# PHASEGO Users Manual

(A toolkit for automatic calculation and plot of phase diagram: PHASE Global Optimization)

VERSION: 3.0.0

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# Contents

# 1 Introduction

## 1.1 About PHASEGO

PHASEGO is designed for the easy implementation of phase transition analysis and plot of phase diagrams. It can also calculate the thermodynamic properties of materials, including the thermal expansion coefficients, the bulk moduli, the heat capacities, the thermal pressures, the Grüneisen parameters, and the Debye temperatures. For the dynamic response properties of materials, PHASEGO can automatically find the Hugoniot pressure-volume and pressure-temperature relations according to the Rankine-Hugoniot conditions [1, 2]. All these qualities can be obtained based on the quasi-harmonic approximation (QHA) and/or full anharmonic free energy corrections (AFEC) from the high-temperature phonon density of states (DOS). More interestingly, with full anharmonic effects the possible phase boundaries of all the structures provided are analyzed and plotted automatically. The decomposition conditions analysis can also be performed according to the Gibbs free energy obtained either from the QHA or after the AFEC. So the high pressure and temperature phase diagram can be constructed and plotted easily by PHASEGO. From the phase diagram and the decomposition conditions analysis, one can manage to predict the synthesis pressure and temperature conditions of materials according to the thermodynamic equilibrium.

## 1.2 Theoretical background

### 1.2.1 The QHA

The QHA is a phonon-based model of crystal lattice vibrations used to describe volume-dependent thermal effects, such as the thermal expansion. It starts from the assumption that the harmonic approximation holds for every value of the crystal volume, and then takes into account part of anharmonic effects by varying crystal volume.

In the framework of QHA, the Helmholtz free energy of a crystal is written as

$$F(V,T) = E_{\mathrm{static}}(V) + F_{\mathrm{zp}}(V,T) + F_{\mathrm{ph}}(V,T), \tag{1}$$

where $E_{\mathrm{static}}(V)$ is the first-principles zero-temperature energy of a static lattice at volume $V$, and $F_{\mathrm{zp}}$ is the zero-point motion energy of the lattice given by

$$F_{\mathrm{zp}} = \frac{1}{2}\sum_{\mathbf{q},j}\hbar\omega_j(\mathbf{q},V). \tag{2}$$

The last term is the phonon free energy due to lattice vibrations, and can be obtained from

$$F_{\mathrm{ph}}(V,T) = k_{\mathrm{B}}T\sum_{\mathbf{q},j}\ln\left\{1-\exp\left[-\hbar\omega_j(\mathbf{q},V)/k_{\mathrm{B}}T\right]\right\}, \tag{3}$$

where $\omega_j(\mathbf{q},V)$ is the phonon frequency of the $j$th mode of wavevector $\mathbf{q}$ in the first Brillouin zone.

For a metallic material, the Helmholtz free energy at high temperature includes the electronic thermal excitation free energy,

$$F(V,T) = E_{\mathrm{static}}(V) + F_{\mathrm{el}}(V,T) + F_{\mathrm{zp}}(V,T) + F_{\mathrm{ph}}(V,T), \tag{4}$$

$F_{\mathrm{el}}$ can be evaluated by the finite temperature DFT with the help of the Fermi-Dirac smearing [3]. At low temperature, $F_{\mathrm{el}}$ is very small and can be neglected, but at high temperature it is large and probably changes final conclusions.

If we write $F_{\mathrm{latt}}$ as

$$F_{\mathrm{latt}} = F_{\mathrm{zp}} + F_{\mathrm{ph}}, \tag{5}$$

it can also be calculated from the phonon density of states $g(\omega)$ via [4]

$$F_{\mathrm{latt}} = \int \left[ \frac{1}{2}\hbar\omega + k_{\mathrm{B}}T\ln(2\sinh\frac{\hbar\omega}{2k_{\mathrm{B}}T}) \right] \mathrm{d}\omega g(\omega), \tag{6}$$

where $k_B$ is the Boltzmann constants. The phonon density of states is written as

$$g_j(\omega) = \frac{V}{(2\pi)^3} \int \mathrm{d}\mathbf{q}\delta\left[\omega - \omega_j(\mathbf{q})\right]. \tag{7}$$

And the total densities of states are normalized to,

$$\int \mathrm{g}(\omega)\mathrm{d}\omega = 3nN, \tag{8}$$

where $n$ is the number of atoms in the unit cell and $N$ is the number of the unit cells.

### 1.2.2 The AFEC

However, the QHA often introduces errors when temperature is high enough or even close to melting temperature at a specified pressure. At this time, the AFEC should be conducted to reduce such errors. At present, PHASEGO performs the AFEC via high-temperature phonon DOS. The high-temperature phonon DOS could be from the molecular dynamics (MD) simulations [5], the self-consistent *ab initio* lattice dynamics (SCAILD) calculations[6], or other simulation methods.

### 1.2.3 The synthesis/decomposition conditions

A compound can synthesized from different components and at different pressure and temperature conditions. It can also decompose into several possible products at specific pressure and temperature conditions according to the thermodynamic equilibrium relations, e.g.,

$$ABO_3 \longleftrightarrow AO + BO_2, \tag{9}$$

or,

$$ABO_3 \longleftrightarrow AO_2 + BO, \tag{10}$$

or,

$$3ABO_3 \longleftrightarrow A_3O_4 + 2BO_2 + BO, \tag{11}$$

or something else. There are many many possibilities when pressure and/or temperature varies. Hence, it is very hard and complicated to analyze which chemical process can really proceed according to the Gibbs free energy criteria.

## 2 Installation and run

The installation of PHASEGO package is very easy. PHASEGO is based on Python, but to increase the computation speed and realize the numerical interpolation and extrapolation, it also uses Numpy and Scipy python libraries.

### 2.1 Installation requirements

The following packages are required:
• Python 2.6 or later.
• NumPy.
• Scipy 0.13.3 or later.
• Matplotlib.

Matplotlib is used for the automatic plot of the HPHT phase diagram. In the Ubuntu system, just simply execute `sudo apt-get install python python-numpy python-scipy python-matplotlib`. In the Windows systems, one can install `pythonxy` package for all the necessary libraries.

### 2.2 Installation

There are two methods to install PHASEGO. When one has the python setuptools module installed, the first method is to execute `python setup.py install` in the PHASEGO root directory as the administrator. As a common user, one can also specify a directory to install using additional "`--prefix=/path/to/install/`". If one has no python setuptools, then the second method to install is: first put the following `PATH` and `PYTHONPATH` environment variable in user's `~/.bashrc` file:

```
export PATH=$PATH:/path/to/phasego/src
export PYTHONPATH=$PYTHONPATH:/path/to/phasego/src
```

or in the `~/.cshrc` file:

```
setenv PYTHONPATH /path/to/phasego/src:$PYTHONPATH
setenv PATH /path/to/phasego/src:$PATH
```

Then, execute `chmod +x /path/to/phasego/src/phasego`. Finally type `source ~/.bashrc` or `source ~/.cshrc`.

### 2.3 Run

Just type `phasego` to run the phase analysis in your work directory contained a controlling file `phasego.in`. All the controlling arguments are detailed below.

## 3 Input and output files

### 3.1 Input files

#### 3.1.1 The QHA calculation

In the QHA calculations, the input files needed by PHASEGO package are the static volume-energy data files and the phonon density of states files for each volume. The structure information can be obtained from the crystal structure prediction codes, such as the packages MUSE [7] and CALYPSO [8]. All the files are placed in the `inp-phasename` directory for each single structure, where `phasename` is the name of this structure named by the user in the controlling file `phasego.in`. The common prefix name of the static volume-energy data files for all structures are specified in the `phasego.in` file, e.g., `ve-`. The full file names of volume-energy data files are this prefix name plus "`T`", where `T` is the temperature at which the volume-energy data are calculated. To include the electronic thermal excitation effects (especially for metallic materials), the energies can be calculated within the framework of finite temperature DFT. There should be a number of volume-energy data files, e.g., `ve-0`, `ve-50`, `ve-100`, `ve-150`, and so on. For nonmetallic materials, `T` equals to 0 and there is only one file, e.g., `ve-0`.

The phonon dos file is named as `ph.dos-volume-0`, where `volume` is exactly the same value in the volume-energy file and "0" means the zero temperature phonon DOS. `ph.dos-` is the common prefix name specified in `phasego.in` for all the structures. The densities of states are normalized to 1 or $3n$, where $n$ is the number of atoms in the unit cell. The unit of frequencies can be chosen from cm-1, THz, meV, and eV.

The following input file example is for the phase transition analysis of GaN at HPHT. The main input file is named as `phasego.in`, in which the lines started with '#' are neglected. Each argument and its value(s) are placed in the same line, in any order and with any number of blank lines. The values of each argument are separated by whitespace and placed after '='. The arguments are all self-explained in their comment line(s).

```
###============================================================###
###==================== PHASEGO input file ====================###
###=============== (PHASE Global Optimization) ===============###
###============================================================###
### Lines started with "#" are omitted.
### Parameter and value(s) are placed in the same line, in any
### order with any number of blank lines.
###
# Note:
###
# A. volume unit can be:  Bohr3 or A3, energy:  Ry, Hartree, or eV.
# B. Num_Formula_Units is the number of chemical formula units
# for energy and phonon dos calculations.
# C. dos files:  dos are normalized to 1 or 3*n, and the unit of
# frequencies can be choosen from cm-1, THz, meV, eV.
#
# EOS Names (number):
# 1.  Murnaghan:  Murnaghan EOS (F. D. Murnaghan, Am.  J. Math.
# 49, 235 (1937))
# 2.  Birch:  Birch EOS (From Intermetallic compounds:
# Principles and Practice, Vol I: Principles.  pages 195-210)
# 3.  BirchMurnaghan:  Birch-Murnaghan 3rd-order EOS (F. Birch,
# Phys.  Rev.  71, p809 (1947))
# 4.  BirchMurnaghan:  Birch-Murnaghan 4rd-order EOS (F. Birch,
# Phys.  Rev.  71, p809 (1947))
# 5.  Vinet:  Vinet EOS (Vinet equation from PRB 70, 224107)
# 6.  Universal:  Universal EOS (P. Vinet et al., J. Phys.:
# Condens.  Matter 1, p1941 (1989))
# 7.  Natural strain 3rd-order EOS (Poirier J-P and Tarantola A,
# Phys.  Earth Planet Int.  109, p1 (1998))
# 8.  Natural strain 4rd-order EOS (Poirier J-P and Tarantola A,
# Phys.  Earth Planet Int.  109, p1 (1998))
# Others:  Fitting Polynomial to F-V data:  pn, e.g., p6
###============================================================###

# The EOS name used for fitting
Eos_Name = 1

# The chemical formula unit (f.u.)  name of the crystal.  It must
# be in correct form and have no brackets, e.g., MgSiO3, WC,
```

```
# BN3, Al2O3, Si, Al3Ti.  The number of atoms for each element
# in the f.u.  will be parsed from it.  Al2(SO4)3 ---> Al2S3O12
Formula_Name = GaN

# The user-defined name for each corresponding structure.  The
# ve and phonon dos files are placed in each inp-name dir.  The
# output files are placed in each out-name dir.
Names_of_Strs = rocksalt wurtzite zencblende

# The number of chemical formula units used for the v-e and phonon
# dos data of each str defined in Names_of_Strs correspondingly.
Num_Formula_Units = 1 2 1

# The prefix name of volume-energy data files for each str.
# The full name is the prefix name plus "T", where T is
# temperature to take into account the electronic thermal
# excitation by finite temperature DFT. If including the
# electronic thermal excitation free energy, the temperature
# start, end, and interval should be the same as Tdata below.
VE_data_File_Name = ve-

# The units for volume and energy respectively,
# volume:  Bohr3, A3; energy:  Ry, Hartree, eV
Units_VE = Bohr3 Ry

# Read_what = dos_data for phonon dos, Read_what = TF_data
# for temperature-helmholt free energy data.
Read_what = dos_data

# Phonon dos file prefix name, i.e., it plus the volume value
# in ve file is the full name.
Ph_Dos_File_Base_Name = ph.dos-

# Unit of frequency in dos data
Unit_of_Freq = cm-1

# Temperature data (K): start, end, interval
#Tdata_Read = 0 3000 50

# Temperature data (K): start, end, interval
Tdata_Write = 0 6000 100

# Pressure data (GPa):  start, end, interval
Pdata = 0 40 1

# If calculate thermal properties, yes or no
If_Incl_Phonon = yes

# Anharmonic phonon from high-temperature phonon DOS
If_Incl_Anharm_Phonon = no
```

```
# If include electronic thermal excitation free energy by
# finite temperature DFT, for metals
If_Incl_Electronic_Excitation = no

# If analyze the potential phase transition P-T points between
# these strs, yes or no
If_Analysize_Phase_Transition = yes

# If plot phase diagram using mathplotlib, yes or no
If_Plot = yes

# If analysize Hugoniot PTV, yes or no
If_Hugoniot = yes

# If calculate Debye Temperature, yes or no
If_Calc_Debye_Temp = yes

########### synthesis/decomposition conditions analysis ##########
# If include decomposition conditions analysis in phase
# transition analysis.
If_Incl_Decomp_Analysis = no

# The reactants/products information on the the synthesis/
# decomposition.
# (Chemical formula)@(Phase name):(Number of chemical formula units)
# pairs, no space for each str.  The number of chemical formula
# units is that used for the ve and phonon dos data of each
# structure of each product.
# e.g., Mg@fcc:1 Mg@sh:1 MgO@B2:1 MgO@B1:1 MgO2@t:1
Products_Info = Mg@fcc:1 Mg@sh:1 MgO@B1:1 MgO@B2:1 MgO2@t:2

########### synthesis/decomposition conditions analysis ##########
```

### 3.1.2 The AFEC calculation

In the AFEC calculations, one should have high-temperature phonon DOS for all the volumes. The high-temperature phonon DOS can be obtained from the MD trajectories by the Fourier transform velocity autocorrelation method [9, 10, 11, 12]. The phonon DOS is,

$$g(\omega) = m \int \langle \dot{\mathbf{r}}(\tau)\dot{\mathbf{r}}(t+\tau)\rangle_{\tau} e^{-i\omega t} \mathrm{d}t, \tag{12}$$

where $\dot{\mathbf{r}}$ is the time derivative of the atom position and $\langle\rangle$ is the ensemble average of MD simulations.

In real calculations, one should prepare such phonon DOS files for PHASEGO. The phonon dos file is named as `ph.dos-volume-T`, where `volume` is exactly the same value in the volume-energy file and "`T`" means the phonon DOS at temperature `T`.

The following input file example is for the AFEC calculations of Cu. The main input file is still named as `phasego.in`.

```
###============================================================###
###==================== PHASEGO input file ====================###
###=============== (PHASE Global Optimization) ===============###
```

```
###============================================================###
### Lines started with "#" are omitted.
### Parameter and value(s) are placed in the same line, in any
### order with any number of blank lines.
###
# Note:
###
# A. volume unit can be:  Bohr3 or A3, energy:  Ry, Hartree, or eV.
# B. Num_Formula_Units is the number of chemical formula units
# for energy and phonon dos calculations.
# C. dos files:  dos are normalized to 1 or 3*n, and the unit of
# frequencies can be choosen from cm-1, THz, meV, eV.
#
# EOS Names (number):
# 1.  Murnaghan:  Murnaghan EOS (F. D. Murnaghan, Am.  J. Math.
# 49, 235 (1937))
# 2.  Birch:  Birch EOS (From Intermetallic compounds:
# Principles and Practice, Vol I: Principles.  pages 195-210)
# 3.  BirchMurnaghan:  Birch-Murnaghan 3rd-order EOS (F. Birch,
# Phys.  Rev.  71, p809 (1947))
# 4.  BirchMurnaghan:  Birch-Murnaghan 4rd-order EOS (F. Birch,
# Phys.  Rev.  71, p809 (1947))
# 5.  Vinet:  Vinet EOS (Vinet equation from PRB 70, 224107)
# 6.  Universal:  Universal EOS (P. Vinet et al., J. Phys.:
# Condens.  Matter 1, p1941 (1989))
# 7.  Natural strain 3rd-order EOS (Poirier J-P and Tarantola A,
# Phys.  Earth Planet Int.  109, p1 (1998))
# 8.  Natural strain 4rd-order EOS (Poirier J-P and Tarantola A,
# Phys.  Earth Planet Int.  109, p1 (1998))
# Others:  Fitting Polynomial to F-V data:  pn, e.g., p6
###============================================================###

# The EOS name used for fitting
Eos_Name = 3

# The chemical formula unit (f.u.)  name of the crystal.  It must
# be in correct form and have no brackets, e.g., MgSiO3, WC,
# BN3, Al2O3, Si, Al3Ti.  The number of atoms for each element
# in the f.u.  will be parsed from it.  Al2(SO4)3 ---> Al2S3O12
Formula_Name = Cu

# The user-defined name for each corresponding structure.  The
# ve and phonon dos files are placed in each inp-name dir.  The
# output files are placed in each out-name dir.
Names_of_Strs = fcc

# The number of chemical formula units used for the v-e and phonon
# dos data of each str defined in Names_of_Strs correspondingly.
Num_Formula_Units = 1

# The prefix name of volume-energy data files for each str.
```

```
# The full name is the prefix name plus "T", where T is
# temperature to take into account the electronic thermal
# excitation by finite temperature DFT. If including the
# electronic thermal excitation free energy, the temperature
# start, end, and interval should be the same as Tdata below.
VE_data_File_Name = ve-

# The units for volume and energy respectively,
# volume:  Bohr3, A3; energy:  Ry, Hartree, eV
Units_VE = Bohr3 Ry

# Read_what = dos_data for phonon dos, Read_what = TF_data
# for temperature-helmholt free energy data.
Read_what = dos_data

# Phonon dos file prefix name, i.e., it plus the volume value
# in ve file is the full name.
Ph_Dos_File_Base_Name = dos-

# Unit of frequency in dos data
Unit_of_Freq = cm-1

# Temperature data (K): start, end, interval
Tdata_Read = 0 1000 50

# Temperature data (K): start, end, interval
Tdata_Write = 0 1000 10

# Pressure data (GPa):  start, end, interval
Pdata = 0 50 10

# If calculate thermal properties, yes or no
If_Incl_Phonon = yes

# Anharmonic phonon from high-temperature phonon DOS
If_Incl_Anharm_Phonon = yes

# If include electronic thermal excitation free energy by
# finite temperature DFT, for metals
If_Incl_Electronic_Excitation = no

# If analyze the potential phase transition P-T points between
# these strs, yes or no
If_Analysize_Phase_Transition = no

# If plot phase diagram using mathplotlib, yes or no
If_Plot = no

# If analysize Hugoniot PTV, yes or no
If_Hugoniot = no
```

```
# If calculate Debye Temperature, yes or no
If_Calc_Debye_Temp = no

########### synthesis/decomposition conditions analysis ##########
# If include decomposition conditions analysis in phase
# transition analysis.
If_Incl_Decomp_Analysis = no

# The reactants/products information on the the synthesis/
# decomposition.
# (Chemical formula)@(Phase name):(Number of chemical formula units)
# pairs, no space for each str.  The number of chemical formula
# units is that used for the ve and phonon dos data of each
# structure of each product.
# e.g., Mg@fcc:1 Mg@sh:1 MgO@B2:1 MgO@B1:1 MgO2@t:1
Products_Info = Mg@fcc:1 Mg@sh:1 MgO@B1:1 MgO@B2:1 MgO2@t:2

########### synthesis/decomposition conditions analysis ##########
```

### 3.1.3 The synthesis/decomposition conditions analysis

A crystal may decompose into some products at the specific pressure and temperature conditions. This information is also very important to evaluate the synthesis possibility of the crystal according to the high-pressure and high-temperature phase diagram. So, it also be regarded as the synthesis conditions analysis, as is the vital information for new materials design.

```
###============================================================###
###==================== PHASEGO input file ====================###
###=============== (PHASE Global Optimization) ===============###
###============================================================###
### Lines started with "#" are omitted.
### Parameter and value(s) are placed in the same line, in any
### order with any number of blank lines.
###
# Note:
###
# A. volume unit can be:  Bohr3 or A3, energy:  Ry, Hartree, or eV.
# B. Num_Formula_Units is the number of chemical formula units
# for energy and phonon dos calculations.
# C. dos files:  dos are normalized to 1 or 3*n, and the unit of
# frequencies can be choosen from cm-1, THz, meV, eV.
#
# EOS Names (number):
# 1.  Murnaghan:  Murnaghan EOS (F. D. Murnaghan, Am.  J. Math.
# 49, 235 (1937))
# 2.  Birch:  Birch EOS (From Intermetallic compounds:
# Principles and Practice, Vol I: Principles.  pages 195-210)
# 3.  BirchMurnaghan:  Birch-Murnaghan 3rd-order EOS (F. Birch,
# Phys.  Rev.  71, p809 (1947))
# 4.  BirchMurnaghan:  Birch-Murnaghan 4rd-order EOS (F. Birch,
# Phys.  Rev.  71, p809 (1947))
# 5.  Vinet:  Vinet EOS (Vinet equation from PRB 70, 224107)
```

```
# 6.  Universal:  Universal EOS (P. Vinet et al., J. Phys.:
# Condens.  Matter 1, p1941 (1989))
# 7.  Natural strain 3rd-order EOS (Poirier J-P and Tarantola A,
# Phys.  Earth Planet Int.  109, p1 (1998))
# 8.  Natural strain 4rd-order EOS (Poirier J-P and Tarantola A,
# Phys.  Earth Planet Int.  109, p1 (1998))
# Others:  Fitting Polynomial to F-V data:  pn, e.g., p6
###============================================================###

# The EOS name used for fitting
Eos_Name = 3

# The chemical formula unit (f.u.)  name of the crystal.  It must
# be in correct form and have no brackets, e.g., MgSiO3, WC,
# BN3, Al2O3, Si, Al3Ti.  The number of atoms for each element
# in the f.u.  will be parsed from it.  Al2(SO4)3 ---> Al2S3O12
Formula_Name = Mg3O2

# The user-defined name for each corresponding structure.  The
# ve and phonon dos files are placed in each inp-name dir.  The
# output files are placed in each out-name dir.
Names_of_Strs = t

# The number of chemical formula units used for the v-e and phonon
# dos data of each str defined in Names_of_Strs correspondingly.
Num_Formula_Units = 2

# The prefix name of volume-energy data files for each str.
# The full name is the prefix name plus "T", where T is
# temperature to take into account the electronic thermal
# excitation by finite temperature DFT. If including the
# electronic thermal excitation free energy, the temperature
# start, end, and interval should be the same as Tdata below.
VE_data_File_Name = ve-

# The units for volume and energy respectively,
# volume:  Bohr3, A3; energy:  Ry, Hartree, eV
Units_VE = Bohr3 Ry

# Read_what = dos_data for phonon dos, Read_what = TF_data
# for temperature-helmholt free energy data.
Read_what = dos_data

# Phonon dos file prefix name, i.e., it plus the volume value
# in ve file is the full name.
Ph_Dos_File_Base_Name = phonopy.dos-

# Unit of frequency in dos data
Unit_of_Freq = cm-1

# Temperature data (K): start, end, interval
```

```
#Tdata_Read = 0 2000 100

# Temperature data (K): start, end, interval
Tdata_Write = 0 5000 50

# Pressure data (GPa):  start, end, interval
Pdata = 600 875 10

# If calculate thermal properties, yes or no
If_Incl_Phonon = yes

# Anharmonic phonon from high-temperature phonon DOS
If_Incl_Anharm_Phonon = no

# If include electronic thermal excitation free energy by
# finite temperature DFT, for metals
If_Incl_Electronic_Excitation = no

# If analyze the potential phase transition P-T points between
# these strs, yes or no
If_Analysize_Phase_Transition = yes

# If plot phase diagram using mathplotlib, yes or no
If_Plot = yes

# If analysize Hugoniot PTV, yes or no
If_Hugoniot = no

# If calculate Debye Temperature, yes or no
If_Calc_Debye_Temp = no

########### synthesis/decomposition conditions analysis ##########
# If include synthesis/decomposition conditions analysis in phase
# transition analysis.
If_Incl_Decomp_Analysis = yes

# The reactants/products information on the the synthesis/
# decomposition.
# (Chemical formula)@(Phase name):(Number of chemical formula units)
# pairs, no space for each str.  The number of chemical formula
# units is that used for the ve and phonon dos data of each
# structure of each product.
# e.g., Mg@fcc:1 Mg@sh:1 MgO@B2:1 MgO@B1:1 MgO2@t:1
Products_Info = Mg@fcc:1 Mg@sh:1 MgO@B1:1 MgO@B2:1 MgO2@t:2

########### synthesis/decomposition conditions analysis ##########
```

## 3.2 Output files

### 3.2.1 The QHA output files

The output files for single phase analysis are placed in the `out-phasename` directory of each structure. The `Alpha.dat` file contains the thermal expansion coefficients data as the function of temperature at fixed pressures. The `B_S.dat` file has the adiabatic bulk modulus data as the function of temperature at fixed pressures. The `B_T_P.dat` and `B_T_T.dat` files contain the isothermal bulk moduli at fixed pressures and temperatures, respectively. The `C_P.dat` file contains the outcomes of heat capacities at fixed pressures. The `C_V_P.dat` and `C_V_V.dat` files have the constant volume heat capacities at fixed pressures and volumes, respectively. The `DebyeT.dat` file has the Debye temperatures as the function of temperature at fixed volumes. The `Enthalpy.dat` is the data file of the enthalpy as a function of pressure. The `Entropy_V.dat` and `Entropy_P.dat` collect the total entropies at fixed volumes and pressures, respectively. The `fittedC_V_V.dat` includes the fitted $C_V$ at fixed volumes. The `fittedE_V.dat` is the data file of the fitted internal energy and pressure. The `FittedHelmFreeE_T.dat` file contains the fitted Helmholtz free energies at fixed temperatures. The `gamma_P.dat` has the thermodynamic Grüneisen parameters as the function of temperature at fixed pressures. The `G_P.dat` and `G_T.dat` files include the Gibbs free energies as functions of temperature and pressure, respectively. The `HugoniotPTV.dat` is the output file of the Hugoniot P-T-V data. The `PV_T.dat` file contains the pressure-volume data at fixed temperatures. The `ThermalP_T.dat` and `ThermalP_V.dat` have the thermal pressure data at fixed pressures and volumes, respectively. The `VT_P.dat` is the output file of the volume-temperature data at fixed pressures. The `C_V-ph-direct.dat`, `Entropy-ph_V.dat` and `E-ph_V.dat` are the constant volume heat capacities, entropy and internal energy of lattice vibrations directly from the phonon density of states, respectively.

The phase transition data and the automatically plotted phase diagram figures are placed in the `Phase-PT` directory. The `P-T.dat` file contains the transition pressures at fixed temperatures, which are obtained by canning pressure at each fixed temperature. Similarly, the `T-P.dat` file contains the transition temperatures at fixed pressures obtained by scanning temperature at each fixed pressure. They can be plotted by other plot softwares. The phase boundaries are indexed by "|" and the phase transitions are labelled by "——>".

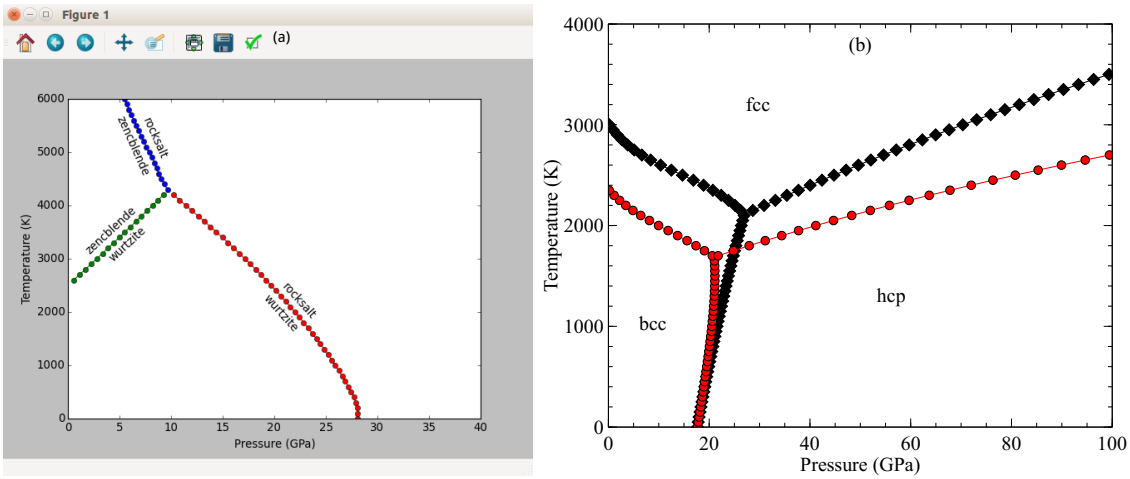


Figure 1: (a) The QHA based high pressure and temperature phase diagram of GaN from the automatic analysis and plot of phase transition. (b) The QHA based high PT phase diagram of Fe with (red symbols) and without (black symbols) electronic thermal excitation free energy corrections.

The phase transition data and the automatically plotted phase diagram figures are placed in the `Phase-PT` directory. The `P-T.dat` file contains the transition pressures at fixed temperatures, which are obtained by canning pressure at each fixed temperature. Similarly, the `T-P.dat` file contains the

transition temperatures at fixed pressures obtained by scanning temperature at each fixed pressure. They can be plotted by other plot softwares. The phase boundaries are indexed by "|" and the phase transitions are labelled by "——>".

Figure 1a is the automatic plot of the phase diagram of GaN. One only needs provide the necessary volume-energy and phonon density of state data for different structures covering the pressure range of interest. The PHASEGO package will gather the Gibbs free energy information and judge the stable field of each structure, and finally plot the phase diagram and label the phase boundary between two structures automatically. The triple point is also clearly shown in the phase diagram. For metallic materials, the electronic thermal excitation free energies at high temperature can not be neglected. In the case of Fe, the results of automatic phase transition analyses with and without electronic thermal excitation free energy corrections are shown in Fig.1b. One notes that the electronic thermal excitation free energies alter the phase boundaries much obviously at high temperature.

### 3.2.2 The AFEC output files

The output files for the AFEC calculations are added the "`_anh`" label and placed in the main output directory of each structure. In the subdirectory, the QHA data from the phonon DOS at different temperatures are placed.

As examples, the zero pressure thermal expansion coefficients of Cu with and without AFEC are plotted in Fig.2a. The Gibbs free energy versus temperature data with and without AFEC at 20 GPa are plotted in Fig.2b.

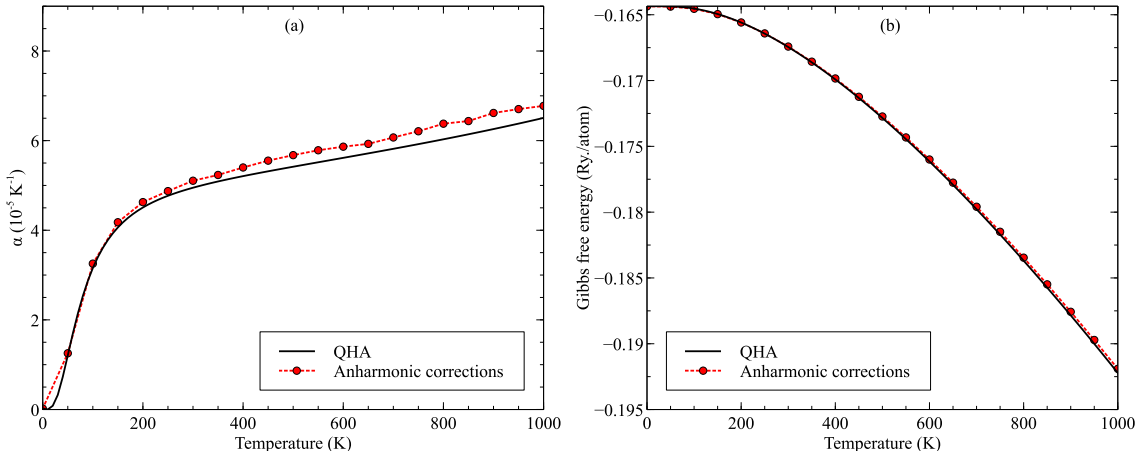


Figure 2: (a) The zero pressure thermal expansion coefficients of Cu with and without AFEC. (b) The Gibbs free energy versus temperature data with and without AFEC at 20 GPa.

### 3.2.3 The output files of synthesis/decomposition conditions analysis

A typical output of the synthesis/decomposition analysis of $Mg_3O_2$ is plotted in Fig. 3. The automatic analysis and plot are obtained by scanning pressure (left) and temperature (right), respectively. The possible decomposition products are fcc-Mg, sh-Mg, B1-MgO, B2-MgO, and t-$MgO_2$. PHASEGO can automatically analyze the possible combinations of all the specified products according to the equilibrium of chemical equation. The predicted decomposition conditions of $Mg_3O_2$ are close to the results in Ref.[13]. The numeric phase boundaries are saved in the `P-T.dat` and `T-P.dat` files in the `Phase-PT` directory.

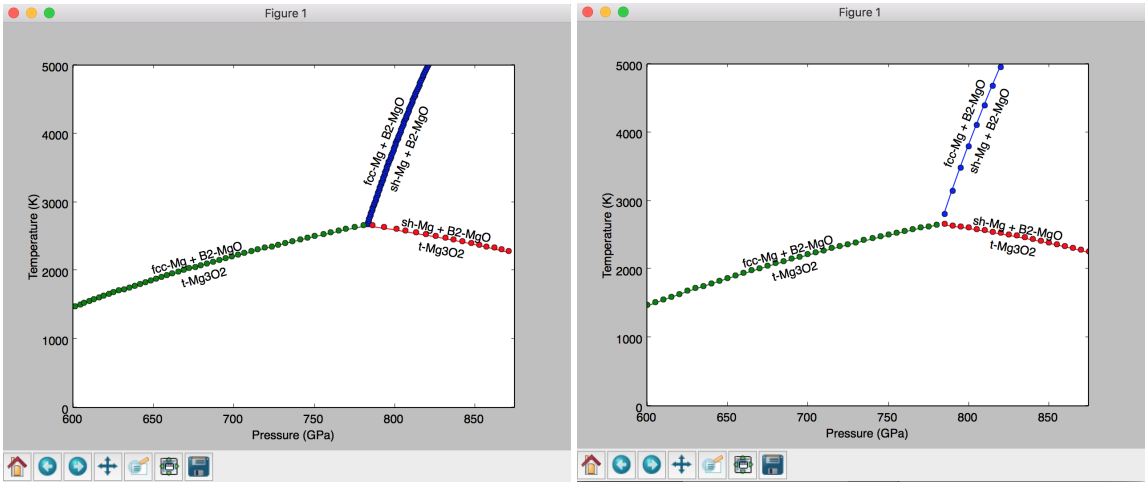


Figure 3: Automatic analysis and plot of the synthesis/decomposition conditions of $Mg_3O_2$ at high pressure and high temperature. left: scannig pressure; right: scanning temperature.

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