



## Calculation of phonons and thermodynamic properties of crystals by Phonon



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### What can be calculated by using Phonon?

#### **Basic functions**

- Force constants  $\Phi_{i,i}(\mathbf{n},\mathbf{m})$
- Impose translational-rotational invariances
- Phonon dispersion relations  $\omega(\mathbf{k},\mathbf{j})$
- Phonon intensities (different filters)
- Irreducible representations at Γ
- Phonon density of states  $g(\omega)$
- Partial phonon density of states for atoms  $g_{u,i}(\omega)$
- Search Brillouin zones for highest phonon intensities
- Animate phonon(s) motion
- Thermodynamical functions: Internal energy E, Entropy S, Free energy F, Heat capacity c<sub>v</sub>
- Thermal mean displacement tensor for atoms  $\langle u^2(\mu) \rangle$
- Neutron coherent and incoherent inelastic scattering of neutrons (x-rays) (multiphonon for incoherent scattering)
- LO/TO splitting from  $Z^*(\mu)$  and  $\varepsilon$ .

## What can be calculated by using Phonon ?

#### **Advanced functions**

- Generate POSCAR and DISCAR for VASP
- Generate structural data file for Wien2k
- Restore symmetry in hexagonal crystals
- Fit phonon dispersion curves  $\omega(\mathbf{k}, \mathbf{j})$  to a set of experimental data
- Generate displacements corresponding to a single, or a set of phonon diplacements.
- Find electronic states strongly coupled to a particular phonon

#### **Pressure dependences**

- Pressure dependence of phonon dispersion relations  $\omega(\mathbf{k}, \mathbf{j})$
- Pressure dependence of phonon density of states  $g(\omega)$
- Gruneissen Parameters
- Pressure dependence of thermodynamical functions
- Pressure dependence of thermal mean displacement tensor for atoms  $<\!\!u^2(\mu)\!\!>$

### What can be calculated by using Phonon ?

#### **Quasiharmonic approximation**

- Temperature dependence of phonon dispersion relations  $\omega(\mathbf{k}, \mathbf{j})$
- Temperature dependence of phonon density of states  $g(\omega)$
- Thermal expansion

#### **Other procedures**

- Searching for soft modes and displacive phase transitions
- Describing the phase transition line, and (T,P) phase diagram
- Phonon contribution to chemical reactions

### Systems which can be calculated by Phonon

### Systems:

- Crystals (230 crystallographic space groups)
- Surfaces (on slab)
- Multilayers
- Interfaces
- Point defects
- Small precipitates
- etc.

System is represented by a **supercell** with periodic boundary conditions. **Basic theory** 

## **Direct method theory**

## **Tutorial for Phonon**

### Direct Method K.Parlinski

**u(1)** 



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

> Φ(n, m) – force constant matrix 3x3 between atom n and m



**u**(2)

**Phonons:** 
$$\omega^2(\mathbf{k}) \mathbf{e}(\mathbf{k}) = \mathbf{D}(\mathbf{k}) \mathbf{e}(\mathbf{k})$$

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

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

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

### Method to calculate phonons

## Part 1 Basic functions

## **Calculation of force constants**

## **Tutorial for Phonon**

#### **Create/Symmetry & Unit Cell** - Construct the unit cell of your system

- Find crystallographic *space group No*
- Find approximate *lattice constants*
- Find *number of non-equivalent atoms*. Set them as *displacive*.

### Example: NiAl

Space group: Pm3m

Lattice constant: a = 2.8920 A

Number of non-equivalent atoms: 2

<u>Use optimized by</u> <u>the DFT program</u> <u>the crystallographic</u> <u>unit cell data</u>

221 Pm-3m O_h^1 Cubic	
Lattice Constant A (angstrems):	2.89235724
Lattice Constant B (angstrems):	2.89235724
Lattice Constant C (angstrems):	2.89235724
Angle Alpha (degrees):	90.0000000
Angle Beta (degrees):	90.0000000
Angle Gamma (degrees):	90.0000000
Number of non-equivalent elastic	particles:

#### **Create/Particles/Particle positions** – Insert atoms into unit cell

- Find *non-equivalent* positions of atoms of the system. Symmetry elements of space group will generate from non-equivalent atom ALL remaining (equivalent) atoms.
- Activate displacive coordinates by (x,y,z)=(1,1,1). Deactivate rotational coordinates (Rx,Ry,Rz)=(0,0,0).
- Insert masses of atoms M.

#### Example: NiAl

#### Non-equivalent atoms are at positions:

Atom	X	У	Z
Ni	0.0	0.0	0.0
Al	0.5	0.5	0.5

Masses: 
$$M_{ni} = 58.690$$
 amu,  $M_{al} = 26.982$  amu





#### **Create/Particles/<u>Electric Charges</u> – Insert Born effective charges**

- Calculate tensors of Born effective charges by Berry phase method for *non-equivalent* atoms. Insert them into **Phonon**. Only independent components should be inserted. Check them in Report.
- Find electronic dielectic constants. Insert it into **Phonon**.

## Example: NiAl

Dielectric constants:  $\epsilon = infinity$ NiAl is a metal, therefore effective charges are not needed



On each supercell S periodic boundary conditions are imposed

Create/Interaction Range/Supercell - Enlarges unit cell to supercell You must define transformation matrix L



#### Exact wave vectors

Wave vectors, which are commensurate with the size of supercell, provide phonon frequencies being ,,exact", <u>independent</u> on the interaction range.

> Special points: Γ, Χ, Μ, R





Example: NiAl

Select 2x2x2 supercell Exact points:  $\Gamma$ , X, M, R

Exact wave vectors are listed in Phonon's Report

> Supercell Exact points



1х1х1 Г



2x2x2 Г, Х, М, R

## Supercell may lower the symmetry of the crystal space group !!!

Pm3m



Supercell 1x1x1

#### P4/mmm



Supercell 1x1x2

Supercell symmetry (P4/mmm) contains only part of Pm3m crystal symmetry elements

If one breaks the crystal symmetry by supercell then:

• phonon dispersion curves have different symmetries and mode degeneracies

• you may **restore symmetry** from supercell symmetry to crystal symmetry.

But we advice to do it only for hexagonal structures

### How to select supercell size and shape?

- 1. Shape of supercell should be close to sphere
- 2. On supercell surface force constant parameters should be 3 order of magnitudes smaller then magnitude of on-site force constants
- 3. It is better if supercell defines more "exact" points

```
Export:
POSCAR = *.d23 for VASP
DISCAR = *.d44 for VASP
Wien2k_position = *.d45 for Wien2k
```

## Displace non-equivalent atoms in non-equivalent directions and calculate HF forces in single ionic loop

- all necessary displacements are listed in Report, \*.d44 file = DISCAR, and Wien2k\_position = \*.d45
- for each displacements calculate HF forces by DFT program

#### **Create/Hellmann-Feynman file/Import H-F File** - name of HF file

NiAl AL	ustenite c	ubic Pm3m	No=221 (	0_h^1) nski (March	2002)		
! Supercell: cubic 2x2x2 (16 atoms)							
Pseudor	potentials	: PAW					
Pressure	ector mesh	R #K: 6X6X	6				
HF for	ces calcul	ated with	#k: 6x6x	6			Commonto
! Maxima	1 HF force	: 0.00000	0 eV/ang	Read and			Comments
Displac	cements: 0	.03 ang,	+ and -,	4 files	IC atoms)		
Ground	state ene	-10	506142 eV	V/cubic unit	cell		
! Lattice	e constant	s of sc 2	x2x2:	a=5.784714	A		
Name	X	Y	z	FX	Fy	FZ	
	0.75000	0.75000	0.75000	0.005186	0.000000	0.000000	Displacement $(Ux,0,0,)$ of Al
1 A	0.75000	0.75000	0.75000	-0.255349	0.000000	0.000000	
2 A	0.25000	0.75000	0.75000	0.068651	0.000000	0.000000	
3 A 4 A	0.25000	0.25000	0.75000	0.009486	0.000000	0.000000	
5 A	0.75000	0.75000	0.25000	-0.004995	0.000000	0.000000	
6 A	0.25000	0.75000	0.25000	0.009486	0.000000	0.000000	
A A	0.75000	0.25000	0.25000	-0.00664/	0.000000	0.000000	
9 N	0.00000	0.00000	0.00000	0.021497	0.021470	0.021470	► Hf forces for Al displaced
10 N	0.50000	0.00000	0.00000	0.020371	-0.019620	-0.019620	
11 N	0.00000	0.50000	0.00000	0.021497	-0.021470	0.021470	
13 N	0.00000	0.00000	0.50000	0.021497	0.021470	-0.021470	
14 N	0.50000	0.00000	0.50000	0.020371	-0.019620	0.019620	
15 N	0.00000	0.50000	0.50000	0.021497	-0.021470	-0.021470	
16 N	0.50000	0.50000	0.50000	0.0203/1	0.019620	0.019620	Displacement (Ux $0.0$ ) of Ni
1 A	0.75000	0.75000	0.75000	0.020507	0.019702	0.019702	
2 A	0.25000	0.75000	0.75000	0.021674	-0.021414	-0.021414	
3 A	0.75000	0.25000	0.75000	0.020507	-0.019702	0.019702	
5 4	0.75000	0.75000	0.25000	0.020507	0.019702	-0.019702	
6 A	0.25000	0.75000	0.25000	0.021674	-0.021414	0.021414	
7 A	0.75000	0.25000	0.25000	0.020507	-0.019702	-0.019702	
8 A 9 N	0.25000	0.25000	0.25000	-0.198509	0.021414	0.021414	Hf forces for Ni displaced
10 N	0.50000	0.00000	0.00000	0.015532	0.000000	0.000000	
11 N	0.00000	0.50000	0.00000	-0.005057	0.000000	0.000000	
12 N	0.50000	0.50000	0.00000	-0.005057	0.000000	0.000000	
14 N	0.50000	0.00000	0.50000	0.017769	0.000000	0.000000	
15 N	0.00000	0.50000	0.50000	-0.006221	0.000000	0.000000	
16 N	0.50000	0.50000	0.50000	-0.004952	0.000000	0.000000	

**Create/Hellmann-Feynman file/Browse H-F File** - browser of HF file

#### File correspondence

Phonon(Windows)	VASP	Wien2k
*.d23 structure	POSCAR	
*.d44 displacements	DISCAR	
*.45 structure+displ.		*.d45



## **Create/Hellmann-Feynman file/Do Report** - calculates force constant matrices $\Phi(n, m)$ from force of HF file

The force constant matrices  $\Phi(n, m)$  are found by fitting all relevant independent parameters of  $\Phi(n, m)$  to all HF forces, taking into account all symmetry elements of the space group. For fitting a *singular value decomposition* method is used.

**Create/Hellmann-Feynman file/Plot Force Constants** - plots elements of force constant matrices  $\Phi(n, m)$  as a function of distance between atoms n and m



**Parameters of force constant matrix** 



Decrease of 3 order of magnitudes of force constant parameters  $\Phi_{i,j}$  guaranties that phonon frequencies at all wave vectors are "exact" Now, we have all force constants of the project

## Part 1 Basic functions

## **Phonon dispersion relations** $\omega(k)$

# **Tutorial for Phonon**

#### **Create/Dispersion Curves/Wave Vectors** - set path of wave vectors

Set points: 6





Wave vector path:  $\Gamma$ , X, M,  $\Gamma$ , R, M

(q<sub>1</sub>,q<sub>2</sub>,q<sub>3</sub>) is a wave number
 (k<sub>1</sub>,k<sub>2</sub>,k<sub>3</sub>) is a wave vector



## **Create/Dispersion Curves/Set Points** - set options of calculuting phonon dispersion relations

- set number of main wave vectors
- set number of wave vectors between each pair of main wave vectors
- set output form of polarization vectors
- $\bullet$  decide to calculate symmetry of phonon modes at  $\Gamma$  wave vector

Number of Main Wave Vectors:	6
Number of Points in Between:	80
Output Eigenvectors: Polariz.	File
Irreduc.Representations k=0:	Yes

#### Tools/High-Symmetry Points - set relation between wave vectors **k** and wave numbers **q**

- Matrix  $\mathbf{A} = (\mathbf{a}_p, \mathbf{b}_p, \mathbf{c}_p)$  of primitive lattice vectors
- Reciprocal matrix  $\mathbf{B} = \mathbf{A}^{-1}$



**Create/Dispersion Curves/Do Report** - calculates phonon dispersion relations

At this point the dynamical matrix is diagonalized for the wave vectors need for  $\omega(\mathbf{k})$ 

## Example: NiAl



#### Neutron measurements and computation of phonon dispersion curves of NiAl



## NiAl

Experiment: M.Mostoller, R.M.Niclow, D.M.Zehner, C.S.Lui, J.M.Mundenar, and E.W.Plummer, Phys.Rev. B 40, 2856 (1989)

Ab initio DFPT of part from Γ to M: G.J.Ackland, X.Huang, and K.M.Rabe, Phys.Rev. B 68, 214104 (2003).



#### Irreducible representation of phonon modes

- **Phonon** writes the irreducible representations of all  $\Gamma$  modes to **Report.**
- Irreducible representation are calculated from polarization vectors, and compared with Tables of representations of point groups.
- If crystal symmetry is broken by supercell symmetry, irreducible representations are not calculated, unless you *restore symmetry*.

#### Example: NiAl

Mu1	ti. Omega	Irreducik	ole Repi	resent
	Wave vector=	0.0000	0.0000	0.00
3	0.019	T1u(I)	acoustic	
3	8.607	Tlu(I)	optic	

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

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



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



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.



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 !!!





#### **Create/Dispersion Curves/Search Brillouin Zones** - search Brillouin zone for highest intensity peaks

- $\bullet$  Wave vector  ${\bf k}$  is determined in the spectrometer of coherent inelastic neutron scattering.
- Wave vector **k** can point to different Brillouin zone centers  $\boldsymbol{\tau} = (h,k,l)$
- Wave vector  $\mathbf{Q}$  of phonon is confined into first Brillouin zone
- Wave vector  ${f Q}$  should be inserted into Seach Brillouin Zones menu of Phonon

 $\mathbf{k} = \mathbf{\tau} + \mathbf{O}$ 

- Wave vector  $\mathbf{Q}$  should be selected parallel to analysed reciprocal wave vector line.
- Phonon itself runs over all Brillouin zones which satisfy  $|\mathbf{k}| < \mathbf{k}_{\max}$
- Intensities written to file are calculated according to dynamical structure factor.
- For a given  $\mathbf{Q}$  intensities are sorted downwords, or upwords.

#### In which Brillouin zone phonon at **Q** has the highest intensity?





## Part 1 Basic functions

## **Phonon density of states** $g(\omega)$

## **Tutorial for Phonon**

**Create/Density of States/<u>Set Points</u> – density of sampling the Brillouin zone** 

DOS  $g(\omega)$  is calculated by random sampling over Brillouin zone

Total DOS  $g(\omega) = \frac{1}{n \, d \, \Delta \omega} \sum_{\mathbf{k}, j} \delta_{\Delta \omega} \left( \omega - \omega(\mathbf{k}, j) \right)$   $\delta_{\Delta \omega}(x) = \begin{cases} 1 & \text{if } \frac{\Delta \omega}{2} < x \leq \frac{\Delta \omega}{2} \\ 0 & \text{otherwise} \end{cases}$ 



Partial DOS

 $g_{i,\mu}(\omega) = \frac{1}{n \, d \, \Delta \omega} \sum_{\mathbf{k},j} \mid e_i(\mathbf{k},j;\mu) \mid^2 \, \delta_{\Delta \omega} \left( \omega \, - \, \omega(\mathbf{k},j) \right)$ 

**Create/Density of States/Do Report** – calculates DOS

**Create/Density of States/Plot DOS** – draws total and/or partial DOSs



## Part 1 Basic functions

## **Thermodynamical Functions**

# **Tutorial for Phonon**

Phonon contribution to harmonic thermodynamic functions (V=const.)

$$E = \frac{1}{2}r \int_0^\infty d\omega \, g(\omega) \left(\hbar\omega\right) \coth\left(\frac{\hbar\omega}{2k_BT}\right)$$

Free energy: 
$$F = rk_BT \int_0^\infty d\omega \, g(\omega) \ln\left[2\sinh\left(\frac{\hbar\omega}{2k_BT}\right)\right]$$

Entropy: 
$$S = rk_B \int_0^\infty d\omega \, g(\omega) \left\{ \left( \frac{\hbar\omega}{2k_B T} \right) \left[ \coth\left( \frac{\hbar\omega}{2k_B T} \right) - 1 \right] - \ln\left[ 1 - \exp\left( -\frac{\hbar\omega}{k_B T} \right) \right] \right\}$$

Heat capacity C<sub>v</sub>:

Internal energy:

$$= r k_B \int_0^\infty d\omega \, g(\omega) \, \left(\frac{\hbar \omega}{k_B T}\right)^2 \frac{e x p(\frac{\hbar \omega}{k_B T})}{\left[e x p\left(\frac{\hbar \omega}{k_B T}\right) \, - \, 1\right]^2}$$

Thermal mean square displacement:  $B_{ij}(\mu) = \langle U_i(\mu) U_j(\mu) \rangle$   $B_{il}(\mu) = \frac{\hbar r}{2M_{\mu}} \int_0^\infty d\omega g_{il,\mu}(\omega) \frac{1}{\omega} \coth\left(\frac{\hbar\omega}{2k_BT}\right)$ 

All thermodynamic functions depend on DOS

C



Create/Thermodynamic F./Plot Free Energy – plots free energy

**Create/Thermodynamic F./Plot Heat Capacity** – plots c<sub>v</sub> Heat Capacity at V=const. **Free Energy** 100  $E \rightarrow (1/2)r \int d\omega \, \omega \, g(\omega)$  $C \rightarrow k_{B}r$ 5 (meV/unit cell) 50 4 0 3 Free Energy 2 -50



-100



**Create/Thermodynamic F./Plot Thermal Displacements** – plots tensor 3x3 of mean square displacements of each atom  $B_{ij}(\mu) = \langle U_i(\mu) U_j(\mu) \rangle$ 

Related to Debye-Waller factor

Example: NiAl

At T = 400 K mean square displacement is: Ni: ~0.10 A Al.: ~0.09 A



## Part 1 Basic functions

## **Neutron Scattering**

**Coherent Inelastic, Incoherent Inelestic** 

# **Tutorial for Phonon**

#### **Create/Neutron Scattering/Coherent Form factor** – plot

Coherent dynamical structure factor:

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

 $F(\mathbf{k},\mathbf{j})$  defines intensities of phonon peaks, which can be different in different B.Z.



#### Create/Neutron Scattering/Set Conditions – geometry of scattering



#### **Create/Neutron Scattering/Incoherent on Mono, Poly** – plot



#### Example: NiAl

2, 3, 4, 5 – phonon scattering on polycrystal



Part 1 Basic functions

## LO/TO splitting

## **Tutorial for Phonon**



### LO/TO splitting from singular term



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

Example: SnO<sub>2</sub> S.C.: 1x1x8

## Part 2 Advance functions

## Generating POSCAR, DISCAR Wien2k\_position files

## **Tutorial for Phonon**

Files:

- POSCAR = \*.d23
- DISCAR = \*.d44
- Wien2k\_positions = \*.d45

are created in Create/Interaction Range/Supercell

	A	в	С
Transform. S=CL	2.0000000	0.0000000	0.0000000
from Crys.Cell C L=	0.0000000	2.0000000	0.0000000
to SuperCell S.	0.0000000	0.0000000	2.00000000
Restore symmetry of o	crystal space	group:	No
Displacement for HF	forces in Angs	troms:	0.03000
Supercell Position F	ile: VASP POS	CAR Displ.+	/-: No

	A	в	С
Transform. S=CL	2.0000000	0.0000000	0.00000000
from Crys.Cell C L=	0.0000000	2.0000000	0.00000000
to SuperCell S.	0.0000000	0.0000000	2.00000000
Restore symmetry of a	crystal space	group:	No
Displacement for HF	forces in Angs	troms:	0.03000
Supercell Position F.	ile: WIEN2k	Displ.+	/-: No

## Part 2 Advance functions

## **Restore symmetry in hexagonal crystals**

## **Tutorial for Phonon**

## **Hexagonal Structure**

Supercell 2x2x2

**First coordination shell** contains all neighbors **Missing atom Second coordination shell** does not contain all neighbors, instead of 12, it has 2 atoms

### **Hexagonal crystals**

There are 3 kinds of hexagonal structures:

- Type A. Trigonal space groups. They have equivalent either hexagonal, or <u>rhombohedral</u> setting. Select rhombohedral and use rhombohedral supercell. Space groups: 146, 148, 155, 160, 161, 166, 167.
- Type **B**. Hexagonal crystals. Select <u>rhombohedral</u> supercell, which has 3 times larger volume. Space groups: 143, 144, 145, 147, 151, 153, 157, 159, 162, 163.
- Type C. Build <u>rhombohedral</u> supercell as in case **B**. The supercell reduces the hexagonal symmetry, thus to recover it, use afterwords *Restore Symmetry*. Space groups: all remaining hexagonal sp. Groups.

Hexagonal structures of A, B, C types can be represented by <u>orthorhombic</u> supercells. These supercells break the symmetry, but, you may *Restore Symmetry*.

## Example: GaN ( type C)



6 neighbors No Z-mirror plane

12 neighbors Z-mirror plane

Atoms and force constants, missing in rhombohedral supercell, are added to dynamical matrix to restore hexagonal crystal symmetry. In this case hexagonal force constants are twice smaller then the rhombohedral ones. Rhombohedral supercell Before *Restore Symmetry* Incorrect degeneracy

After *Restore Symmetry* 









Hellmann-Feynman F.

Calculate force constants of original supercell (with reduced sym.)

**Restore symmetry of calculated force constants** 

## Part 2 Advance functions

## Fit phonon dispersion curves ω(k,j) to a set of experimental data

# **Tutorial** for Phonon

### Fit phonons to experimental data

We want to shift LA mode at k=X from  $\omega$ =6.019 THz to  $\omega$ =7.5THz

Useful:

- To combine phonon frequencies from supercell of several shapes, and different 'exact' points.
- To see what force constants cause a give phonon frequency shift.
- To fit calculated phonon dispersion curves to experimental points

Option should be used at 'exact' points only.

## Example: NiAl



WAVE VECTOR

#### Procedure to fit mode to experimental value





## Part 2 Advance functions

# Collective displacements corresponding to a phonon mode

# **Tutorial for Phonon**

## **Create/Dispersion Curves/Mode Displacements/Show Position File** - generates multi-displacement file for phonon modes

At 'exact' wave vectors one may generate files POSCAR, Wien2k\_porticle, which contain position of atoms in supercell displaced according to polarization vectors of selected phonon modes.

POSCAR = \*.d68MODECAR = \*.d67 - similar to DISCAR but with multi-displacements Wien2k\_position = \*.d69

Multidisplacement files can be used to:

- calculate precisely HF forces for a given phonon mode
- to trace energy profile with respect to phonon mode
- study shift of electronic levels againt phonon displacements







## Part 3

## **Quasiharmonic Approximation** (scalling temperature T to pressure P)

# **Tutorial for Phonon**



Volume (A3/atom)

### Phonon dispersion curves as a function of pressure P for W



### Phonon density of states $g(\omega)$ as a function of pressure P for W



#### Free energy and quasiharmonic approximation 0K 300K 600 Harmonic free energy as a 600K 300 function of temperature 900K 1200K 500 -300 1500K 0 (meV/atom) P = 0 kB(meV/atom) -500 -600 1800K -1000 -1500 -900 2100K Free Energy -2000 Energy 2400K -1200 -2500 -3000 -1500 2700K -3500 Free 1000 2000 3000 4000 0 Temperature (K) -1800 3000K -2100 3300K **Stable** -2400 3600K Harmonic free energy as function of -2700 volume for different temperatures. 20 22 14 16 18 Minimum defines *stable state* Volume (A3/atom)

### Relations following from quasiharmonic approximation



Scalling between tempearature T and pressure P for quasiharmonic approximation



#### Thermal expansion of lattice constant of W



Volume thermal expansion of W

## Phonon dispersion relations in quasiharmonic approximation at different temperatures (from pressures)



Temperature shifts of phonon peaks

## Phonon density of states $g(\omega)$ in quasiharmonic approximation at different temperatures (from pressures)



## Part 3

## Soft modes. Crystal instability

# **Tutorial for Phonon**

**Create/Dispersion Curves/Do Report** - calculate phonon dispersion relations

Example: austenite NiTi



Polarization vector of soft mode indicate symmetry lowering caused by phase transition

K.Parlinski and M.Parlinska-Wojtan, Phys.Rev.B 66, 0604307 (2002)

#### Phonon, ver. 4.22



## http://wolf.ifj.edu.pl/phonon/

Copyright Krzysztof Parlinski

## **The End**