Lattice dynamics with PHONON

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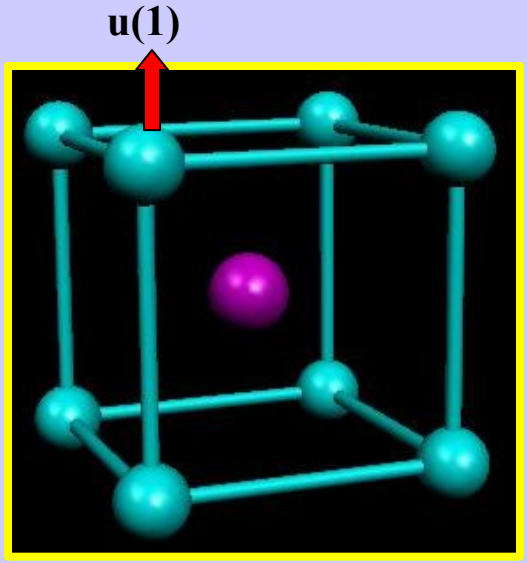
Method to calculate phonons

Direct Method K.Parlinski



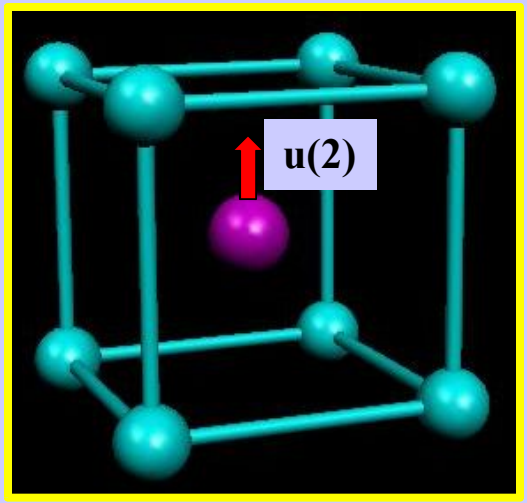
Potential: $V = \frac{1}{2} \sum_{n,m} \Phi(n, m)\, u(n)\, u(m)$

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

Dynamical matrix:

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

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



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

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

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

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

Strategy

DFT codes

VASP **Kresse, Hafner**

MedeA **Wimmer, Wolf**

Wien2k **Blaha, Schwartz**

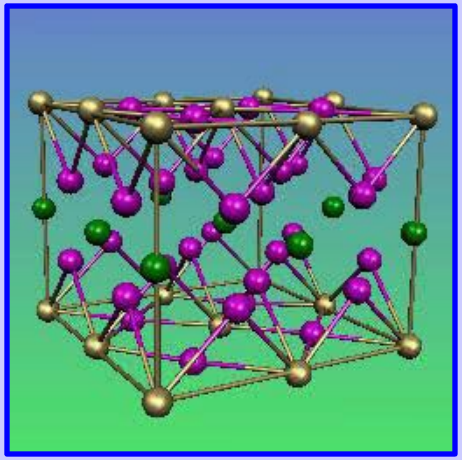
Ab initio calculations for supercell
Structure, energy, HF forces
T = 0 K

Phonon **Parlinski**

HF forces
Direct method

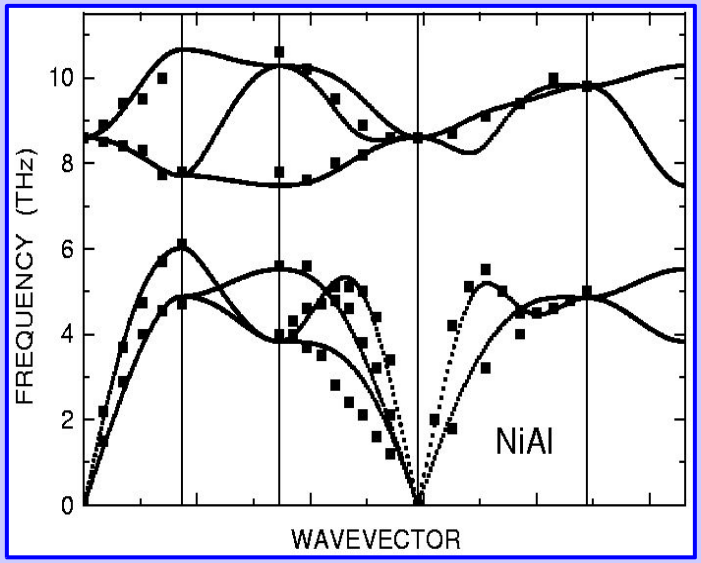
Phonons.
Teperature dependences.
Thermodynamics. Spectroscopies.
Phase diagrams. Phase transitions
T > 0 K

$PuCoGa_5$
T=300K

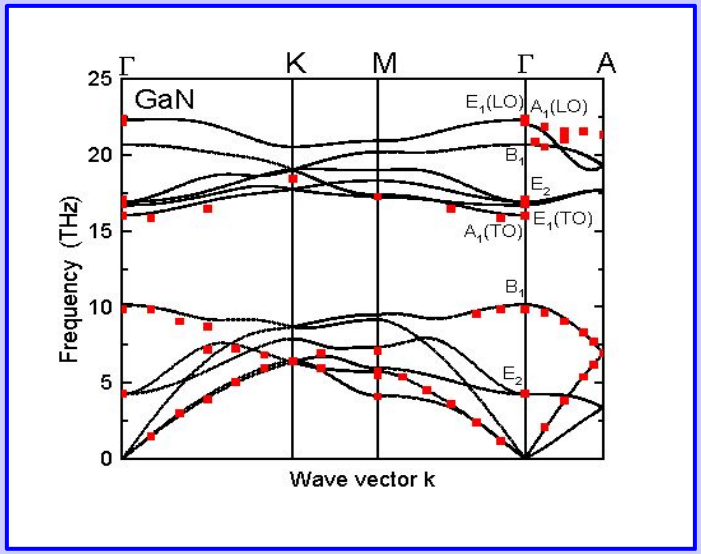


Comparing computer phonon dispersion curves with experiment

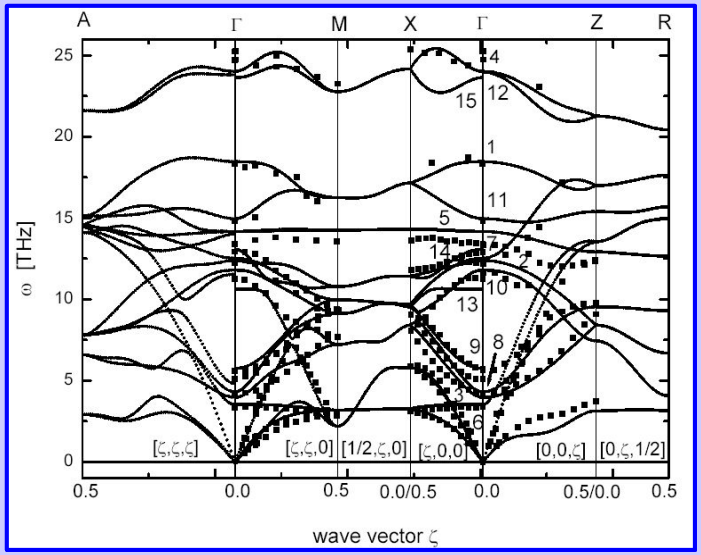
NiAl



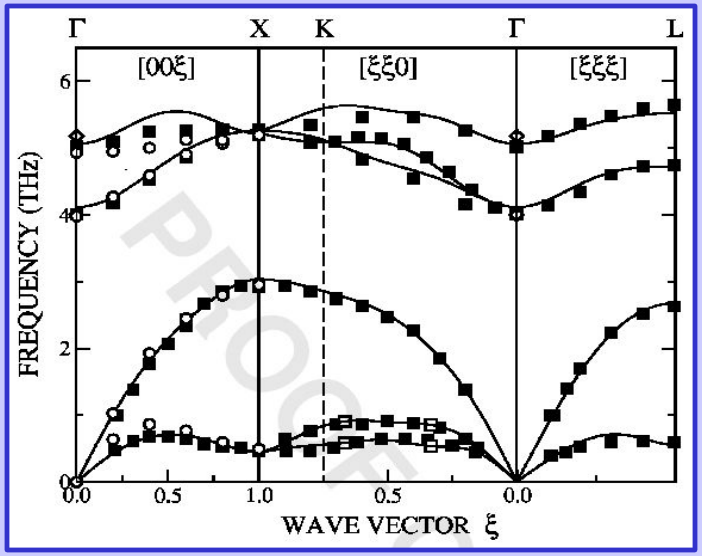
GaN



TiO_2

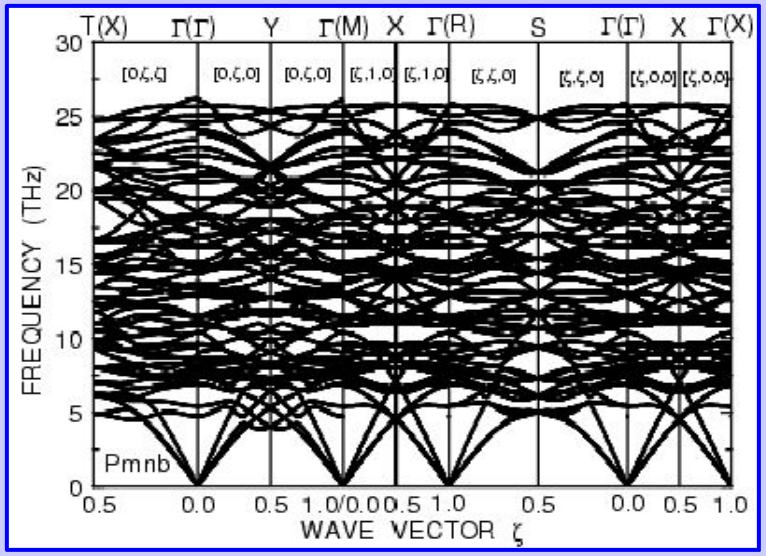


HgSe

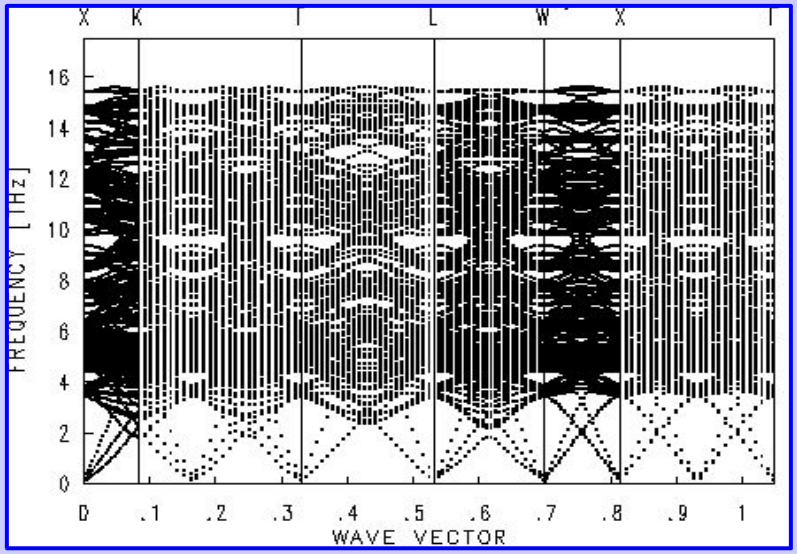


Phonon dispersion curves of more complex systems

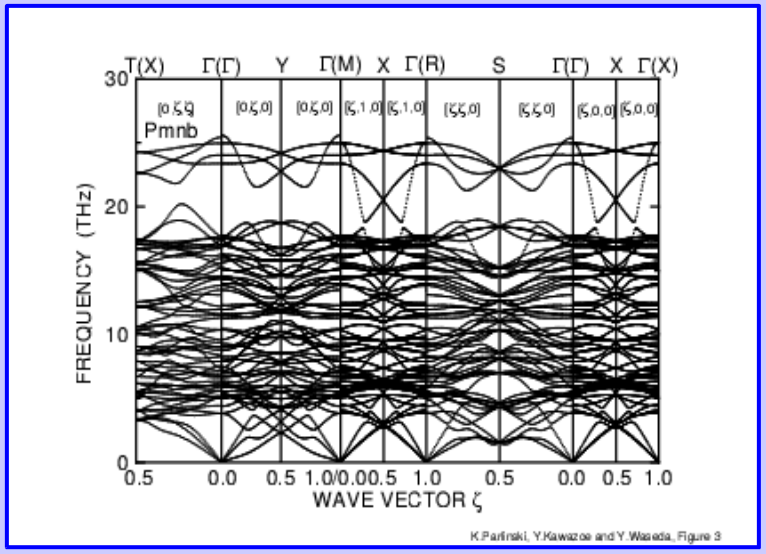
$MgSiO_3$ orthorhombic



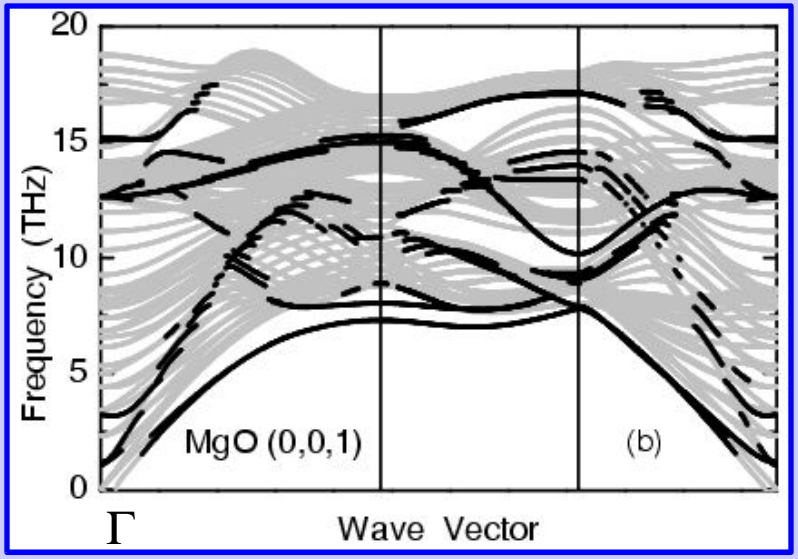
Cubic CoO + one vacancy



$CaTiO_3$ orthorhombic

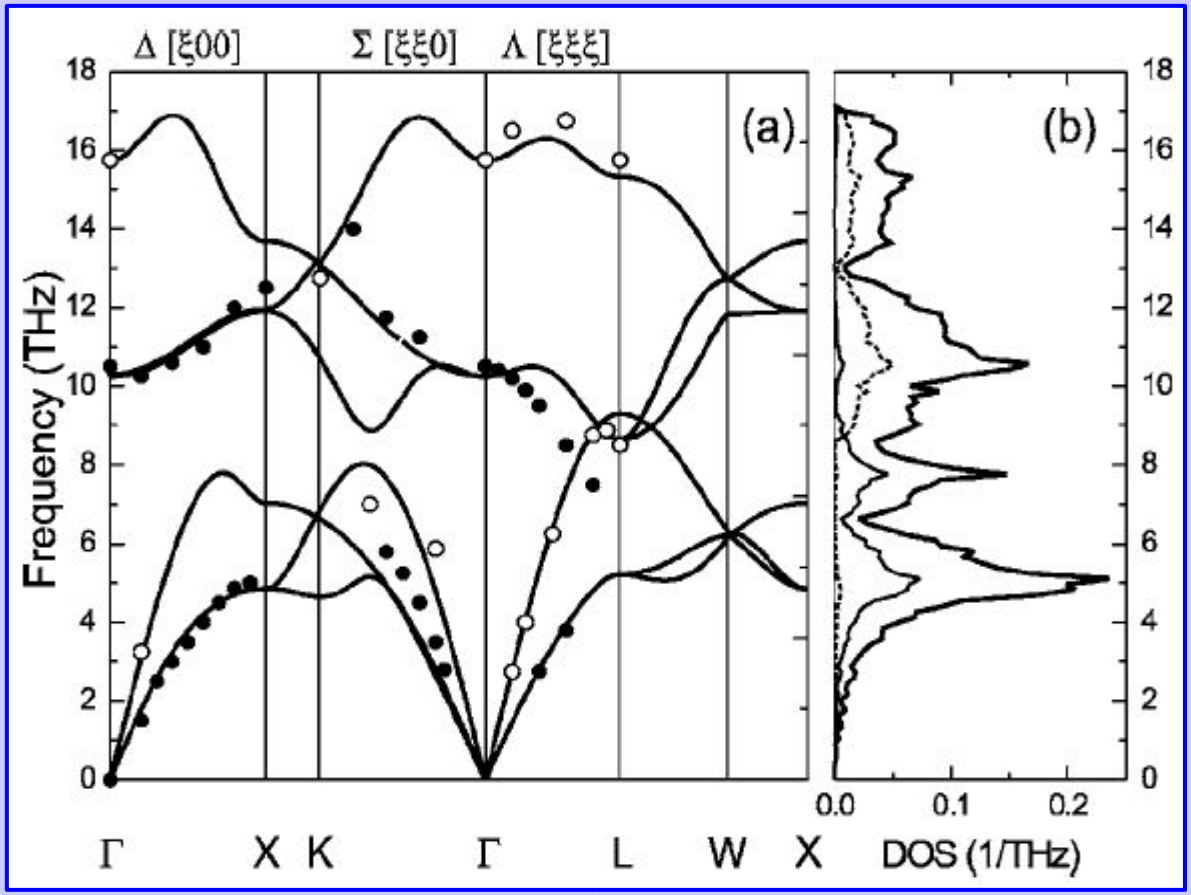


Surface MgO(001) M X Γ



CoO crystal cubic NaCl - type

PAW, GGA+U, Local Coulomb repulsion U = 7.1 eV
Pu: *5f* Hund's exchange J = 1.0 eV



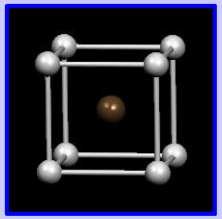
Phonon dispersion curves calculated for U=0 and J=0 shows imaginary frequenscies

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)

Intermetallics NiAl, NiAl-Fe

Supercell 16 atoms
Concentration of defects ~6%

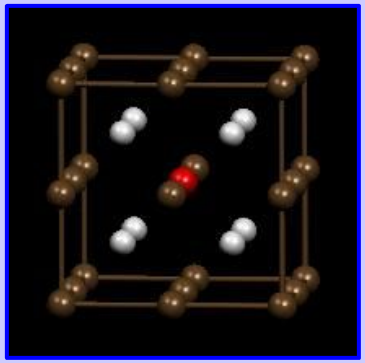
NiAl



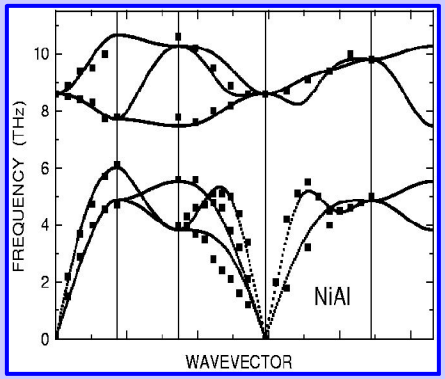
Ni(Fe)Al

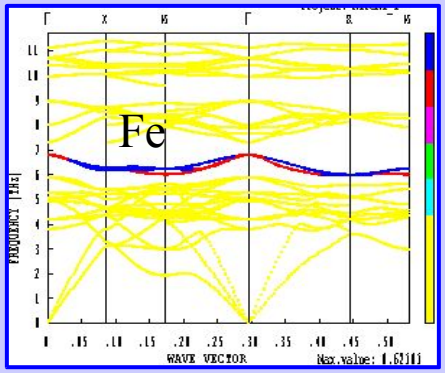
48 modes

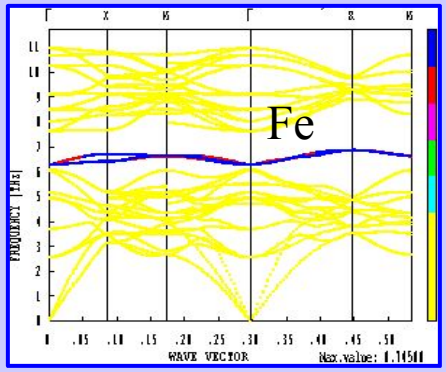
NiAl(Fe)



48 modes



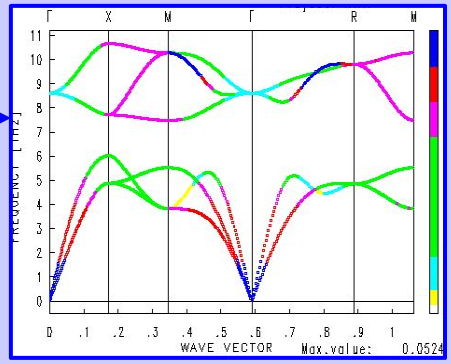


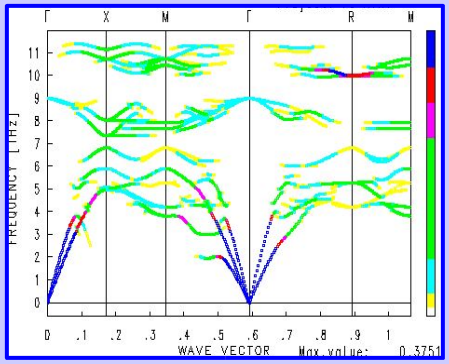


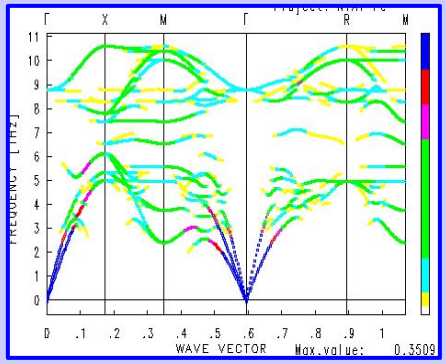
Filter O

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

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







K.Parlinski, P.T.Jochym, O.Leupold, A.I.Chumakov, R.Rueffer, H.Schober, A.Jianu, J.Dutkiewicz, and W.Maziarz, Phys.Rev.B **70** 224304 (2004).

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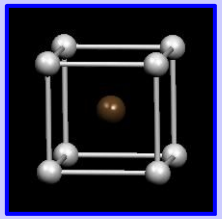
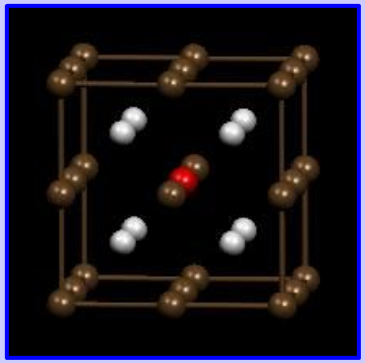
NiAl



Ni(Fe)Al

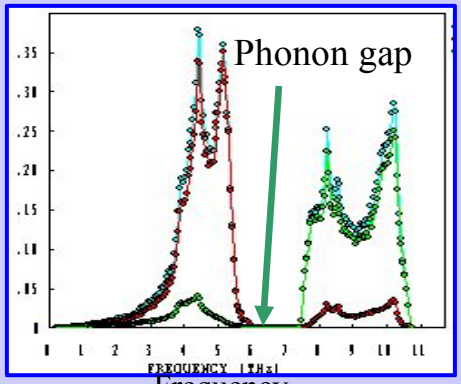
NiAl(Fe)



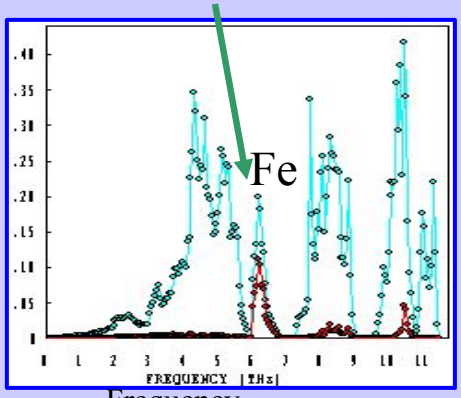
Local mode in phonon gap

Local mode in phonon gap

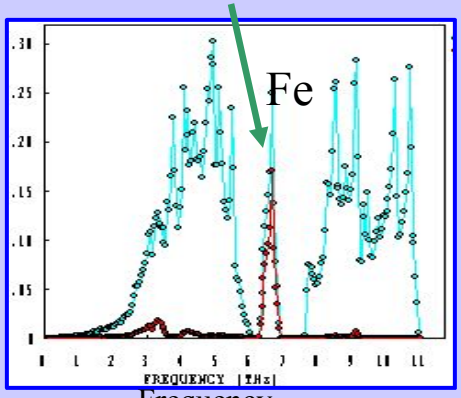
DOS
Phonon
density of states



Frequency

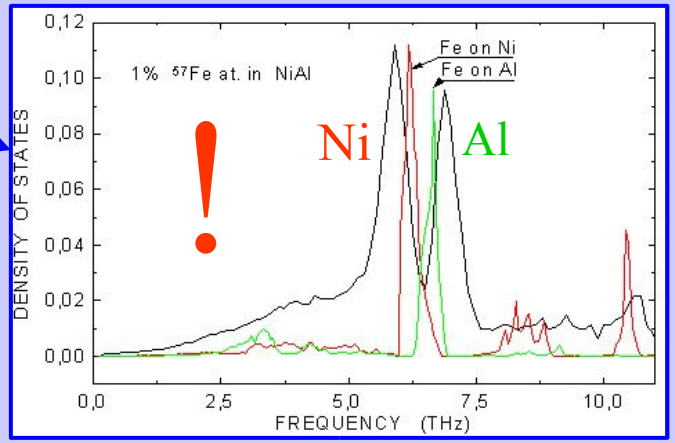


Frequency



Frequency

Measurements of Fe local modes
by Nuclear Inelastic Scattering (NIS).
1% at. ^{57}Fe in NiAl



K.Parlinski, P.T.Jochym, O.Leupold, A.I.Chumakov, R.Rueffer, H.Schober, A.Jianu, J.Dutkiewicz, and W.Maziarz, Phys.Rev.B **70** 224304 (2004).

Quasiharmonic approximation

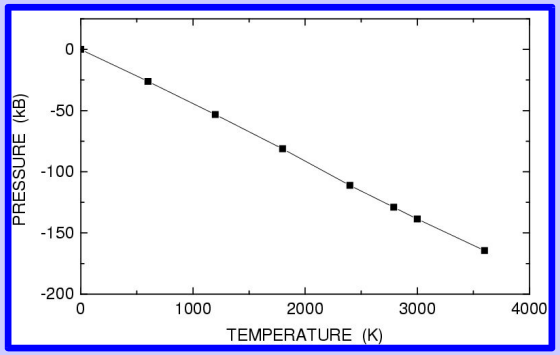
1.Aim: temperature dependence of quantities..... **A = A(T) = ?**

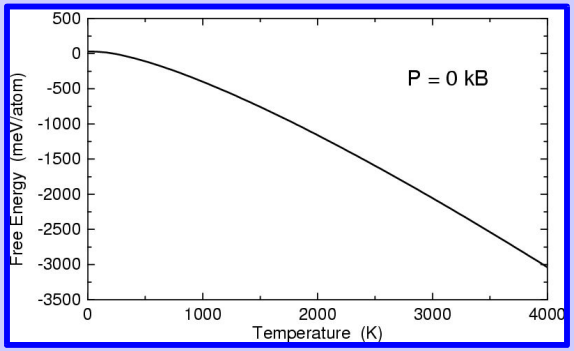
2.Find structure & phonons for different supercell volumes **V**..... **A = A(V)**

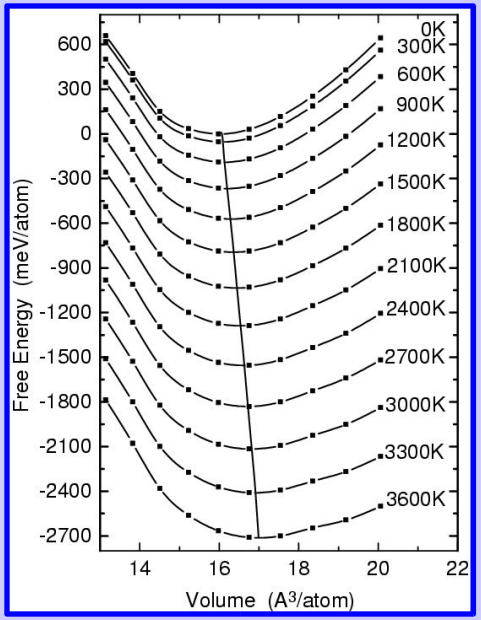
3.Establish relation volume - tempeature via free energy minima... **V = V(T)**

4.Replace..... **A(T) = A(V(T))**

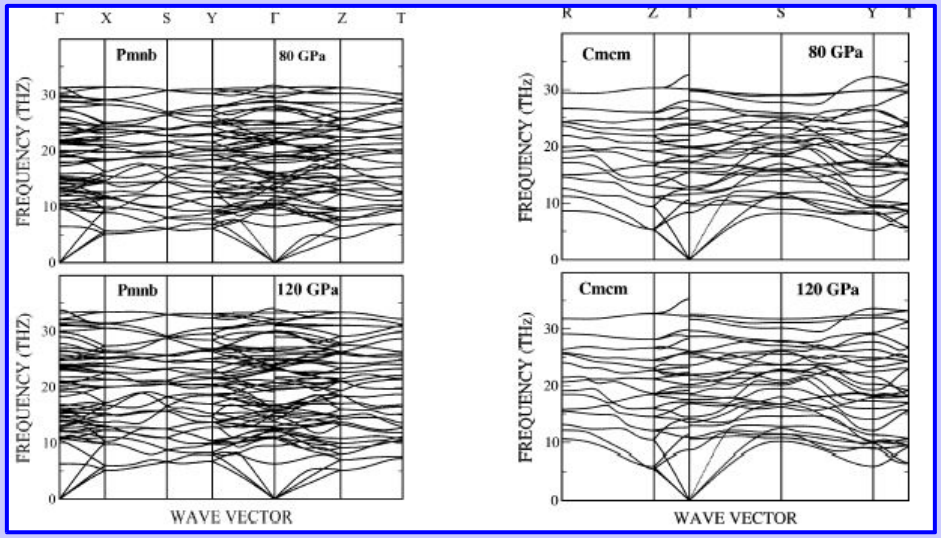
W (element)







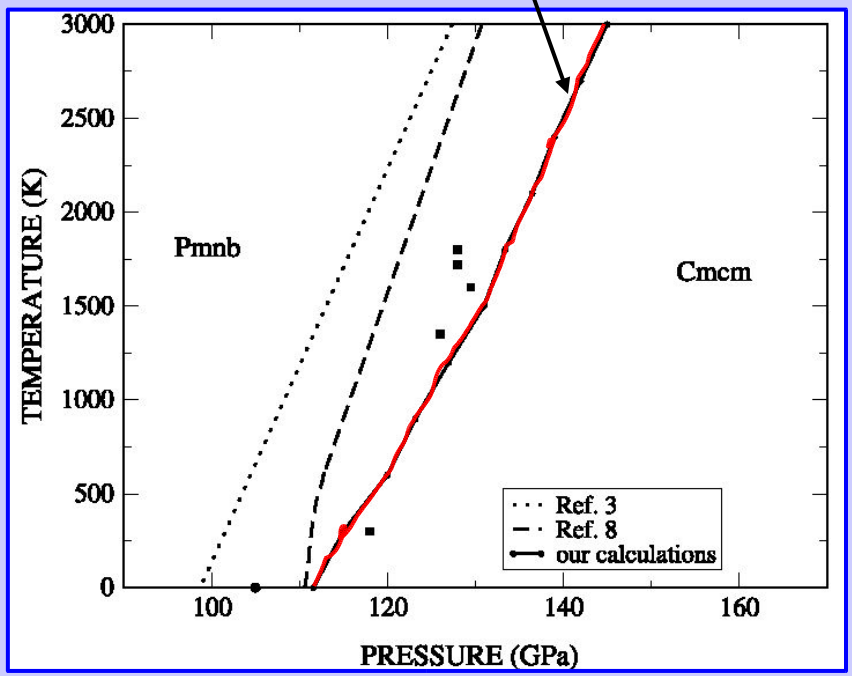
P-T phase diagram of $MgSiO_3$



Perovskite

Post-perovskite

M.Sternik, and K.Parlinski,
J.Phys. Chem. Solids, **67**, 796 (2006).



Pressure experiment:
A.R.Oganov, S.Ono, Nature **430**, 445 (2004)

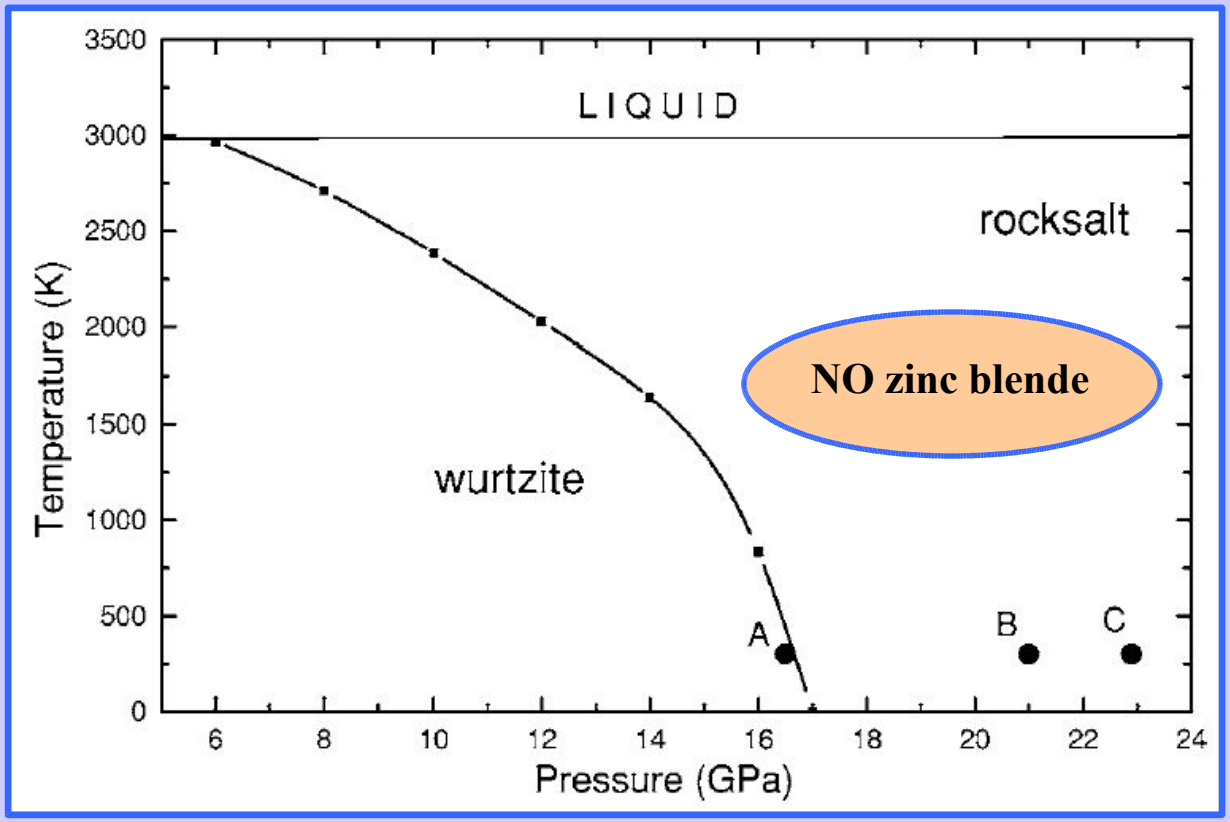
T-P phase diagram of AlN

AlN

Wurtzite
$P6_3mc$ (hexag.)

Zinc blende
F-43m (cubic)

Rocksalt
Fm-3m (cubic)

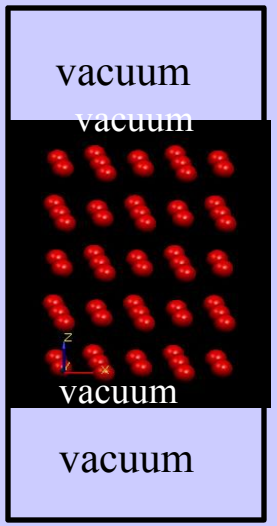


A.Siegel, K.Parlinski and U.D.Wdowik, Phys.Rev. B74, 104116 (2006).

Surface phonons. Filling slab approach*/ **Fe (110)**

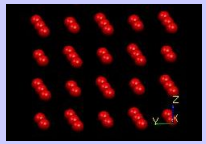
The method devides a thick slab into:

2. Thin slab with surfaces and vacuum: 5Fe
3. Section of bulk crystals: Fe
4. The two results are collected into single system with Hellmann-Feynman (HF) file
5. HF used in PHONON calculations

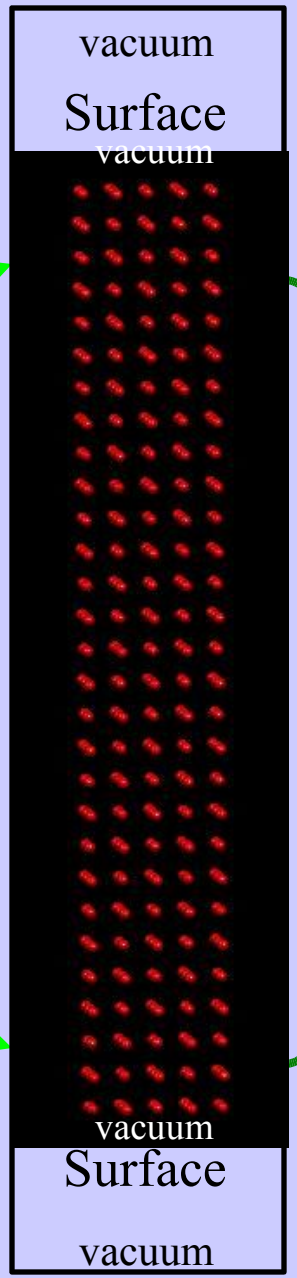


5Fe

Bulk supercell with periodic boundary conditins



Supercell



29Fe layers

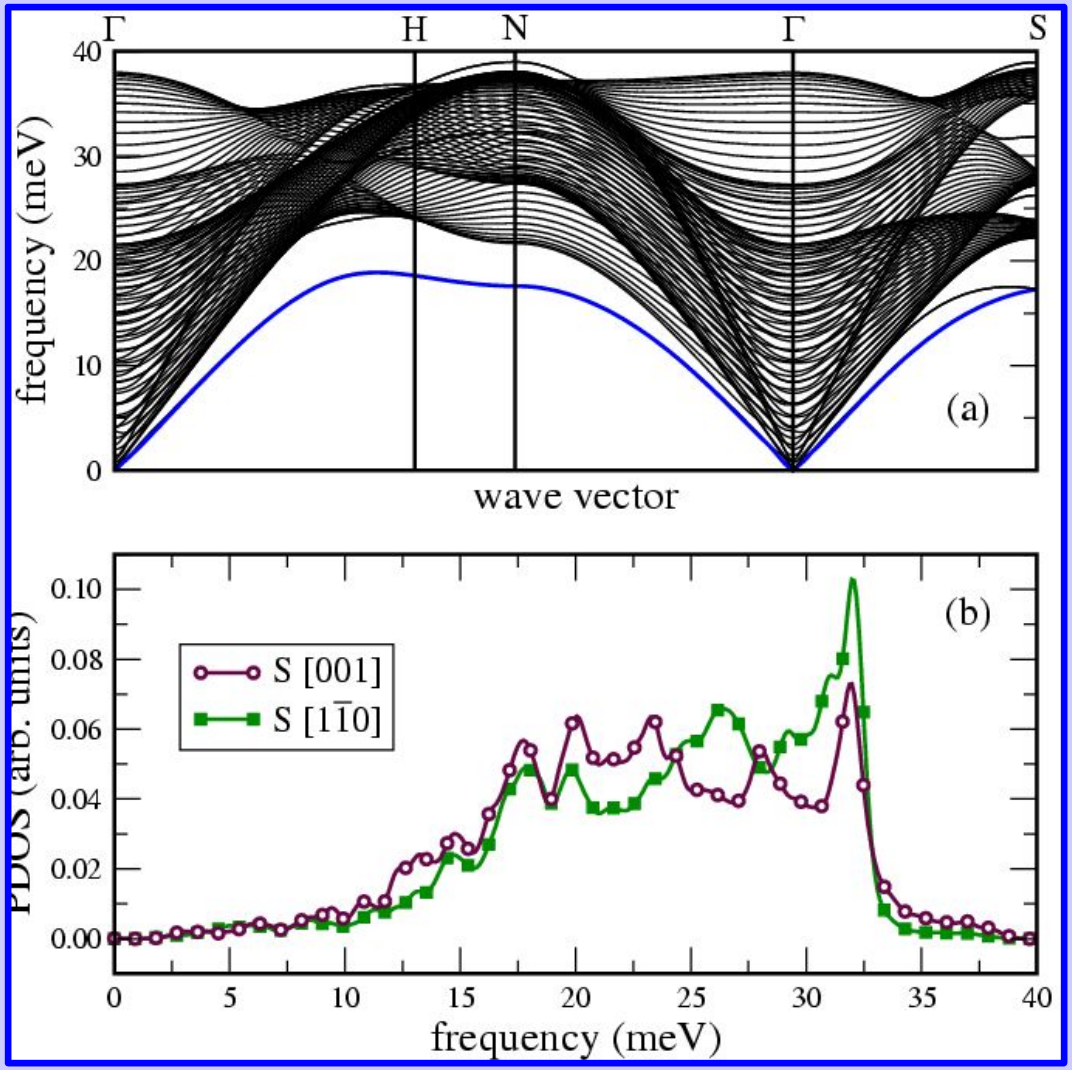
Bulk

6 x supercell

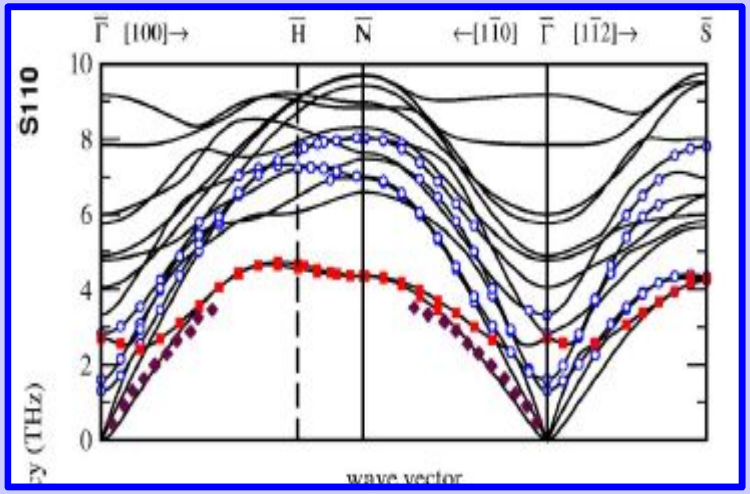
*/ J.Fritsch and U.Schroeder, Phys.Rev. 309, 209 (1999)
E.W.de Wette, Surface Phonons, vol.21, Springer Series, p.67 (1991)

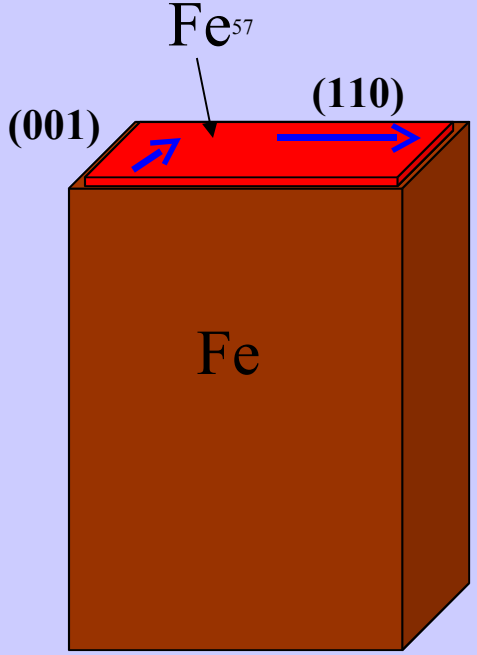
K.Parlinski, Phys.Rev. B74, 184309 (2006)

Slab of 29 layers of Fe (110)



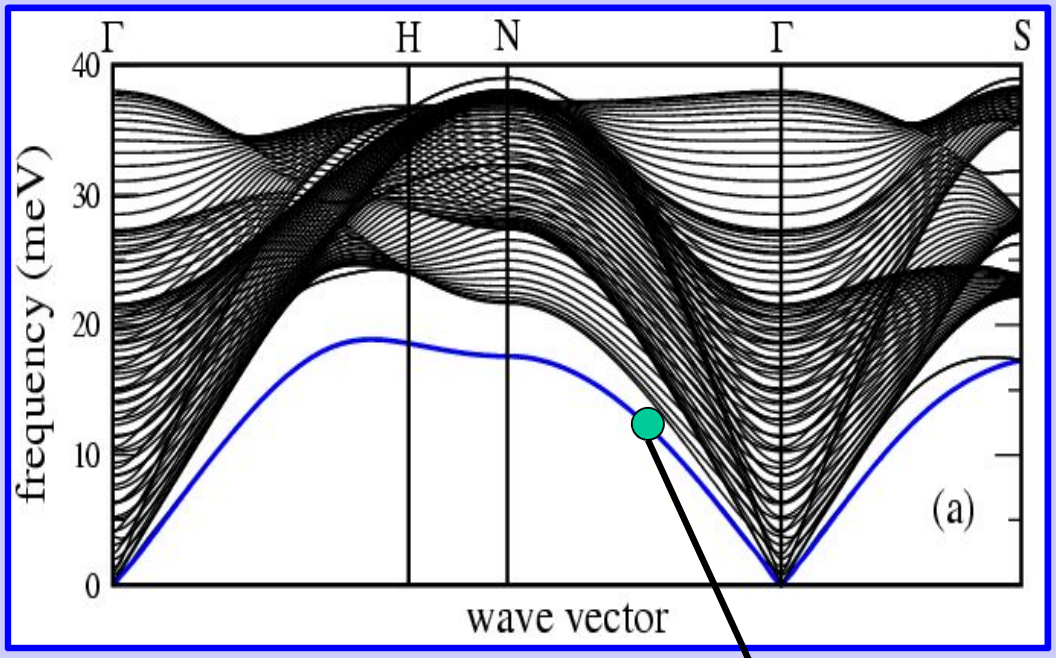
5 layers (110)

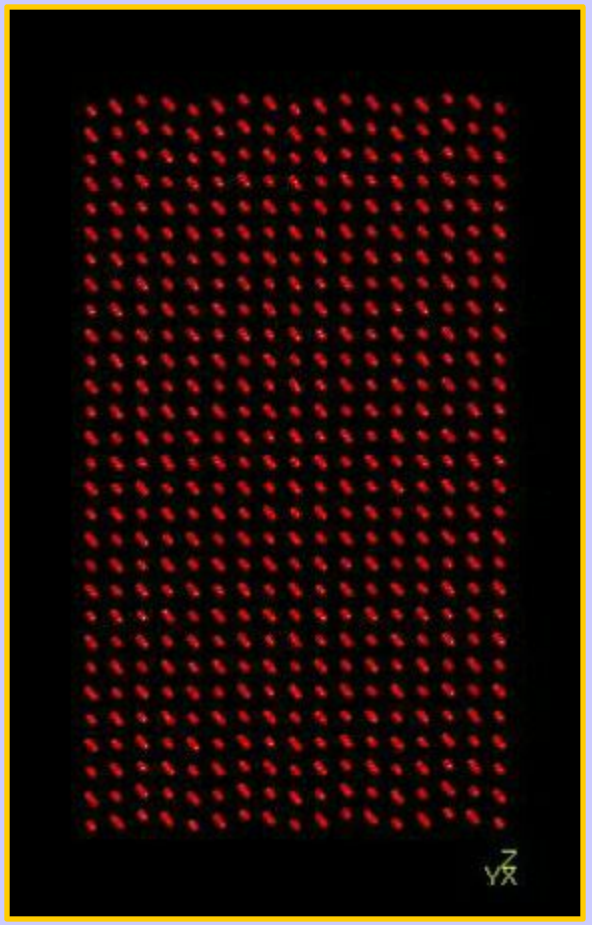




Fe (110) slab

Rayleigh mode of (110) surface in Z direction



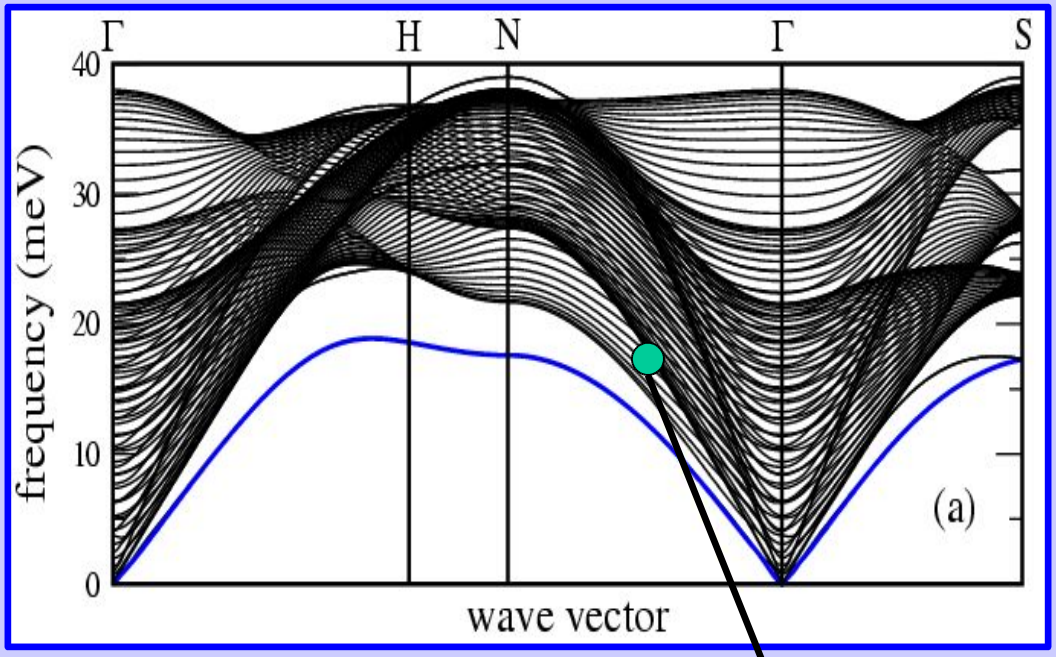


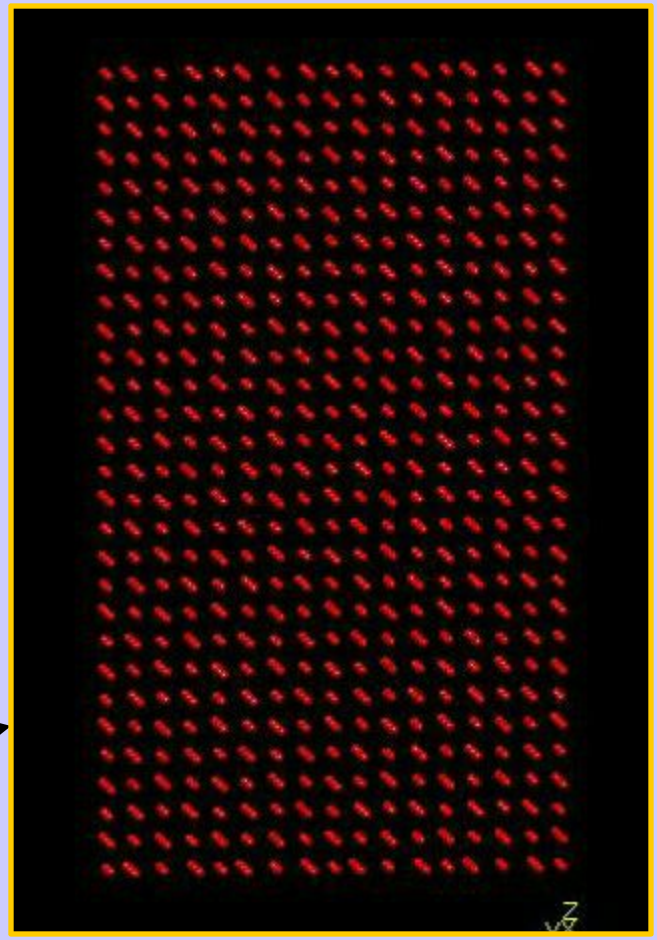
[1,-1,0]

Only surface atoms are vibrating with polarization perpendicular to the surface

Fe (110) slab

Surface mode of (110) surface in [110] direction





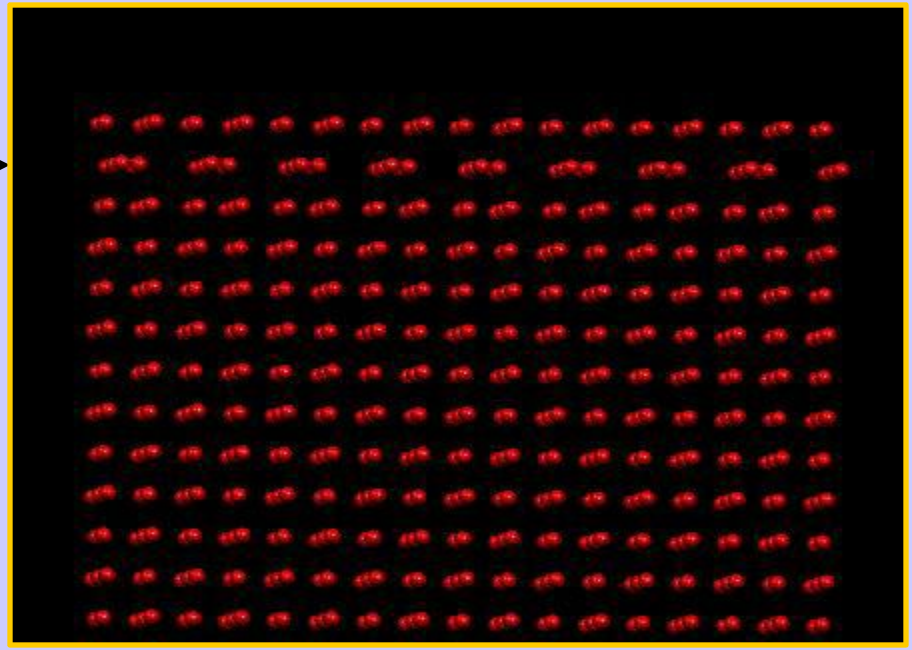
Longitudinal surface mode

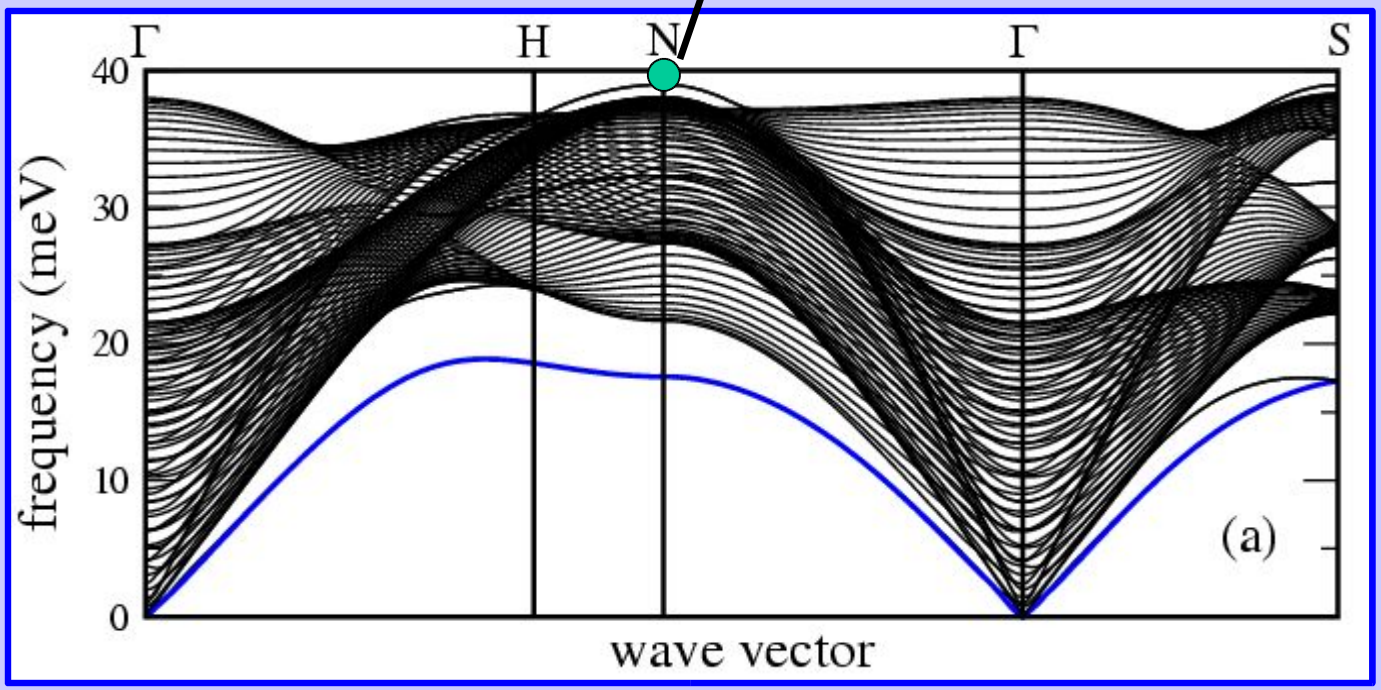
[1,-1,0]

atomic displacements [1,-1,0]

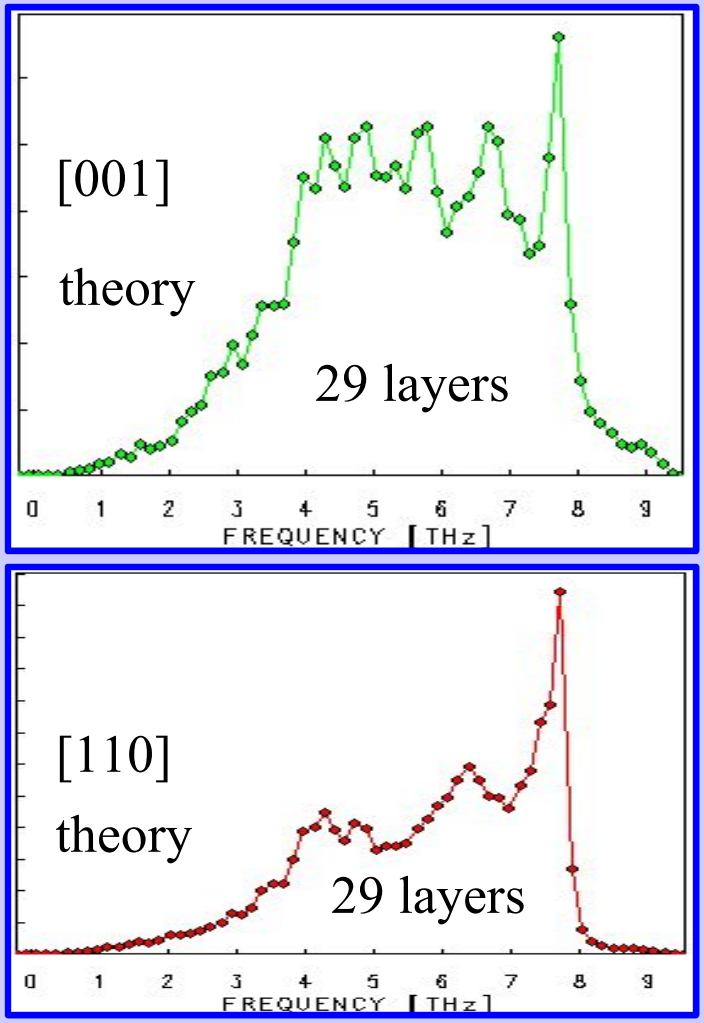
Fe (110) slab

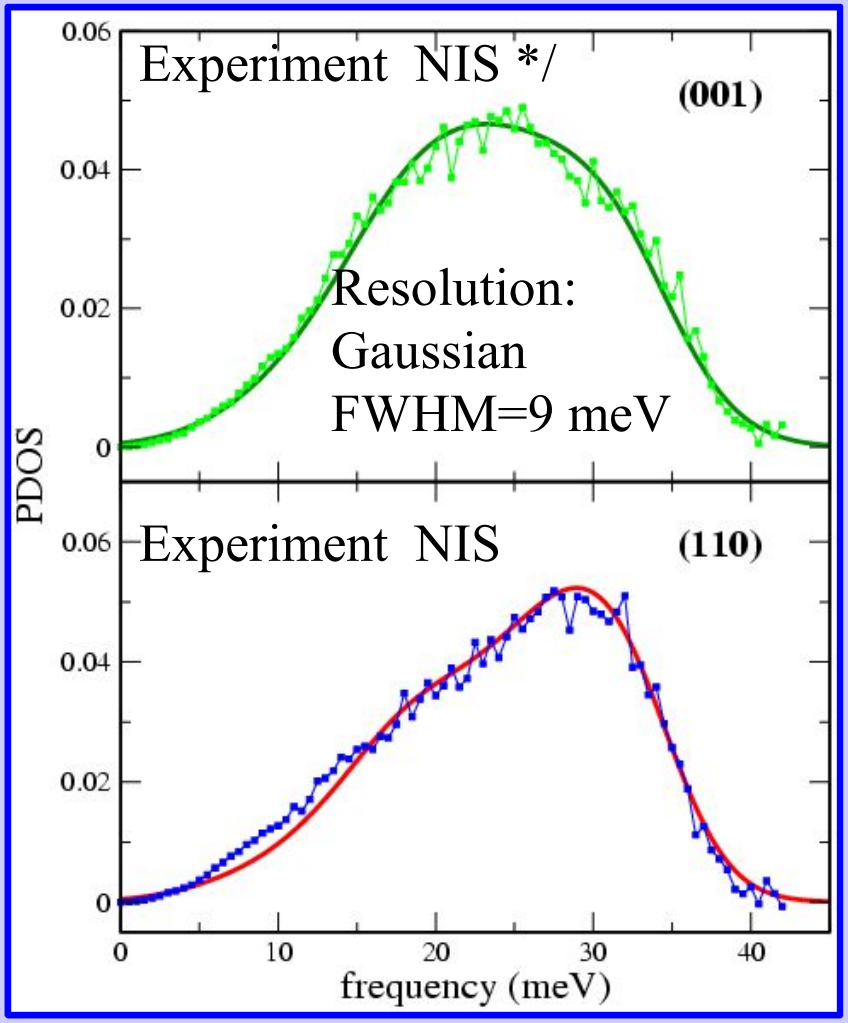
„Local mode" in sublayer with frequency splitted off from phonon band. **New !**





Measured partial density of states of surface monolayer of Fe(110)





NIS - nuclear inelastic scattering (resonanse scattering of γ –ray from Fe^{57}).
Only surface atoms were marked with Fe^{57}

*/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)

What can be calculated using DFT + Phonon ?

Properties:

Phonon dispersion relations $\omega(\mathbf{k},j)$
Phonon intensities (different filters)
Irreducible representations at Γ
Phonon density of states $g(\omega)$
Partial phonon density of states $g_{\mu,i}(\omega)$
Phonon intensities in Brillouin zones
Animate phonon(s) motion
Thermodynamical functions: E, S, F, c_V
Debye-Waller factor $\langle u^2(\mu)\rangle$
Neutron (x-rays) inelastic scattering
LO/TO splitting from $Z^*(\mu)$ and ε
Gruneissen parameters
Fit $\omega(\mathbf{k},j)$ to an experimental data
Displacement pattern for $\omega(\mathbf{k},j)$
Find electronic state coupled to $\omega(\mathbf{k},j)$
Thermal expansion

States:

Ambient: (T = 0 K, P = 0 GPa)
Pressure depend.: (T=0 K, P=0GPa)
(from DFT code)
Temperature depend.: (T>0K, P=0GPa)
(Quasiharmonic approximation, needs phonons)
(T,P) dependence

Systems:

Crystals (230 space groups)
Surfaces (on slab)
Multilayers, interfaces
(Point) defects, small precipitates, etc.

Other procedures:

Searching for soft modes
Construct (T,P) - phase diagram
Phonons in chemical reactions

End

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