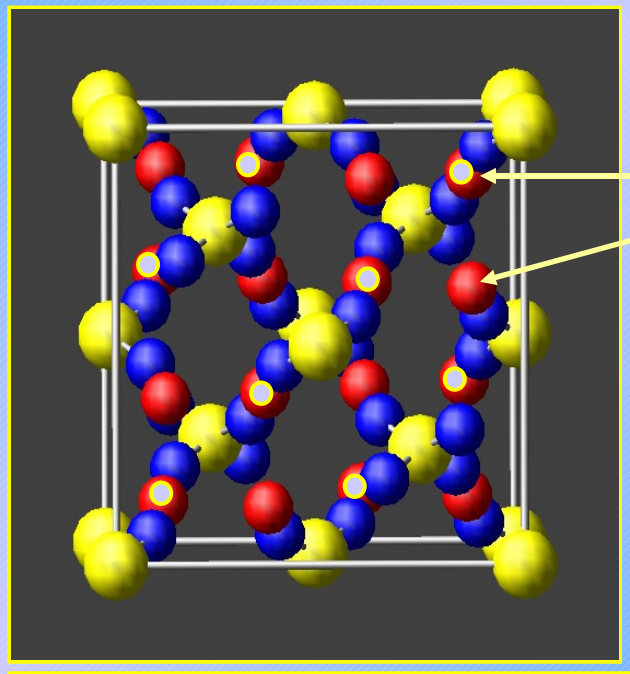
- Magnetic system is treated without magnetic interaction, or with wrong magnetic structure.
- Interatomic potential range must be taken longer.
- Exists a proper soft mode, and imaginary frequency is correct.
- Electron correlation is neglected.
- ?

Fe_2SiO_4

FM

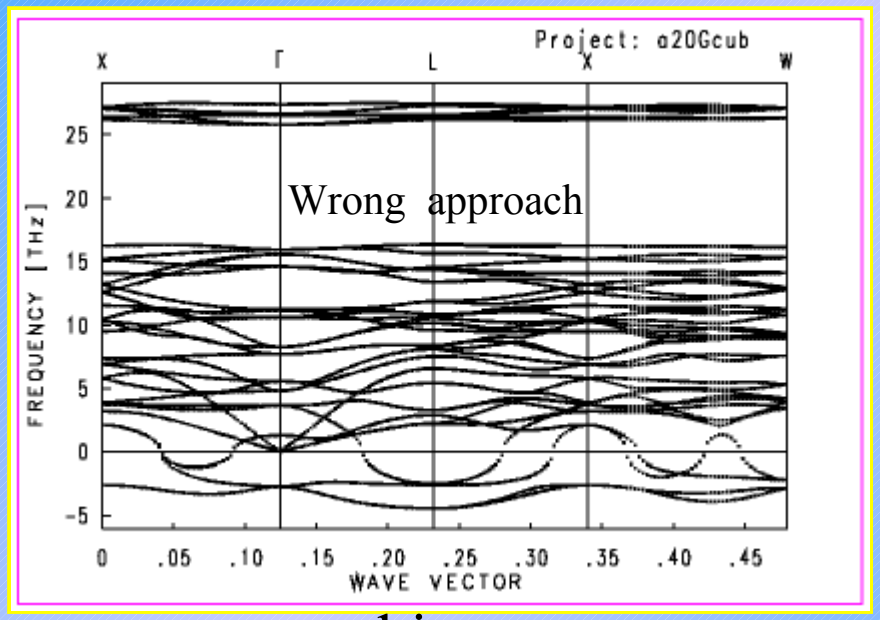
3 HF force lists as required by cubic **Fd-3m**



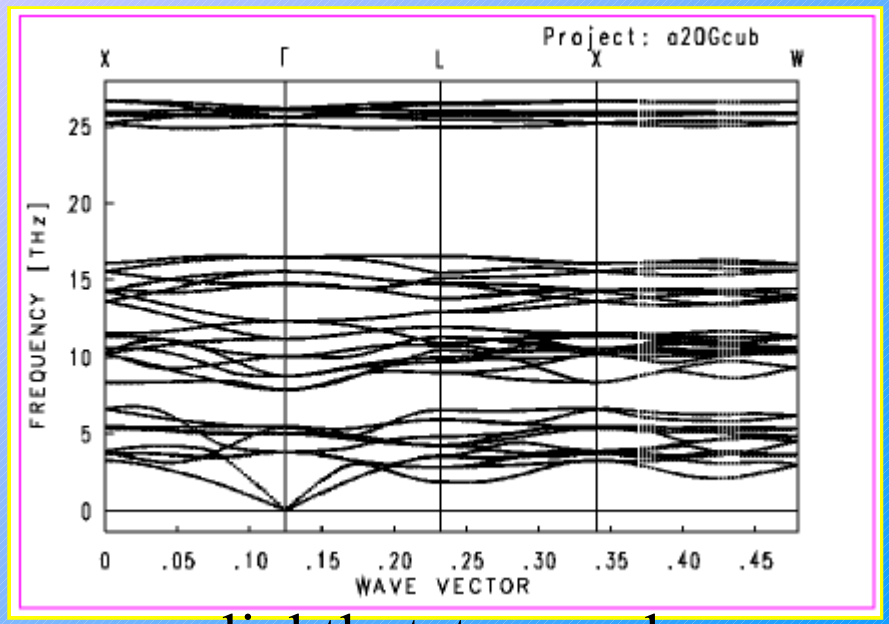


AF

8 HF force lists as required by tetragonal **$I4_1/amd$**



cubic



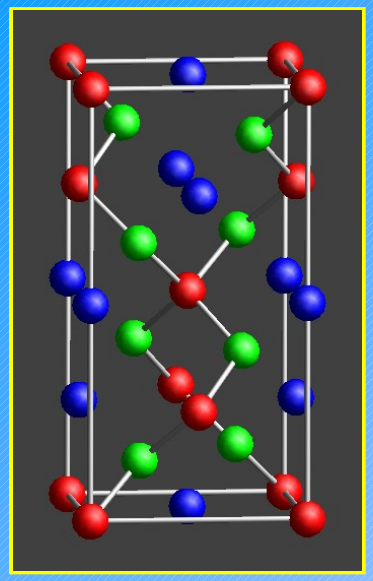
slightly tetragonal

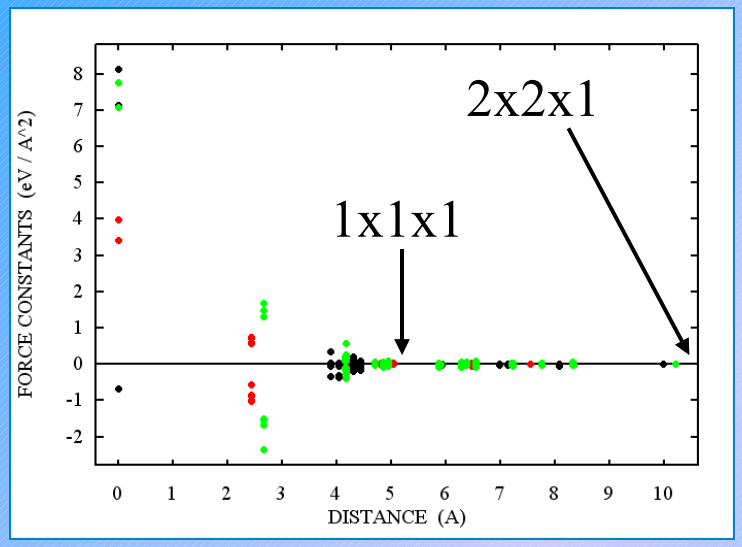
M.Derzsi, P.Piekarz, P.T.Jochym, J.Łażewski, M.Sternik, A.M.Oleś, K.Parlinski, Phys. Rev. B 79, 205105 (2009).

Short interatomic potential

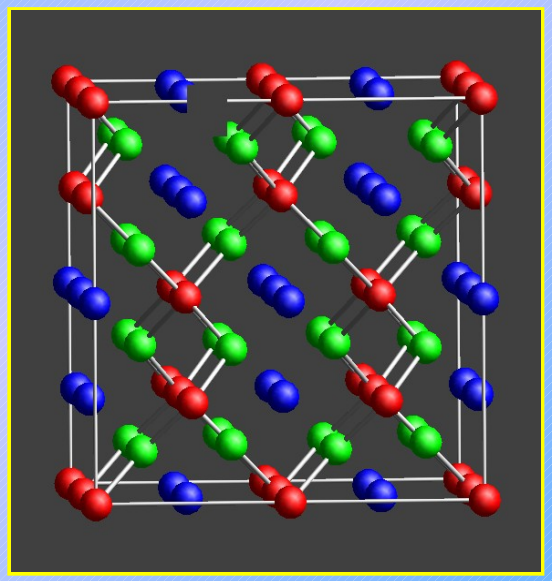
$CuInSe_2$

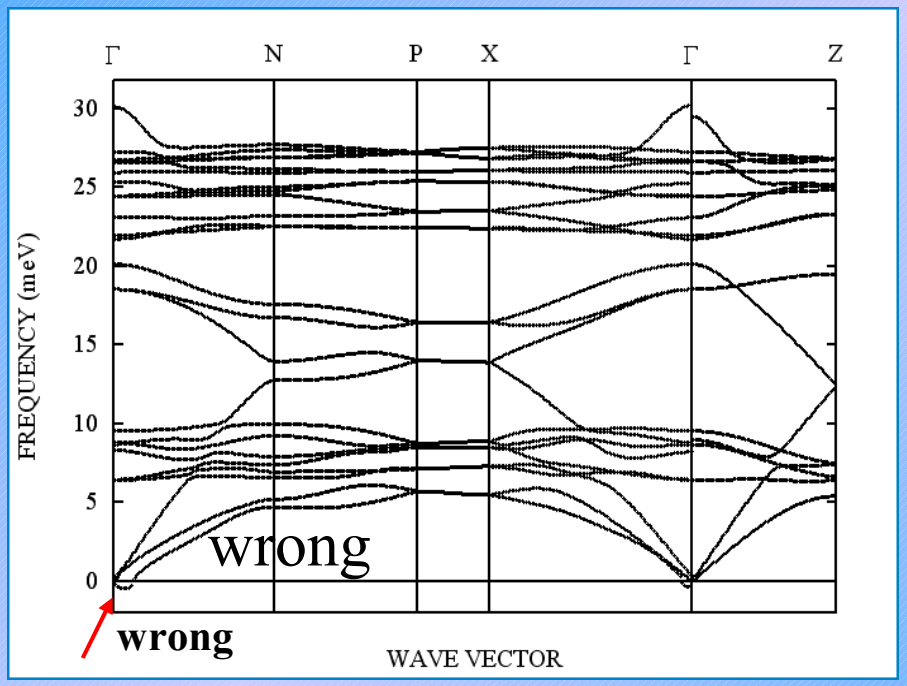
1 x1 x1

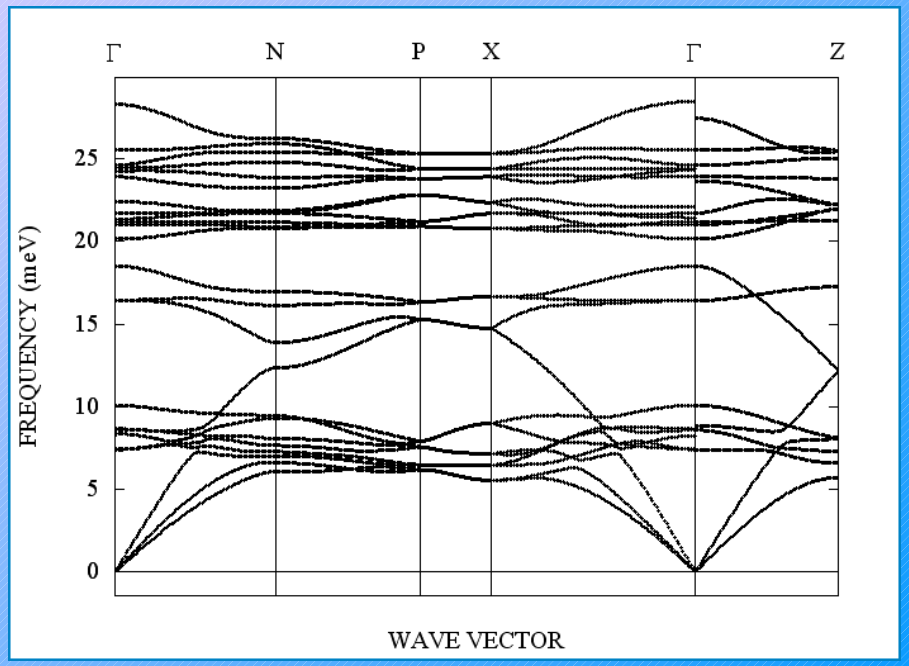




2 x 2 x1







J.Lazewski, H.Neumann, K.Parlinski, G. Lippold, and B.J. Stanbery, Phys.Rev. B 68, 144108 (2003).

Space subgroups induced by a phonon mode

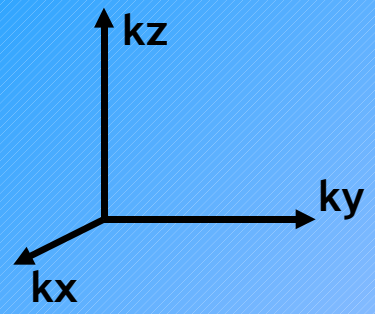
Space group analysis can be useful in:

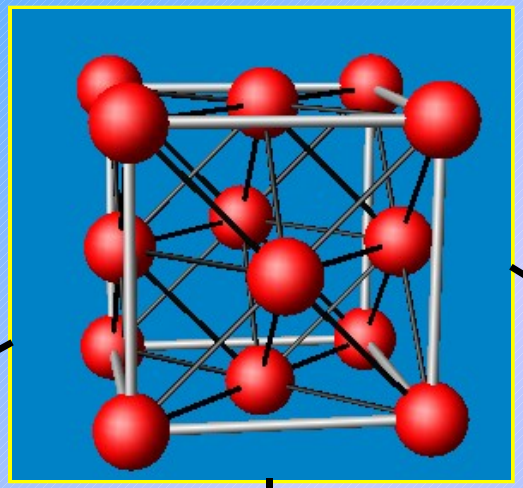
- structural phase transitions
- linear electron-phonon coupling
- magnetic-phonon coupling

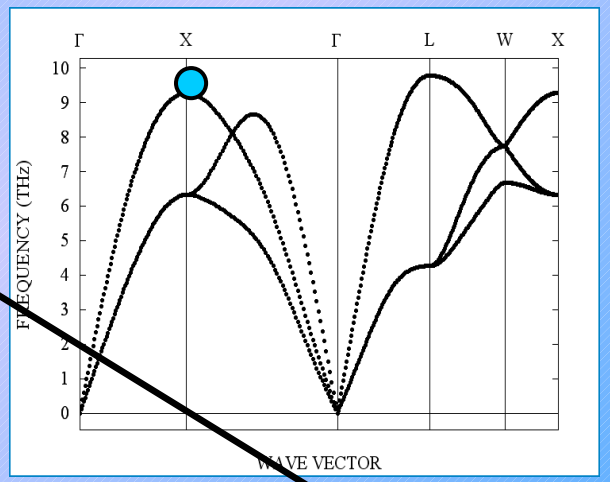
Example: Space subgroups induced by a phonon mode „X3-" in fcc Al

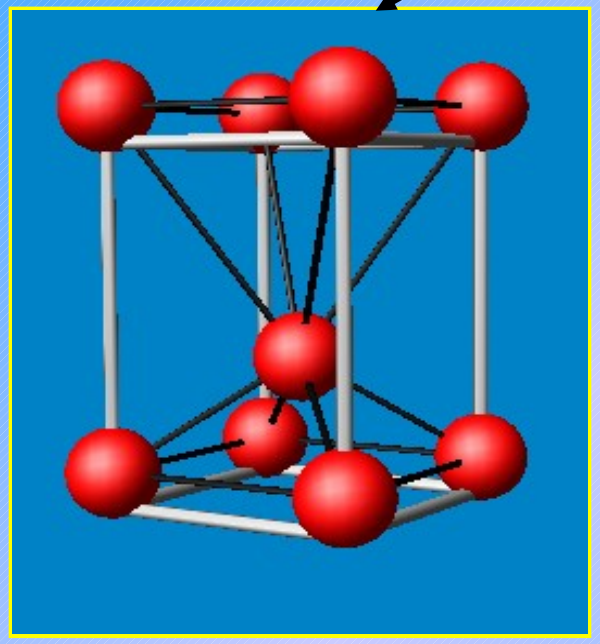
Fm-3m, No=225, (000)

Irreducible star {kx} has 3 arms

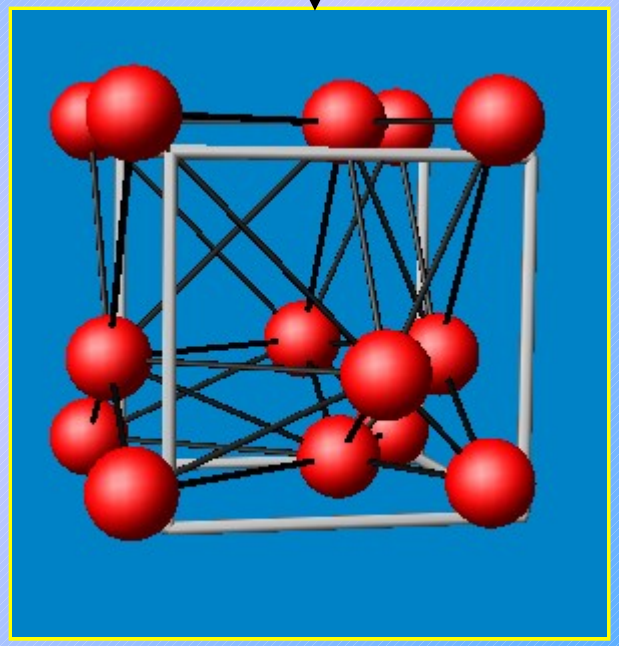




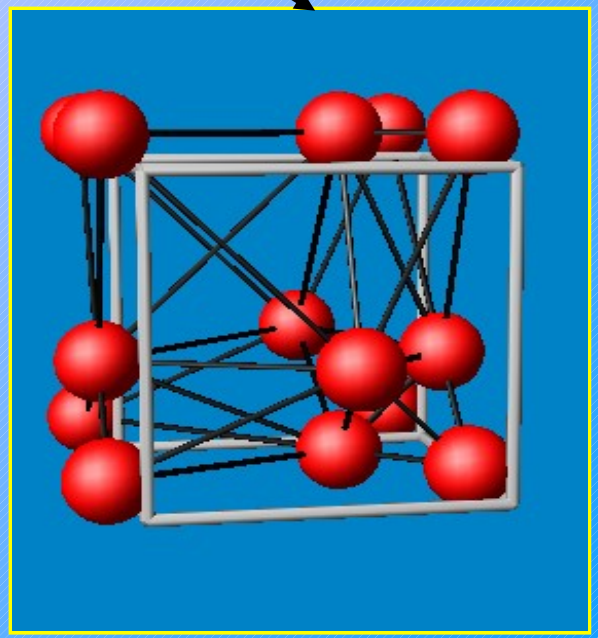




P4/nmm, No=129, (a00)



P4_2/mcm, No=132, (aa0)



P-43m, No=215, (aaa)

H.T.Stokes, D.M.Hatch, and B.J.Campbell, „Findsym" in ISOTROPY, (2007), http://stokes.byu.edu/isotropy.html

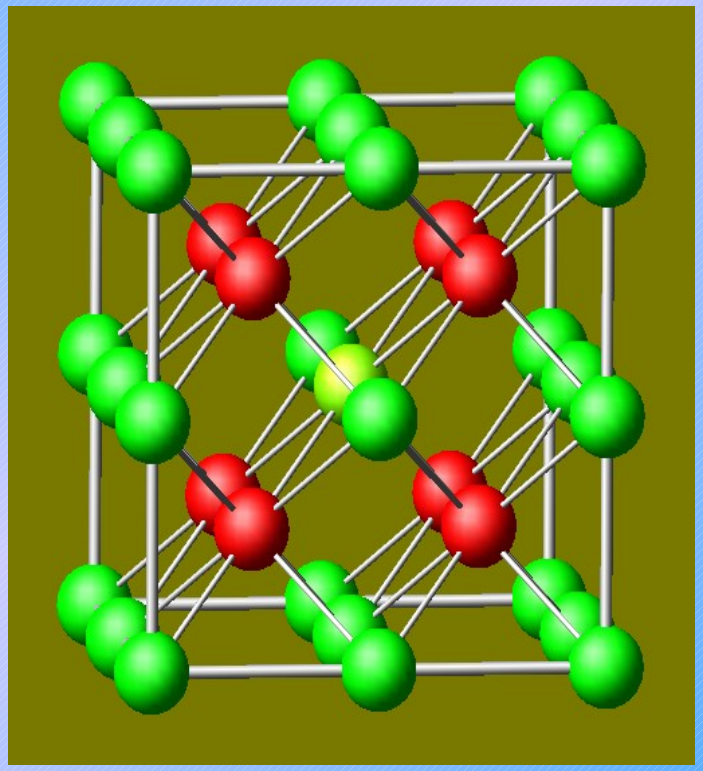
Towards crystals with point defects

Is description of phonon dispersion curves of primitive and supercell equivalent?

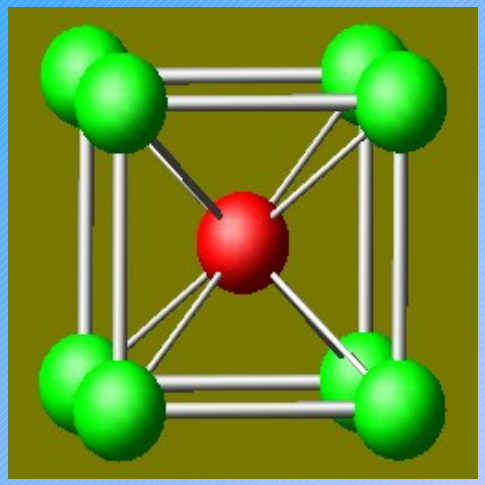
Yes, it is, but filters should be used.
Example.

Model crystal AB

2x2x2



1x1x1



Reminder:

$$\frac{1}{\mathbf{k}^2}\left|\sum_{\mu,i}\frac{\mathbf{k}\cdot\mathbf{e}_i(\mathbf{k},j;\mu)}{\sqrt{M_\mu}}\right|^2$$

Average over orientations

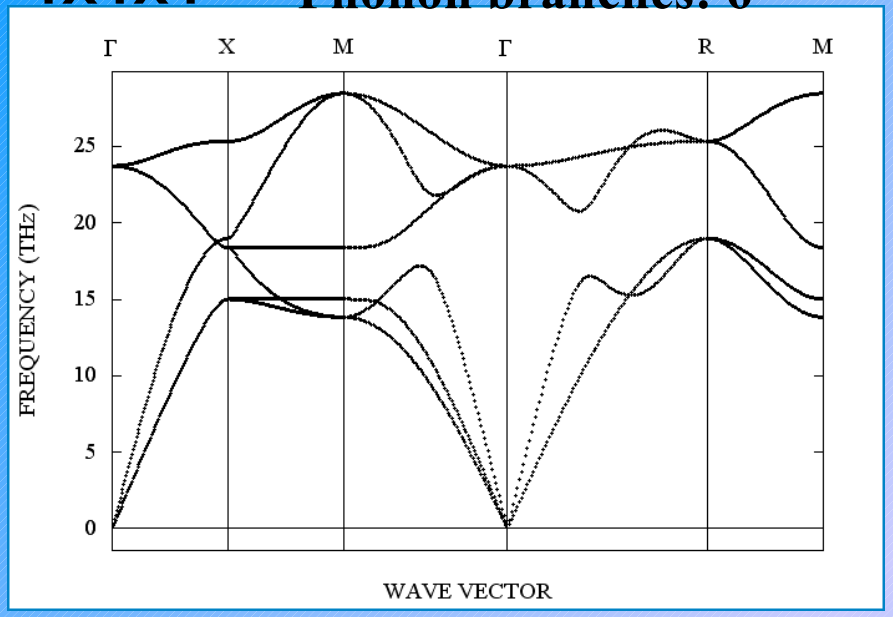
$$\left|\sum_{\mu,i}\frac{\mathbf{e}_i(\mathbf{k},j;\mu)}{\sqrt{M_\mu}}\right|^2$$

Intensity of coherent neutron scattering averaged over orientations (k.e) gives Averaged Filter (AF)

AF

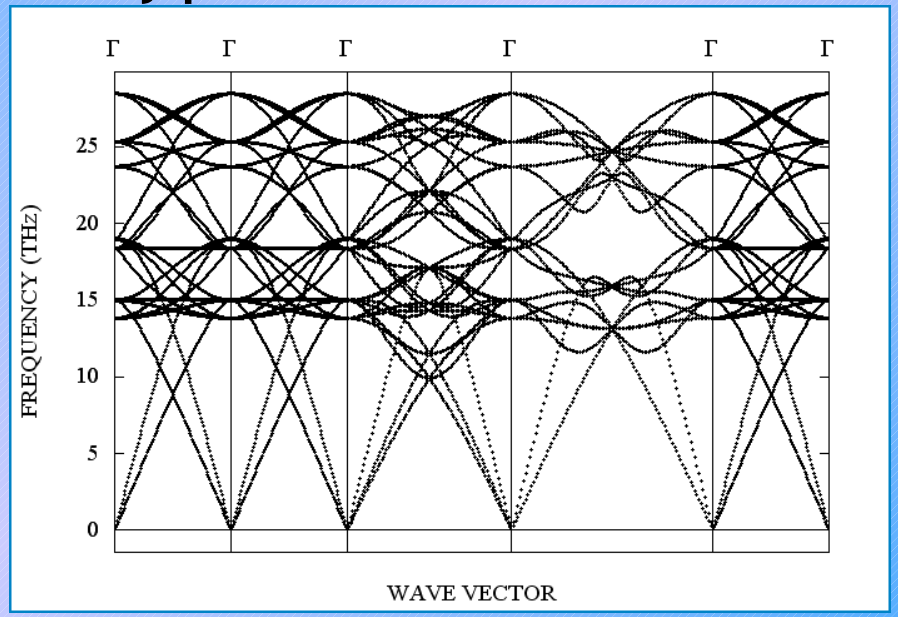
Model crystal AB

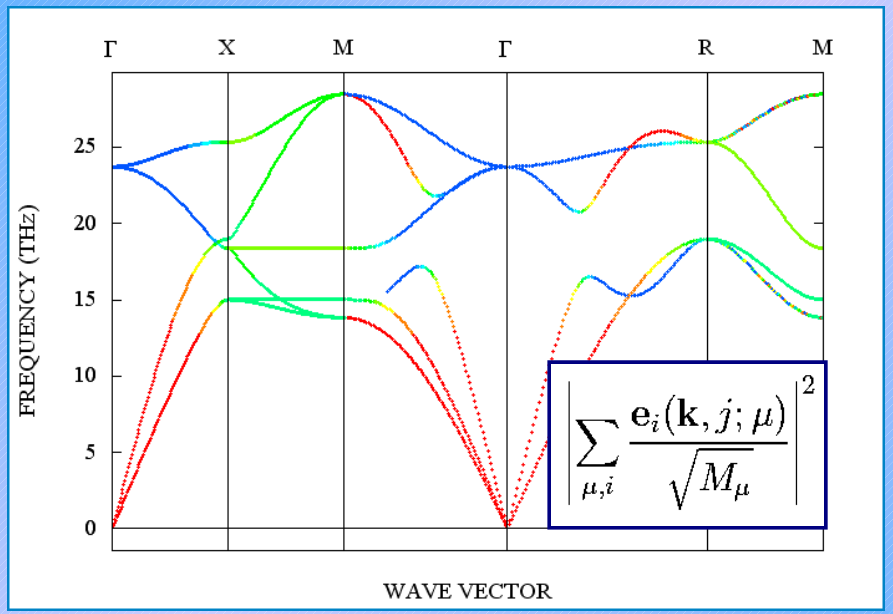
1x1x1 **Phonon branches: 6**

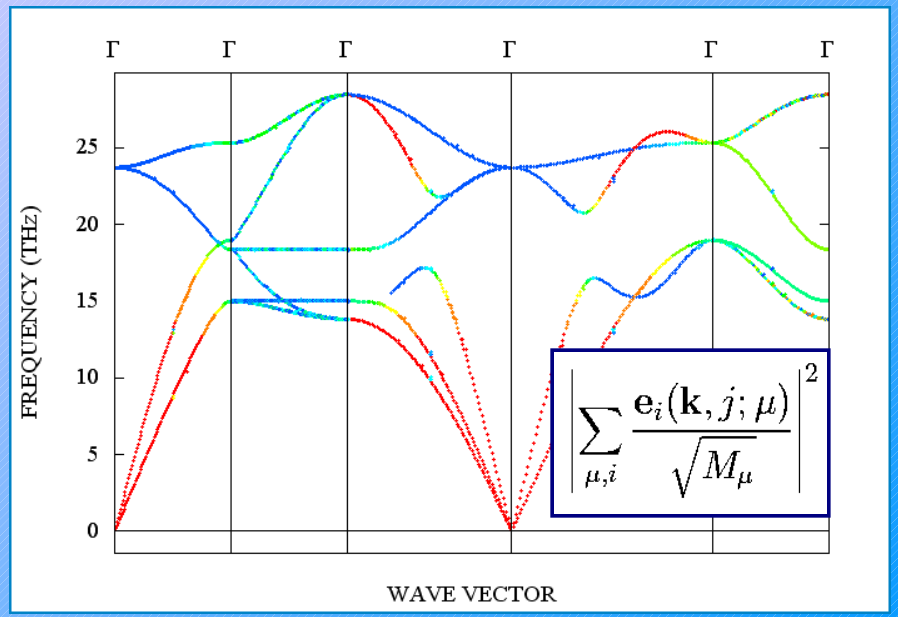


2x2x2 **Phonon branches: 48**

Many phonon modes are inactive



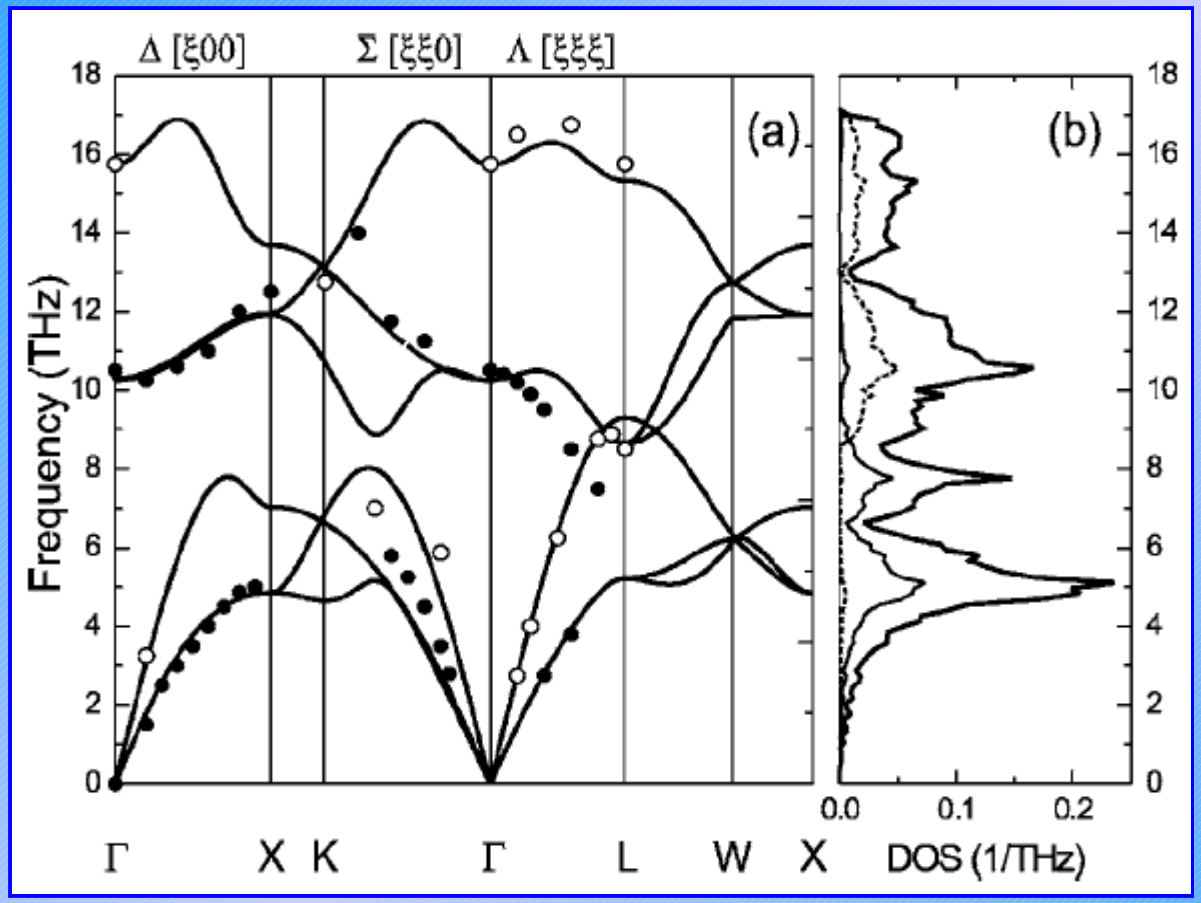




CoO crystal

Strong electron correlation. LDA+U, GGA+U

PAW, GGA+U, Local Coulomb repulsion U = 7.1 eV
Hund's exchange J = 1.0 eV

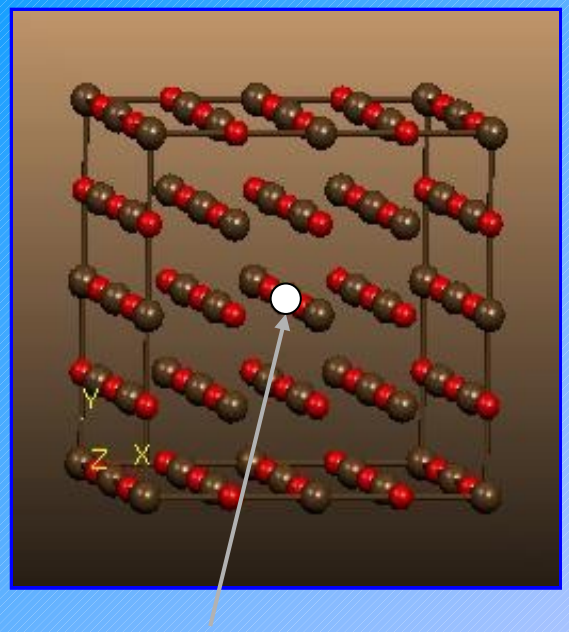


cubic NaCl - type

Phonon dispersion curves calculated for U=0 and J=0 shows imaginary frequenscies

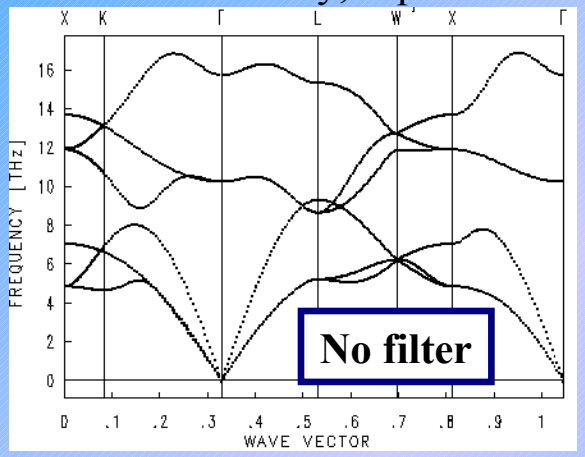
Experiment: J.Sakurai, W.J.L.Buters, R.A.Cowley, and G.Dolling, Phys.Rev. **167**, 510 (1968)
Calculations: U.D.Wdowik, and K.Parlinski, PRB, 75, 104306 (2007)

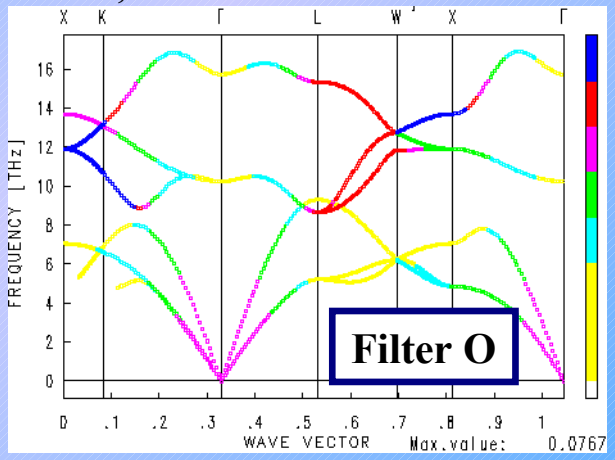
CoO, cubic type of NaCl Crystal CoO with Co vacancy



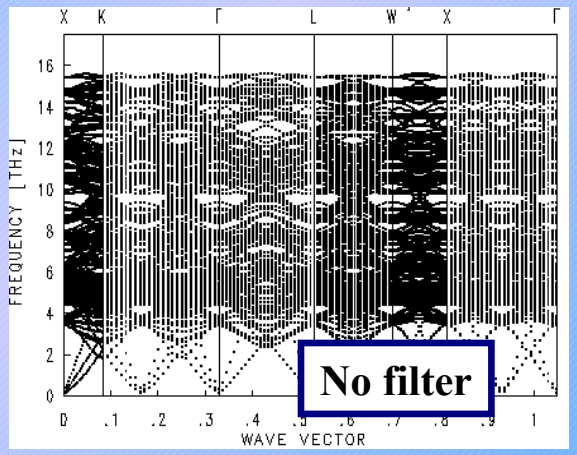
Cobalt vacancy of concentration ~3%

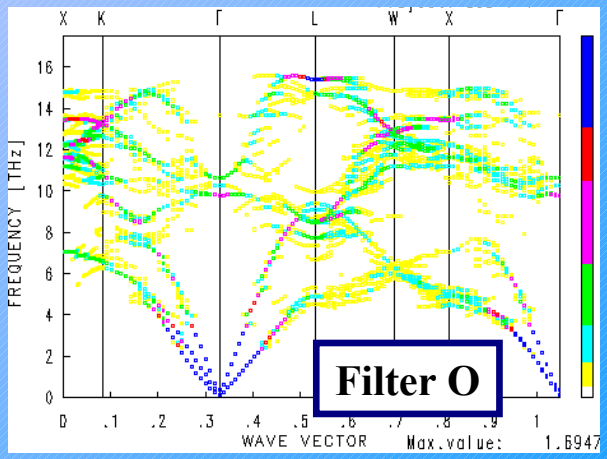
CoO no vacancy, supercell of 64 atoms, 6 modes





CoO with vacancy at Co, supercell of 63 atoms, 189 modes





VASP, LDA+U
Local Coulomb repul. U = 7.1 eV
Hund's exchange J = 1.0 eV

Filter O → **Intensity colour** ~

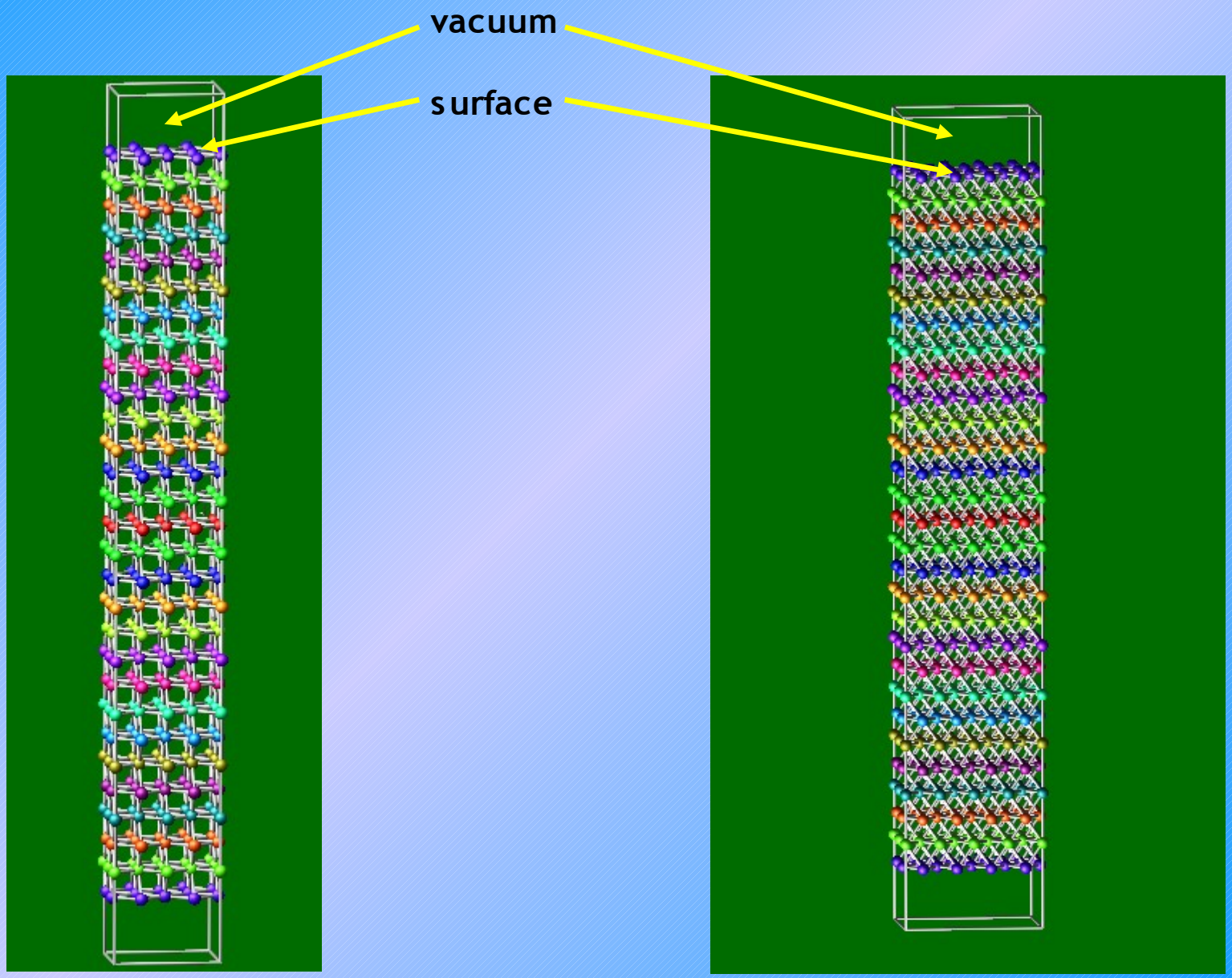
$$\left| \sum_{\mu,i} \frac{\mathbf{e}_i(\mathbf{k}, j; \mu)}{\sqrt{M_\mu}} \right|^2$$

Indicates occupation of phonon branches. Independent on size of unit cell. Depends on B.Z.

U.D.Wdowik, and K.Parlinski, PRB, 75, 104306 (2007)

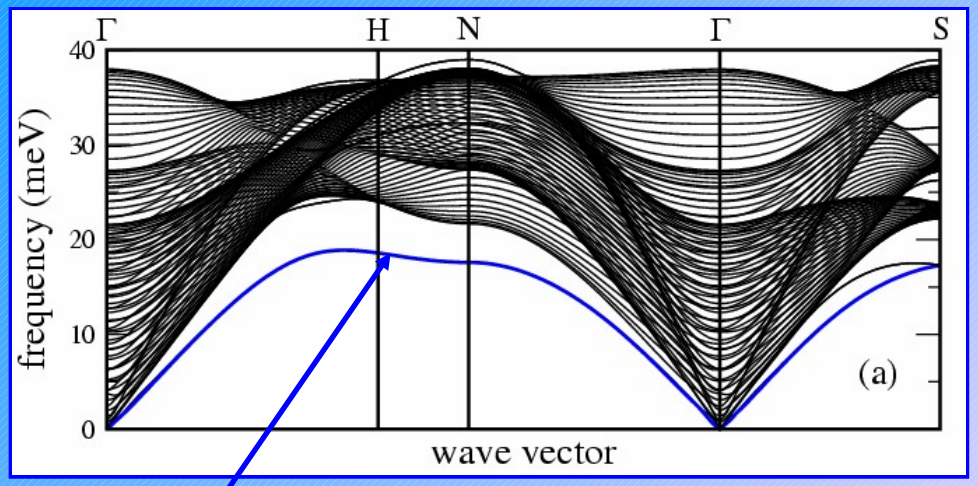
Phonons on surface
Fe (110)

Supercell with 3d periodic boundary conditions for surface calculations



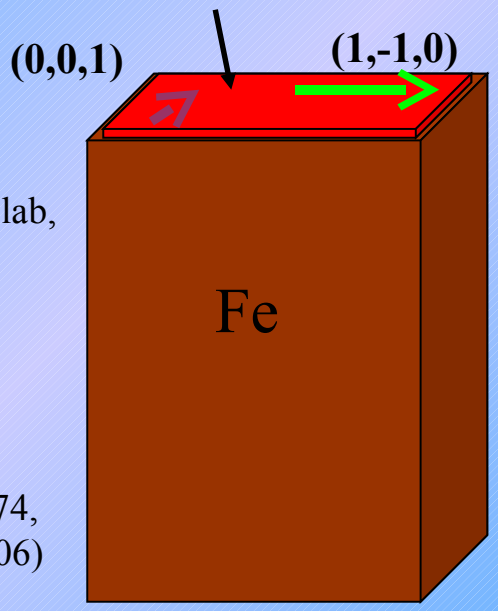
Phonons on Fe (110) surface

Slab of 29 layers of Fe (110)



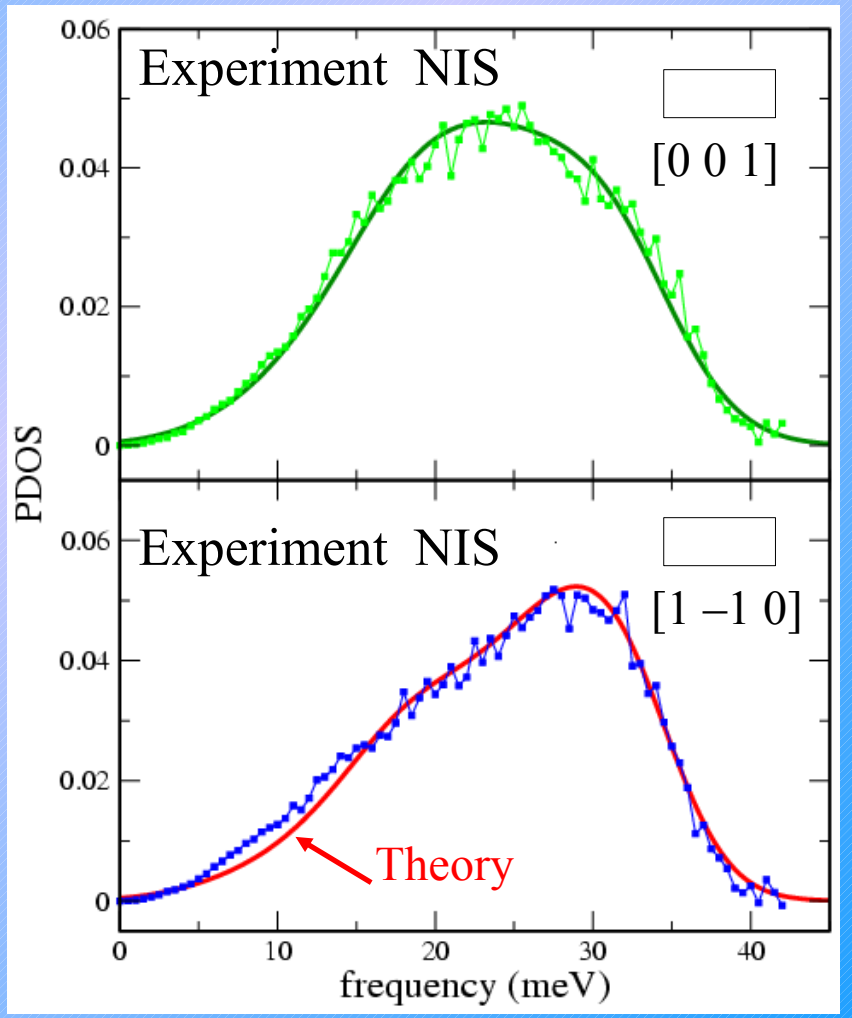
Rayleigh mode

Fe^{57} single crystal



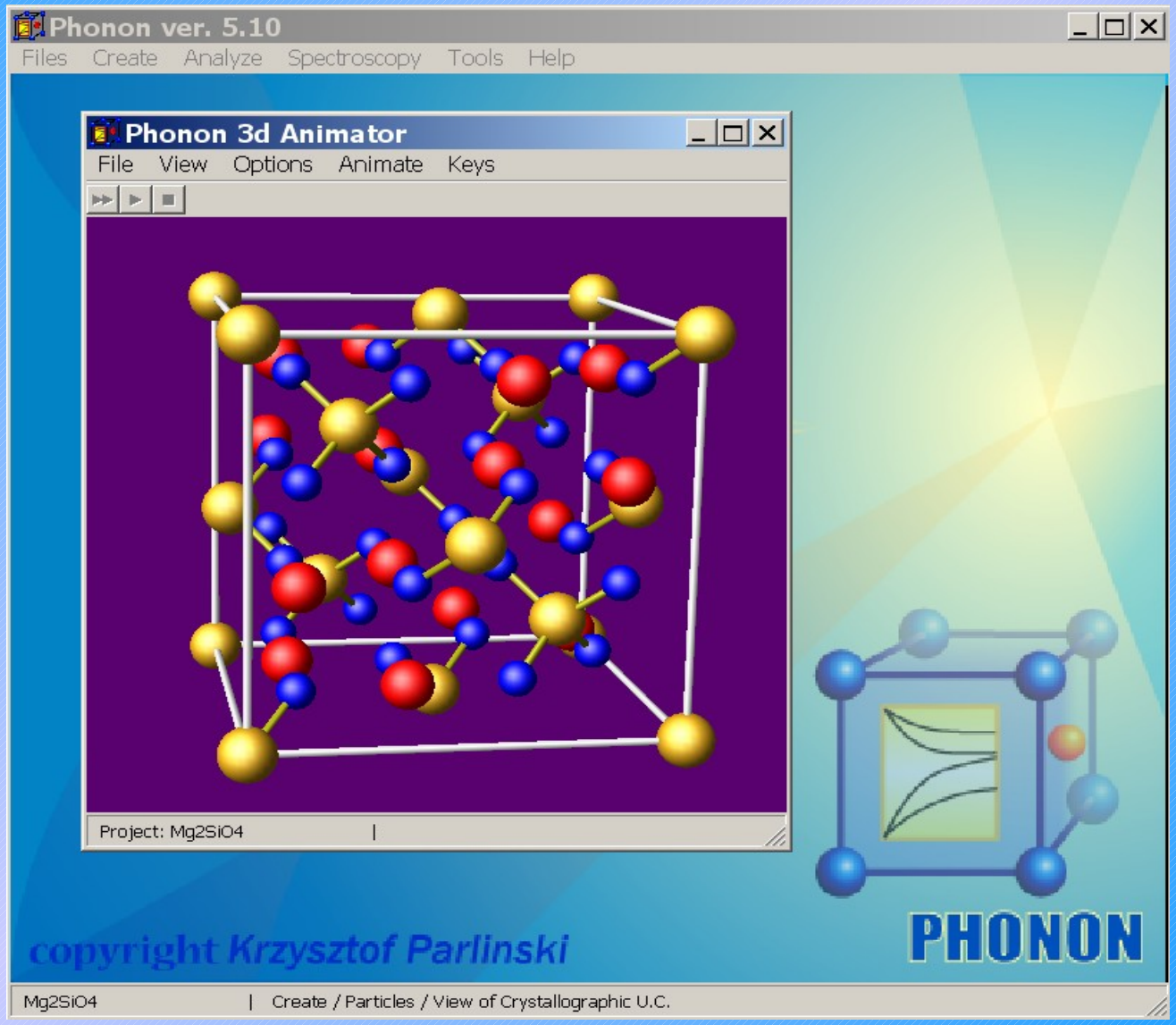
Filling slab approach:
5 layers (110) of surface slab,
6 times 4 slabs of bulk Fe

K.Parlinski, Phys.Rev. B74, 184309 (2006)



T. Ślęzak, J. Łażewski, S. Stankov, K. Parlinski, R. Reitinger, M. Rennhofer, R. Rüffer, B. Sepiol, M.Ślęzak, N. Spiridis, M. Zając, A. I. Chumakov, and J. Korecki, Phys.Rev.Lett. 99, 066103 (2007)

Phonon Software, ver. 5.10



http://www.ComputingForMaterials.com/

Phonon ver. 5.10

http://www.ComputingForMaterials.com/

A new PHONON version 5.10 (32bits), for Windows and Linux.

New option:

- entirely new interface for Windows and Linux
- separated ab initio and modelling options
- automatic updating of lattice constants and atomic positions after DFT optimization
- plot of phonona's intensities by adjustable colours
- easier setting of wavevectors and wave numbers in Brilloun zones
- plot parameters set now by User
- any selected phonon mode can be fully animated by PHONON internal routine
- finds low symmetry space group created by commensurate phonon modes
- plots x-rays scattering with atomic form factor and nuclear inelastic scattering
- calculates dielectric constant (phonon part) and infrared absorption
- provides symmetry analysis of LO/TO

Thank you !